WASTE DISCHARGE INTO THE MARINE ENVIRONMENT

Principles and Guidelines for the Mediterranean Action Plan

Published under the joint sponsorship of the World Health Organization and the United Nations Environment Programme

Pergamon Press

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PREPARED IN COLLABORATION WITH THE INSTITUTE OF SANITARY ENGINEERING,
POLYTECHNIC OF MILAN, ITALY

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PREFACE

Following its establishment in 1972 by the United Nations General Assembly, the United Nations Environment Programme (UNEP) selected the Mediterranean Region as one of its "concentration areas" providing assistance to the coastal states in their endeavours to secure measures for the adequate protection of the marine and coastal environment.

In collaboration with a number of United Nations Specialized Agencies including WHO, UNEP convened in Barcelona from 28 January to 4 February 1975, the Intergovernmental Meeting on the Protection of the Mediterranean. During that meeting, which was attended by 16 of the 18 coastal states, an Action Plan was approved comprising three substantive components: legal (framework convention and related protocols), scientific (research, monitoring and assessment) and management (integrated planning). Its final objective was to assist Governments in improving the information base on which environmentally sound national development policies could be formulated; and in improving their ability to identify various options and to make rational choices and appropriate allocations of resources.

The legal framework of the Action Plan was adopted in the Final Act of the Conference of the Plenipotentiaries of the Coastal States of the Mediterranean Region for the Protection of the Mediterranean Seas (*) convened by UNEP in Barcelona from 2 to 16 February 1976. This Conference approved the texts of three legal instruments, namely:

- Convention for the Protection of the Mediterranean Seas against Pollution;
- Protocol for the Prevention of Pollution of the Mediterranean Sea by Dumping from Ships and Aircraft; and
- Protocol concerning Co-operation in Combating Pollution of the Mediterranean Sea by Oil and other Harmful Substances in Cases of Emergency.

Considering that the Convention was too broad to provide meaningful protection on its own, it was agreed that no State could be a Contracting Party to the Convention without also becoming a party to at least one of the protocols.

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* Mediterranean Action Plan and the Final Act of the Conference of Plenipotentiaries of the Coastal States of the Mediterranean Region for the Protection of the Mediterranean Sea, UNEP, 1978.

The Convention and the two protocols came into force on 12 February 1978 and have been ratified as of March 1981 by fifteen Mediterranean States and the EEC.

A Conference of Plenipotentiaries of the Coastal States of the Mediterranean Region for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources took place in Athens from 12 to 17 May 1980 and made the decision to adopt a further Protocol, covering the protection of the Mediterranean against pollution from land-based sources.

The present volume has been prepared in order to assist responsible national authorities in the implementation of this protocol, by providing principles and guidelines for the issuance of permits by national authorities for the discharge of certain types of waste and other matter into the marine environment.

The preparation of this volume has been entrusted to the Institute of Sanitary Engineering of the Polytechnic of Milan (Italy), but the contents of the various chapters were developed by a multi-disciplinary team of experts from the Mediterranean States, together with UNEP and WHO staff. The first draft was reviewed by a study group comprised of authors of the individual chapters together with additional specialists in the fields covered by the document. The views expressed should not,however, be construed as representing the official policies of either WHO or UNEP.

It is hoped that the material presented will be useful both in relation to the Mediterranean Action Plan and for other programmes relating to marine pollution control. It is intended that it will form the basis for the development of a model code of practice for the management of waste from coastal sources. Any comments and suggestions for the improvement of the present text would be welcomed and should be addressed to the Director, Promotion of Environmental Health, World Health Organization Regional Office for Europe, Scherfigsvej 8, 2100 Copenhagen Ø, Denmark.

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PART A. Guidance of the Control of the Discharge of Potentially Harmful Substances into the Mediterranean Sea

CHAPTER 1

1.1 THE NEED FOR ACTION

1.1.1 The Developing Situation

During recent decades a considerable increase has taken place in the rate of disposal of liquid wastes into the Mediterranean. Not only has there been a widespread growth of population in the coastal zones but the extension of the water carriage system to serve larger proportions of the population together with higher standards of living are giving rise to much greater quantities of domestic sewage per head discharged into the sea. Superimposed upon the normal population is the continually growing tourist population resulting in the production of peak quantities of domestic sewage which may lead to a tenfold increase in the normal flow. These peak discharges of sewage will, of course, coincide with the maximum recreational uses of the coastal waters. Furthermore the influx of tourists from many different countries will increase the diversity of pathogenic organisms in the sewage.

In addition industry is expanding in the coastal zones and producing large volumes of liquid wastes which find their way into the sea. The character of many of these wastes is changing as new substances are introduced into processes and products and new uses found for existing materials. Completely new organic chemicals with novel properties and characteristics are being synthesised and brought into large scale use. Even domestic sewage has been altered by the extensive substitution of synthetic detergents for soap. Many of these new chemicals pose additional threats to the waters into which they are discharged and their treatment and control give rise to new problems.

The liquid wastes discharged into the Mediterranean continue to increase in both volume and complexity and there is a developing situation.

1.1.2 The Effects of Coastal Pollution

Article 2 of the Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona Convention) gives the following definition:

> "Pollution" means the introduction by man, directly or indirectly, of substances or energy into the marine environment resulting in such deleterious effects as harm

> to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water and reduction of amenities

This definition is similar to those incorporated in other marine conventions and the deleterious effects may be classed in three groups (health, natural resources, and amenities) and considered very briefly.

The hazard to health arises almost entirely from the presence of pathogenic organisms which may cause infection by direct contact during bathing and other water sports or by the consumption of infected sea food. It must be remembered that the chances of infection during water sports are influenced by the time of exposure in the warm water of the Mediterranean will be much longer than in the colder waters of Northern Europe and some other parts of the world.

The sea food likely to carry pathogens is mainly shell fish which is a popular food with both the indigenous and the tourist population and is usually eaten raw. The pathogenic organisms reach the water mainly, if not entirely, through the discharge of domestic sewage and the increased mobility of large numbers of people around the world enhances the chances of the transfer and distribution of epidemic diseases between countries.

The Mediterranean is famous for the clarity and attractive appearance of its water, and this is one of the reasons for its popularity not only for bathing and water sports of all kinds but also as an amenity for those less active. Domestic sewage and some industrial wastes carry fine particles of matter in suspension which can, in quite small concentrations, seriously affect the transparency and appearance of the water.

Domestic sewage may also affect the clarity of the water indirectly by its content of plant nutrients encouraging the growth of minute free swimming algae which cloud the water. These nutrients may also promote the growth of seaweed beaches giving rise to unpleasant conditions, particularly when the plants decompose. The presence on a beach of any matter obviously of sewage origin or of discarded plastic or other materials can be unaesthetic and offensive.

Fisheries may be affected in several ways by pollution of the water. There may be acute toxic effects or, as is more common, longer term chronic consequences in which the health, growth and reproducibility of the fish may be impaired. This can result in smaller fish, reduced numbers or the virtual disappearance of the fish from a polluted zone. Interference with some stage of the food chain of fish can act indirectly but with similar consequences. Discharges which lead to blanketing of the sea bed with sediment may destroy the spawning ground of fish with damage to fishing over a much greater area than the polluted zone.

In the Mediterranean the effects of the polluting discharges tend to be confined to the coastal and inshore areas in the vicinity of the discharges. Further offshore dilution and decay reduce the concentration of most of the offensive substances to harmless levels and the transfer of pollution across international frontiers is confined largely to coastal boundaries.

1.1.3 The Consequences of Pollution

Tourism is a major commercial interest in the Mediterranean; between 1960 and 1971 the numbers of tourists increased from 24 million to 65 million annually and may now exceed even 100 million. Pollution which has an observable effect in reducing the attractiveness of the beaches and the inshore waters is likely to have an adverse effect upon the popularity of the particular locality. Any outbreak of ill health attributable to contaminated sea water, either through bathing or the consumption of sea food tends to receive widespread international publicity with adverse consequences for the area. These are matters about which international tourists are highly sensitive.

Inshore and offshore fishing are major Mediterranean industries and the average unit value of the catch is five times the average world price. Fisheries are of considerable economic and social importance in the region and the consequences of any harm resulting from pollution can be serious.

Apart from commercial interest in the control of coastal pollution there is a strong general movement to preserve the natural marine ecology of the region and to conserve endangered species, or at least to keep to a minimum and to closely limited areas any significant deterioration in the natural ecology of the Mediterranean.

The control of coastal pollution adequate to maintain satisfactory conditions throughout the Mediterranean region cannot be carried out without the expenditure of what may appear to be substantial sums of money. But the need for this expenditure is a direct consequence of our greatly increased affluence and our higher standards of living. The cost should be treated as a charge, presented for payment, against our easier and more comfortable living. It is a contra-account which is relatively insignificant compared to the expenditure, and the benefit, on the other side of the account.

1.2 THE PURPOSE OF THE GUIDE

1.2.1 The Code of Practice

The methods developed by the various Mediterranean countries to deal with coastal pollution differ in several ways. With the growth of the problem in recent years it has been realised that a co-ordinated, integrated approach is desirable for a variety of reasons, scientific, economic and political and this has led to the proposal for a Protocol, with relevant technical annexes. At the Seminar on the Control of Coastal Pollution held in Athens in July 1977 it was recommended that an advisory Code of Practice on the control of the discharge of potentially harmful substances should be prepared. The present guide is a part of this Code of Practice which will also include the following topics:

(a) Information systems for coastal control
(b) Design of collection, treatment and disposal systems
(c) Environmental impact assessments
(d) Administrative, financial and allied aspects
(e) Manpower and training

1.2.2 Potentially Harmful Substances

Harmful substances are for the purposes of control divided tentatively into two groups. The first comprises those which are toxic, persistent and accumulate in living organisms. The number of these substances is limited but the proposed recommendations in the Protocol are that discharge of these specified substances should be strictly regulated to prevent pollution. This guide is not concerned with this group of substances.

The second group comprises potentially harmful substances which are, or may be, noxious according to circumstances but whose harmfulness is reduced by dilution or natural processes and whose scope for causing damage is limited in both space and time. These potentially harmful substances should only be discharged in accordance with a legal authorisation embodying such restrictions as are necessary to protect the quality of the receiving waters.

The purpose of this guide is to provide assistance in formulating suitable authorisations for the discharge of potentially harmful substances. It covers the successive steps involved in the process and is intended to help in establishing a common, rational approach. It does not propose uniform standards or treatment but indicates a general methodology to be applied to local problems producing a solution appropriate to individual circumstances. The manual is advisory and in no way mandatory.

In compiling the manual the various authors have drawn upon the extensive literature on the subject combining it with their own specialist knowledge.

It contains little which is novel but it presents the relevant information and the underlying considerations in a form intended to provide guidance in the preparation of authorisations for potentially harmful substances as envisaged in the suggested Protocol.

1.3 METHODS OF CONTROL

1.3.1 The Main Choices

Various methods have been employed to control the discharge of polluting matter to water. The oldest is probably that involving the imposition of identical limits to all discharges, often termed "uniform emission standards". This rigid method is sometimes modified to treat the original limits as a "norm" and to supplement these with a number of permitted but fixed variations. This method is now being superseded in some countries by control based upon reference to the environmental or ambient quality levels necessary to maintain the receiving water in a fit state for its required uses. The required limits for each discharge are normally determined by the controlling authority. In some instances the control exercised has been financial, an effluent charge being imposed according to the polluting load discharged and the theoretical cost of its treatment. In its simple form this method leaves the decision as to the degree of pollution and the quality of the receiving water to be made by the discharger.

The two principal methods, uniform emission standards and environmental quality requirements, are considered in more detail below.

1.3.2 Uniform Emission Standards

Under this system limits for various constituents and characteristics are fixed and imposed upon all discharges irrespective of their volume and nature, or of the volume and use of the receiving water. The advantage of this method is its ease of application. The imposition of limits, the monitoring and the enforcement are administratively and technically simple. The staff required is small and having no discretionary powers, they are not vulnerable to political and local pressures.

Another advantage claimed for the method is that all dischargers are treated equally and for industrial dischargers there is no unfairness or distortion of commercial competitiveness arising from differences in the location of factories in the same industry. This argument is not however invoked in respect of other manufacturing costs such as water supply, transport or labour, all of which are influenced by the location of the factory. When the siting of a new factory is under consideration the cost of the effluent treatment and disposal will be ignored and the comparative economics of different sites will not be correctly evaluated.

The disadvantage of the method is that for the majority of discharges the fixed requirement is either insufficient to prevent pollution or is too stringent and involves unnecessary treatment. The requirements are either too little and ineffective or too much and waste money, and both these situations may occur with two adjoining effluents discharging into the same water. Furthermore under the widely differing social, economic and industrial conditions in the Mediterranean countries a system of this nature is impracticable.

1.3.3 Environmental Quality Requirements

The basic philosophy of this method is to control the discharges so that the quality of the sea water at any specified place is suitable for the purposes for which it is required at that place. In this way the optimum use is made of existing resources and money is spent to best advantage.

The application of the method calls for more technical information and skill than does the uniform emission standards method. The degree of precision with which the individual discharge requirements are determined will depend upon the technical facilities available but expenditure on technical resources will be offset by savings in treatment and disposal and more reliable protection of water quality. It is a more flexible system permitting the exercise of judgement according to local conditions.

Figure 1 illustrates the procedure for the control of discharges by ambient quality levels.

The first step is to define the area in geographical terms, determining its boundaries and then to decide the uses of the water in that area. Next the criteria to determine the suitability of the water for the purposes for which it will be used are selected. The criteria are then used to stipulate the quality levels necessary for the defined uses and where there is more than one use the most stringent level for each quality characteristic will be considered.

It is customary to employ two levels for each quality characteristic. One is the desirable level which would be accepted as satisfactory and requiring no further improvement, the other is a less stringent requirement regarded as the maximum tolerable limit. If this limit is exceeded the water is unfit for the use. Wherever water quality is in the grey area between the two levels the objective of attaining the lower level should always be maintained.

1.3.4 The Authorization Process

Figure 1 shows the successive steps in the issue of an authorization and its implementation.

It shows on the upper left the derivation of the environmental quality levels by consideration of the area and the local uses. The quality requirements for a specific use will be similar throughout the Mediterranean and the process of deciding upon appropriate quality levels in individual cases will be simplified if uses are classified and criteria and quality requirements attached to each use. This is indicated on the upper right of the diagram.

Recommendations have been made for the preparation of a classification of uses with relevant criteria and levels and a guide for Mediterranean purposes is to be prepared.

An example of a use/quality level is the E.coli level for bathing water which was adopted as an interim criterion at a review meeting of the WHO/UNEP Project on Coastal Water Quality Control / MED VII /.

> highly satisfactory bathing areas should show Escherichia coli counts consistently less than 100 per 100 ml and to be acceptable, bathing waters should not give counts consistently greater than 1000 E.coli per 100 ml.

This requirement for bathing water is applicable to all coastal waters throughout

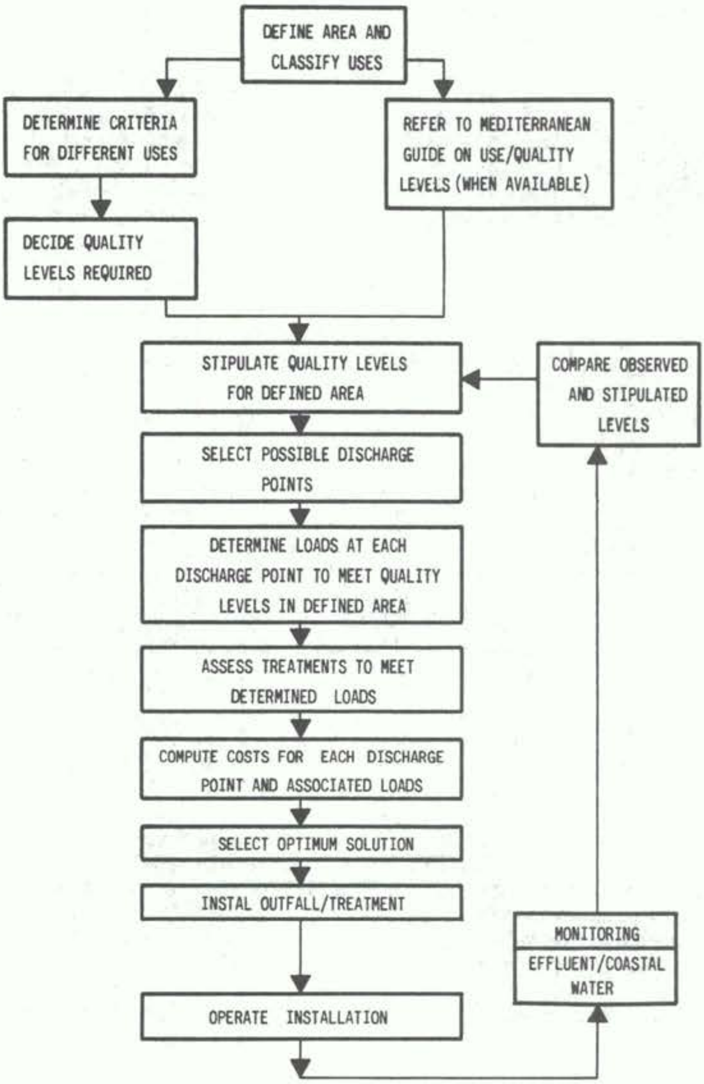

Figure 1 Diagram illustrating procedure for control of discharges by environmental quality requirements based on water use.

the Mediterranean region. It incorporates the dual "desirable/satisfactory" and "maximum tolerable" levels referred to earlier.

The next stage is to decide what conditions and restrictions must be applied to the discharge in order to achieve the required quality levels. There are two variables to be considered, the location of the discharge point and the pollution load of the effluent. In general terms the longer the pipeline the greater the acceptable pollution load, and vice versa. For a defined bathing water area there will be a seaward limit and the pipeline should discharge beyond this limit. For any given point of discharge the concentration of E.coli in the effluent must be such that the dilution, dispersion and death rate will reduce the E.coli concentration at the boundary of the bathing area to within the limits given above. The longer the pipeline the greater the distance and time of travel of the sewage to the bathing zone and the greater the dilution when it arrives there. Depending upon local physical conditions it may be possible to position the outlet so that the discharge plume does not reach the bathing zone.

It is at this stage that comprehensive information about the physical, hydrological, chemical and meteorological conditions in the area is required in order to predict the behaviour of waste water discharged at different points. As has been indicated the precision with which these assessments can be made will depend upon the extent of the information available and the experience and skill of the technical staff. The ideal is to prepare, from the data, a set of mathematical relations which will assist in predicting the way in which the discharge will travel and disperse under different conditions at different potential discharge points, and what effect it will have upon the zone of use. The acceptable load for each discharge point can be estimated and the accuracy with which this can be done will depend to a considerable extent upon the amount of data available. Existing information will probably need to be supplemented by surveys and investigations within the area. The work involved at this stage is described comprehensively in Chapter 5. Pipelines and treatment plants are expensive and expenditure on exploratory surveys is relatively small but even a limited survey can still provide valuable guidance and may result in substantial economies.

Estimates are prepared of the cost of the installation of the different pipelines and the associated treatments. These will indicate the relative costs of different solutions and be valuable in arriving at an overall optimum solution taking into consideration other aspects such as ease of operation and maintenance.

The succeeding stages are the installation of the disposal system, monitoring of the results and feedback to assist in future decision.

1.4 THE OPERATION OF A CONTROL SYSTEM

In the operation of a control system as outlined in the preceding section a number of aspects which need considering are described below.

1.4.1 The Authorization

It may be considered desirable to ask the discharger to declare which of the listed potentially harmful substances are present or likely to be present in the effluent and to authorize, up to stipulated levels, the discharge of these substances only. If the discharger wishes to include any of the other substances he has to apply for a new or additional authorization.

The authorization will give consent to the discharge of the listed substances present and stipulate the maximum concentration which may be present in the effluent. A temperature limit may be required also. The polluting effect is a function of both concentration and volume and will have been taken into account in determining the appropriate conditions of the authorization. There should therefore be one limit for the maximum daily volume and one for the maximum rate of discharge, the latter being necessary to prevent flush discharges.

The authorization should be subject to review at stated intervals, perhaps one or two years.

Experience shows that all discharges, whether of domestic or industrial origin, vary with time in their composition. The variations may be cyclical, as a result of social habits or industrial activity, or they may be random and of uncertain origin. This means that the concentration of listed harmful substances in a discharge will fluctuate about a median value and on occasion they may exceed the stipulated limit, without causing serious harm. It may therefore be desirable to indicate a required frequency of compliance with the limits as a percentage of samples which must be within the limits.

The fluctuations will not be the same for all substances, some being much more variable than others, and percentage compliance figures will be required for each substance. It is not easy to select figures without some information about the effluent and a decision may be deferred until there is a sufficient number of analyses available to permit statistical evaluation of the data to indicate suitable compliance requirements. These may be reviewed periodically as data accumulates.

1.4.2 Monitoring

The controlling authority will carry out sampling and analysis of the effluent to ensure that the discharge is within the prescribed limits, and of the seawater to confirm that the environmental quality within the defined zone meets the use requirements.

Sampling from a submerged outlet is usually impracticable. It will normally suffice if the sample is taken from the pipeline near the shore line, and when installing new pipelines it should be a requirement that facilities be provided to take representative samples by the provision of a suitable access chamber. It is also desirable that provision be made for gauging the flow, perhaps by spot checks for small discharges but for major discharges a continuous flow recorder and integrator should be installed.

If the discharge point is outside the defined use zone the monitoring of the environmental quality will be near the boundary where the maximum concentration of the effluent will be expected. Where the outlet is situated within a use zone, then the question arises of where the receiving water should be sampled and what dilution if any should be taken into consideration. If the extreme case of no dilution were to be enforced the discharge would need to be of the same quality as the use quality of the receiving water. If a dilution zone is permitted the sample will presumably be taken at a specified distance or at a point on a fixed perimeter. Within this area the environmental quality standards will not apply. The size of the zone will influence the quality of the effluent required and therefore the extent of treatment necessary. Relatively small differences in the size of permitted dilution zones may involve substantial differences in treatment costs and the maintenance of use quality for a small volume of water may be disproportionately expensive. It would be difficult to justify the existence of a dilution zone in a bathing area but it could be argued that no outlets should be permitted in such an area.

The question of permitting a dilution zone and on what scale, will of course have to be considered during the formulation of the authorization, because it influences directly the effluent load and the corresponding treatment. It is a matter of importance and is dealt with in detail in Chapter 5.

1.4.3 Enforcement

Contravention of the conditions of an authorization will render the discharger liable to prosecution. The decision whether or not to take action will depend upon the magnitude and consequences of the pollution, the difficulties facing the discharger and the vigour with which attempts are made to overcome them. Penalties for persistent transgression should be such that it is cheaper to carry out effective treatment than to continue paying the fines.

1.5 TREATMENT CONSIDERATIONS

1.5.1 Treatment For Sea Discharges

The selection of treatment methods for municipal and industrial wastes before discharge to the sea needs to be based upon the particular quality requirements and to have regard to the absorptive capacity of the sea.

All domestic sewage, or industrial wastes carrying large solids, should be screened to remove solids and floating material. An oil separator should be installed and a grit chamber to reduce the risk of blockage of the pipeline. This preliminary treatment should be regarded as the minimum for virtually all discharges.

If unsettled sewage is discharged into a zone where there are no strong currents or tidal movements the suspended matter will deposit in the vicinity of the outlet blanketing the bed and giving rise to anaerobic conditions. The bulk of the settleable matter should be removed before discharge by treatment in conventional sedimentation tanks. Settlement will also bring about a reduction in the heavy metal content of the effluent.

Proposals for the provision of secondary treatment should be thoroughly investigated and justified. The rate of dispersion and the degree of dilution in the sea is normally such that the biological oxygen demand is unlikely to cause any significant oxygen depletion. The reduction in the concentration of coliform bacteria by conventional treatment is usually about 95%, which is equivalent to the quite low dilution factor of twenty times.

The oxidation of ammonia to nitrate before discharge may have a deleterious effect because the nitrate will encourage a more rapid growth of algae near the outlet than the ammonia from which it is derived.

If further treatment is needed the use of chemical coagulants before settlement will assist in precipitating out the heavy metals and by reducing the colloidal matter present result in an effluent of greater transparency.

1.5.2 Existing, New and Altered

All new discharges require authorization but an existing discharge may be increased to a volume which warrants a reconsideration of its effect upon the receiving water or an industrial effluent may change in composition. Changes of an existing discharge should be subject to scrutiny and a new authorization issued.

When effluent control is introduced industries and municipalities already discharging into the sea may face formidable problems in meeting the requirements imposed by the new controls. Both within the factories and within the town the drainage systems may not be integrated but split up into numerous small drains discharging round the periphery or along the coast. Before any treatment can be installed or long pipelines brought into use redrainage of the factories or extensive modification to the existing sewerage system must be carried out. These are expensive and lengthy processes and when they have been completed there is often difficulty in finding land available for treatment plant.

When a new factory is built or a new urban area is developed it is relatively easy and cheap to instal an integrated drainage or sewerage system and to incorporate in the layout provision for treatment plant.

It is therefore desirable when introducing a new control system to distinguish between existing and new sources of pollution. The existing discharger should be required to prepare a plan for the redrainage and treatment or the extension or duplication of pipelines to enable the new control limits to be met, and there should be a programme and an agreed timetable for its execution and completion. Progress should be reported annually to the control authority. In the absence of such arrangements the new discharger, who is expected to comply with the controls without delay, will feel unfairly treated and resist the demands made upon him.

1.5.3 Industrial Sewages

Many of the potentially harmful substances occur mainly, and some exclusively, in industrial effluents. When these effluents are discharged directly from the factory into the sea the authorization is given to the factory and the responsibility for limiting the concentration of potentially harmful substances to comply with the authorization rests upon the factory.

It frequently happens that the factory effluent is not discharged into the sea but into the local sewerage system. This practice is to be encouraged for it has a number of advantages, for example the domestic sewage dilutes the factory waste. The authorization for the outfall of the sewerage system is given to the sewerage authority and it carries the responsibility of ensuring that the concentrations of potentially harmful substances are within the limits of the authorization. In order to do this it may be necessary to reduce the quality of certain of these substances discharged from a factory to the sewer. If the sewerage authority cannot require the factory to reduce its load it cannot meet the conditions of the authorization. It might be possible for the sewerage authority to instal special treatment for the reduction of the substance before discharge of the sewage into the sea but this is almost certain to be more expensive than reduction at source and the question of who meets the cost of any extra treatment of the sewage will have to be decided. It is essential that a sewerage authority has powers to control the volume and composition of all industrial waste discharged into its sewers. Industrial waste entering the sewers should be subject to an authorization issued by the sewerage authority.

1.5.4 Multiple Discharges

The environmental quality control system makes use of the absorptive and dilution capacity of the receiving water. The question may arise where there is a single discharge to a defined area whether the full available capacity be taken up or should a reduced load, requiring more extensive treatment before discharge, be authorized in order to reserve capacity for any future dischargers? The decision may depend upon judgement as to the likelihood of new discharges arising in the future.

If the full capacity has been taken up and a new discharger applies for authorization is it refused? Or is the capacity shared between the new and the old? This again is an aspect which should be taken into account when issuing authorizations.

1.5.5 Diminishing Returns

The cost of treatment for the removal of a specific substance from water is not directly proportional to the quantity removed because as the concentration is progressively reduced the cost of unit removal increases. An analogy is with the effort required to dig a hole or to sink a well which becomes increasingly difficult as it gets deeper. This phenomenon should be borne in mind when there are two or more discharges requiring treatment but resources and finance are limited. As a simple example if there are two similar discharges the cost of removal of 50% of the substance from each may be about the same as 75% removal from one discharge and none from the other. While in the first instance a total residue of 50% will be discharged in the second instance the residue will be 62.5%. The arithmetic may not, in practice, be so simple but the principle is of general application in the optimisation of limited resources.

A compromise solution of this nature should be regarded as a temporary measure pending the installation of treatment to meet the full environmental requirements.

1.5.6 Chlorination

For domestic sewage the fecal coliforms are probably the most useful indicator of its presence and its concentration. If the effluent is chlorinated before discharge the fecal coliform count will be reduced but the other constituents of the sewage will be little affected and the fecal coli count loses its value as an indicator of the sewage concentration in the water. It may be argued that it is preferable to rely on the natural processes of dilution and decay than the artificial process of chlorination. There is also the possibility that the chlorinated compounds formed by chlorination are themselves harmful.

1.5.7 Zero Discharge

The concept of zero discharge should not be applied to potentially harmful substances. The Mediterranean has a capacity to absorb these substances, by dilution to harmless levels, by precipitation and adsorption and by decay and decomposition. This capacity should be utilised and money should not be spent on unnecessary treatment.

Zero discharge means, in effect, below the level of analytical detection, which is not zero. During recent years instrumental methods of analysis have been developed which are extremely sensitive and can determine minute concentrations. In many instances these concentrations are well below known harmful levels and the analytical results are not alarming, but reassuring.

1.6 UTILIZATION AND CONSERVATION

1.6.1 Disposal

The objective of schemes of sewerage and treatment tends to be confined to safe disposal but consideration should always be given to other approaches and possibilities.

1.6.2 Aquatic Nutrients

Much of the Mediterranean sea is oligotrophic, that means the water is deficient in nutrients to an extent which limits the number and size of the fish. The discharge of domestic sewage containing nitrogen and phosphorus is beneficial and will improve fish production in the area. The process is not merely disposal but use and is analogous to the distribution of manure on agricultural land as a means of recycling nutrients. Care must be taken that the location of the discharge does not give rise to health hazards.

Treated sewage has been used for the cultivation of algae as a crop providing animal feeding stuff.

1.6.3 Water Re-use

In some of the Mediterranean coastal zones there is a serious shortage of water. In these regions full consideration should be given to the feasibility of treating the sewage, if necessary, to a quality suitable for use for agricultural irrigation instead of discharge to the sea. In these areas advantage may be taken of climatic conditions to use low cost treatment methods such as oxidation ponds. Re-use in this way will either extend the area of land available for agriculture or, where clean water is already used for agriculture enable an equivalent amount of that water to be diverted to potable and domestic use.

1.6.4 Industrial Recycling And Conservation

In many industries using water a careful investigation of the processes and methods will enable substantial economies in water to be made saving both water and effluent costs. It is often possible to recycle water or to use water successively in processes with less stringent quality requirements, such as the use of discarded process water for cooling.

In some industries it has proved possible to substitute dry for wet processes or to employ processes using less water. A typical example is the replacement of acid pickling by shot blasting in the iron and steel industry.

1.7 THE ORGANIZATION OF THE CONTROL OF COASTAL POLLUTION

1.7.1 The Role Of Central Government

The Mediterranean countries exhibit a wide spectrum of stages of political, social and economic development and the most appropriate form of control organisation will vary accordingly. Experience in different countries does provide, however, some general guidance. A major consideration is the extent to which the responsibilities are apportioned between central and local government.

Central government determines national policy, enacts legislation and retains overall, ultimate control. It has been found advantageous at central government level to arrange for formal consultation and liaison between the ministries concerned with the various interests in coastal pollution such as health, industry, tourism, fisheries, local affairs, navigation and marine matters.

The extent to which central government itself carries out executive duties or delegates them to local or regional authorities will be influenced by the resources and technical capabilities of the regional and local authorities. It must also be borne in mind that the municipalities will usually be responsible for sewerage and disposal. They will be dischargers and it might be deemed inappropriate for an authority to issue, and enforce, authorizations to itself.

The attached Figure 2, which supplements Figure 1, illustrates the machinery of control which may be divided into information, control and monitoring.

1.7.2 Information

Information supply covers the assembly and processing of existing information together with the collection of additional information and the accession of routine monitoring data. The evaluation of the data on which to determine the conditions to be attached to the authorization may be carried out at the information stage and passed to the control stage at which the authorization is issued.

The discharge is monitored to ascertain the extent of compliance with the authorization, and the receiving water also to confirm its quality. The monitoring consists of the collection of samples, their transport to a laboratory and analysis.

The analytical results are fed back to the control authority who is normally responsible for enforcement. The analyses will also be supplied back to the information collection stage.

At regular intervals the data will be scrutinised and at agreed intervals the conditions of the authorization reviewed. An annual report may be prepared and

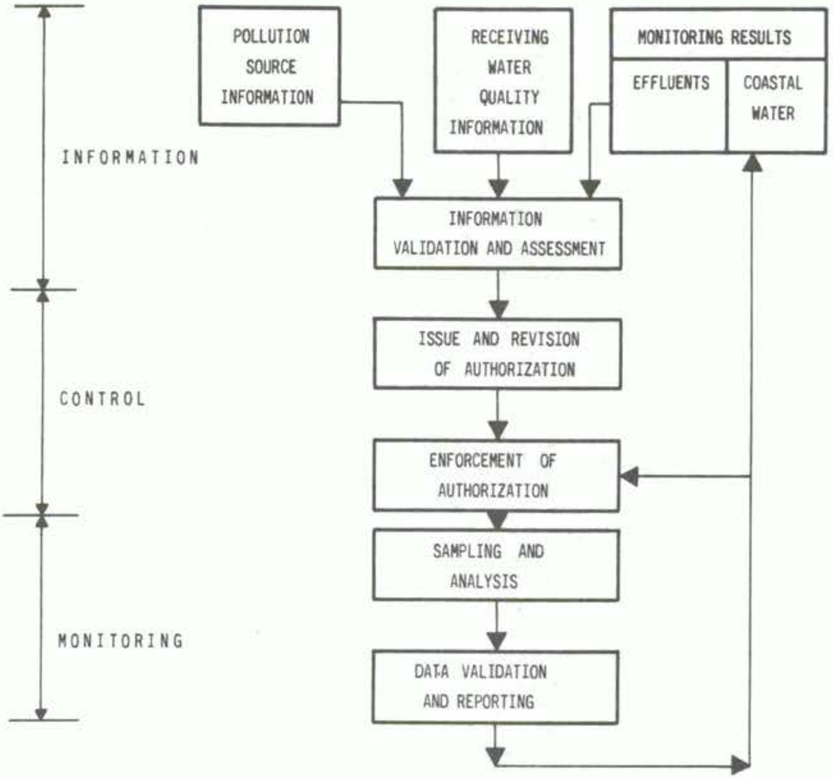

Figure 2 Diagram illustrating the executive functions of coastal pollution control.

published.

The collection and interpretation of the data is a complex operation calling for a high degree of technical skill. In some countries facilities may exist for this work to be carried out regularly. Where for example there are authorities for the management of inland waters they may have or acquire the competence to carry out this work. For many countries the data collection and evaluation may best be carried out by single specialised institutions serving the whole country.

1.7.3 Control

The issue of the authorization and its enforcement may be the responsibility of a local organization, either a suitable existing organization who might accept the additional responsibility, or an authority established for the purpose. Alternatively central government may retain authorization and enforcement powers operating either centrally or through local offices.

In many countries the most suitable form of organization may be found to be control by central government operating through regional offices with centralized analyses for most of the listed harmful substances but with bacteriological determinations carried out in existing, local laboratories. It is sometimes held that in making decisions central government will take into consideration national interests which may be overlooked by a local control body.

1.7.4 Monitoring

The frequency of monitoring may vary, for example it might be less frequent or suspended during the colder months when little or no bathing is taking place. The sampling calls for a measure of knowledge and skill but is not usually carried out by the laboratory staff.

The analysis of the listed harmful substances can be carried out satisfactorily by the older, and slower, analytical techniques. These substances can now, however, be analysed more rapidly and with less effort by instrumental methods. The equipment is costly and its use is only justified when large numbers of samples are to be analysed. If adequate transport of samples from the various sampling points can be arranged the use of a centralized laboratory with modern analytical facilities should be seriously considered. It may be a separate governmental laboratory, or it may be attached to an existing institution.

The most numerous determinations are likely to be for total and fecal coliforms which, because of the time of transport, are less suitable for centralized determination. These determinations could be carried out in a public health laboratory or the laboratory of a local hospital or the microbiology laboratory of a university, suitably extended.

1.8 THE SCOPE OF THE GUIDE

The guide is intended to provide guidance on the various technical aspects of the subject. Each chapter, prepared by one or more specialists, covers a specific topic. There follows a brief account of the field covered by each chapter and its scope.

1.8.1 The Characteristics And Composition Of The Wastes

This chapter deals with wastes containing the listed potentially harmful substances most likely to be encountered in practice. It includes seven of the metals, cyanides, fluorides, industrial inorganic phosphorus, phenols and aromatic compounds likely to taint fish and industrial nitrogenous compounds.

For each of these substances or groups it lists the industries and processes employing them and resulting in their discharge in liquid wastes. It thus gives an indication of the types of factory likely to be responsible for the presence of these substances in a receiving water and also what contaminants to look for from various industries.

For each substance there is a brief description of the industry, the types of waste it produces, the form of the wastes, the total quantities, the discharge patterns and the concentration to be expected.

All this information should prove particularly useful when discussing with industrialists the composition, characteristics and qualities of their wastes and the conditions of the authorization.

1.8.2 Characteristics Of Waste Constituents With Respect To Their Harmfulness

In the first part of this chapter the authors discuss the various characteristics of substances which cause them to be harmful, the mechanism of damage and the interaction between the substances and the marine environment.

In the second part of the chapter the toxic, bioaccumulable and other harmful effects of the potentially harmful substances are described and discussed individually.

The first chapter (see 1.8.1) described the substances likely to be discharged, the form and the concentrations. This second chapter is the logical sequence in considering the harmful effects of these substances, in quantitative terms, to assist in determining the necessary limits in the aquatic environment, to ensure its suitability for use and to avoid serious interference with the ecological balance.

1.8.3 Characteristics Of A Discharge Site And The Receiving Marine Environment

Having ascertained what substances are likely to be present in a discharge and in what concentrations and quantities, and having utilized the information to determine what concentrations are acceptable in the receiving water the next task is to relate these two. This means deciding what restrictions must be placed upon the discharge, and incorporated in the authorization, in order to ensure acceptable conditions in the receiving water. Advice on reaching a rational decision is contained in this chapter of the Guide.

The early section of the chapter is concerned with the definition of the area likely to be affected by one or more discharges and the behaviour of the discharge plumes. It then proceeds to consider the hydrographic data which is required to assess the behaviour of the discharged water in a defined area and describes in detail methods of obtaining the data. It also deals with meteorological, geological, chemical and other factors which influence the absorptive capacity of the receiving water.

It considers the location of the discharge in relation to the use of the water zones and the preparation of descriptive maps.

There follows a comprehensive account of the phenomenon of initial dilution, the various factors affecting it, their assessment and the computation and prediction of the degree of initial dilution.

The next section deals with events following the initial dilution such as dispersion, mixing and transport and refers to modelling of such phenomena.

The chapter concludes with a discussion of the chemical and biological conditions and problems in the defined discharge area.

This chapter indicates the scope of the information needed to relate a given discharge at a given place to its effects upon the receiving water.

The collection and processing of all the data described in this chapter is likely to be beyond the resources of many of the Mediterranean countries at present. This should not deter the utilization in accordance with the relevant sections of this chapter, of such data as is available or readily obtainable. The methods described can be developed progressively as more data is collected and the situation can be reassessed periodically when the authorization is reviewed.

1.8.4 Availability Of Water Treatment Technology

When the conditions of an authorization have been issued the discharger has to consider what steps he must take to enable the effluent to comply. The next chapter describes the waste treatment technology available to reduce the polluting components of the effluent.

The various (potentially harmful) substances and groups of substances are each dealt with individually with the exception of the less common elements which are considered together.

For each of these substances the chemistry underlying the treatment processes available is described together with their application in terms of chemical engineering processes. The employment of biological treatment both for industrial wastes and domestic sewage is also included as is disinfection for the reduction of pathogens. There is a section on the cooling of warm discharges when these give rise to thermal pollution and not to thermal enrichment.

This chapter will be of value not only to the discharger but also to those responsible for the formulation of authorizations in providing them with information on the feasibility, and difficulties, of complying with proposed limits.

1.8.5 Potential Impairment Of Marine Ecosystems

The last chapter considers the harmful effects of coastal and marine pollution. It refers to the potential effects upon human health and upon the aesthetics of the coast and the sea. It also refers to the longer term consequences of interference with marine ecosystems and resources and warns against increasing threats to the system. This chapter in effect summarises the objectives of the Mediterranean Project.

PART B. Technical and Practical Aspects Governing the Issue of Authorizations for the Discharge of Wastes containing Harmful Substances

CHAPTER 2

Introduction

It is opportune to draw attention to the fact that the interest of this Guide lies not so much in the novelty of the information it provides, as in its particular design, which has purposes of an applicative and administrative character.

In fact, the information presented, available in the abundant technical literature, is concerned with the characterization of contaminating discharges, the destination of contaminants in the sea and their effects on the various uses.

It was considered useful to prepare a report on "Principles and Guidelines" because the direct utilization of the abundant technical literature, for the derivation of criteria that can be responsibly adopted by authorities in considering the granting, or otherwise, of authorization to discharge wastes to the marine environment, is neither immediate nor easy.

A re-elaboration of the extensive material available from this point of view and a presentation favouring as far as possible its use for the purposes indicated, automatically implies the explicit formulation of certain hypotheses with regard to standards.

These purposes, as also the whole of the abundant material concerning marine pollution, may be called into question. It may be alleged, for example, that the purposes of the report have no real justification, in that the typical scheme of the criteria, on the basis of which a decision concerning such an authorization can be made in a proper manner, consists of the exact definition of the qualitative and quantitative characteristics of the discharges, their precise evolution in relation to the phenomena of dilution, transport, transformation, accumulation, etc. that occur in the marine environment, of the precise evaluation, parameter by parameter, of the effects on the various organisms and on the ecosystem, naturally taking into account, synergistic effects and finally, of the prospects of evolution with time (of the contaminating load, on the one hand, and, on the other, of the natural environment itself).

Although such a scheme is certainly an ideal model at which the various standards should aim, it is fairly generally recognized that this level of perfection in the prediction of the effects of contaminating discharges is at present considerably beyond not only the administrative possibilities of most of the countries concerned, but also of the effective level of knowledge available on the subject.

While all those studies which serve to bridge the gaps of knowledge should obviously be encouraged, it should also be acknowledged that certain impediments to achieving perfection should not discourage, or obstruct, the adoption of prediction models of an approximate character. These models, which are more or less accurate but in any case err on the side of safety, take into account in some manner (that is, according to what is known, has been tested in practice and, also is possible and feasible from the administrative point of view, as has been demonstrated by the experience of a number of other Mediterranean countries which have developed this aspect in a rational way) the indicated relations of cause and effect. In this case the result achieved will be based on a modicum of rationality instead of being left to chance, as is the case when standards are adopted in which none of the aspects listed in this Guide are taken into account.

In this respect, it can also be pointed out that the search for an immediate and perfect solution has proved more of a brake than an encouragement to a careful policy of sanitation of the coastal waters. For example, the acknowledged difficulty of preparing a system of standards has given rise - admittedly only in an isolated case - to the formulation of discharge criteria (non-criteria) which, considering only the quality of the effluents, completely ignore the terms of the problem, with the result that the pollution caused by a certain contaminating discharge in a certain sea zone evades every form of control.

The criteria that govern the authorization of a discharge, that is the methods by which the capacity of a certain sea zone to receive a certain discharge without negative effects can be judged in a adequately systematic manner, must necessarily take into account the aspects indicated in this guide, even though their exact evaluation is not at present possible. This, then, is the fundamental principle that has determined the preparation and presentation of the various aspects dealt with in the chapters of this report.

This realistic approach, apart from being implicit in the decisions which led to the preparation of the report, has, in practice, been adopted by numerous countries in and outside the Mediterranean Basin. It is strongly favoured today and, one could say, justified by the fundamental distinction made between the various categories of contaminants (*).

Such a distinction is fundamental to any proposal concerning the criteria that can govern the authorization of a discharge and reflects the ample technical literature and the administrative practice of the countries most advanced in this sector.

For a graphic synthesis of these preliminary considerations, one can refer to Fig. 3, in which three curves A, B, and C, are shown.

(*) The various categories of contaminants are divided tentatively into two groups:

Group I. Substances, families or groups of substances which are toxic, persistent and accumulate in living organisms and for which intervention at source is necessary in all cases; this Guide is not concerned with this group of substances.

Group II. Substances , families or groups of substances which are generally less toxic or are more readily rendered harmless by natural processes and therefore normally affect only limited coastal areas. These potentially harmful substances should only be discharged in accordance with a legal authorization embodying such restrictions as are necessary to protect the quality of the receiving waters.

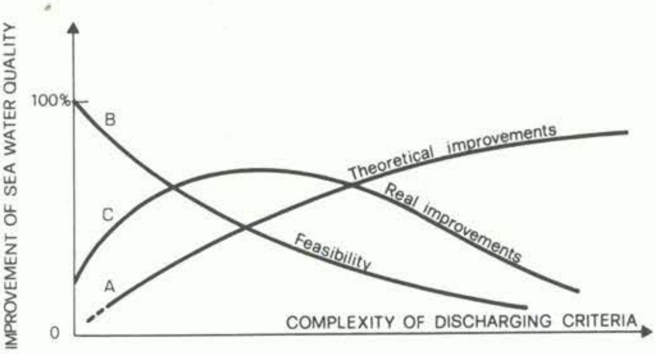

Figure 3 Schematic representation of the efficiency and applicability of a more or less complex system of standards for the control of pollution in coastal waters.

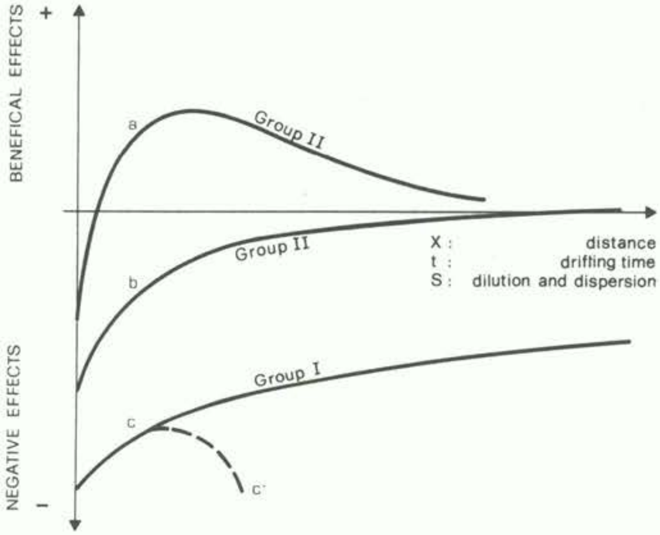

Figure 4 Indicative and schematic representation of phenomena of marine pollution caused by the discharge of wastes containing substances of Groups I and II.

The degree to which a certain system of regulation adopted by a country intends to take into consideration the various aspects contemplated in this report, for the purposes of sanitation of the coastal waters, appears in the abscissa.

The environmental benefit theoretically achieved (Curve A), and (Curve B) the practical possibility and probability that the standard criteria have a practical effect appear in the ordinate as percentages.

Curve C represents the real benefit and derives, so to speak, from the product of Curve A and Curve B; in other words, the Curve C indicates the real environmental benefit achieved in relation to the complexity, adequacy and ambition of the standard criteria, as well as to the probability that such criteria can be applied.

As can be seen, there exists a situation, that of compromise between the feasible and the perfect, in which the best results are to be expected (this is near the highest point of the Curve C).

Whereas a system of regulation that is extremely ambitious and complex would in theory promise great benefits in terms of the quality of the environment, the great improbability that this system of standards will be carried into effect reduces its real effect practically to zero.

On the other hand, a simple system of standards is extremely easy to apply. The separation of cause from effect, however, makes the benefit, often achieved at the cost of great waste of resources, very modest.

In cases where these extreme conditions have been expressed by corresponding systems of standards, they have proved to be unsuitable for the purpose.

Another graph (Fig. 4) illustrates in an indicative manner the methods of action of the various contaminants of Group I and II and consequently justifies certain hypotheses regarding standards that permit a simplification of the problem, favouring the achievement of those "compromise" solutions which, as has been said, adapt the requirements of an adequate protection of the environment to what is presently feasible from the administrative and cognitive point of view.

Fig. 4 is inspired by a graph proposed by Foin for the purpose of illustrating certain distinctions between one type of marine pollution and another and, thus, between one type of system of standards that can be proposed and another, and also, naturally between one type of suitable technical solution and another.

The interval between the time of the discharge and the moment of observation, or the distance of the place examined from the discharge point, or the degree of dilution (and possibly of assimilation and transformation) of the substances discharged is indicated in the abscissa. The three parameters are of course related to each other by laws that vary from case to case but usually in the sense that the average ratio of dilution and the average rate of assimilation and transformation achieved increase with increasing distance from the discharge point and drift time.

In the ordinate, the upper part (+) indicates the field in which a certain discharge has a beneficial effect with regard to certain uses; the lower field (-) indicates when the effect of a discharge on the marine environment is harmful.

Curves "a" and "b" refer to the substances of Group II, while curve "c" refers to the substances of Group I. As can be seen, curve "c" reveals a minimum value (that is, a maximum of harmful effect) in exact correspondence with the discharge point, where the concentrations are effectively greatest and the harmful consequences more probable.

Even in the case of the contaminants of Group I, the progressive dilution with movement away from the place of discharge brings about a reduction of the polluting concentrations and thus, in general, a diminution of the harmful effects. The curve climbs very slowly to signify the small benefit achieved even by efficient dispersion systems with regard to certain substances such as cadmium, mercury, pesticides and the persistent hydrocarbons, because generally, and as a result of the persistant nature and the large scale of action of these contaminants, the benefit achieved in a local environment and in terms of reduced concentrations in the coastal waters, represents, above all in the Mediterranean, only a partial and inadequate solution. The control of such forms of pollution requires drastic intervention at source, whether by controlling the quantities produced or by providing really efficient purification treatment.

The dotted curve c' correctly illustrates the harmful effects of substances which are subject to accumulation (in sediments or organisms) possible even at a considerable distance from the discharge point. Thus, instead of an at least partial recovery of the quality of the environment, there may be a deterioration where there is accumulation or in relation to certain uses (mussel cultivation, fishing).

To anticipate what will be discussed more fully later on in the report, the characteristics indicated above render manifestly uncertain, or at any rate inadequate, a form of control that seeks to protect the marine environment by imposing limits on the concentrations of such substances in the sea closest to the discharge.

Naturally this does not mean that, by virtue of its inadequacy, this form of control should be completely ignored. It means, however, that the criteria given in the chapters of this Report (concerned with the disposal of substances of Group II) do not lend themselves to application to the substances of Group I, for which an intervention at source is always necessary.

It should be made clear that in any case phenomena of accumulation cannot be hypothesized in the dissolved phase. In the course of a progressive mixing with less polluted waters, accumulation cannot occur in any way in this phase. This is of considerable importance in that it might be thought that in certain unfavourable current conditions, the contaminants may concentrate instead of diluting. Anticipating what is explained more fully in Chapter 5, it is possible to ensure that the effect of subsequent dilution cannot ever lead to an increase in concentration after the initial dilution.

This means that when a certain contaminant in the dissolved phase has a concentration below a certain limit considered acceptable in the proximity of the discharge point it will not be able, as a result of a hypothetical concentration and accumulation, to appear in other places in a greater concentration.

Considering now the curves "a" and "b" referring to the contaminating substances of Group II, it is to be observed first of all that the behaviour of the discharges, under the aspect of the pollution induced in the marine environment, is in its turn sub divided into two different hypotheses, to which the two curves "a" and "b" refer.

The curve "a" relates to a category of substances that often cause pollution prevalently associated with urban discharges and run-off from agricultural land. These are nutrient and organic substances that, where they are present in high concentrations that are destined to persist for a long time (in relation to the slow exchange of the water masses affected by the discharge) may give rise primary, and above all secondary, organic pollution. These are phenomena of considerable gravity not only for the aquatic life - in relation to the phenomena of dystrophy and, worse, of anoxia that may be produced - but also with regard to the aesthetic qualities of the coastal waters and thus to tourism and to the well-being of the coastal populations more directly concerned by the phenomena.

However, where these substances are adequately dispersed in an environment naturally poor in these substances, which is the case of large parts of the Mediterranean basin, they can have a beneficial effect on primary productivity and thus on fishing activities. In this way it is possible for discharge methods which take into account the characteristics of the receiving waters, to convert phenomena of pollution attributable to these substances into beneficial results for fishing activities, without in any appreciable manner reducing the transparency of the coastal waters and, thus, the quality of the same from the point of view of recreational activities.

A similar argument, with appropriate reservations, may be considered valid for other types of pollution such as thermal pollution.

Many of the substances of Group II give rise to phenomena of pollution that can be indicatively illustrated by the curve "b". These are substances which have a harmful effect on the marine environment, but which are less harmful than the substances of Group I, or else they are rendered harmless more quickly by the natural processes of dilution and self-purification, and therefore affect coastal zones which are generally smaller.

The curve "b" in fact runs above the curve "c", and tends to zero in relatively shorter times, thus indicating the reduced scale and harmfulness of these substances. The essential characteristics of these substances determine the choice of criteria that may be adopted for the control of the pollution they produce. In fact, with regard to the substance of Group II represented by the curve "b", it is generally considered opportune to exercise a systematic control at source to limit the total quantity discharged. It is in fact considered desirable, whatever the conditions of discharge, to reduce the quantity discharged (with reference particularly to the number of product units, the type of industry and the average contribution per inhabitant).

At the same time, the substances for which intervention at source is necessary represented by the curve "b" can be controlled, as far as their final effect on the marine environment is concerned, by limiting the relative concentrations at pre-established points (for example, for the sake of simplicity and for precautionary reasons, near the most heavily polluted point, that is, the point of discharge).

While leaving each government free to decide on the technical methods of intervention and even on the types of standard to adopt, it can be said that, where the substances now under consideration (curve "b") are concerned, a certain maximum concentration in proximity to the discharge point should be proposed as an essential objective. This position, apart from being directly precautionary with regard to aquatic life, has the further advantage of being more acceptable to the various countries that border the Mediterranean Sea. In fact, whereas sub-division of the pollution load discharged into the Mediterranean by the various countries would be difficult and uncertain, it is in the direct interest of these countries to maintain a coastal water quality adequate for health protection and social and tourist activities.

An important contribution of the Assessment component of the Mediterranean Action Plan consists of giving an authoritative and founded justification to this sub-division of contaminating substances and correlative effects. It can in fact be affirmed that, with particular reference to the substances of Group II, a sufficient guarantee for the maintenance of the Mediterranean waters in a satisfactory condition would be constituted by the maintenance in that condition of the coastal waters directly affected by the discharges, and thus potentially the most polluted.

If one thinks of the wide differences of opinion - sometimes not supported by experimental data - that have so far characterized the subject of the pollution of the Mediterranean, with the consequent dispersion of effort and the poor results that have on occasions been obtained, one can fully appreciate the usefulness of the systematic and homogeneous work of surveying the real situation carried out within the context of the "Assessment" programme.

On these bases, important not only for what is new about them, but also for the systematic operation of scientific screening organized by various experts and, thus, the considerable authority with which the programme is endowed, it becomes effectively possible to make certain distinctions and simplifications (indispensable in this complex field of intervention) which serve to bring into being mechanisms of pollution that permit a real defence of the Mediterranean waters, concentrating the effort on the graver aspects of pollution as documented and, above all, using rational methods.

The credibility of the justified warnings, that placed the various governments on their guard against the immediate consequences of the grave deterioration of large coastal zones and of the no less grave prospects of an extension of this state of pollution (mainly in relation to the substances of Group I), was in some cases compromised by statements of a pessimistic or optimistic character, which may have disorientated the authorities as to the scale and necessity of the remedies to be adopted.

In the conditions of greater objectivity that exist today in consequence of the development of the "Assessment" programme, it is considered possible to put forward, with good prospects of their being applied, a series of principles and guidelines which, together with the distinctions to be established rationally for Groups I and II, can affectively be introduced into the various systems of regulation prepared by the various governments. There is comfort in the knowledge that numerous systems of regulation (e.g. those of Yugoslavia, Israel, France, Spain, and other countries) have for some time been moving in this direction, in perfect agreement with the principal international organizations (UNEP, WHO, ECE, ...).

Reverting to the discussion concerning curve "b" of Fig. 4, it will perhaps be useful to point out that this expression does not refer solely to the various substances of Group II of typical industrial origin, but also to certain typical components of urban sewage, with regard to the discharge of which a systematic control would thus be opportune. The substances in question are, for example, macroscopic solids, floating substances, a certain part of the suspended solids the limitation of which is generally considered opportune in nearly all discharge conditions.

To these correspond, on the other curve, other substances typical of urban sewage, such as nutrients, biodegradable organic substance expressed as BOD, pathogenic organisms, with regard to which an indescriminate limitation at source is senseless, in that any limitation should be conditioned by the particular circumstances of the discharge, and may be considered opportune in some cases and not in others.

It would be preferable to adopt a system of regulation which related to the quality of the receiving water.

In the course of these introductory remarks it is also considered opportune to point out that the treatment of the subject has been extended to all liquid discharges that may contain, even in relatively small quantities, the various substances of Group II. In fact a fundamental distinction between the various types of contaminating discharge is now fairly uniformly accepted, that is, the discharges have been subjected to a first sub-division as follows:

A) substances of Group I, with regard to which it is proposed that there be a rigorous control at source to the point of their complete elimination;

B) substances of Group II, with regard to which it is proposed that in each case an examination should be made of the acceptability of the discharge, in relation to the total quantities discharged, the characteristics of the sea zone receiving such discharges, the presence of other discharges, etc.

C) wastewaters of domestic origin or effectively similar, which can be subjected to criteria of acceptability of a fairly general character, provided that, by respecting certain standards of quality in the receiving waters, the local conditions are taken into account.

The main objective of these Principles and Guidelines should consist of the development and presentation of criteria useful for assessing the advisability in each individual case of granting or not granting authorization for the discharge of substances to be listed in Group II. This is the case of discharges of a prevalently non-domestic nature, though some of the substances of Group II could be related to typical aspects of domestic pollution too (presence of pathogenic organisms, inorganic phosphoric compounds, etc.). The treatment together of domestic sewage and wastes of industrial origin initially containing for example relatively high concentrations of heavy metals, cyanides, etc. could give rise to a certain confusion of ideas with regard to:

a) scale of action;
b) type of harmful effects;
c) criteria desirable for regulation and control.

Under these aspects, in fact, industrial discharges and other discharges to be listed in Group II and domestic or similar discharges differ.

It was deemed possible to solve this problem in a satisfactory manner by proposing, later in the report (see Chapter 5), a number of criteria serving to distinguish between typical domestic discharges (and others comparable to them) and discharges not comparable to typical domestic discharges. With regard to the domestic discharges there are then outlined a number of criteria of a general character based mainly on the existing standards, as well as on suggestions that emerged in the course of a meeting recently organized by WHO and UNEP(*).

It appeared opportune to draw the distinction between discharges of domestic origin. In the absence of an agreed criterion of distinction, it would be possible to consider all urban discharges as domestic or, conversely, to assume that discharges of a domestic nature do not exist.

Another question about which it is opportune to give some explanation concerns the possibility of making use within the Mediterranean Basin of experience and criteria derived and tested outside it.

On the one hand, any extension of formulae, criteria or solutions should obviously be carried out with care (one can call to mind the poor results obtained when an attempt was made to apply solutions and criteria generally considered suitable for rivers to the problems of the sea), whilst on the other hand it can be admitted that the various experiments and the numerous studies carried out in non-Mediterranean countries could be useful for the purposes of this report and for the sanitation of the coastal waters of the Mediterranean.

(*) WHO/UNEP Workshop on Coastal Water Pollution Control (Athens 27/6 - 1/7/77) and other organizations.

Mention can be made of factors of a general character, particularly of the efficiency of the various methods of wastewater treatment in removing contaminating substances (also bearing in mind the greater or lesser degree of efficiency of the personnel responsible for these processes). Even toxicity tests on particular marine organisms using sea water are not without significance with regard to the use of such data in other seas. The formulae governing the processes of initial dilution are the same in the ocean, in the North Sea and in the Mediterranean. In each particular case the result of the application of these formulae is determined by the different water densities (and in particular the different density gradients) and the local current conditions.

The methodology for the evaluation of phenomena of bacterial disappearance, for the simulation of dispersion phenomena using tracers, etc. though largely developed outside the Mediterranean are fully applicable in the Mediterranean area as also is the definition of "Broad scale dispersion models".

In short, a certain methodological approach to the control of coastal pollution (caused by substances to be listed in Group II) may be considered substantially valid, irrespective of the exact geographical locality in which it was developed. The purpose is in fact that of restoring or maintaining satisfactory environmental conditions even in proximity to the most heavily polluted point - in relation to the protection of aquatic life - or in relation to the hygienic conditions (e.g. for bathing, mussel cultivation) in nearby zones susceptible to pollution.

Thus, when the "scale" of the pollution phenomena is of the order of a few hundred metres or, at the most, a few km, whether the basin measures 1000 or 10,000 kg is immaterial.

In any case various motives of differentiation should be brought into evidence, with regard to criteria and practices concerning the disposal of wastewaters in the Mediterranean, compared with other seas, always bearing in mind, however, that a distinction between a situation in the Mediterranean and situations outside the Mediterranean is not scientifically acceptable for it would suggest that the Mediterranean basin has characteristics so homogeneous that in very point the same techniques would always be appropriate for a particular discharge. It can be affirmed, instead, that the differences of physiographical characteristics between two localities even only a few kilometers apart on the same stretch of Mediterranean coast may be greater than the differences between either and other localities on other sea coasts (North Sea, the oceans).

It seems opportune to make this point since, the enclosed form of the Mediterranean basin, has caused it to be inappropriately compared to a lake which, as far as discharge criteria and the consequent sanitation interventions are concerned, could be considered as a homogeneous whole.

Indications can be given of a number of salient characteristics that in general distinguish the Mediterranean coastal environment from analogous ocean environments.

Heavy metal concentrations in Mediterranean water and sediments are generally greater than in the ocean for natural reasons, even in uncontaminated areas. The same is also true with regard to certain marine organisms. Thus, the threshold levels determining a state of pollution, may not be the same as those appertaining to uncontaminated ocean waters.

This consideration is relevant with regard also to the definition of the maximum tolerable limits of certain substances to be listed in Group II, e.g. lead and chromium in the waters immediately surrounding the discharge point (that is, after the initial dilution).

This acceptability threshold may be established by dividing a certain characteristic value derived from short-term toxicity tests by an application factor.

For the sake of precision it could be proposed that this criterion be adopted when the resultant value is lower than the one indicated by experiments relating to chronic toxicity effects or effects on the behaviour of organisms. This, of course, is in order to be on the safe side.

It may be that the concentration expressed by acute toxicity tests divided by the application factor gives a lower value that the typical concentration in sea water. In this case the indication is to be considered to be without significance, in that, in order to achieve the relative objective, it would be necessary to dilute the sea water with discharge water.

A significant characteristic of the Mediterranean waters - with the exception of bays, port zones, coastal strips characterized by poor water exchange (sometimes due to the existence of constructions like breakwaters and groynes designed to reduce beach erosion), shallow waters, inflows of river water loaded with nutrients - is the great transparency of the waters and their light blue colour. These characteristics derive mainly from the scarcity of nutrients and from a limited primary production, although the latter is considerable in relation to the scarcity of nutrients.

The high degree of transparency, already compromised in numerous localities by domestic and industrial discharges or by inadequate forms of treatment and disposal of the same, is one of the main tourist attractions and thus one of the main economic assets of the Mediterranean countries. Another asset is the favourable social consequences of a healthy and agreeable environment.

The methods of treatment, re-use and disposal of wastewaters in a manner that does not bring about any appreciable alteration of the above characteristics thus acquire a greater importance than elsewhere.

Particular care must thus be taken to avoid the occurrence of eutrophication or significant replenishment in waters used for recreational purposes. Greater attention must be dedicated to the advisability of removing a certain part of the suspended solids and floating substances than is the case with other seas, which are generally more turbid and thus less sensitive to the harmful effects of an aesthetic nature mentioned above.

The shortage of water, typical of many zones of the Mediterranean basin, would make the re-use of water particularly advisable (e.g. for agricultural irrigation). Where this possibility is impeded by factors of an economic agronomic or hygienic character other forms of re-use of suitably treated sewage could be considered e.g. these nutrients could be transported to sea zones where, in view of their relative scarcity, they would have a beneficial effect.

The Mediterranean waters are also characterized by a high rate of disappearance of coliforms. These are well-known indicator organisms and there is some debate as to the measure in which their disappearance, as a result of phenomena of natural or artificial purification, reflects that of the various pathogenic bacteria. However, a good measure of agreement has been reached that, even in Mediterranean waters, a sufficiently low concentration of faecal coliforms (e.g. less than 100 faecal coliforms/100 cc in 80% or 90% of the samples) could provide a satisfactory protection against hypothetical infective risks associated with bathing.

In fact, despite its well-known limitations, this parameter (colimetric) has proved suitable for the protection of drinking waters and also, it would appear, for the consumption of shell-fish.

To complete the picture, it should be mentioned that it has been claimed that in the Mediterranean the coliform bacteria do not diminish in number in the sea water but simply are diluted. However, these are isolated claims and are neither justified by the majority of authors, nor confirmed by simple experimental surveys. On the other hand, the rapid disappearance of coliforms may give rise to incorrect evaluations concerning purification phenomena of another type occuring at the same time as bacterial disappearance. In other words, in comparison with other coastal waters (North Sea, coast of California), the same colimetric limit in the coastal waters may permit the use of shorter pipelines, and thus give rise to less developed phenomena of dilution, dispersion and transformation of other contaminants.

For this reason it may be justifiable in the case of Mediterranean waters to establish relatively low colimetric standards, possibly accompanied by a standard for a minimum total dilution in proximity to the beaches.

Since these objectives are feasible from the engineering point of view, it would appear reasonable to take them into consideration wherever it is economically possible. This would be prudent and, in any case, would favour the improvement of the quality of the coastal waters, for example, for the disposal of organic loads and as regards eutrophication.

An element that favours more stringent colimetric standards, at least with regard to the waters used for mussel cultivation, is the unfortunately high level of infective diseases in many coastal zones of the Mediterranean.

Thus the pathogenic organism coliform ratio grows and, in consequence, the health risk remaining unchanged, the microbiological limit considered adequate for protection of the quality of shell-fish should be lowered. The considerations set forth above are supported by the fact that the Mediterranean coasts are the destination of a considerable tourist influx coming, in part, from countries in which the frequency of water-transmissible diseases may be much lower.

It is appropriate to point out that, even though the extension of microbiological pollution is characterized by its small scale (at the most a few kilometers from the major sources), episodes that give evidence of unhygienic conditions in the coastal zones of a country reflect a widespread discredit on the tourist attractions of other zones of the same country, or of other countries of the Mediterranean basin.

For this reason, even though pathogenic organism pollution is not the most serious form of pollution in Mediterranean waters, and is not a type of pollution of irreversible character, it is attributed a notable importance in the context of this report (Chapter 7).

As regards the control of pollution from urban discharges, this parameter will thus remain a key one, although related aspects should also be taken into account, in particular, the toxicity of sewage in relation to the possible industrial contributions or to chlorination processes (carried out to reduce the bacterial and, in some measure, the virus load).

If it is borne in mind that for every ton of chlorine produced, about 250 grams of mercury are released into the marine environment, and that the most serious phenomena of mercury pollution frequently occur in proximity to the pipelines of factories producing chlorine, the importance attributed by this report to the control of microbiological pollution in all its many aspects and consequence will be seen to be justified.

Another element differentiating hydrographic situations recurring frequently in the Mediterranean from those found in other coastal zones (North Sea, coast of California, etc.) is that the coastal currents are less influenced by the tides and are usually subject to frequent changes of direction and intensity. This fact is of no particular significance in terms of its consequences. Faster currents, on the one hand, give rise to greater initial dilution (since, diffuser lengths being equal, greater volumes of dilution water are available) but on the other, to a quicker return to the shore of the substances discharged, thus allowing less time for the phenomena of absorption or disappearance of the substances in question (this is of particular relevance to the control of microbiological pollution).

In general it can be said that in the Mediterranean a precise knowledge of the hydrographic characteristics will call for particularly accurate surveys and, where possible, correlation with anemometric data rather than with the tides (without, however, leaving the tides or other possible factors out of consideration).

The persistent hydrocarbons do not fall within the scope of this report and are to be listed, presumably, in Group I. However, "crude oils and hydrocarbons of petroleum origin" different from those to be listed in Group I are included in Group II.

Although for this class of oils and hydrocarbons, more easily degradable and of more modest toxic effect, the possibility of long-term damage to the Mediterranean ecosystem is to be considered less serious than in the case of the substances of Group I, the presence of considerably variable currents, in some circumstances running towards the shore has induced the author to treat the subject for the time being only in relation to the characteristics of the effluent, since at least under the aesthetic aspect, the control of this form of pollution from discharges coming from the land takes little advantage of the processes of dilution and assimilation which may, on the other hand, be of considerable importance for other substances.

Long before the problem of pollution became public domain, prevention of pollution of the sea from the discharge of effluents containing radioisotopes was recognized as an important problem. In fact already in 1958 the UN Conference on the Law of the Sea adopted a Convention of the High Seas, art. 25 of which provides that every state shall take measures to prevent pollution of the seas from the dumping of radioactive wastes, taking into account any standards and regulations which may be formulated by the competent international organizations. From that time the International Atomic Energy Agency (IAEA), Vienna, has called on several panels of experts to formulate principles and guide-lines for establishing limits for the release of radioactive materials into the environment and especially into the sea, (1 - 6).

The basic objectives of radiation protection are the prevention of the occurrence of acute effects and the limitation of the probability of later somatic and genetic effects to levels deemed to be acceptable, (4).

The effects of radiation exposure on man are based on the recommendations of the International Commission of Radiological Protection, (7). The ICRP which has been operating since 1928, periodically reviews new evidence and revises, if necessary, previous recommendations.

Radiation effects on marine organisms and ecosystems have been reviewed by the IAEA panels on Effects of Ionizing Radiation on Aquatic Organism and Ecosystems, (6), and by the panel on the Radiation Effects on Population Dynamics in Ecosystems, (5).

These recommendations are used as guidelines for the assessment of the safety of the proposed radioactive waste disposal into the marine development.

Practically without exception these guidelines and criteria have been used by national authorities to elaborate legislation for the issuing of authorizations for the discharge of wastes containing radioisotopes into the environment including the coastal waters. The authorization for release is based on an environmental impact statement for each nuclear installation. This document contains data on background levels of radioactivity in the environment and also estimates the radiation dose to the public that results from normal plant operation.

Legislation based on ICRP recommendations is in force in France, Italy, Yugoslavia, Spain, Israel, Greece and in other Mediterranean countries.

The present Guide is aimed at delineating principles and guidelines for establishing criteria for an authorization of discharge of wastes containing various substances into the Mediterranean from land-based sources.

For each substance the work encompasses the major possible land-based source. Such sources are industries, municipalities, agriculture and natural runoff and drainage. The description of the various potential sources is given regardless of the actual potential harmfulness to the marine environment or to the present conditions of the Mediterranean. For long-term planning it should be assumed that the industrial development of Mediterranean countries may result in establishing new industries which do not necessarily exist at present and which might affect the Mediterranean by direct or indirect discharge (through streams and estuaries). It should be noted that a certain substance of Group II can appear in a multitude of wastes in different chemical forms which in turn might have different effects on the marine environment.

Each substance of Group II, according to the various potential dischargers (sources), is dealt with according to a list of a factors. Thus the various sources and pollutants are characterized and analyzed according to factors ranging from their composition, mode of discharge, potential harmfulness, discharge site consideration, possible treatment methodology and their final impact on the marine ecosystem and its beneficial uses.

The matrix of substances, sources and factors affecting their discharge is schematically illustrated in Figure 5 as a three dimensional axial pattern.

The text of this Guide and the system fit the abovementioned matrix; it is divided into five chapters according to the groups of factors.

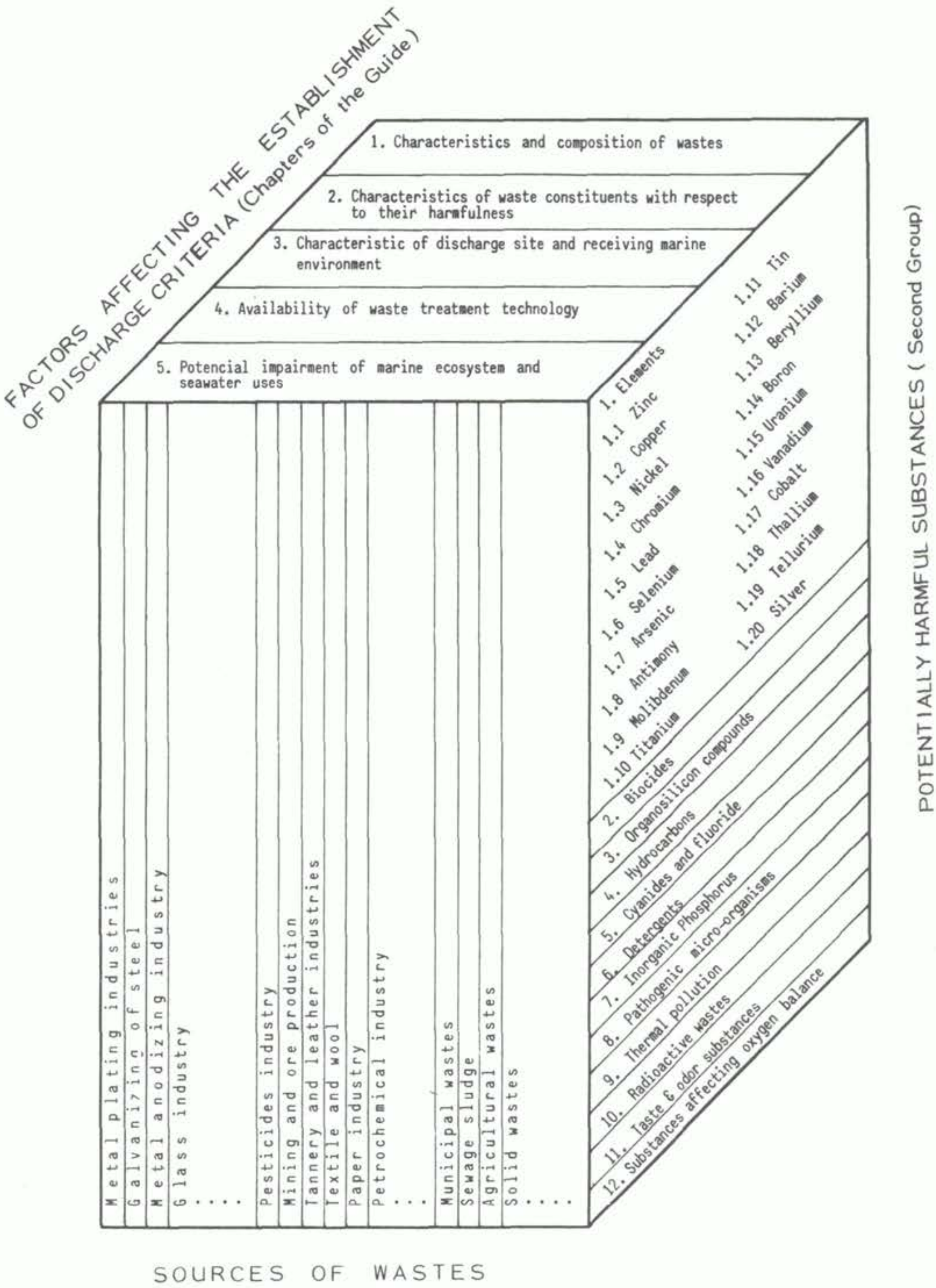

Figure 5 Schematic structure of discharge authorization guideline.

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CHAPTER 3

Characteristics and Composition of the Wastes

3.1 INTRODUCTION

Characteristics and composition of the wastes containing elements and substances of Group II are given in this Chapter according to the various sources such as industrial wastes, municipal wastes as well as some reference to agricultural wastes and natural runoff and drainage.

For each source of waste the detailed description of amounts, form of wastes and concentration are given.

The sources are not listed in any order of importance regarding their actual effect on a given marine environment (in this case the Mediterranean) nor with any regard to their presence or magnitude in a given country. It merely indicates the inventory of possible sources of substances of Group II, an inventory which will hopefully be useful to the various authorization procedures for such sources (dischargers).

It should be further noted that with the recent advancements in analytical equipment and procedures, which have resulted in increasing detection in resolution of chemical substances, most substances of Group II can be found in municipal sewage and even in natural runoff and drainage waters, although their concentration will be quite small. Therefore, only major contributors of substances of Group II have been analyzed in this Chapter. Due to the rapid increase in technological advancement, diversity and sophistication by industry, it was hard to encompass the multitude of new processes which might emit substances of Group II of which the exact composition of the wastes is not known to the authors at this stage. For example, large pharmaceutical industries emit almost any substance in various concentrations, at various times, still they are not classified as "classical" producers of a given wastewater containing a given substance.

Table I summarizes the various major sources which produce in their wastes substances of Group II but this table does not attempt to encompass all sources and all substances.

TABLE 1. MAJOR SOURCES OF ELEMENTS AND SUBSTANCES OF GROUP II

SOURCES OF WASTE \ POLLUTANT	Zn	Cu	Ni	Cr	Pb	Se	As	Sb	Mo	Ti	Sn	Ba	Be	B	U	V	Co	Tl	Te	Ag	Biocides	Si-org	Hydrocarbons	CN^-	F^-	detergents a AN	detergents b CAT	detergents c NON	P	Pathogenes	Thermal	Radioactive	Taste & Odor a	Taste & Odor b	Taste & Odor c	a BOD	O_2- balance N-eut.	O_2- balance Fe^{++}	O_2- balance $S^=$, $SO_3^=$
METAL PLATING IND.	x	x	x	x	x					x	x			x			x			x				x	x			x			x								
GALVANIZING OF STEEL	x		x											x											x						x								
METAL ANODIZING	x		x											x										x															
VISCOSE RAYON & FIBRE	x																																						
ELECTRIC WIRES		x																																					
GLASS INDUSTRY				x		x	x					x		x										x	x						x								
CERAMICS & PORCELAIN				x			x			x		x		x						x					x						x								
PESTICIDES		x			x	x	x		x									x			x																		
JEWELLRY & ORNAMENTAL																				x																			
ARTIFICIAL SILK	x																																						
MINING & ORE	x	x	x	x	x		x		x	x										x	x				x														
ELECTRONIC PRINTING CIRCUIT	x	x			x	x																		x	x														
FOUNDERIES		x	x																												x								
TANNERY & LEATHER				x										x							x					x	x		•	x				•	x		•		•
PHOTOGRAPHY				x	x									x						x																			
TEXTILE & WOOL				x										x												x		x		x	x				x				
COOLING WATER (close)	x			x																	x										x								
INKS, DYES & PAINTS	x			x	x	x	x			x		x								x	x																		
BATTERIES					x																																		
TETRA-ETHY-LEAD					x																																		
PRINTING					x																																		
EXPLOSIVES					x																																x		
PAPER	x	x			x	x															x										x				x				x
RUBBER																						x	x	x		x		x			x			x	x		x		x
ALLOYS			x	x				x	x							x	x			x											x								
METALLURG			x	x			x	x	x			x				x	x			x											x				x			x	x
NYLON										x																					x								
NUCLEAR POWER													x	x																	x								
FOSSILE FUEL POWER								x				x			x																								
DETERGENTS													x												•	x	x	x		x					•		x		x
LAUNDRIES													x													x	x	x		x	x			•			x		x
COSMETICS & PHARMACEUTIC													x											x			x		x			x	x	x	x		x		x
FERTILIZERS													x	x										x	x				x										
CANNING & FRUIT										x			x						x											x						x	x		x
COAL															x								x														x		
COKE																						x	x	x					x		x			x					x
REFINERIES	x	x		x								•		•								•	x	x	x				x		x		x		x	x	x		x
PETROCHEMICAL	x	x		x																	x	x	x	x			x		x		x		x	x	x	x	x		x
CHEMICAL (catalytic)																						x																	
GAS SCRUBBING									x				x	•								x	x								x			x					x
SOLICON																						x																	
TITANIUM OXIDE (sludge)																																						x	
PHOSPHORIC ACID																									x														
DOMESTIC SEWAGE	•	•	•	•	•	•	•	•	•	•	•	•	•	x	•	•	•	•	•	•	•		•	•	•	x	x	•	x	x				•		x	x	•	•
SEWAGE SLUDGE	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•		•	•					x	x		•		•		x	x	•	•
AGRICULTURAL WASTES		•												x							x		•	•		x	x		x	x				•		x	x		•
SOLID WASTES	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	x		•	•					x	•		•	•		•	x	x	•	•

3.2 INORGANIC ELEMENTS AND THEIR COMPOUNDS

3.2.1 Zinc, Zn

3.2.1.1 Introduction. Processes which give rise to zinc in their waste solutions include zinc and brass metal works, zinc and brass plating, steel galvanization, silver and stainless steel tableware manufacture, viscose rayon yarn and fibre production, battery production, paint and dye manufacturing, anticorrosion in cooling towers (together with chromium), as well as pulp and paper manufacture.

Zinc is mainly found in the rinse solution of plating and metal processing industries (galvanization). Separation of zinc through treatment is very difficult due to its association with other metals in waste streams. It is not economical to separate and recover zinc.

3.2.1.2 Principal industries.

(a) Metal Plating Industry

Type and Size of Industry

Zinc is used in the electroplating process (for zinc plating) in cyanide solutions. Zinc may also be used in metal colouring process plants. Zinc is used in the anodizing plants and also zinc plated steel may be treated with phosphoric acid. Industry sizes vary from small electroplating shops with a few tons per week capacity to major metal works with platings of tens of thousands tons of finished product per year.

Types of Wastes

The origin of zinc bearing wastes is mostly electroplating dipping baths. In most cases the bath solution is alkaline and it contains zinc-cyanide, NaOH, Na_2CO_3, Na_2SO_4, NaCN and Rochell salt.

Following electroplating, most zinc compounds appear in the wastes in the form of $Zn(CN)_2$ and some in the form of $Zn_2Fe(CN)_6$.

As with other plating wastes, zinc concentrations will vary according to plant management. Average concentration of zinc in general electroplating wastes is 5 to 8 mg/l but concentrations may vary from 11 mg/l in silverware plants, to 110 mg/l in cyanide bearing wastes from automobile manufacture. However, plating solution may contain as much as 34,000 mg/l of zinc. Processes which give rise to zinc bearing wastes are Pickle baths ($>$ 40 mg/l), brass mill wastes (40-1500 mg/l), zinc plating (70-350 mg/l) and silverware (5-220 mg/l).

Form of Wastes

Zinc bearing wastes are of a similar type to other plating wastes, they are in a clear liquid form and most zinc is soluble in alkaline solution of pH above 9. Sometimes zinc compounds form a suspension with white grey milky form. Most wastes are generally cyanide bearing and may include aluminium, lead and copper depending on the other process steps. Solutions may include both insoluble zinc and dissolved zinc as well as floating scum and oil.

Total Amounts

Zinc plating of one ton of product usually discharges 0.4 kg of zinc with a flow of approximately 8 m^3 of total liquid wastes. Bath water including cleansing and rinsing amount to 60 litres of wastes per 1 m^2 of plated surface in water-saving plant.

Discharge Pattern

Zinc coating and silverware processing are both batch processes leading to semi-continuous discharges of wastes. Most plants operate one or two shifts per day. Weekly cleaning of baths may result in peak flow on a certain day of the week. There may also be peak discharges due to accidental or unintentional spills and dumpings.

Effluent Concentrations

Zinc treatment is part of an overall treatment process. This generally involves firstly destruction of associated cyanides by oxidation, followed by pH changes leading to chemical precipitation followed by sedimentation or filters.

Cyanide destruction can be accomplished by chlorination which yields also $Zn(OH)_2$ which form a precipitant by pH adjustment. The following chemical process takes place:

$$Zn(CN)_2 + 2HOCl \longrightarrow Zn(OH)_2 + 2CNCl$$

$$2CNCl + 3HOCl + H_2O \rightarrow 5HCl + 2CO_2 + N_2$$

following such treatment, plant effluent contains less than 1 mg/l of Zn and under optimal operational conditions zinc concentration of less than 0.2 mg/l can be accomplished.

Zinc containing sludge should be dried by evaporation and disposed of in a solid form, usually by land filling in sites where there is no danger to ground and surface waters.

(b) Steel Galvanizing Plants

Type and Size of Industry

Steel galvanizing industry, specifically galvanized pipes, is usually large, as far as individual plants are concerned. Plants with capacity of 5,000 to 50,000 tons per year are in existence. Most plants use the Hot Dip Galvanization technique which is in many aspects similar in principle to the zinc electroplating (paragraph 3.2.1.2 (a) above) but the industry is more mechanized and processes are more continuous and are usually with automatic control.

Type of Wastes

Two forms of steel galvanization exist, namely: (1) galvanization in alkaline solution, usually with the presence of cyanides, and (2) galvanization with acidic solution with the presence of zinc sulphate. The galvanization in alkaline solution is almost similar to the zinc electroplating technique described in the preceeding paragraph.

The acidic galvanization wastes originate mostly from the process of fluxing which in large galvanization plants is continuous and wastes contain zinc sulphate together with other salts.

Form of Wastes

Wastes are in a clear or slightly coloured liquid solution with pH levels of between 2 and 3. Wastes contain zinc and iron ions as well as sulphate and chloride anions.

When pH levels are raised, a milky suspension is formed which finally yields a slurry type sediment.

Total Amounts

Large galvanization plants produce approximately 5 to 15 m^3 of total plant wastes per ton of galvanized steel capacity. Approximately 5 to 10 percent of these wastes are galvanization fluxing wastes i.e. approximately 1 m^3 of process wastes per ton of plant production capacity.

Discharge Patterns

In small plants with batch operation discharge is semi-continuous (depending on number of batches per day). In larger plants discharge is continuous for at least 12 hours per day. For a plant to become economical at least two-shift operation is required.

Effluent Concentrations

Fluxing wastes contain 20 to 60 mg/l of zinc while total plant wastes contain 1 to 5 mg/l zinc.

Treatment by pH adjustement, precipitation and settling, preferably of fluxing wastes before mixing with total plant wastes, results in zinc concentrations of 2 to 4 mg/l which bring the concentration to less than 0.5 mg/l in the total plant's wastes.

Zinc-containing sludge should be dried by evaporation and disposed of in a solid form, usually by land-filling. Sites should be selected carefully to prevent ground water and surface water pollution by zinc-containing leachate.

Physical, Chemical and Biochemical Properties of Wastes

Zinc sulphate is highly soluble and quite toxic to natural fauna. With dilution with sea water zinc salts which are largely insoluble will be formed with time, but until then the zinc toxicity might become harmful.

(c) Viscose Rayon Production

Zinc is discharged from the viscose rayon production process. General rayon wastes may contain from 250- 1 000 mg/l of zinc. Ion exchange recovery of zinc may reduce concentrations to 20 mg/l.

(d) Groundwood Pulp Production and Newsprint Production

Little information is available as to the concentrations of zinc in wastewaters from these processes. It has been noted that a large groundwood pulp mill used 6 tons of zinc per day.

(e) Cooling Water

The use of a commercial process 'Cathanodic Treatment' leads to zinc being discharged in the blow down of circulating water systems. Zinc concentrations of 6 ml/l have been found.

(f) Paint Production

Zinc has been found in the wastes from the paint industry in concentrations ranging from 0.3-10 mg/l.

3.2.2 Copper, Cu

3.2.2.1 Introduction. Copper metal is used both in industry and for jewellery and ornamental industry. Copper bearing solutions arise in the metal plating bathing operations with subsequent rinses while jewellery processing also involves plating of or on copper. Copper is also a major component in the electrical wiring industry. Electroplating and etching of printed circuits in the electronic industry also produces copper bearing wastes.

3.2.2.2 Principal industries

(a) Metal Processing and Plating

Type and Size of Industry

Industrial copper utilization occurs in large industrial complexes involving copper mills, and appliance manufacturing. The production of electrical cables and automobile radiators is another major use of copper. Electroplating also involves copper waste flows. Size of plants vary from small shops processing a few tons of copper per year to large industries processing hundreds of tons of copper and brass products per year.

Type of Wastes

Copper is electroplated using four types of baths, alkaline cyanide, acid sulphate, pyrophosphate and fluoborate - all made using the copper salts. Copper is electroplated where a thick coat is required.

Chromates are often coated on to copper. Immersion plating is used to put a copper coat on steel, gold on copper and tin on copper.

Plating process wastes may contain up to 120 mg/l of copper, brass mill wastes may be up to 400 mg/l, while other processes may lead to waste concentrations up to 50 mg/l generally. Exceptions are copper wire mills (800 mg/l average) 1000 mg/l in silver plating.

Total plant wastes usually contain 20 to 80 mg/l of copper according to amounts of rinse waters. Continuous rinsing (following dipping) and stationary rinsing contain between 5 to 20 mg/l of copper.

Two major types of copper plating processes exist, namely: the alkaline cyanide process and the acid sulphate process. Both processes produce respectively different types of wastes.

The alkaline cyanide copper plating involves electroplating in baths containing 15,000 to 60,000 mg/l Na_2CO_3, 5000 mg/l to 10,000 mg/l NaCN or KCN and 20,000-40,000 mg/l $Ca(CN)_2$. pH levels are maintained at 11-12.5.

Plating baths wastes contains small monocline crystals of $Cu_2(CN)_2$ and dissolved $CuK_3(CN)_4$ as well as KCN, NaCN and other salts and heavy metals. Wastes are strongly alkaline with pH between 11 and 12.

The acid sulphate copper plating involves electroplating in baths containing 50 gr/litre sulphuric acid and 200 gr/litre copper sulphate. In many cases thiourea-dextrin molasses are added. All the bath substances appear in the bath wastes and in the various rinsing operations.

Form of Wastes

Alkaline cyanide process wastes are turbid with dark colour and they contain suspended matter and small crystals in suspended and sludge form. They have a typical copper cyanide odour and should be kept in their alkaline form to prevent the emission of HCN. Wastes can contain oils and other metals. Acid sulphate wastes are clear with the typical light blue colour of copper sulphate.

Total Amounts

Alkaline cyanide processes produce 30 to 40 m^3 of wastes per ton of plant product. Acid sulphate processes produce 20 to 30 m^3 of wastes per ton of plant product.

Discharge Patterns

Small plants produce frequent batches when baths are being emptied after plating (dipping) which produce extremely concentrated wastes. Stationary (fixed) rinsing, following plating, produces medium concentrated wastes and continuous or semi-continuous rinsing produces wastes with decreasing concentrations.

Large plants produce the wastes virtually continuously. In a very well-managed waste handling plant the concentrated (hot) wastes from plating and stationary rinsing are segregated from the concentrated sequential rinsing. In a few plants, an attempt to recover some of the chemical substances from the "hot" wastes was made. The economics of such recovery is still controversial.

Effluent Concentrations

Concentrations of untreated wastes are mentioned above in the paragraph on Type of Wastes. Alkaline cyanide copper plating wastes can be treated by complexization with iron salts to $Cu_3Fe(CN)_4SO_2$ which is removed by precipitation and sedimentation.

An alternative treatment is by the use of active chlorine following the chemical reaction (not stoichiometric):

$$Cu_2CN_2 + Cl_2 + NaOH \longrightarrow N_2 + Cu\,CO_3 + CuCl_2 + NaCl + H_2O$$

Both $CuCO_3$ and $CuCl_2$ form a precipitant at elevated pH and can be removed by sedimentation.

Such treatment can produce effluent with less than 0.1 mg/l copper and in well managed plants, levels of copper are below 0.05 mg/l.

Acid sulphate copper plating wastes can be treated by lime according to the following chemical reaction:

$$Cu\,SO_4 + Ca(OH)_2 \longrightarrow Cu(OH)_2 + CaSO_4$$

$Cu(OH)_2$ is insoluble and forms a precipitant.

Lime treatment of copper wastes produces effluent of less than 0.5 mg/l of copper and in a well managed plant after filtration concentrations of 0.05-0.1 mg/l can be accomplished.

Recovery of copper firstly involves in-plant measures of waste stream segregation and flow reduction. Recovery processes include evaporation, ion exchange and electrolytic techniques.

Copper containing sludges are dried by evaporation and disposed in land fills and old quarries in locations where groundwater and surface water pollution can be prevented.

Physical, Chemical and Biochemical Properties

Copper sulphate is a known algacide. Most copper precipitants will remain insoluble in a weak alkaline environment, but will tend to be redissolved in acidic environment such as produced in anaerobic bottom layers when mixed with biodegradable organic sediments.

(b) Electric Wire Treatment

Type and Size of Industry

Electric wire plants can vary from 500 to 2000 tons of wires produced per year with a few exceptions of larger plants.

Type of Wastes

When wires are drawn from the melted copper they are pickled with sulphuric acid to remove layers of copper oxides. Sodium carbonate is used for neutralization. Wastes contain copper sulphate and copper carbonate together with sodium sulphate.

Form of Wastes

Turbid solution containing dissolved copper sulphate and suspended and sludge of copper carbonate with orange colour.

Total Amounts

Approximately 2 to 5 m^3 of wastes are produced per ton of wires processed. Flow reduction, which is advisable for metal recovery, can bring down the amount to between 1.5 to 2.5 m^3 per ton of wires. Plant raw wastes contain 50-100 mg/l of copper sulphate and 50-100 mg/l of copper carbonate.

Discharge Patterns

In smaller plants operation is intermittent and discharge is for a few hours per day or on certain days per week. Larger plants have a continuous or semi-continuous flow.

Concentrations

Well managed plants recover copper from the wastes by electrolytic methods and they also dry the copper carbonate and sell it as a by-product.

Following such treatment the final effluent contains less than 0.5 mg/l of copper and with careful operation effluent with less than 0.05 mg/l can be produced.

(c) Copper Ornamental Industry

Type and Size of Industry

Copper ornaments, jewellery and souvenirs are "blackened" in small shops or larger copper ornament industries.

The industry is limited in size but is a significant waste producer because it is difficult to control.

Type of Wastes

Following coating of copper products they are washed with sulphuric acid and sulfide-containing substances such as $K_2S_2O_2$, K_2S etc. Copper oxides and copper sulphate are produced in the wastes together with oils, detergents and salts.

Concentrated bath wastes can contain between 100 and 300 mg/l of copper while sequential rinse waters will contain between 5 to 20 mg/l.

Wastes are very acidic and most copper is in solution.

Form of Wastes

Turbid acid solution containing suspended matter and greyish sludge.

Total Amounts

Approximately 5 m^3 of wastes per ton of copper products.

Discharge Patterns

Usually intermittent batches of concentrated bath wastes and rinse waters.

Effluent Concentrations

Mixed raw wastes can contain 20 to 100 mg/l of copper. Following neutralization by lime and precipitation of copper hydroxide, final effluent may contain less than 0.5 mg/l of copper and in a well managed waste treatment less than 0.2 mg/l.

(d) Electronics Printed Circuit Industry

Type and Size of Industry

This is a developing industry usually of medium and small size establishment producing 1000 to 6000 m^2 of printed circuit per year. A few major electronics firms have opened large printed circuit factories with capacities of 10,000 m^2 of printed circuits per year and more. It should be noted that the trend is to reduce the size and increase the sophistication of printed circuits, thus measuring surface area is not adequate for plant capacity nor for its waste discharge.

Type of Wastes

Wastes contain mainly copper associated with other metals such as chromium, tin, zinc, nickel and cadmium. Pickling of copper components by chromic acid forms an especially problematic waste containing $Cu_3(CrO_4)_2$, and H_3CrO_4. Process wastes from plating baths and stationary rinsing contain 80,000 to 150,000 mg/l of copper while total plant wastes can contain 100 to 250 mg/l copper.

Form of Wastes

Clear bluish acid solution.

Total Amounts

15 to 30 m^3 of wastes are produced per square meter of printed circuits produced. Copper discharge in wastes might reach 2 to 4 kg per m^2 of printed circuits.

Discharge Patterns

Batch in small establishments followed by intermittent rinsing. Virtually continuous in large establishments with occasional peaks in concentration due to spills, emptying and cleaning.

Effluent Concentrations

Chromium should pass by reduction to Cr+++. Copper is removed by pH adjustment, precipitation and settling as described above. Following treatment, copper concentration is usually less than 1 mg/l and with careful treatment concentrations of 0.1-0.2 mg/l can be achieved.

(e) Other Industries with Wastes Containing Copper

Copper wastes may also originate from the following processes: wood preserving, pulp and paper mills, paper and paper board mills, fertilizer manufacture and petroleum refining.

3.2.3 Nickel, Ni

3.2.3.1 Introduction. Nickel is found in the wastes from metal processing and plating industries. These include tableware plating, and metal finishing plants. Copper and brass plating plants produce wastes which contain little or no nickel (< 1 mg/l).

3.2.3.2 Principal industries

(a) Metal Processing

Type and Size of Industry

Types of industry are tableware plating, metal finishing, appliances and business machine manufacture, and general plating plants. The size of plants varies.

Type of Wastes

Typically the wastes arise from plating and pickling processes as well as rinsing. Nickel plating is performed using a sulphate boric acid - chloride solution as well as baths of the nickel salts of sulfonate, chloride and fluoborate. Baths for nickel plating contain approximately 300 gr/litre of $NiSO_4$, 40 gr/litre of $NiCl_2$, together with 40 gr/litre of H_3BO_3.

For thick metal coatings, nickel is used as a primary coating of complex objects. Nickel is usually in an acidic bath. Nickel is also coated on steel using immersion baths. Nickel may be in concentrations in the range of 10-130 mg/l for tableware plating plants, 2-50 mg/l for metal finishing plants, 10-40 mg/l for business machines and appliances manufacturing, and up to 1000 mg/l for general plating.

Wastes are acidic and contain besides $NiSO_4$ and $NiCl_2$, H_2SO_4 and H_3BO_3. Spent plating baths, stationary rinsing and primary dipping contain high concentrations of nickel. If the concentrated wastes are segregated, rinsing water contains between 5 to 20 mg/l nickel.

It is associated with other metals used in the general metal processing industry.

Form of Wastes

Wastes appear as acid green solutions.

Total Amounts

Between 20 to 50 m^3 of liquid wastes are produced per ton of processed products.

Discharge Patterns

Discharge of rinse waters and the process associated occasional spills, will give rise to a continuous discharge with peaks in concentrations.

Effluent Concentrations

Treatment by lime raising the pH over 10 produces $Ni(OH)_2$ precipitate which is removed by sedimentation (settling) according to the following reaction:

$$NiSO_4 + NiCl_2 + 2Ca(OH)_2 \longrightarrow 2Ni(OH)_2 + CaCl_2 + CaSO_4$$

Alternative methods include complexization with other waste metals and cyanides in an alkaline environment to produce precipitant or ion exchange methods.

Segregation of concentrated plating and dipping baths from rinse waters is recommended with possibilities of recovering nickel from strong solutions.

The above mentioned treatment produces effluent with less than 1.0 mg/l nickel while careful treatment can produce effluent with less than 0.5 mg/l nickel.

Nickel-containing sludges following sedimentation can be disposed of after drying by evaporation in land fills or old quarries in such a manner as to prevent leaching into susceptible groundwater and surface waters.

3.2.4 Chromium, Cr

3.2.4.1 Introduction. Chromium compounds are ubiquitous in industries and in their wastewater. Chromium appears in many alloys and plated metals and as an anticorrosion inhibitor, used in cooling water to protect pumps and heat exchangers. Thus, it can be found in a multitude of wastewaters.

Chromium is used in the electroplating and alloy industry, chromium compounds are used in dyes including some of the common textile dyes and chromium oxides, specifically Cr_2O_6 is used as an effective oxidant, and softener, especially in tannery wastes.

Due to its ubiquitousness in many products and emission from small industries and laboratories, chromium concentration in general municipal wastes can reach 5 to 10 mg/l while their most common concentrations are below 1.0 mg/l.

3.2.4.2 Principal industries.

(a) Tannery Industry

Type and Size of Industry

Tanneries can vary from very small at village level, processing less than 10 tons of hides per year, to major tanneries producing between 5000 and 20000 tons of hides per year.

The type of wastes depends on the degree of processing of the hides to leather, form of hides (raw, cleaned, with or without hair, etc.)

Type of Wastes

Raw hides are passed through about 30 stages of hide pickling, cleaning (using oxidants) and softening. Chromate salts are used at various stages, particularly in the tanning-oxidizing and in the pulp chrome finish stages usually in a strong acidic solution with the aid of sulphuric acid.

Hexavalent and trivalent chromates are used but during the processes almost all hexavalent chromium is reduced to trivalent, particularly due to the presence of sulfides. Besides chromium compounds, tannery wastes contain sodium chloride, ammonia, enzymes, detergents, suspended and flotable organic matter, greases, lanolines, dyes and dissolved organic matter.

Chromium dosages are in the form of $K_2Cr_2O_7$ and H_2CrO_4 but following reduction trivalent $Cr(SO_4)_3$ is formed. Sequential processes involve the use of strong alkaline solutions where $Cr(OH)_3$ is formed.

BOD and COD concentrations of 5,000 to 20,000 mg/l respectively, are common in some of the tannery processes waste streams while BOD levels of about 1000 mg/l are common in the overall tannery wastes stream. In tanneries where water-saving measures were adopted, chromium concentrations in the total raw tannery wastes can vary between 2000 and 1500 mg/l as chromium, while approximately 500 mg/l chromium should be regarded as average. Other tanneries discharge between 50 to 200 mg/l chromium in the total effluent, usually after some precipitation has occurred in the waste holding basins.

Form of Wastes

Tannery wastes are very turbid, coloured (usually red) foamy and malodorous. The wastes are usually alkaline with pH of between 9.5 to 12. Most chromium appears in the form of $Cr(OH)_3$ which forms a greenish precipitate at higher pH levels. At neutral and acidic pH levels and progressing part of the chromium solubilized.

Total Amounts

Tannery wastes amount to between 20 to 100 m^3 per ton of hides processed, depending on type of process and on degree of water-saving measures which are taken within the plant. Consumption of chromium salts can reach 10 to 40 kg per ton of hides processed with discharge of 5 to 15 kg chromium per ton of processed hides. Thus, a 2,000 tons per year tannery can discharge between 40,000 to 160,000 m^3 of wastes per year containing chromium wastes amounting to 25-35 percent of total plant wastes (20-25 m^3 per ton of hides). They can be treated separately.

Discharge Pattern

Hide soaking, pickling and polishing is usually done in tanks, baths and basins, which are filled and emptied in batches. In large tanneries this will form a semi-continuous flow (such as daily batches, or a few batches per day), while in small plants, batches are discharged every few days or few weeks. When earth basins are used, discharge is infrequent and even seasonal when basins are emptied to allow the evaporation, drying and disposal of the tannery sludges.

Effluent Concentrations

Most tanneries use large retention holding basins where precipitation of chromium hydroxide and chromium salts occur. A series of precipitation basins where chromium containing sludges are subsequently dried by evaporation constitute the minimum treatment. Such minimum treatment facilities will result in effluent containing less than 50 mg/l of chromium. The removal of chromium is due to the relative insolubility of $Cr(OH)_3$ in an alkaline environment. Using pH adjustment, mechanical sedimentation basin and chemical precipitation (such as ferric and aluminium coagulation) results in a relatively high effluent quality with concentrations of chromium of less than 10 mg/l and even less than 5 mg/l following well-operated treatment plants.

Chromium concentrations in total wastes of large plants following well-operated treatment is 1-2 mg/l.

Physical, Chemical, and Biochemical Properties

Due to the highly reducing environment in tannery wastes caused by the presence of sulfide and degradable organic matter, virtually all chromium appears in the less toxic trivalent form. Due to the high pH of the wastes, following the merging with alkaline stream, insoluble $Cr(OH)_3$ is formed.

When $Cr(OH)_3$ traces reach a marine environment, it is most likely that they will be found in bottom sediments in their trivalent less-harmful form.

(b) Electroplating and Alloy Industries

The Type and Size of Industry

The industry may vary in size from small 'shop' levels to large highly-developed industrial complexes. Metal profile coating and anodizing industries with capacity of 10,000 tons per year and more of product are in existence. Car and automotive industries maintain chromecoating and plating production facilities with capacities of tens of thousands of tons of chromium-coated parts per year. The type of industry may be electroplating of common metals, previous metals or specialty metals. There are finishing processes, such as anodizing, coating as well as chemical etching and milling.

Type of Wastes

Wastes may vary from innocuous and non-toxic wastes, to highly lethal and toxic wastes. The former are the result of good plant management and the latter may be due to intentional or unintentional spills of concentrated process solutions. For typical plating operations the chromium concentrations may vary from 100 mg/l for car grill manufacture, to 50 mg/l for a metal fastener plant. Total plant wastes including both plating and rinsing wastes usually contain 10 to 30 mg/l of chromium. Associated with the chromium may be compounds such as zinc, iron, lead, aluminium and cyanide, and sometime fluorides. Chromium is introduced in the form of CrO_3 together with sulphuric acid to form H_2CrO_4 acid solution.

The wastes usually are generated in the rinsing of processed items after removal from baths. However, the intermittent dumping of spent process solution will also cause major peaks in concentrations.

In the alloy industries, the electrolytic chromium gives rise to the highest concentrations of chromium. While other processes may give rise to concentrations less than 10 mg/l, in the electrolytic process the concentration may be as high as 2000 mg/l. The waste will have a low pH and high concentrations of ammonia, iron and manganese.

Form of Wastes

The wastes are usually coloured with floating scum, oil and metal particles. There will be both suspended and dissolved solids. In typical acidic wastes most chromium is in soluble form, mostly as CrO_4 salts. Colour of wastes is clear, greenish or reddish according to the type of the process and the pH.

Total Amounts

Chromium electroplating plants produce between 20 to 100 m^3 total plant wastes per ton of plated product. In well managed plants the total plant wastes will be between 30 to 40 m^3 per ton. Raw waste levels of chromium may be up to 1 kg/ton processed with a pH ranging from 2-13 depending on the process. If the pH is high the chrome will be an insoluble green precipitate which is soluble at low pH. Galvanising process may use up to 2500 gallons/ton.

Discharge Patterns

The process wastes are discharged continuously because they usually are the result of a series of batch processes. The discharge of spent bath solutions will be intermittent if there is no flow equalization or re-use of the solutions.

Effluent Concentrations

Total plant raw wastes can contain between 10 to 50 mg/l of hexavalent chromium. There are various types of treatment all aimed at reducing the chromium to its trivalent hydroxide form $Cr(OH)_3$ which can be precipitated.

With non-cyanide wastes reduction by ferrous sulphate and liming is used according to the following chemical reactions:

$$H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O \quad (1)$$

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3 + 3CaSO_4 \quad (2)$$

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 3CaSO_4 + 2Fe(OH)_3 \quad (3)$$

Other treatment methods involve reduction of hexavalent chromium to trivalent by the use of sodium thiosulphate or removal of chromium ions by ion exchange.

Cyanide-containing wastes should pass an oxidizing step to remove the cyanides before removal of chromium.

Following treatment, the concentration of chromium in total plant wastes is 0.1-0.2 mg/l and all residual chromium is in the trivalent form. $Cr(OH)_3$ precipitated sludge should be dried by evaporation and disposed safely in a dry form, usually by land filling.

Physical, Chemical and Biochemical Properties

Raw chromium plating and anodizing plant effluents contain high concentrations of soluble hexavalent chromium which is highly toxic to natural fauna and flora. Polluted receiving bodies of water usually provide a reducing environment to turn the chromium into a trivalent form and with neutral and alkaline pH will render the chromium insoluble. However, before this "natural" removal will occur, the damage of hexavalent chromium can be significantly harmful.

Residual amount of $Cr(OH)_3$ in the treated effluent will find their way into bottom sediments and remain there virtually harmless.

(c) Textile and Wool Dyeing

Type and Size of Industry

Textile and wool dyeing processes are quite common in most countries. Size of factories will vary from small dyeing and re-dyeing establishments to large dyeing plants within a textile and wool plant or as a separate plant. Size of plant can reach 50,000 tons of fabric dyed per year.

Type of Wastes

A significant number of textile and wool dyes contain, or are based on, chrome-acid and metachrome substances. Textile and wool plants contain several streams from various processes among them alkaline wastes, chlorine wastes, acidic wastes, detergent wastes and fibrous suspended matter wastes. Dyeing facilities wastes are usually separated from the wastes of the entire plant and they contain between 20 and 70 mg/l of chromium both in hexavalent and in trivalent forms.

Form of Wastes

Liquid coloured wastes with some suspended matter, pH vary according to the combination of dyes.

Total Amounts

Dyeing process wastes can amount to between 20 to 60 m^3 per ton of fabric dyed.

Discharge Patterns

Dyeing, soaking and rinsing are done in batches which in large plants form a continuous or semi-continuous flow.

Effluent Concentrations

Chromium concentrations in raw dyeing process wastes may vary between 10 to 120 mg/l according to degree of process stream separation. Final concentrations depend on separation of waste streams, type of dyeing processes and degree of treatment. Most chromium containing dyes are highly soluble and they are difficult to treat. Treatment by bleaching, coagulation and activated carbon may result in chromium concentration of less than 2 mg/l. Some concentrated dyeing process wastes are separated and disposed of into evaporation basins with no liquid discharge. Dry residue is hauled away and buried.

(d) Use of Chromate as an Anti-Corrosion Inhibitor

Type and Size of Waste Source

Chromate salts are added to closed cycle cooling systems, usually those which are based on cooling towers. The addition of zinc salts and/or dispersants can reduce the concentration of chromates.

Closed cycle water cooling systems are very common in many industries such as refineries, petrochemical industry, thermal combustion industry, chemical industry, ceramic and glass industry, metal industry, freezing works, large air conditioning facilities and small and medium scale power generation plants. Closed cycle cooling systems are used when open flow through systems are not feasible due to shortage of natural cooling waters or when measures to prevent thermal pollution have been taken.

Type of Wastes

Water cooling wastes are usually in the form of spent bleed-off or renewals of the cooling system waters. Chromate salts are added with various salts containing $CrO_4^{=}$, usually in the form of $K_2Cr_2O_7$ or $Na_2Cr_2O_7$.

Cooling water spent bleed-off contains, beside chromates (hexa-valent chromium), also zinc, dispersants, dust,algae, slimes and dissolved solids of the natural water origin but in two to three-fold concentration.

Form of Wastes

Clear water, occasionally with some colour and turbidity and some dust or grit.

Total Amounts

Amounts depend on size of plant, climate, shortage of water, composition of water, presence of scale-forming substances such as calcium, magnesium, iron and manganese, type of heat exchanger and cooling towers, corrosiveness of piping etc. A common medium to large size refinery, for example, requires approximately 10 million m^3 per year of cooling water of which between two to four millions are spent bleed-off.

Discharge Patterns

In small cooling systems, bleed-off water is spent intermittently while in large systems continuously or semi-continuously with occasional complete renewal of the cooling system which is usually coupled with cleaning of the entire system plus removal of scale, rust and slime.

Effluent Concentrations

When zinc salts and/or dispersants are used, chromate concentrations which are maintained in the system are 10 to 30 mg/l. With higher levels of zinc the chromate concentration can be reduced to between 5 to 20 mg/l as Cr_2O_3. Where no zinc is added, chromate concentrations increase to between 50 to 150 mg/l.

Batch or intermittent bleed-off wastes may contain up to 500 mg/l as Cr_2O_3 while continuous or semi-continuous bleed-off waters (where zinc additives are used) contain between 10 to 40 mg/l as Cr_2O_3 or between 7 to 27 mg/l of hexavalent chromium ion.

Following treatment of reduction of the hexavalent chromium to trivalent chromium followed by pH adjustement to form settleable $Cr(OH)_3$ or removal of chromium by ion exchange, chromium concentrations can be reduced to below 0.5 mg/l chromium.

Physical, Chemical and Biochemical Properties

Untreated cooling water spent bleed-off contain the most harmful and toxic hexavalent chromium ion. Contrary to the false common belief that spent cooling waters are basically "pure waters" and because of the large amount of wastes, especially in cooling system renewal, discharge of these wastes can be very harmful to the receiving bodies of water. The relative increased temperature of cooling system wastes can only enhance the toxicological effects of the hexavalent chromium.

(e) Other Industries with Wastes Containing Chromium

Chromium has also been found in the wastes originating from the production of paint pigments and plastics.

3.2.5 Lead, Pb

3.2.5.1 Introduction. Lead was formerly used in many of the original water piping installations in many countries. Hence, in older areas, used water coming from houses was found to contain lead. This lead was found in both untreated and treated sewage. Industrially, lead is used in a number of industries. The major ones being metal electroplating, battery production and paint production.

Recently lead has been the subject of much investigation because it is an additive to petrol (gasoline) and hence is an air pollutant. Lead from the combustion of petrol will also find its way into drainage and sewage through spills, washing out by rain and sedimentation onto the roads.

3.2.5.2 Principal industries.

(a) Battery Production Industry

Type and Size of Industry

The production of batteries requires the use of lead for the plates used within the batteries. The plates may be either newly made or produced from used batteries.

Type of Wastes

The wastes are generated in the plate forming areas and also where the batteries are cleaned and filled. The wastes will be acid and highly corrosive due to the use of sulphuric acid.

Form of Wastes

The wastes will be $PbSO_4$ in the ionic form. The wastes will be white in colour, and turbid. There may be some particulate lead from the plate forming areas.

Total Amounts

Wastes from the plate forming areas will contain 1-50 mg/l lead. The wastes from the cleaning and filling areas will be about 10-12 mg/l lead. The volume of wastes are 4-5 litres/battery.

Discharge Patterns

Continuous due to continuous plating operation.

Effluent Concentrations

The effluents may be initially treated using sedimentation to remove particulates. The addition of calcium hydroxide will cause the following reaction:

$$Ca(OH)_2 + PbSO_4 \longrightarrow CaSO_4 + Pb(OH)_2$$

The $Pb(OH)_2$ will precipitate out leaving a final lead concentration of about 0.2 mg/l. Following sand filtration the effluent lead concentrations can be brought down to 0.05 mg/l and less.

(b) Metal Plating Industry

Type and Size of Industry

The electroplating of lead is a process sometimes used. The lead may come from anodising baths. Electronic printed circuit production involves lead plating and welding, usually in combination with tin and copper plating.

Type of Wastes

The wastes will arise from rinsing of plates after processing and spills of process bath solutions. Plating baths are highly concentrated and initially contain 900 gr/litre of lead fluoborate $Ph(BF_4)_2$, 30-40 gr/litre H_3BO_3, 10 gr/litre HBF_4 as well as metallic lead and sulphuric acid. Wastes might contain also other metals such as tin, copper, zinc and nickel.

Form of Wastes

The wastes could contain insoluble lead and will be grey-white containing suspended $PbSO_4$. There will be both floating and settleable material. However, when the wastes are strongly acid, the lead will be mostly soluble.

Total Amounts

The lead-bearing wastes in the form of either lead or lead sulphate will be produced at a rate of 8 m^3/ton of processed metal. The concentrations of lead will be about 8-10 mg/l in total plant wastes.

Discharge Patterns

The discharge of waste will be continuous with peak concentrations associated with spills.

Effluent Concentrations

Using lime treatment techniques, previously outlined, or other techniques for pH adjustement, the final plant effluent can contain less than 0.2 mg/l lead. Using more sophisticated techniques such as ion exchange or chemical complexization with other waste metals may yield effluent of approximately 0.05 mg/l and less.

(c) Petroleum Additives

The production of tetraethyl lead as a petroleum additive gives rise to lead waste. Additionally after the fuel is burnt the lead may be found in the air or on road surfaces. Hence, rainfall, and the resulting urban runoff will also be lead-bearing wastes. The production wastes may contain lead in the range of 100-200 mg/l as organic and inorganic lead.

(d) Other Industries with Wastes Containing Lead

Lead may also be found in the waste from printing, pigment, fuel, photographic, match and explosive industries. In the paint and pigment industry 1.0-10.0 mg/l lead has been found in waste waters.

3.2.6 Selenium, Se

Industries using selenium include paint, pigment, and dye producers, eletronics, glass manufacturers, insecticides and metallic sulfide ores. However, very little information is available on the concentrations.

One known non-conventional source of selenium is scrubbing water from incinerators which burn layers normally containing the element. The concentration of the element in this water was found to be few micrograms per litre.

Another source is represented by metallic sulfide ores where selenium occurs as an impurity. Selenium has also been found in the cooling water blow down from electricity generating stations.

3.2.7 Arsenic, As

Arsenic and its associated compounds have been found in the wastes of the following industries: metallurgical, glassware and ceramic, tannery, due and pesticides. However, as the inorganic pesticide industry is on the decline it is thought that this waste source will also diminish. Concentrations of AsO_2 in raw inorganic pesticides industries were found to be between 100 and 500 mg/l.

3.2.8 Antimony, Sb

Industries whose wastes contain significant concentrations of antimony are rare and information is extremely meagre.

3.2.9 Molybdenum, Mo

Molybdenum has been monitored in air emissions from a number of industries. Therefore molybdenum will also be found in liquid wastes. The processes are mining (copper), molybdenum refinering metal alloy production, electrolytic manganese production and some oil and coal burning processes. No reliable information concerning the concentrations of molybdenum in the various wastes is available.

3.2.10 Titanium, Ti

The processes producing titanium containing wastes include the mining industry, metal processing, ferro-titanium production, ceramics and fibre glass, pigment production, plastic production and some incineration processes. No information is available regarding effluent concentrations

3.2.11 Tin, Sn

3.2.11.1 Introduction. Tin plating is a common process used in the metal processing industry; there are two methods, hot-dipped tin plating and electrolytic tin plating. The latter process is usually preferred. The process involves electrolytic alkalinic cleaning, pickling and plating with numerous rinsing steps. Production of cans for food preserving and canning industry involves large scale tinning operations while metal recovery of solid wastes involves detinning processes.

3.2.11.2 Principal industries.

(a) Tin Plating

Type and Size of Industry

Tin plating is associated with large metal processing plants, as well as the electronics printed circuit industry. Tinning of cans involves industries with thousands of tons per year capacity while small tin metal ware is done in small shops, usually in the less developed regions.

Type of Wastes

The wastes are the rinsing water and process bath spills. The baths contain boric acid HBF_4, free tin, $Sn(BF_4)_2$ and H_2SO_4. Wastes are acid in character.

Form of Wastes

The wastes will be warm, turbid with dissolved and floating material associated including oils and metal particles.

Total Amounts

The concentration of tin may be in the range 50-130 mg/l from plating operations. The pH may be almost neutral and the waste tin load will be about 1-5 lb/ton plated.

Discharge Patterns

Discharge is continuous from continuous processes with peak concentrations when dumping or accidental spills occur.

Effluent Concentrations

Using techniques of precipitation, flocculation and clarification tin concentrations may be reduced to 1.0 mg/l. Using ion exchange or complexization technique can produce effluent with less than 0.2 mg/l of tin.

3.2.12 Barium, Ba

Barium as barium sulphate is used in the production of white paint. Barium is also found in the following processes: metallurgy, glass, ceramics and dyes and rubber vulcanization. Little information is available on waste concentrations.

3.2.13 Beryllium, Be

Beryllium is found in small concentrations in the air-borne wastes originating from many incineration processes, e.g. coal boilers, municipal waste (including sludge) burners. As wet scrubbing or electrostatic precipitation are common air pollution control measures a beryllium-containing waste water flow will be generated from incinerators which use air pollution control equipment. Beryllium will be found in liquid wastes emitted from wet scrubbers quenching wastes as well as in drainage water from sites where electrostatic precipitator residue is disposed of.

Beryllium alloy production gives rise to waste flows. No information regarding beryllium concentration in the above mentioned wastes is available.

3.2.14 Boron, B

3.2.14.1 Introduction. Boron is a metal used in a number of industries. However, not a great deal is known about concentrations in processes wastes and final effluents. This is because boron is generally discharged together with heavy metals which are often of greater interest.

Boron is found in the process bath waters in the metal finishing industry. Boron is also used in the fruit packing industry and as a chemical in the photographic industry.

3.2.14.2 Principal industries.

(a) Metal Processing

Type and Size of Industry

Hydroboric acid is a component in the process bath water for many metals such as lead, nickel, copper and tin. The boric acid is particularly important in the nickel treatment industry.

Type of Wastes

In the metal plating industry the major processes are metal preparation, metal coating and finishing. All these processes use rinse waters. The source of wastes are process solution spills and disposal as well as rinse water disposal. As mentioned in the above sections. the wastes contain the heavy metals themselves, plus borate, fluoride, possibly cyanide. There will also be sulphates and chlorides and they will be acidic.

Form of Wastes

In the case of nickel the wastes are a green acid solution containing many other ions apart from dissociated and undissociated boric acid (H_3BO_4). The wastes may be warm. The boric acid is in the dissolved state.

Total Amounts

The concentrations of boron are of the order of 1-2 mg/l in both process and plant wastes. Waste flows are of the order of 20-50 m^3 per ton of processed metal.

Discharge Patterns

The discharge of waste will be intermittent.

Effluent Concentrations

As the effluent concentrations are quite low it is difficult to treat specifically. In particular it is associated with heavy metals which are the major object of treatment. Ion exchange is a possible technique for specific removal of boron.

(b) Fruit Canning and Packing

Type and Size of Industry

In the washing of fruit, which is the first stage of processing and packing of fruit, boron is used. Hence boron is discharged primarily during the fruit canning season. The fresh citrus exporting industry use boric acid and sodium borate to clean the fruit before waxing. This is a major source in Mediterranean countries which are citrus exporters.

Type of Wastes

The wastes originate in the washing process and are likely to be mixed with other process wastes. Those from the peeling, canning, cooking etc. process. In this first washing section the fruit is washed with water, then dipped in a $NaBO_3$ solution and then washed again. Hence the borate will appear through the second rinse and spills and disposal of the $NaBO_3$ solution.

Form of Wastes

The process wastes are an aqueous solution of $NaBO_3$ in water. It has no colour or odour. The waste is dissolved. However, this waste stream when mixed with other wastes will be similar to that described in section 3.2.3.2 (a).

Total Amounts

Waste flows amount to 3 m^3 per ton of fruit processed. The concentration of the boron in both the plant and process wastes is of the order of 2-3 mg/l.

Discharge Patterns

The wastes will be discharged continuously.

Effluent Concentrations

Waste flows will be reduced through the reuse of water after appropriate treatment. However, removal of boron is likely to be small and is difficult due to small concentrations. However, with treatment boron tends towards zero concentration.

(c) Detergent Production

Sodium perborate is used as a bleach in household washing powder. Hence it has been found in raw sewage in appreciable amounts as well as in detergent manufacturing wastes. Sodium perborate is also used in laundries and cleansing facilities due to its degreasing properties.

Boron concentrations in raw municipal sewage can amount to between 2 and 6 mg/l. In countries where reclaimed effluents are used extensively, for agricultural irrigation, strict measures should be applied to restrict the use of sodium perborate in order to reduce boron concentrations in the effluent. This is due to the sensitivity of many agricultural crops to boron.

3.2.15 Uranium, U

Sources :

3.2.15.1 Nuclear industry. Wastes containing uranium may be produced by uranium ore, production of nuclear fuels and from nuclear power stations. Such wastes are dealt with according to codes of practice of radioactive wastes which are beyond the scope of this chapter.

3.2.15.2 Phosphate fertilizer industry. Uranium naturally appears in phosphate rock and therefore in phosphate fertilizers. Middle Eastern, North African, Brazilian, Peruvian and North American phosphate rocks contain in average between 100 and 150 grams of uranium per ton of phosphate rock with radiation activity of between 10 to 150 p Cig^{-1}.

Although uranium may be contributed to the marine environment through washout and runoff of agricultural drainage area, flood water and leachates and runoffs from phosphate mining operations, the main point source is phosphate bulk loading and unloading in major port terminals. Phosphate powder and dust which is wind blown, spilled or washed to the sea near major harbours is the single largest contributor of uranium to the marine environment.

3.2.16 Vanadium, V

Vanadium oxides residues are found in wastes from the alloy and metallurgy industries as vanadium is an important component of alloys used for the tooling industries.

Vanadium oxides are emitted from stocks of thermal power stations where C oil and other fossil fuels are the sources of fuel as well as from coal gasification and coal processing industries.

Any liquid wastes from air pollution control equipment such as wet scrubbers will contain significant amounts of vanadium.

Traces of vanadium are also present in wastes of sulphuric acid production, where vanadium serves as a catalyst.

No reliable information is available regarding vanadium concentrations in various liquid wastes.

3.2.17 Cobalt, Co

Cobalt is used in the metal plating and ionizing industries as cobalt compounds give a golden colouration to finished metal products. Its concentration in various wastes is quite small and the effluent characteristics as well as treatment are almost similar to nickel containing wastes. Manufacturing of cobalt produce liquid wastes as well. Cobalt is also found in wastes originating from the production of electrolytic manganese and in wastes of certain plastic industries.

Cobalt is also used in the metallurgy and alloy industries as well as being present in radioactive wastes. Concentrations of cobalt vary from industry to industry and reliable data is scarce.

3.2.18 Thallium, Tl

Thallium compounds are used in the pesticide industry particularly in rodent poisons. The concentration of thallium in wastes from such industries is unknown due to scarcity of information.

3.2.19 Tellurium, Te

Insufficient information is available regarding tellurium-containing industrial wastes and its concentration in various wastes.

3.2.20 Silver, Ag

3.2.20.1 Introduction. Silver plating is used for cutlery and jewellery. It is an age old process. A newer process is the development of photographic films. This process also involves the use of silver. Because of its high value, the recovery of silver is most desirable, thus the elimination of silver from the waste stream can become an economically profitable operation.

3.2.20.2 Principal industries.

(a) Silver Plating

Type and Size of Industry

The industries are silver plating of cutlery, jewellery and ornaments. Apart from a few rather large cutlery plating plants most industries are small town silversmith shops.

Types of Wastes

Little particulate silver and suspended silver oxides are found in the wastes as well as some dissolved silver. The bath solutions are made of silver cyanide, potassium cyanide, potassium carbonate, metallic silver and free cyanide. Bath spills contain high concentrations of silver while rinse waters contain 2-5 mg/l of silver.

Form of Wastes

The wastes are mainly soluble AgCN. Associated chemical pollutants are Ag, K_2CO_3 and KCN. The wastes are alkaline, sometimes slightly turbid and without colour.

Total Amounts

Approximately 8 m^3 of waste are produced per ton of treated metal.

Discharge Patterns

Discharges are continuous with peak concentrations due to spills and dumping of process solutions. Due to the value of silver intentional dumping is unlikely.

Effluent Concentrations

Generally cyanide ion will interfere with the precipitation of silver chloride so the destruction of cyanide, usually by chlorination, is the first process. Cyanide destruction also involved the production of silver oxide which is a black precipitate and some silver chloride which forms white greyish precipitant. The reaction is (not stoichiometric):

$$AgCN + Ag + 5Cl_2 + NaOH \longrightarrow Ag_2O + CO_2 + NaCl + N_2 + H_2O$$

Following complete destruction of cyanide and pH adjustment, sodium chloride will lead to the formation of silver chloride and its removal, using sedimentation and skimming. Other techniques include ion exchange, reductive exchange and electrolytic recovery. Following such treatments, concentrations in waste streams of 0.1 mg/l silver may be achieved.

(b) Photographic Industry

Type and Size of Industry

The developing of photographic and x-ray film utilizes silver solutions. This is usually a small size industry, except for major film development centres.

Type of Waste

The development process involves the conversions of AgBr to Ag_2S which is on the negative. The films are rinsed in a number of solutions at various stages.

Form of Wastes

The silver in in the ionic form and is associated with $K_4[Fe(CN)_6]$, KBr, K_2S, $Na_2S_2O_3$ and Na_2SO_3. The wastes are all soluble and will have a light white colour.

Amount of Wastes

The concentrations of silver are of the order of 1-2 mg/l up to 8 mg/l in x-ray film developing.

Discharge Patterns

The wastes are discharged intermittently. Due to the smallness and vast distribution of film and x-ray development establishments, control and surveillance is extremely difficult. On the other hand, due to the high value of silver recovery, contractors are seeking the collection of concentrated wastes.

Effluent Concentrations

Electrolytic recovery of silver has become an economically profitable endeavour. The problem is the collection of wastes from the various emitters. Concentration of effluent following electrolytic recovery is less than 0.1 mg/l silver.

(c) Various Industries with Wastes Containing Silver

Silver metal is used in the food and beverage processing industries. Silver nitrate is used in porcelain and ink manufacturing industries. Insufficient information is available on silver concentration in such wastes.

3.3 BIOCIDES

3.3.1 Introduction

Most biocides belong to the organo-haloginated substances (mostly haloginated hydrocarbons) and the organophosphorus substances, both covered by Table 1 and beyond the scope of this work.

Other biocides contain arsenic, lead, mercury, copper, chromium which are dealt with in earlier sections or in Table 1. Organo biocides which do not fall within the above categories are Triazines, Phenosyalkanoic compounds, Carbamates, Urea-substituted compounds and amine compounds. Inorganic bacteriocides such as chlorine derivatives, peroxides and permancyanates for example are quite common but are also beyond the scope of this work.

Organic phosphorus is a component of a number of pesticides. The wastes from these pesticides may be a problem in two ways - as a waste directly from the production process and through washout after application of the pesticides. Both ways the wastes may cause death of plant and animal life due to the natural effect of the pesticide or in small concentrations may lead to eutrophication. Pesticides other than organophosphoric may additionally cause problems because of accumulation due to their non-biodegradability. Most organophosphorus pesticides are biodegradable although their rate of biodegradability depends on specific circumstances.

Triazines, Carbamate pesticides and organic phosphorus are brought forward here as examples of point sources of biocides cited.

3.3.2 Principal Industries

(a) Production of Triazo Organic Nitrogen

Type and Size of Industry

The production of organo-nitrogen pesticides reaches 30,000 tons per year, the main process being Triazine synthesis.

Type of Wastes

The wastes are aqueous solutions of organic compounds plus other organics. The wastes may also be characterized by use of BOD, TSS, TOC, TDS and nitrogen concentrations.

Form of Wastes

The wastes are aqueous solutions of organic and nitrogen compounds. The main organo-nitrogen compounds are Triazines. The wastes have a yellow-brown colour and are acidic. It should be noted that the solubility of Triazines is 50 mg/l, so only part will be dissolved in the process wastes.

Total Amounts

Total plant waste streams amount to 2000 m^3/d with process wastes of about 100 m^3/d. The Triazime concentrations are about 100 mg/l in the process wastes but fall to 5 mg/l in the plant wastes. They give rise to 10 kg per day or 1 ton per year. Alternatively waste is produced at a rate of 0.003% per ton of product.

Discharge Pattern

Wastes are discharged discontinuously.

Effluent Concentrations

The wastes may be treated using filtration and biological treatment. Concentration in the effluent in a well-run plant may reach 0.5 mg/l. Waste segregation and dry clean up will further reduce waste quantities.

(b) Production of Carbamate Pesticides

Type and Size of Industry

The industry described here produces Carbaryl pesticides also known as carbamate pesticides. The quantities produced are about 4000 tons/year.

Type of Wastes

The wastes are aqueous solutions of organics. Process steps such as synthesis separation, recovery, purification and process finishing all give rise to wastes. Process solutions may also contain intermediate products.

Form of Wastes

The main product is $C_{10}H_7$-O-CO-NH-CH_3 but other components of the waste are tetraline, methylamine and hydrochloric acid. Hence the solution will have a low pH. Wastes are typical of those from chemical plants. Part of the chemical will be soluble while another part is insoluble in the process waste. Other typical parameters in the waste streams are characterized as COD, BOD, TS, Na, Cl, etc.

Total Amounts

The total plant wastes amount to 600 m^3/d, while the process wastes of 30 m^3 are mixed with about half the total plant waste. The concentrations in the plant waste are about 5 mg/l. This amounts to 3 kg per day or 1 ton per year. Based on production the waste is about 0.03% of the production per year.

Discharge Patterns

The discharge is discontinuous depending on the cycle times and cleaning of equipment.

Effluent Concentrations

Treatment of these organic wastes can be accomplished using conventional secondary waste treatment such as activated sludge or trickling filters. Effluent concentrations should be of the order of 0.5 mg/l.

(c) Phosphorus (Organic) from Chemical Pesticide Production

Type and Size of Industry

The industry produces some 30,000 tons per year using organic synthesis techniques.

Type of Wastes

The wastes originate in the various process synthesis steps. These include decanter units, distillation towers, hydrolyzing, and product and equipment washing. The wastes may be characterized by BOD, TSS, COD, TOC and phosphates.

Form of Wastes

The wastes will be aqueous solutions of $PO_4^=$, organophosphate, and other organic compounds and solvents. Most of the phosphate will be soluble.

Total Amounts

The plant produces some 2000 m^3/d of wastes of which 100 m^3/d is from the organophosphorus pesticide process. The concentration of organophosphorus in the process waste is 1000 mg/l while its concentration in the plant waste is 50 mg/l as phosphorus. Hence some 100 kg per day or 10 tons per year are produced.

Discharge Pattern

Discharge is intermittent depending on cycle times and process cleanup.

Effluent Concentration

Treatment of the wastes may include biological treatment and/or precipitation and sedimentation with chemical addition. The final phosphorus waste stream concentration may reach 5 mg/l as phosphorus. The use of dry cleanup systems will also reduce waste flows overall.

3.4 ORGANOSILICON COMPOUNDS

Organosilicon compounds are emitted almost exclusively from the organosilicon production industry.

Insufficient information was available to the authors at this stage regarding the characteristics and composition of such wastes.

3.5 CRUDE OILS AND HYDROCARBONS

3.5.1 Introduction

This section includes oil and hydrocarbons originating from processes other than oil refinery processes. Oil refinery process wastes are covered in Table 1.

3.5.2 Principal Industries

(a) Mineral Oils from Garages and Car Washes

Type and Size of Industry

There are many garages and car washes to be found throughout the cities and country. Each of these establishments will give rise to waste mineral oils either directly through oil changes or accidentally through spills and leakage.

Type of Wastes

The wastes will be a mixture of oil, water, petrol, some heavy metals and detergents. The wastes may be segregated or combined depending on the reuse possibilities entertained.

Form of Wastes

The wastes will be aqueous with foam. They will be dirty, black with floating and dissolved oils. They can be characterized by BOD, TSS, COD, pH, oil and grease, and some heavy metals.

Total Amounts

The amount of oils used will vary with engine size. However, an average car uses 150 litres/year while buses use 300 litres/year. This may give rise to oil concentrations of 50-60 mg/l.

Discharge

Discharge may be continuous during part of the day for car washes. For garages discharges will be intermittent.

Effluent Concentrations

The effluent treatment should begin at the source with separation of the oils before mixture with other wastes. Also the first waste treatment step should be oil separation in e.g. API separator. Detergent could be added to dissolve the oil. Also air flotation and skimming can be used. Final oil concentrations of 5-8 mg/l can be attained.

(b) Iso-Amyl Alcohol

Type and Size of Industry

The chemical iso-amyl alcohol is used in the production of both phosphoric acid and potassium nitrate. The industry produces some 12,000 tons per year of phosphoric acid.

Type of Wastes

The iso-amyl alcohol is used to separate hydrochloric acid from potassium nitrate and also for the separation of phosphoric acid from the process solutions. Hence the chemical will be found in wastes from the reaction stages as well as purification and recovery stages.

Form of Wastes

The chemical formula of iso-amyl alcohol is $(CH_3)_2CH\ CH_2CH_2OH$. The other components in the waste streams will be Ca, P, Cl^-, Fe, Mg, K, F, $PO_4^=$. The wastes will mostly dissolve and will have a distinctive odour. The specific gravity of the chemical is 0.812.

Total Amounts

Plant wastes are about 1000 m^3/d while the wasted chemical will be about 100-200 mg/l in concentrations. This will give rise to about 150 kg/day.

Discharge Patterns

As this is a large continuous plant the waste streams will be continuous also.

Effluent Concentrations

As the alcohol is dissolved, it is not possible to treat the wastes.

(c) Oils from Meat Processing

Type and Size of Industry

The meat cooking and processing industry is quite large. One plant produces about 1000 tons per year.

Type of Wastes

Wastes are produced in all phases of production. Oils are produced in the cutting section, rendering sections and the cooking and packing sections.

Form of Wastes

Wastes are aqueous mixtures of blood, waste, meat, oils etc. They may be characterized through the concentrations of BOD, SS, DS, COD, colour, pH, grease, P, N, Cl etc. In general, the wastes are coloured with soluble and insoluble components. There will also be odours arising from the waste flows. The oils will be organic in nature.

Total Amounts

There are about 150-200 m^3/day of waste flows with all these flows originating from oil bearing processes. Oil will be at about 100-180 mg/l or about 20 kg/day.

Discharge Patterns

As the plant operates continuously, with care for hygienic conditions and cleanliness there will be continuous waste streams.

Effluent Concentrations

The oils can be flocculated and separated. Oil flotation and skimming are an alternative. The general plant flows would also be treated using conventional primary and secondary treatment processes.

(d) Organics and Oils from Palm Processing

Type and Size of Industry

The industry gives rise to about 16,500 tons/year of palm oil.

Type of Wastes

The wastes are generated in three esterification and purification steps of oil production. Also washing down of plant floors gives rise to wastes. The process involved is

PALMOIL + ESTER → FREE FATTY ACIDS

Form of Wastes

The wastes are aqueous solutions with oils, mainly dissolved but with some separation of phases. The wastes will be odourous and will be warm, 20-100°C. There are also constituents such as sulphuric acid, sodium sulphate and sodium chloride.

Total Amounts

The process and washing down produces about 10 m^3/d of wastes, with 1/2 actually process wastes. There will be 1200 mg/l oils and waste COD is about 16,500 mg/l. There is about 0.1 m^3 of waste/ton of product. The TAS is about 330 gram/l.

Discharge Patterns

The batch process is operated twice per day throughout the year. Hence wastes are discontinuous.

Effluent Concentrations

The wastes can be treated in ponds or anaerobic biological treatment.

(e) Fruit Processing

Type and Size of Industry

The fruit canning and juicing industry uses many organic compounds such as fructose and other sugars. The fruits include oranges, apples, lemons, grapefruit, grapes.

Type of Wastes

The main processes are washing, peeling, concentrating, filtering and product packaging. All the processes give rise to waste streams including washing water, wash down water, spills and disposal of excess material.

Form of Wastes

The wastes contain many organic compounds such as those of formulae $C_6H_{12}O_6$ and $CH_2OH\ (CHOH)_3\ COCH_2OH$.

There will be some colour and possibly some odour. There will be floating and dissolved materials.

Total Amounts

About 4 m^3 of wastes are produced from each ton of fruit or about 1.6 m^3 per ton of produce. The organics in process wastes are at about 3200 mg/l but fall to 1280 mg/l in plant wastes.

Discharge Patterns

The wastes are discharged continuously during the season which lasts from September to May.

Effluent Concentrations

The wastes may be treated using coagulation and sedimentation, ponding and other biological treatment techniques. Reuse of water will greatly reduce waste water flows. Process waste organic concentration may be reduced to 300 mg/l and plant waste concentrations to 150 mg/l.

3.6 CYANIDES AND FLUORIDES

3.6.1 Cyanides

Cyanide wastes arise from a number of different industries. In the aquatic environment they are highly toxic to plant and animal alike. Pollution of water sources or recreational areas causes a situation of extreme danger to human beings. Industries which discharge cyanides are metal processing industries, organic chemical industries and petrochemical industries.

(a) Metal Processing Industries

Type and Size of Industry

Zinc plating is conducted in cyanide baths as is silver and gold. In general cyanide baths are also used in copper production. Industries can vary from small shops to large metal processing plants. Sometimes smaller establishments are more problematic than larger plants because of difficulties of surveillance and control.

Type of Wastes

Wastes are generated in the cyanide bathing processes. Cyanide is generally associated with many other heavy metals such as zinc, copper, iron, nickel, aluminium. Mixed wastes contain on the average 50 to 70 mg/l CN^- while typical total plant wastes contain an average of 15-30 mg/l CN^-. Concentrations of cyanides from general process wastes are 200-1500 mg/l for electronic hardware, 70 mg/l for silver-ware and up to 130 mg/l in general plating wastes. The wastes are generated by the rinsing of plates and occasional spills.

Form of Waste

Most cyanides appear in alkaline bath solutions since acidic environment can produce highly toxic HCN vapour.

The wastes are aqueous turbid solutions with dissolved CN^- ion, associated are oils and detergents as well as suspended floating and dissolved metals. They may be warm and coloured.

Total Amounts

Quantities of cyanides will depend on the particular bathing process being used. Quantities of wastes per ton of product are given in the sections on respective metals. Primary plating baths may contain between 30 to 50 grams per litre of cyanide salts. Approximately 10 to 30 kg of cyanides are used per ton of plated products.

Discharge Patterns

In small shops or plants discharge is intermittent or semi-continuous. In larger plants discharge is continuous with peaks depending on spills and dumping of process solutions.

Effluent Concentrations

Cyanide presence interferes with of heavy metals by pH variation and precipitation. Hence it is important to separate concentrated cyanide streams if possible. Cyanides can be destroyed by oxidation usually by chlorine according to the following reaction (not stoichiometric):

$$CN^- + Cl_2 + NaOH \rightarrow N_2 + CO^=_3 + NaCl$$

If waste segregation and separation are not possible, cyanide destruction must be conducted before metal treatment. Other methods of cyanide treatment are activated carbon adsorption, ion exchange, liquid-liquid interaction and acidification volatilization.

Effluent qualities of below 5 mg/l of CN^- can be accomplished.

In well managed treatment, concentrations of CN^- in the final effluent may be as low as 2 mg/l for the cyanide bearing wastes and below 0.5 mg/l in total plant wastes.

(b) Petrochemical Industry

Type and Size of Industry

The petrochemical industry can be subdivided into a number of production categories namely: crude oil distillation, cracking, petrochemical production, lubrication oil manufacturing and coke manufacturing. Larger plants are usually integrated to produce various combinations of the above. Plants may vary in size, but to render the plant economical its production capacity should be at least 50,000 tons per year.

A medium to large size refinery and petrochemical plant processes between 1 and 10 million barrels of oil per year.

Type of Wastes

Cyanides are produced in small quantities in all process steps. However, in the cracking process (thermal) up to 10 mg/l of CN^- may be found. In other process wastes concentrations of up to 0.2 mg/l of CN^- are found.

Form of Wastes

Cyanides are dissolved ions of CN^- in the waste streams. Wastes vary in each process and they usually contain oils, dissolved organics, sulphates, nitrates and ammonia, and phenols.

Total Amounts

Old refineries and petrolchemical plants produce enormous quantities of wastes of between 2 to 5 m^3 of wastes per ton of crude oil processed. New refinery technology has cut amounts of wastes to approximately 0.2-0.3 m^3 per ton of crude.

Approximately 1.0-1.5 kg of cyanide is used per ton of cracking plant input.

Discharge Patterns

Discharge is intermittent with varying frequencies according to plant operation.

Effluent Concentrations

Following destruction of cyanides by chlorination as described in earlier paragraphs concentrations of below 0.2 mg/l can be readily achieved.

(c) Other Industries with Wastes Containing Cyanides

Cyanide wastes are also found in a number of other industries.

These include the photographic industry where concentrations of 6 mg/l have been found. Cyanides were found in the process wastes of the ferroalloy industry at up to 30 mg/l. Cyanides may also be found in the wastes from the pharmaceutical industry, as well as the rubber and plastics industries.

3.6.2 Fluorides

Fluorides appear in wastes of numerous industries among them the fertilizers industry, metal processing industry, glass and ceramics industries, in some petrochemical and pesticide industries and in various mining and mineral processing wastes. Only the principal fluoride emitters are described here.

(a) Phosphate Fertilizer and H_3PO4 Industry

Type and Size of Industry

Phosphate fertilizer industries, as well as producing ortho phosphoric acid for industrial purposes are usually large in size with capacity of at least 5000 tons of H_3PO_4 per year. Major fertilizer plants can reach capacity of 10,000 to 100,000 tons of phosphate (as H_3PO_4). As in other mining and mineral industries, fluoride is present in the raw material (rock) and is emitted into the waste-stream during the recovery and processing of the commercial product being superphosphate fertilzer and ortho phosphoric acid in this example.

Type of Wastes

Phosphate rock is treated with hydrochloric acid to produce H_3PO_4, $CaHPO_4$ and $Ca(H_2PO_4)_2$.

Fluoride ions are dissolved from fluoride salts and complexes in the rock and they appear in the wastes in the form of CaF_2, HF, NaF and KF. Wastes contain H_3PO_4, $CaCl_2$, $CaSO_4$, HCl, iso-amyl-alcohol and other dissolved salts and minerals. When the industry is producing other fertilizers (usually nitrogenous) ammonium and nitrate salts will also be present in the plant waste stream.

Concentrations of fluoride in the phosphate acidification process are between 1000 and 4000 mg/l depending on fluoride content in the raw material (rock) and on the amount of water used in the process. Total fertilizer plant wastes might contain between 200 and 800 mg/l of fluorides.

Ortho phosphoric acid production processes contain 2000-4000 mg/l of fluorides and total plant wastes contain approximately 1000-2000 mg/l of fluorides.

Form of Wastes

Waters are in a turbid, milky solution, due mainly to the content of calcium sulphate suspension.

Total Amounts

Phosphate fertilizer plants produce approximately 10^3 of waste per ton of product. Fluoride discharge can reach 10 to 30 kg per ton of produce expressed as H_3PO_4.

Discharge Patterns

Discharge is normally continuous.

Effluent Concentrations

Lime treatment at elevated pH levels will form relatively insoluble CaF_2 precipitant. Final effluent after such treatment may contain 10-15 mg/l and with further adsorption of CaF_2, 1-2 mg/l. Total plant wastes contain 4-6 mg/l fluoride ion.

(b) Electronic Industry

Type and Size of Industry

Processing of printed electrical circuits and conductors and special plating processes involve the use of fluoride-containing compounds. Industries vary in size and they are usually small with a few exceptions, the major electronics industries.

Type of Wastes

HBF_4 is added to plating and processing baths, usually when copper and special alloys are used (sometimes also in zinc, nickel and silver plating).

Process wastes contain 20-30 mg/l of F^- while total plant wastes might contain process copper and other metals.

Form of Wastes

Usually clear or slightly coloured solution.

Total Amounts

Total plant wastes amount to approximately 10 to 20 m^3 per m^2 of plated or processed surface while process wastes amount to 1-2 m^3 per m^2 of plated or processed surface.

Approximately 20 g of HBF_4 is discharged per m^2 of processed surface.

Discharge Patterns

Intermittent batch production, almost a continuous flow in larger plants. Peak concentrations when spills occur.

Effluent Concentration

Fluoride is removed by ion exchange on special resins producing effluent with approximately 0.5-1 mg/l F^-. Total plant effluent contains therefore 0.1-0.2 mg/l fluoride ion.

(c) Glass Industry

Type and Size of Industry

Fluoride is generally found in the wastes generated from glass surface treatment processes. This involves the removal of surface faults such as minute cracks and flaws. It is also used in the production of frosted surfaces such as for frosted glass or light bulbs.

Type of Wastes

The wastes from the glass industry include cooling and boiler water, and washwater from plate, float and automotive subcategories.

Hence, the fluoride wastes will be due to the washing of glass after frosting at HF treatment.

Form of Wastes

The wastes will be acidic containing mercury, diofluoric acid, sulphuric acid, oils and abrasions and silicon compounds. The wastes may be warm and turbid. There will be associated suspended solids but little BOD.

Amount of Waste

The concentrations in the wastes will be

HF	:	1000-3000 mg/l
H_2SO_4	:	500-1200 mg/l
Oils	:	50- 150 mg/l
Abrasions	:	1500-3000 mg/l

About 46,000 l of wastewater/ton of glass processed will be produced.

Suspended solids concentrations may be as high as 15,000 mg/l giving 700 kg/ton of glass.

Discharge Patterns

Discharges may be intermittent due to batch processing.

Effluent Concentration

The effluent may be treated in a series of lime neutralization and acidification steps followed by precipitation tanks. The wastes can be then neutralized and stored in lagoons. Effluents of less than 20 mg/l can be achieved.

(d) Other Industries with Wastes Containing Fluorides

Fluoride is a component of the bath solutions of many electroplating and metal treatment processes. Fluorides are also specifically used in steel and aluminium production plants. Fluorides are also produced as wastes from the water treatment industry.

3.7 NON-BIODEGRADABLE DETERGENTS

3.7.1 Introduction

Hard detergents are detergents which are either non-biodegradable or very slowly biodegradable. They may be anionic, cationic and non-ionic. Some effort has been made in recent years to convert to soft detergents i.e. those that are easily and quickly biodegradable. Slow, hard detergents are still being used, and therefore they are found in the waste streams originating from the production process itself, in laundry wastes, in car wash wastes, and in the wastes from metal degreasing processes. Hard detergents are also found in urban runoff and in raw sewage.

3.7.2 Hard Detergent

Type and Size of Industry

Hard detergents such as Benzil sulphonate (DDBS) are produced as a by-product of the petrochemical industry. The size of the industry is 5.5×10^6 tons/year.

Type of Wastes

Depending on the success of waste segregation there will be larger or smaller amounts of water with the waste products. The wastes originate in all stages of the detergent preparation process.

Form of Wastes

The wastes contain DDBS as well as NH_4^+, K, BOD, COD, SS, fats. They may also be characterized by using MBAS - methylene blue active substances. The DDBS is generally dissolved.

Total Amounts

The plant gives rise to 3000 m^3/day of wastes with a concentration of 600 mg/l, hence some 1800 kg/day of product are found in the waste streams. The BOD of the waste streams may be in the range of 60-3500 mg/l, the COD 100-2000 mg/l and MBAS 50-1400 mg/l.

Discharge Patterns

The discharges will be intermittent depending on process operation, washing down and production requirements.

Effluent Concentrations

In theory it should be possible to separate by aerating which would cause foam and then remove the foam. Other treatment techniques are primary sedimentation, skimming and biological treatment.

3.7.3 Laundries

There are many types of laundry processes including industrial laundries, linen only, auto washes, carpet and upholstery cleaning, laundromats and dry cleaning. Concentrations of 100 mg/l ABS have been found in waste streams.

3.8 INORGANIC COMPOUNDS OF PHOSPHORUS AND ELEMENTAL PHOSPHORUS

3.8.1 Introduction

Phosphorus like nitrogen is ubiquitous in the natural environment. Given sufficient other nutrients the addition of P may stimulate plant life leading to a deterioration of the water and the aesthetic quality of the environment by eutrophication.

Phosphorus is a waste product from the production of phosphoric acid for fertilizer production. It will also be found in urban waste-streams such as urban runoff, urban sewage and urban treated sewage.

3.8.2 Principal Industries

(a) Fertilizer Production

Type and Size of Industry

Phosphate fertilizer is produced by a series of ore treatments (washing steps) followed by production of phosphoric acid. This may then be used to produce $(NH_4)_3PO_4$, H_2SO_4 and triple superphosphate.

Type of Wastes

Wastes are generated in all steps including all pollution treatment steps.

The use of wet scrubbers gives rise to a wastewater stream. Cleaning of process equipment and areas gives rise to waste flows.

Form of Wastes

The wastes include $PO_4^{=}$ as well as $SO_4^{=}$, Ca and fluoride. There may be ammonia and aluminium. The ions will be dissolved and the solution will be coloured with a low pH (1-2).

Amounts

Approximately 10 m^3 of wastes are produced per ton of phosphates (expressed as H_3PO_4). The P_2O_5 concentration in actual treatment process wastes may be as high as 5000 mg/l. But in overall plant wastes, the P_2O_5 concentration is about 100 mg/l. Other compounds are: suspended solids 1000 mg/l, $SO_4^{=}$ 4000 mg/l, and fluoride 8000 mg/l.

Discharge Patterns

Waste discharges may be intermittent depending on batch processing, water treatment and any reuse of waste streams.

Effluent Concentrations

Treatment of phosphate wastes may most easily be achieved using chemical precipitation using lime. This is done by a two-stage neutralization process. The phosphorus concentrations following such treatment should be reduced to less than 1 mg/l as phosphorus.

(a) Chemical Production of H_3PO_4/KNO_3

Type of Industry

About 12,000 tons/year of ortho phosphoric acid are produced in one large plant.

Type of Waste

The process involves treatment of elemental phosphorus with hydrochloric acid. This produces phosphoric acid plus by-products. Wastes originate in purification process and plant wash down steps.

Form of Wastes

The wastes are an acidic aqueous solution containing $SO_4^=$, $NO_3^=$, $PO_4^=$, and F^-.

Total Amounts

Process waste concentrations of $PO_4^=$ are in the range of 3000-6000 mg/l while plant wastes are about 3500 mg/l $PO_4^=$. Process wastes are 850 m^3/d out of a total plant wasteflow of 1000 m^3d. The wastes are dissolved with some floating and settleable solids. About 3500 kg/day of $PO_4^=$ is found in the waste stream.

Discharge Patterns

Discharges are continuous.

See paragraph headed "Effluent Concentrations" above.

(c) Metal Processing

Type and Size of Industries

Phosphatization of metals in plating and metal processing industries is quite common. Specific metal plating industries are described above.

Type of Wastes

Metals are washed in baths and ponds containing 20-50 g/litre of $NaPO_4$ together with 20-50 g/litre of Na_2CO_3, 10 g/litre of NaOH and 5-20 g/litre of Na_2SiO_3.

Concentration of phosphate in process wastes including rinsing may reach 200-500 mg/l as P_2O_5.

Form of Wastes

Wastes are alkaline, usually clear with light yellowish colour and foam.

Total Amounts

Approximately 8 m^3 per ton of metal products are discharged from the phosphatization metal treatment.

Discharge Patterns

Intermittent rinsing.

Effluent Concentrations

Lime and magnesium treatment at elevated pH cause precipitation of calcium phosphate producing effluent with less than 10 mg/l P. Ion exchange methods can produce effluents with less than mg/lP.

(d) Other Sources of Phosphorus

Phosphorus may also be found in the wastes originating from water cooling processes. Phosphorus is a component of runoff both rural and urban. Indicating concentrations is very difficult because of the variability of runoff flows and variability between areas. However, concentrations may average 1-2 mg/l or less. Municipal sewage also includes some phosphorus usually in the form of phosphate.

Phosphorus concentrations in raw municipal sewage are between 6 mg/l and 18 mg/l (as P). Lime, or alum or ferric chloride treated effluents, contain less than 2 mg/l of phosphorus and with a proper filtration of such effluents concentration of phosphorus can reach below 1 mg/l.

3.9 PATHOGENIC MICRO-ORGANISM

3.9.1 Introduction

Pathogens are emitted to receiving bodies of water by municipal sewage discharge, discharge of sludges, discharge of some industrial wastes and in animal wastes. Runoff water, especially from animal husbandry and agricultural areas may also contain animal pathogens.

Due to the difficulty of isolating and identifying specific pathogens in wastewaters by routine monitoring, non-pathogenic indicator organisms are used, notably bacteria of the coliform group.

The following are the main sources of pathogens that might affect the marine environment.

3.9.2 Municipal Sewage

The municipal sewage might contain many pathogens most notably Salmonella, Shigella, Vibrio cholerae, Salmonella typhimurium, bacillary dysentery causing bacteria, amoeba cysts, poliomyelitis viruses, infectious hepatitis viruses, various enteric viruses, ECHO viruses, coxsackie viruses, and Ascaris eggs. Total coliforms and faecal coliforms and less after faecal streptococci serve as indicator organisms to all pathogens, specifically bacterial pathogens, whilst a direct count of plaque forming units (PFU) is used for virus enumeration mostly in research and special surveys.

Type and Size of Source

Municipal wastewater in most sewered countries amounts to between 80 and 300 litres per inhabitant per day (including contribution by public facilities). Amounts depend on the standard of living, availability of water supply and local customs. This will constitute the average sewage flow when a separate (segregated) sewage system exists but the flow may dramatically increase when combined sewage-flood water collection is practised.

The amounts of wastewater emitted by a municipality will be dramatically reduced when no central sewage exists i.e. when the community is served by individual septic tanks or night-soil collection.

Form of Wastes

Pathogens in wastewater will be in the form of individual bacteria and virus particles or associated with other suspended and settleable matter.

Total Amounts

An individual human emits between $5x10^9$ to 10^{12} coliform bacteria per day and between $0.5x10^6$ and $3x10^6$ enteric virus units per day. Various factors have been suggested to relate pathogenic organisms to indicator organisms.

Total Concentrations

Concentrations of coliforms in ordinary municipal wastewater usually range between 10^7 and $5x10^8$ per 100 ml while concentration of faecal coliforms usually amount to between 10 to 60 percent of the total coliforms.

Enteric virus concentrations vary between 400 to 2000 plaque forming units (PFU) per 100 ml m in ordinary municipal wastewater.

Sludges, septic tank pump-out and night soil might contain much higher concentrations of coliforms and viruses according to their solid content and the time lapse until discharge.

Effluent Concentration

Primary treatment reduces coliform organisms by 40 to 80 percent while a reduction of between 1 and 2 orders of magnitude is expected in conventional biological secondary treatment thus bringing about coliform concentrations of approximately $5x10^4$ - $5x10^6$ per 100 ml. Chlorination might bring coliforms to below 1000 per 100 ml but coliform regrowth might be expected. Various pathogens might be more sensitive to treatment and disinfection than the coliform indicator bacteria while other pathogens (especially some viral pathogens) can be more resistent to treatment and disinfection.

Virus removal in a full secondary biological treatment might be between 1 to 3 orders of magnitude and its efficiency of removal depends to a large extent on the temperature.

Lime treatment is very effective in removal of both bacteria and viruses and reduction by 3 to 5 orders of magnitude has been reported.

3.9.3 Industrial Wastewater

Industrial wastes which include pathogens may originate in the following industries: diary products, fruit processing, food canning, textile and leather industry, feed lots, timber industry and laundries. Bacteria which may be found in the wastes from these industries include Pseudomonas, Chromobacteria, Achromobacteria, Corynae bacteria, Enterobacteria, Micrococci, Brevibacteria, Caulobacteria, yeast and viruses. In most cases industrial wastes enter the sewage system and are treated there. This may be after some treatment at the industrial site. This treatment is generally for the reduction of BOS, S.S., and metal concentrations.

Although there is very little evidence of effective pathogenicity to humans through the marine environment with such wastes they contain a large concentration of coliform organisms.

Type and Size of Source

Industrial wastes may be up to 50% of the mean dry weather sewage flows. Individual industries will generate waste flows depending on their size, the season (packing plants) and water reuse considerations.

Form of Wastes

The wastes may be carried in solid or liquid media. The liquid medium may be discharged to sewers or receiving wastes. The solid wastes would generally be disposed to the land. The pathogens in the form of living bacteria, viruses or spores, will therefore be found in sewage streams and at land disposal sites. Some bacteria etc may enter the groundwater. Some industrial wastes from the food, beverage and brewery industries might contain non-pathogenic coliforms and klebsiella micro-organisms, which can give a high coliform count on beaches which are close to points of discharge of such wastes.

Total Amounts

Amounts will be similar to those in section 3.9.2.

Total Concentrations

See section 3.9.2.

Effluent Concentrations

Effluent treatment whether industrial treatment or conventional sewage treatment will reduce pathogens by those factors mentioned in section 3.9.2 (under Effluent Concentration). No information was available regarding ground water quality near solids disposal sites.

3.9.4 Runoff, Drainage And Agricultural Wastes

The amount of human pathogens in streams and floodwater reaching the marine environment and which contain, among other things, runoff water, drainage water and agricultural wastes depends on the amount of sewage and other human wastes that find their way into the stream or its watershed as well as the degree of treatment of such wastes and the time esplased. Agricultural wastes might include Salmonella, brucelosis organisms, anthrax organisms and other organisms of animal origin.

Nevertheless, streams and floodwaters that reach the marine environment and which are fed by watersheds with intensive agricultural activity may contain a high concentration of coliform, faecal coliform and faecal streptococci indicator organisms. These organisms will give a high coliform background concentration to the marine environment and in certain cases might surpass the allowable coliform standards at beaches close to river mouths and esturies. In certain cases such "naturally occurring" indicator organisms may mask the presence of human point source of sewage.

3.10 THERMAL POLLUTION

Once-through cooling systems that can create thermal pollution of the marine environment are usually near-shore large fossil fuel and nuclear power stations, refineries, petrochemical industries, liquified natural gas (LNG) facilities etc. Bleeding-off of closed recycling cooling waters usually do not affect the heat balance of large bodies of water.

Only fossil fuel power production facilities are discussed in this work; other sources of cooling water are basically similar in their basic characteristics although quantities of cooling waters and the temperature gradients may be different.

Type and Size of Waste Source

Fossil fuel steam-electric power stations that can significantly affect the marine environment range in size from 50 megawatt to the largest power plants of 1500 megawatts and more. Economy of scale and the diminishing availability of near-shore sites direct the increase in size of power stations to the range of 1000-3000 MW_e.

Quantities and Heat Gradients

Flow of cooling water from power stations depends on size of plant, temperature gradients, efficiency of the plant and its heat exchangers, etc. Cooling water flow may range between 2 and 12 m^3/sec per 100 megawatts installed capacity with temperature gradients between inflow and outflow, t_c, of between 4 to 10°C.

The discharge of warm waste is likely to be continuous. However this is also likely to be seasonal e.g. more electricity is used in winter hence more cooling water may be required. Alternatively in summer when e.g. sea waste is warmer it may be necessary to use larger flows.

As the 'blowdown' or removed cooling water has already been cooled it is unlikely that further cooling will be attempted.

3.11 RADIOACTIVE EFFLUENTS

3.11.1 Introduction

Radiation may be of natural and anthropogenic origin.

The natural radionuclides in the environment are of two general classes. Cosmogenic nuclides have their origin from the interaction of cosmic rays with atoms present in the atmosphere and in the radioactive decay of radioisotopes produced during the formation of the solar system.

Anthropogenic sources of ionizing radiation are the processes involved in the production of energy with the fission fuel cycle, fallout from nuclear weapon tests, use of radioisotopes in researches, industry and medical applications and consumers goods.

With regards to a release of radioactive effluents into the marine environment the sources of concern are wastes produced during the nuclear fuel cycle and (to a lesser extent) wastes from industrial research and medical applications.

3.11.2 Type And Size Of Industry

The amount of wastes produced in the various steps of the nuclear fuel cycle depend on the energy production. At present few nuclear installations are in operation in the Mediterranean basin.

On Dec. 31, 1977 4 gas/graphite reactors (GGR) with a nominal power of 1336 MW(e), 2 boiling water reactors (BWR) with a nominal power of 620 MW(e), one pressurized water reactor (PWR) with a nominal power of 250 MW(e) and one fast breeder reactor (FBR) with a nominal power of 233 MW(e) were in operation in the Mediterranean basin, Table 2. These reactors are sited in France, Italy and Spain. From Jan. 23, 1964 when the first reactor (Garigliano, Italy) was connected to the electrical grid, these 8 reactors have generated circa 110.10^9 kWh (=12.600 MW year) of electricity up to December 31, 1977.

By 1990 about 25 additional nuclear reactors, 1000 MW(e) each, should be in operation in the Mediterranean basin.

This could bring the total nominal power installed by 1990 from the present 2440 to about 27500 MW(e).

Only two civilian fuel processing pilot plants (Italy) exist at present in the Mediterranean basin. Their capacity is estimated at 0.1 tons uranium per year. The installation of future fuel processing plant in the Mediterranean basin is still uncertain.

3.11.3 Origin And Average Composition Of Waste

The nuclear fuel cycle produces wastes along its various steps: mining, milling, feed material preparation, fuel fabrication, energy production by fission in reactors and fuel processing. At each step different type and quantities of wastes are produced. Of the three fuel cycles (uranium, thorium and uranium/plutonium) only the uranium and the uranium/plutonium cycles are used in the Mediterranean countries.

Although all artificial radioactivity is produced in the nuclear reactors by far the greatest amount of these wastes arise in the fuel processing plant. 99.99 percent of these wastes are permanently stored.

In accordance with national requirements of radiation safety, only minor amounts are released into the environment.

Airborne release will only marginally influence the marine environment. Liquid releases may reach the sea indirectly or directly. As will be shown in this section on effects the release into the marine environment of the same quantities results in much lower dose to human than a release into fresh water environment.

Mining, milling, feed material preparation and fuel fabrication produce low level effluents containing uranium, plutonium and thorium and its decay products (daughters). At present no sites are known which discharge directly or indirectly through a discharge into a river and thence into the sea.

In 1977 4 different reactor types (PWR, BWR, GGR and FBR) were operating in the Mediterranean basin.

The radioisotope composition and the amounts in the effluents released into the environment depend on the reactor type and on the waste processing system used. Therefore, even the composition and amount of the effluents released from the same reactor type may vary widely. In general older reactors release larger amounts of radioactive effluents than recent ones.

The amount of radioactive effluents produced is related to the amount of electric energy produced and the quantities released are normalized into curies per MW(e) y electricity produced.

3.11.4 Form of Waste

Reactors produce airborne and liquid effluents and solid wastes. The main radioisotopes in airborne effluents are the noble fission gases krypton and xenon, the activation gases 41-Ar, 14-C, 16-N, 35-S and tritium, radioactive halogens and particulates.

Liquid effluents contain, besides various fission products (FPs), activation

TABLE 2 - Production of electric energy by nuclear reactors in operation in the Mediterranean basin by December 31.1977 (MED X 1978, Notiziario II/1978)

Country	Name	Location	Type	Distance from sea km	MW (e) nominal size	Connection with grid	Total electric power produced 10^9kWh	MW y	Utilization in percent
Italy	Garigliano	coast	BWR	15	160	23. Jan. 1964	12	1370	63
	Latina	coast	GCR	0	210	12. May 1964	16.5	1880	66
	Torino	Po	PWR	400	250	22. Oct. 1964	16.75	1900	58
	Caorso	Po	BWR	300	900	-	-	-	-
France	G 2 + 3	Rhone	GCR	90	86 (2 units)	1960	9.9	1125	77
	Bugey-1	Rhone	GCR	350	540	15. Apr. 1972	16.7	1900	61.5
	Bugey-2	Rhone	PWR	350	925	21. Apr. 1978	-	-	-
	Phenix	Rhone	FBR	90	233	13. Dec. 1973	3.8	433	46
Spain	Garona	Ebro	BWR	700	460	2. March 1970	16.9	1930	52.5
	Vandellos I	coast	GCR	0	500	6. May 1972	18.4	2100	70
					4.264		110.95	12.638	

products (APs). The average composition of liquid effluents is given in Table 3. All values are normalized per NW of electric energy produced. It should be noted, however, that even within the same category of reactors the amounts and the isotopic composition vary widely. With the possible exception of France, spent fuel elements are stored or processed outside the Mediterranean basin. The release of radioactive materials from the fuel reprocessing plant depends upon the type of fuel, irradiation history, cooling time and the specific waste processing systems of the reprocessing installation.

3.11.5 Total Amounts Discharged

Approximate release can be estimated from the normalized releases and the amount of MW(e) y produced. Future release from nuclear installations may be estimated from the installed power assuming an utilization factor of 0.7. These releases will be lower since waste treatment technology will improve. Solid low level wastes are sometimes dumped at sea (but so far no solid wastes have been dumped in the Mediterranean). Wastes from other civilian nuclear uses are often sealed sources, which are not dispersed in the environment. The isotopic composition of non-nuclear wastes to be discharged into the environment is difficult to estimate. Production and import data may be consulted.

3.11.6 Discharge Pattern

Airborne effluents are discharged more or less continuously from BWRs. The amount and relative isotopic composition depend on the hold up times of the gases before release. In older reactors the hold up time is short (20 to 30 min). In modern BWRs hold-up times of two hours and more allow short living isotopes to decay. Since in PWRs the primary loop is rarely opened the release is two orders of magnitude less than that from BWRs. The low temperature Magnox reactors discharge insignificant amounts of airborne effluents.

The frequency of release of liquid wastes varies considerably with reactor type and waste treatment plant. Leakage of the primary system to the secondary system and to the auxiliary building means that the amount of floor drainage wastes, from laundry decontamination, wash-down, etc. are important parameters. Then number and capacity of collector tanks and treatment of these wastes and those from the spent fuel pits are other parameters.

3.11.7 Physical, Chemical And Biochemical Properties

The main characteristic of a radioactive waste is its radioactivity. Radioisotopes decay under emission of different forms of radiation which in turn have different effects on living organisms.

The chemical form depend on the form of waste treatment before release and of the origin in the reactor system.

The nuclides may be in ionic form, complexed with organic ligands, particulated and colloidal. According to their form they will follow a different distribution pattern in the marine environment and also different pathways to man.

In general ionic radioisotopes are more readily taken up than complexed forms by components of the marine environment.

On the other hand particulate and colloidal forms are preferentially accumulated by the so-called filter-feeders, e.g. mussels and copepodes. (*)

(*) For a recent review see: Bernhard M., Zattera A.: The role of chemical speciation in the uptake and loss of elements by marine organisms; International Symposium on Interaction between Water and living Matter; Odessa, Oct. 1975 (In press)

TABLE 3 - Radionuclides in normalized liquid effluents from reactors in μ Ci per MW(e) year(*)

PWR	1200000	30	-	-	-	-	180	120	-	88	13	42	-
BWR	100000	20	200	-	-	-	580	1900	-	1700	46	6100	230
GGR	270000	90	-	770	18000	1300	670	42	3700	-	27	710	83

	89 Sr	90 Sr	90 Y	91 Y	91 Zr	95 Zr	95 Nb	99 Mo	103 Ru	106 Ru	106 Rh	125 mTc	110 mAg
PWR	14	2.2	-	-	4.1	-	6	3.4	24	-	-	-	18
BWR	800	98	-	-	-	12	-	160	-	-	-	-	5.9
GGR	680	11500	11500	370	-	-	110	-	-	2300	2300	1900	-

	124 Sb	125 Sb	131 I	132 I	133 I	134 Cs	137 Cs	141 Ce	144 Ce	144 Pr	147 Pm	154 Eu
PWR	98	-	2300	13	1300	1000	1700	-	82	-	-	-
BWR	-	-	3600	150	-	17300	25000	9.1	340	-	-	-
GGR	420	7500	-	-	-	13600	68300	-	960	960	3800	150

(*) Data from UNSEAR 1977: Sources and Effects of Ionizing Radiation; UNSCEAR 1977, report to the UN General Assembly; UN, New York pp. 725.

3.12 SUBSTANCES CAUSING TASTE AND/OR SMELL IN FISH AND OTHER MARINE FAUNA (Phenols and Aromatic Organic Compounds)

3.12.1 Introduction

Phenolic compounds are prevalent in the wastes of many industries. These are particularly dangerous because they are toxic to marine life, create oxygen demand and also cause taste in drinking water after chlorination.

Industries giving rise to phenol wastes are coke production, organic chemical production, plastics production, pharmaceutical industry, the gas production industry and, most important, oil refineries.

Phenolic compounds and other aromatic compounds such as benzenic compounds, toluene and xylene are particularly of concern because they bring about a distinct bad taste and odour to fish, fish products and other marine products. Benzenes, toluenes and xylenes are emitted from many organic industries such as petrochemical industries, refineries, dye industry, coal gasification etc.

3.12.2 Principal Industries

(a) Oil Refineries and Petrochemical Industries

Type and Size of Industry

The petrochemical industry can be subdivided into a number of production categories. They are crude distillation, cracking, reforming, visbreaking, petrochemical production, lubrication oil manufacturing and coke manufacturing. Plants may also be partly or fully integrated to include a number of these processes. Most integrated plants are large in size with capacity of at least 100,000 tons of products per year.

Type of Wastes

Phenolic wastes are discharged from almost all steps of processing. After the crude oil fractionation, wastewaters contain, beside phenols, sulphides, ammonia chlorides and mercaptans. Cracking either chemical, catalytic or hydrocracking give rise to major phenolic wastewater flows. Concentrations of phenols in flows from crude distillation are 50-200 mg/l, cracking 20-100 mg/l, petrochemical 5-50 mg/l and fully-integrated 5-50 mg/l. Associated components of waste streams are BOD (up to 800 mg/l) suspended solids ($<$ 300 mg/l), oil and grease ($<$ 500 mg/l) and sulphides ($<$ 60 mg/l) to mention a few. Benzenes, toluenes and xylenes are products of petroleum and petrochemical production, especially from processes such as cracking, reforming and visbreaking. Their concentrations may vary between 20 and 100 mg/l.

Form of Wastes

The wastes are a nucleus of floating and dissolved oils in fractions. The water may be usually black in appearance. It may be warm and contains both dissolved and suspended solids. There will be dissolved chemicals including heavy metals, cyanides, ammonia and phosphate.

Total Amounts

Based on 1000 m^3 of oil produced the phenol production is 0.04 kg from crude distillation, 4 kg from cracking, 7.7 kg from petrochemical, 8.3 kg from lube oil manufacture and 3.8 kg from integrated systems. Waste flows have been reduced greatly with the introduction of new technology. For example, 100 gal/barrel of waste was produced from crude distillation using older technology. In a new plant this has been reduced to 10 gal/barrel. Similarly for catalytic cracking 85 gal/barrel has been reduced to 10 gal/barrel.

Discharge Patterns

The discharge of wastes from all processes is continuous. However, economics of operation show the high benefit of wastewater reuse.

Effluent Concentrations

With the inclusion of wastewater treatment facilities and the reuse of water, effluent quality should be improving. Typical treatment processes include API separators, lagoons, activated sludge treatment, sedimentation and chemical addition. After treatment, phenol concentration and concentration of aromatic compounds should be almost zero.

(b) Organic Chemicals

Type and Size of Industry

The types of organic chemical industries may be divided into categories: they are, non-aqueous processes (e.g. vinyl chloride), processes with process contact with water as steam (e.g. methanol, acetone), aqueous liquid phase reactions (e.g. acetic acid, iso butylene) and batch or semi-continuous processes (e.g. fatty acids tannic acids).

Type of Wastes

Wastes arise from steam condensate, washing down of facilities, preparation of products and regeneration of catalysts. Phenolic concentrations for the categories described under Type and Size of Industry above are: 0-15 mg/l, 0-6000 mg/l and 0-150 mg/l, respectively. Associated waste components are BOD, suspended solids, cyanides, TOC, oil and metals.

Form of Wastes

The wastes will be aqueous possibly coloured and milky. There will be some floating material and the wastes may be warm.

Total Amounts

Total production quantities will be dependent on the particular chemical being produced.

Discharge Patterns

As the major phenolic wastes come from the aqueous phase reactions which are continuous the effluent will also be continuous.

Effluent Concentrations

Treatment systems similar to those employed in the oil refineries; biological treatment and sedimentation can be used. Adsorption on activated carbon, is a possible alternative. Effluent qualities approaching zero should be attained.

(c) Melamine and Resin Industry

Type and Size of Industry

Melamine formaldehyde and phenolformaldehyde industries are of medium and large size. Phenolic compounds are emitted from both resin production and melamine covered plywood and furniture board industries.

Production of glues and adhesives for plywood, insulation boards etc. also produce phenol and aromatic solvent wastes.

Resins such as ureaphenolaldehyde and moulding powder production are also associated with emission of phenols and other aromatic substances.

Type of Wastes

Process wastes contain up to 100 mg/l phenols associated with carbolic acid, aldehydes, acetone and various ketones. Wastes are usually acidic. Total plant wastes produce 5 to 10 mg/l of phenols.

Form of Wastes

Wastes are turbid, and odorous, red-black in colour with suspended solids and sludge.

Total Amounts

Approximately 100 m^3 of wastes are produced per ton of resin of which approximately 5 m^3 per ton of product are process wastes rich in phenols.

Discharge Patterns

Intermittent discharge of phenol-rich process wastes.

Effluent Concentrations

Lime tréatment will produce calcium phenolate precipitate which can be evaporated to form a thick slurry to be discharged to hazardous wastes landfilling sites or incinerated. Following such treatment phenol concentration in process wastes is less than 10 mg/l or 0.5 mg/l in total plant wastes.

(d) Paint and Dye Industry

Solvents such as benzenes, toluenes, xylenes and other solvents are emitted from the paint and dye industries. Due to the diversity of such industries, no specific details are given here.

(e) Pharmaceutical Industry

Phenols, benzenes and other aromatic substances are emitted from the pharmaceutical industry. Due to the diversity of such industries, no specific details are given here.

3.13 SUBSTANCES WHICH HAVE AN EFFECT OF THE OXYGEN BALANCE

3.13.1 Introduction

Discharge of any biodegradable organic wastes into the marine environment will have an effect on the oxygen balance due to exertion of immediate oxygen demand and biochemical oxygen demand (BOD). The main sources of such wastes are municipal wastes and industrial wastes, particularly the food and beverage industries, breweries and distilleries, paper industries, tanneries, refinery and petrochemical industries, sugar refineries, canning industries as well as meat packing and processing and fishmeal production.

The effect of land-based point source of biodegradable organic wastes on the oxygen balance of the wide-open sea will be limited to the immediate surrounding area of the point of discharge. This is because of the enormous dilution rate in the open sea. However, the effect of oxygen depletion will be much more marked in confined areas of the sea such as estuaries, lagoons, marinas, close narrows bays and sea-enclosures. For example, raw municipal sewage with a 5-day BOD of 300 mg/l will have a negligible impact when the total dilution and dispersion in the open sea reaches a factor of 100 (usually attained within the first hour after discharge).

Sulphides, sulphites and other chemical reducing agents, whether from industrial sources or from septic municipal sewage, exert an appreciable immediate oxygen demand that might cause substantial fish kills in the vicinity of discharge, particularly in sea enclosures.

The most important factor that can affect the major oxygen balance in larger areas of the sea, still when a certain degree of enclosure exists preventing free exchange of seawater with the open sea, is eutrophication. Nitrogen constitutes the major limiting factor to algal growth in the marine environment rather than phosphorus and this chapter will discuss some of the major sources of nitrogen that might reach the sea.

3.13.2 Biodegradable Organic Matter

Raw municipal wastes might exert between 200 to 1000 mg/l of 5-day BOD, depending on water consumption and the contribution of industrial wastes to the municipal sewerage system. Such wastes might exert an immediate oxygen demand of up to 30 mg per litre per hour, particularly when the sewage is septic and contains sulphides and other reducing agents.

Industrial organic wastes such as those coming from distilleries, meat packing, paper making, tanneries and petrochemical industry might have BOD_5 values measured in thousands and tens of thousands mg/l.

It should be noted that as far as ordinary municipal sewage is concerned, especially following primary treatment bringing BOD_5 levels to between 150 and 300 mg/l, a well engineered deep enough marine outfall with a proper diffuser will usually not significantly affect the oxygen balance in the open sea when the normal current situation exists.

When discharging into estuaries, lagoons or other sea-enclosures, secondary treatment of wastes can bring about BOD_5 values of less than 50 mg/l and immediate oxygen demand of less than 2 mg/l per hour.

3.13.3 Reducing Chemicals

Septic sewage might contain a multitude of reducing agents as indicated by oxidation-reduction potential (ORP) of much below -200 millivolt. Sulphides, mercaptans and reduced metals constitute a major part of these reducing agents. Strong septic municipal sewage may exert an immediate oxygen demand of up to 50 mg/l per hour and more which might cause a severe depletion of oxygen in the immediate vicinity of the point of discharge unless the immediate dilution is large enough.

A multitude of industries discharge reducing agents with their wastes, such as sulphides, sulphites, reduced metals, etc.

Usually good aeration system and occasionally chemical oxidation (or mixing the wastes with oxidizing wastes) can eliminate the problem. In a few occasions excess thiosulphate used for dechlorination causes oxygen depletion in the immediate point of discharge. In the design of large municipal sewerage collection systems and outfalls it is advisable to prevent severe septicity by various methods such as aeration, cascaded flow and other methods which also are essential to prevent sulphide-borne corrosion.

3.13.4 Eutrophication Control

Introduction

Nitrogen is a major limiting factor in the marine environment and a few sources of nitrogen will be briefly discussed herein.

Nitrogen Sources

Municipal Wastewater

Municipal raw wastewater contain between 40 to 120 mg/l of nitrogen usually in the form of organic nitrogen and ammonia. Ordinary primary and secondary treatments do not remove nitrogen, although good secondary treatment can oxidize the nitrogen into nitrates.

Applying ammonia stripping or nitrification-denitrification techniques can produce effluents with less than 10 mg/l of nitrogen.

Runoff, Drainage Water and Agricultural Wastes

Depending on the intensity of agricultural utilization of the watershed, streams and rivers might contain appreciable amounts of nitrogenous compounds that might cause severe eutrophication in enclosed and semi-enclosed marine bodies of water in the areas surrounding the river mouths. Good agricultural waste management can reduce this problem.

Nitrogenous Compounds from Industrial Wastes

Introduction

Nitrogen compounds are ubiquitous in nature and industrial processes. They may be of the following forms: nitrate, nitrite, ammonia and organic nitrogen. Most commonly they will be found in the effluents from nitrogenous fertilizer plants, urban wastewater, water treatment plants, nitric acid plants, tannery wastes and textile wastes.

The nitrogen compounds, being so common in nature, may be easily utilized in the environment. The results of these may be the degradation of the environment through the process eutrophication by affecting the oxygen balance of the receiving body of water.

Ammonia will be toxic if discharged at concentrations higher than 10 mg/l. The fertilizer effects of nitrogen compounds can cause problems in both inland waters and the sea.

Principal Industries

(a) Fertilizer Industry

Type of Industry

The production of fertilizer may involve the production of the following chemicals: ammonia, urea, ammonium nitrate, nitric acid and ammonium sulphate.

Type of Wastes

The wastes are aqueous solutions produced from potassium nitrate processes. The potassium nitrate is produced from potassium chloride and nitric acid. These are nitrate wastes. Ammonia wastes arise from the production of ammonia and ammonium salts.

Form of Wastes

The wastes are usually soluble ions in aqueous solutions. There may be smells arising from ammonia wastes.

Total Amounts

The potassium nitrate plant produces 10 m^3 of wastes per ton fertilizer with 1.5 m^3 per ton from the potassium nitrate process. The process wastes are 4000 mg/l NO_3^- while the plant wastes are 20,000-40,000 mg/l. From the ammonia fertilizer plant, about 5000 m^3/day of waste are produced. The ammonia process wastes are about 400 mg/l NH_4^+.

Discharge Patterns

Discharges of nitrate wastes are continuous while the ammonia wastes are intermittent.

Effluents

Effluent treatment will involve biological treatment causing nitrification followed by denitrification or ion exchange. Zero effluent quality can be achieved.

(b) Tannery Wastes

Type and Size of Industry

See Section 3.2.4.2 (a), Type and Size of Industry.

Type of Wastes

See Section 3.2.4.2 (a), Type of Waste.

Form of Wastes

The wastes contain various forms of ammoniacal nitrogen including $(NH_4)_2SO_4$, NH_4OH etc. They will be associated with oils, fat, hair etc. The ammonia is soluble, without colour.

Amounts

The nitrogen will be about 400 mg/l as N in about 1000 m^3/day of waste. This is about 400 kg/day of NH_3 as N.

Discharge Patterns

The discharges are intermittent.

Effluent

See Section 3.13.4 (a), Effluents.

(c) Oil Refinery

Type and Size of Industry

Integrated plants producing heavy oils as well as petroleum products and LPG. The annual production can vary between 100,000 and 10 million tons per year.

Type of Wastes

The wastes originate in the thermal fractionation of the oil as well as in cooling water and drainage water (washing down).

Form of Wastes

The nitrogen is in the form of ammonia (dissolved) and is associated with many other pollutants such as oils, scum, phenols, chlorides and sulphates. The waste also smells, is opaque (turbid) and warm.

Amounts

Total plant waste flows are about 10-20 m^3 per ton of oil processed. Ammonia concentrations are about 300 mg/1.

Discharge Patterns

Discharges are intermittent depending on plant operation and water recycle requirements.

Effluent Concentrations

Treatment using biological techniques can reduce to low ammonia concentrations. Stripping with air in cooling towers will also reduce NH^4 concentrations.

(d) Textiles

Type and Size of Industry

The textiles industry may be divided into two subsections, raw fibre treatment, and processed fibre finishing. The former may involve wool scouring, wool finishing and dry processing while the latter involves woven fabric production and finishing, as well as dyeing and carpet production. Plant size may vary between shop size and large industrial complexes.

Type of Wastes

The wastes originate in all the process steps particularly in the raw fibre processing. Urea is used in some processing which gives rise to organic ammonia.

Form of Wastes

The wastes are dirty, containing floating oil, scum, and chlorides. They may be turbid and smell. They may be coloured with dissolved pollutants. Generally the wastes are characterized by BOD, suspended solids and grease.

Total Amounts

The BOD from raw fibre processing may reach 8000 mg/1 while in other processes the range is up to 2000 mg/1. The suspended solids may be up to 10,000 mg/1 for the former and up to 800 mg/1 for the other processes. Organic nitrogen is of the order of 15-20 mg/1. Overall flows of 20,000 m^3/day are found nationwide. Hence approximately 200-500 kg/day of nitrogen are produced.

Discharge Patterns

Discharges will be batch for small operations but for large industrial complexes they may well be continuous.

Effluent Concentrations

Effluent treatment should involve primary sedimentation (perhaps combined with chemical precipitation). Then some form of secondary treatment such as activated sludge or trickling filtration. Lagoons may also be used.

(e) Electronics Printed Circuit Industry

Type and Size of Industry

Type and size of industry is specified in the metal plating sections above (copper).

Type of Wastes

Metal plating circuits especially when copper is used involves the use of NH_4OH, $(NH_4)_2SO_4$ and $Cu(NH_4)_4SO_4$. Plating baths wastes may contain 160-200 grams of ammonia per litre while total plant wastes 200-400 mg/1.

Form of Wastes

Slightly turbid bluish alkaline wastes with ammonia odour.

Total Amounts

Total plant wastes are 15 m^3 per square meter of printed circuits while ammonia containing bath and rinsing wastes are 1-2 m^3 per m^2 of circuits.

Discharge Patterns

Batches of concentrated bath wastes and semi-continuous rinse water.

Effluent Concentrations

Following ammonia stripping by towers, the concentration of ammonia is below 15 mg/1.

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CHAPTER 4

Characteristics of Waste Constituents with Respect to their Harmfulness (*)

The substances, the families and groups of substances and the sources of pollution have to be classified with regard to the criteria which define their danger to the marine environment which will receive them.

The criteria adopted for this classification are not and cannot be specifically defined, but can only be defined in relation to their concentrations and to their reactions with the environment and the organisms in it.

The concept of toxicity or, more generally speaking, of the capacity to damage of a given substance is directly dependent on its concentration and on its destiny in the water body which receives it.

In fact, an ecosystem is the result of the geological changes in the chemical and physical parameters of the environment and of the interaction between these parameters and the biological forms which, in the evolutionary process, have adapted themselves to the variations in environmental factors.

Therefore a discharge which could cause a rapid change in the environmental parameters, albeit without toxic substances, can be highly detrimental.

In fact, the biotic component of the ecosystem, built in the biotope which shelters it, is the stable result of a long period of selective adaption and of interaction between biotic and abiotic factors.

This long biogeochemical process in the formation of an ecosystem explains why a mature community of integrated organisms does not exist in a polluted environment which is, of necessity a recent formation, transitory and often unstable as well.

On the basis of the determination of the characteristics of a discharge and the consequent changes it will cause in the receiving water consistent with the safeguárding of aquatic life, it is necessary first to define the levels of toxicity and tolerance.

(*) Complete data concerning sources, uses and concentrations in water, sediments and biota are extensively reported and commented on the document: "IRPIC Data Profiles on Substances for Evaluation of Environmental Hazards".

These levels can be thus defined by (**):

1. the determination of environmental factors and of the concentrations of materials favourable to natural waters;

2. the determination, based on laboratory studies, of the sensitivity of those organisms relative to the various environmental factors, of the supportability intervals and of optimum growth;

3. the determination, based on studies carried out on different bioassay of the physiological, morphological and behavioural reactions of species when in the presence of toxic materials and of the concentrations of those materials which show themselves to be detrimental after continuous exposure;

4. experimentation at laboratory scale to ascertain their compatibility with the aim of protecting the biological resources of aquatic environments.

One should also bear in mind that:

- some natural complexes of dissolved materials to which the aquatic organisms have adapted themselves can be favourable, whilst other concentrations or compositions can be detrimental;

- material of an artificial nature introduced by man can be detrimental;

- altering the quantity of those substances which normally are to be found in the environment can be detrimental;

- toxicity is a term of quantitative value, that is to say any materials can become toxic when their concentration exceeds certain levels.

Finally one must consider that:

- unfavourable conditions endured over long periods by adult beings can be detrimental to the survival of the species

- those conditions unfavourable to the elimination of entire populations or groups of species can also operate for only a few hours

- levels of environmental factors and concentrations of toxics which seem innocuous over short periods of exposure, can show signs of being detrimental over long periods or with repeated exposure, (1).

We therefore take into consideration the following characteristics of the constituents of the waste in relation to their damaging effects:

1) Persistence (physical, chemical, biological) in the marine environment.

2) Toxicity and other harmful effects.

3) Accumulation in biological systems or sediments.

4) Biochemical transformation producing harmful compounds.

5) Adverse effects on the oxygen balance.

(**) in accordance with the F.W.P.C.A. (USA)

6) Susceptibility to physical, chemical and biochemical changes and interaction in the aquatic environment with other seawater constituents which may produce harmful biological or other effects on seawater uses and on marine ecosystems.

4.1 PERSISTENCE IN THE MARINE ENVIRONMENT

The significance of persistence is directly related to that of degradability of a determined substance, even if the relative definitions express varying concepts.

Therefore one can apply that definition, adopted by Portmann for organic substances, to all substances; that they can be considered persistent if they are "only slowly degraded in the course of the effluent treatment or in the marine environment or which, under particular circumstances, may persist in the marine environment", (2).

Again according to Portmann, persistence is an unusual characteristic in a discharge and this happens in the sea when "the input or the pollutants is such as to exceed the rate of removal via dilution, dispersion and degradation or by adsorption, and immobilisation in the sediments". If a substance is not readily degraded in the sea, the possibility of problems arising are increased since with time a toxic concentration may build up in the area of discharge or disposal.

If the persistent substance is bio-accumulated then, although it does not necessarily follow that bio-accumulated substances are toxic, the probability of ecological damage and harmful effects is increased, (2).

It is obviously unrealistic to think that we can totally eliminate even the traces of those persistent substances having toxic effects from the discharge, but it is necessary that in defining levels of concentration for such substances one also bears in mind the quantity contained in the discharge and the size and the characteristics of the receiving area.

Finally, the definition of danger level is in relation to the ecological structure of the zone, to the type of trophic chain which exists there and to the exploitation which man makes of this chain in the given area.

4.2 TOXICITY AND OTHER HARMFUL EFFECTS

The toxicity of a substance to different groups of aquatic organisms is defined as LC_{50}, i.e. the concentration of the substance at which half of the test specimens were killed within a certain time limit.

In the literature the results given by toxicity tests show a great variety. There are several reasons for this. Various species of organism with very different physiology have been used in the tests and even when the same species is used, the results are varied. This might be because the test conditions are varying. Different experimental time, different physical and chemical properties, e.g. temperature, oxygen tension, pH and salinity, etc. are used in the various tests.

The developmental stage of the test specimens also affects the results, as fry and larvae often show a much higher sensitivity than the adult specimens. A standardization of toxicity tests is required.

The LC_{50} is determined by bioassays. The LC_{50} thus defined has many conceptual limitations and is ill-suited to be used as a gauge of the toxicity of the water in models of dispersion of the receiving water, (3).

The conceptual limits are due to the fact that a test on every single species, especially those not belonging to the community concerned with the discharge, does not permit evaluations of acute limits and limits of chronic tolerability for the other species, or of the effects on the structure of the biological community and on its capacity to adapt and evolve.

The LC_{50} is a parameter of the discharged water and reflects its own strength in inhibiting biological processes and therefore the preservation of life and the fulfilling of the intra- and interspecific biotic factors, which are the foundation of the success of an organism which colonizes a given biotope and of a community in order to build up to a biocenosis climax.

Therefore the real significance of the LC_{50} does not lie in the value itself but "in the correlations that may be established between a wastewater's LC_{50} and the condition of the community for receiving water organisms", (3).

The toxic concentration of the wastewaters, defined as $100/LC_{50}$ and given in toxic units (4), can be used in a dispersion model like any substance from wastewaters and multiplied by the flux gives the total toxic capacity and thus allows predictions of the toxic concentration in the receiving waters.

In order to ensure the validity of an acceptability limit of a discharge, the toxic concentration for this limit must ensure not only the correct equilibrium for the species but also the full vitality of the marine community.

The dispersion model for wastewaters to predict the toxic concentration in a bay (*) has brought into evidence an interesting relationship between the variety of the benthic species, acting as an index of the biological health of the community concerned, and the toxicity concentration, (5).

Analyses of multiple linear regression show a significant inverse relationship between high toxicity concentration and diversity index.

It has been shown that a concentration of toxicity of 0.04 toxic units in the receiving water has a noticeable effect on the diversity index and vitality of the benthic community. This relationship is even more significant as it is well-known that the benthic communities act as integrators of environmental factors and therefore the long-term reaction of the biogenosis at high levels of toxicity can be foreseen. Using these methods it has been ascertained that in the same bay the daily average of toxic emission from discharge points was made up to 56% from urban sources and the remaining 44% from industry, (6). Also it was noted that a primary effluent contains an average toxicity of 2.21 TU (toxic units) corresponding to a TL50 = 45%, whilst a biological treatment plant can reduce the toxicity to 0.5 TU.

The substances principally responsible for the toxicity in treatment plant effluents are, it seems, in this case ammonical nitrogen and more importantly ABS,(alkyl benzene sulphonate).

Chemical precipitation, followed by a primary sedimentation, brings the toxicity of the effluent to 1,3 - 1,6 TU, (7). The toxicity of an effluent is considerably increased by chlorination, (10).

Apart from the lethality to the organisms, other detrimental effects more or less correlated with it are caused by discharging to ecosystems, with the effect of reducing the specific diversity, the quality, and also at times the quantity of the biomass.

Alterations of the cellular structure and of more important functions, such as the metabolism and reproduction, have been observed in the organisms, (9, 9, 11, 12).

(*) San Francisco Bay, California (USA)

4.3 ACCUMULATION IN BIOLOGICAL SYSTEMS OR SEDIMENTS

Data on accumulation in water, in sediments and in aquatic organisms are presented in this survey. They are stated as concentrations in the tissues of the organisms, in the sediments and in the seawater. In some cases data are presented as concentration factors, i.e. the concentration in the organisms divided by the initial concentration of the substance.

The methods of chemical analysis of wastewaters cannot give information on the phenomena of transformation and metabolic concentration of detrimental substances in marine life.

A good way to study in vitro these phenomena, in order to recognize the dangers of these substances at the various levels of the food chain, is the trophic-dynamic chain system, (13).

Research on the processes of bio-accumulation includes a study of those damaging products which are accumulated in the three matrices which form the ecosystems: water, organisms and sediments.

It is also necessary to study which are the factors favouring the accumulation in the different matrices, and finally what is the action of the accumulated products on the large predatory animals and on man.

In the literature the most significant studies are in regard to products which have been found toxic to man, in particular some metals, the hydrocarbons and their degradational products, also the halogen-composed organics.

Bio-accumulation of metals is increased in the proximity of discharge points because of the presence in the discharge of physico-chemical forms of metallic complexes directly absorbable by marine organisms.

The ways by which this concentration is carried out are as follows, (14).

1. the ingestion of suspended particles;
2. pre-concentration in food;
3. metallic complexes of specific molecular organics;
4. incorporation of the metallic ions in important physiological systems;
5. ionic exchange at the level of the mucus of molluscs.

In the study of bio-accumulation it is important to define the concentration factor regarding the accumulation and transfer of a substance. The concentration factor is defined as the ratio of the concentration in the organism to the concentration in an equal amount of the water, (8).

The discharge of waste waters can also produce an accumulation of organic material in the sediment with changes in the pH and Eh, and with the trapping of various pollutants.

It has been proved that, (15), 25-75% of the heavy metals trapped by the sediments are subsequently released to the water and become available to organisms. About 5 to 7% of the organic substances produced each year is lost in muddy sediment and 33 to 88% can return in a dissolved form by way of water.

As regards the regeneration of phosphorus its release from the sediments is augmented by the lowering of the pH, provoked by pollution, but is hindered in reduction conditions. Studies carried out on a polluted fjord (Askeroefjorden, 50 km north of Gothenburg, Sweden) show a return of 25% of phosphorus and 1/3 or more of the materials containing nitrogen in the water.

The greater part of the copper, and approximately half of the zinc, free themselves from the sediment during the first phases of the diagenetic reactions. An appreciable amount of cobalt, nickel and lead return to the water. Consequently there is a strong recycling and a massive presence of these metals in the aquatic organisms without there being a dependence of the Eh values, (15).

4.4 BIOCHEMICAL TRANSFORMATIONS PRODUCING HARMFUL SUBSTANCES

Wastes discharged into the environment undergo various transformations. Physical, chemical and, especially biological agents will interact with the various components of the waste and change the original composition by decomposition of the organic matter, by changing the physico-chemical form of elements, incorporation into living matter, adsorption onto particles, adsorption onto sediments, etc.

It is well known that inorganic mercury can be transformed in sediments (and probably also in other matrices) into the more toxic methyl-mercury and other organic mercury compounds,, (16). Methylation of several other elements, (Pb, Sn, Pd, Pt, Au, As, Se, Te, etc.) is possible, (17). Methylated arsenic is less toxic than inorganic arsenic, lead and mercury, for example are more toxic in organic form. However the toxicological and environmental significance of these transformations is not clear. In marine organisms the percentage of methyl-mercury varies from 1 to about 95 percent.

In non-polluted coastal environments marine organisms high in the food chain (e.g. fishes and mammals) have higher percentages of methyl-mercury than organisms low in the food chain (e.g. algae, crustaceans and molluscs). In marine teleost fishes, however, the percentage of methyl-mercury depends on the total mercury concentration. Fishes and marine mammals with low total mercury concentrations have 80 to 95 percent methyl-mercury, if, however, these organisms possess high mercury body burden (greater than 50 ppm FW) the methyl-mercury is reduced to a few percent. There is now evidence that an inert Hg/Se compound is formed in marine mammals with a high total mercury body burden. Whether this protection mechanism functions also in polluted environments is not clear at present.

Chlorine treatment e.g. in discharge canals of power stations used to combat fouling, has been reported to form toxic chloramines and by exchange with bromine the toxic bromamines may also be formed.

The decomposition of detergents and surface active agents can result in products which are more toxic than the original wastes.

The toxicity of waste components can, of course, also be increased by synergistic effects.

4.5 ADVERSE EFFECTS ON THE OXYGEN BALANCE

The dissolved oxygen (D.O.) requirements of marine organisms, and, in particular of benthic ones, are little known. Above all, taking as a base the level of DO which causes fish mortality or dystrophic phenomena, one sees that a concentration between 5,3 and 8 mg/l is sufficient to assure the accomplishment of the growth and reproduction of marine organisms. Lower concentrations are generally lethal for most species, especially if the level of DO is reduced to 1,25 mg/l in 24 hours. Adult individuals generally manage to survive low oxygen concentrations over a longer period of time. Coastal environments ensure satisfactory conditions for aquatic life if the DO concentration does not fall, for more than a few hours, to below 5 mg/l, (18).

The reduction of the level of dissolved oxygen in the water represents a risk for marine life, and could trigger off, in estuarine and coastal waters, a modification of the composition of the species and of the abundance of the marine organisms. A reduction of the concentration of dissolved oxygen affects the growth rate and swimming velocity as can be demonstrated in laboratory tests.

The pollution which causes the most frequent oxygen crises in the marine environment is that due to the emission of organic material, in particular nutrients and bio-stimulants.

In the case of entrophication the effects of this kind of pollution are indirect or secondary, in that the chemical-physical conditions of the environment are altered because of the increased biological activity which is produced in the waters.

These phenomena are all the more evident in coastal zones having low water exchange and which are highly populated especially in summer.

The dispersion and dilution of suitably treated discharges (generally primary sedimentation is sufficient using chemical precipitation when necessary) are almost always sufficient to resolve these unfavourable effects with advantageous consequences for the productive capacities of offshore water and particularly those of the Mediterranean, which is well-known for being poor in nutrients.

The balance of the nutrient salts and the primary productivity in the various biogeographical sectors of the Mediterranean bear witness to the non-existence of a state of diffused eutrophia even in the more critical basins, such as the Adriatic, and there is the probability that accumulation phenomena, such as would make a medium-term dystrophic situation a reality, are presently forming or likely to occur in the next decade. The hydrology of the Mediterranean and its relation with the Atlantic testify to a balance of nutrient salts which shows a definite deficit as regards the Mediterranean.

Consequently the unfavourable effects of nutrients and bio-stimulants on the oxygen balance are only to be expected as the result of an erroneous choice of location and of the methods of eliminating those discharges characterized by an excess of organic substances, of nutrient salts and of bio-stimulants. The discharging of cooling waters can have effects locally on the concentration of DO, by reducing the solubility of oxygen in sea water. However, in this case the responsibility for the damage can also be attributed to the erroneous location of the discharge and to the disposal methods (19-20).

4.6 SUSCEPTIBILITY TO PHYSICAL, CHEMICAL AND BIOCHEMICAL CHANGES AND INTERACTION IN THE AQUATIC ENVIRONMENT WITH OTHER SEAWATER CONSTITUENTS WHICH MAY PRODUCE HARMFUL BIOLOGICAL OR OTHER EFFECTS ON SEAWATER USES AND ON MARINE ECOSYSTEMS

This characteristic of the constituents of discharge is extremely complex to evaluate and to attribute experimentally to the substances involved in precise quantities. Its effects, however, are easily noticeable by comparing the morphological and physiological reactions of single organisms to various environments or of communities in different stages of the same biotope.

Only by starting from these preliminary facts can we eventually suggest bioassays for routine checks of the effects of these substances and determine suitable factors to apply in order to establish those levels of acceptability in the bodies of water which receive them.

It is known that alterations in the salinity, the pH, the turbidity and the temperature can considerably change the critical toxicity of a pollutant. To give an example of the influence of temperature it is sufficient to quote the example of pesticides composed of chlorinated hydrocarbons which are more toxic in summer, and that of the toxicity of detergents which rises with an increase in salinity, (1).

4.7 HARMFULNESS OF WASTE CONSTITUENTS

4.7.1 Elements Considered in Paragraph 1.1.1 Of Chapter 1(*)

Unlike many contaminants, the elements listed in paragraph 1.1.1 of Chapter 1 are normal constituents of the marine environment and traces at least are always found in seawater. Table 4 gives the natural concentration in seawater and in different groups of marine organisms.

TABLE 4 - Concentration of elements in different groups (ppm/dry wt)

Elements	Seawater ppb	Phytoplankton	Zooplankton (copepodes)	Bivalve molluscs	Fish	Seaweeds
Ag	0,28	0,2	0,1	0,3	0,1	0,2
As	2,3			15	10	20
B	4440					
Ba	2	33				
Be	5.6×10^{-3}					
Co	0,05	1	1	1	0,1	0,7
Cr	0,3	1,5	1	1,5	0,5	0,9
Cu	2	7	10	10	3	15
Mo	10	2	2	2	1	0,5
Ni	2	3,2	2	3	1	3
Pb	0,03	4	3	5	3	4
Sb	0,3			0,05	0,02	0,1
Se	0,2			3	3	1
Sn	0,01	3		0,5	0,4	1
Ta	0,002					
Te						
Ti	1					
U	3,2					
V	2,5	3	3	2	1	3
Zn	4,9	38	113	100	80	90
% dry wt			11	20	25	20

(*) Data profiles of some of these are reported in the document: "IRPIC Data Profiles on Substances for Evaluation of Environmental Hazards".

Persistence

Obviously the elements are immutable. This means that once one element is mobilized in the environment, its total amount there remains the same, regardless of form, until it is immobilized again. Its form may be altered by biogeochemical processes, so that the particular salt in which it originally entered the environment no longer exists but the total amount of the element present as other compounds or ions remains unchanged.

Toxicity and other harmful effects

At suitable concentrations some of the elements considered are essential to enzyme activity. At least zinc, copper, nickel, chromium, selenium, molybdenum, tin, vanadium and cobalt are known to be essential to living organisms.

There is little evidence that larger marine organisms ever suffer from metal deficiencies and presumably the optimum concentrations are those occuring naturally.

When the natural concentrations are exceeded the effect on the individual organisms is either dramatic death, or the production of sublethal effects such as morphological and physiological changes or behavioural effects.

Metals in their pure state present little hazard, except those having a high vapour pressure, such as mercury, and those which may be present in a particular form in the atmosphere, such as vanadium. It is the soluble compounds of the metals which create problems in aquatic environments. Some of the metallo-organic compounds are among the most toxic compounds known, e.g. methyl-mercury and tetraethyl lead.

Waldichuk, (21), gave a list based on LC_{50} values for marine species:

$Hg > Ag > Cu > Zn > Pb > Cd > As > Cr > Sn > Mn > Al > Be > Li$

The National Academy of Science, (22), has concluded, on the basis of acute toxicity to fish, synergism of some metals in combination, sublethal effects, bio-accumulation and the danger to man of consuming sea-food, that the pollution hazard of some of the most prominent metals in seawater can be ranked as follows:

$Hg > Cd > Ag > Ni > Pb > As > Sn > Zn$

The LC_{50} concentration for a particular metal in a particular species can be changed by a whole range of factors which are summarized in Table 5.

Relative toxicity of metals

There are comparatively few examples where the toxicities of several different metals have been compared in the same species. An idea of the relative toxicities of some metals may be gained from the results of Tarzwel and Henderson, (85), who studied their effects on the fathead minnow Pimephales promelas in hard fresh water. The following order was found:

$Cu > Cd > Be > Sb > Ni > V > Pb > Ti > U > Zr > Mo$

Wood and Goldberg, (87), have given a classification of elements according to their toxicity (Table 6).

TABLE 5 Factors influencing the toxicity of heavy metals in solution

Form of metal in water	inorganic organic	soluble	complex ion ion chelate ion molecule
		particulate	colloidal precipitated adsorbed
Presence of other metals or poisons	joint action	more than additive	
	no interaction	additive	
	antagonism	less than additive	
Factors influencing physiology of organism and possibly form of metal in water	temperature pH dissolved oxygen light salinity		
Condition of organism	stage in life history (egg, larva, etc.) changes in life cycle (e.g. moulting, reproduction) age and size sex starvation activity		
Behavioural response	additional protection (e.g. shell) adaptation to metals altered behaviour		

Accumulation in biological systems or sediments

Organisms. Because certain elements are required in life processes, most organisms have a capability of concentrating them. This capability is increased by certain feeding and metabolic processes which can lead to enormously high concentration factors. The invertebrates appear to have a particularly high capability for concentrating metals, along with other foreign materials found in their environment, when they filter plankton during feeding. Because of the ability of many metals to form complexes with organic substances, there is a tendency for them to be fixed in the tissue and not to be excreted. In other words, they have a long biological half-life.

Accumulation in sediments. Metals can be accumulated in sediments by three processes:

a. precipitation;

b. adsorption;

c. absorption and modification by marine organisms.

a. Precipitation. If the concentration of a metal is higher than the solubility of the least soluble compound that can be formed between the metal and anions in the water, such as carbonate, hydroxyl or chloride, precipitation will occur. With the exception of metals such as iron, which is readily precipitated leaving very little in solution, many heavy metals can remain in seawater at concentrations which are orders of magnitude higher than those occuring naturally.

The solubility can be increased still further if complexing ions not usually found in seawater are present as contaminants, or, alternatively, the solubility may be reduced, as happens in anoxic water, when hydrogen sulphide is present. In the presence of hydrogen sulphide metals such as Zn, Cu, Cd, Pb, Hg, and Ag, having very insoluble sulphides, tend to be precipitated leaving small amounts in solution. On the other hand, higher concentrations of iron and manganese are found, because their sulphides are more soluble than the hydrated oxides which are precipitated in aerated seawater.

b. Adsorption. Metals can be removed from seawater by adsorption on the surface of particles such as hydrated ferric oxide, hydrated manganese dioxide, clay minerals and phytoplanktonic organisms; of the hydrated oxides, ferric oxide is usually more important in coastal regions than manganese dioxide since it is usually more abundant and is much more readily precipitated.

c. Absorption and redistribution by organisms. The removal and deposition of metals from seawater is often promoted by biological processes. For example, Sorokin, (23), has described the role of benthic filter-feeding animals in accelerating the deposition of particles and their associated heavy metals by consolidating them in faecal material. Vertical transport of metals by agencies such as the moulted exoskeletons and faece of zooplanktonic animals has been described recently by Lowman et al, (24), Small and Fowler, (25). It has been calculated by Lowman et al that the vertical distribution of metals in the sea will be affected by biological action mainly in areas near land where nutrients for high biological productivity are available from upwelling of the ocean or from runoff from the land. Although many zooplanktonik species migrate diurnally and can in this way transport metals, Lowman et al, (24), have concluded that generally more than 90% of the vertical transport of heavy metals occurs in the form of faecal pellets, crustacean moults and dead animals and plants. Whether this process results in the sedimentation of the metal depends on the depth of the sea, since in deep water the metals may be returned to solution long before they can sink to the bottom.

Although the behaviour of metals in contaminated or indeed in normal sediments is not fully understood, the present evidence shows that under suitable conditions some metals are returned to the overlying water following remobilization and upward diffusion. As a result, contaminated sediments may persist as sources of metals when the original source has been removed. In estuaries, conditions for the mobilization of metals may be particularly favourable in view of the fluctuating salinity and the disturbance of the sediments by currents or by dredging, (Table 7).

4.7.2 Biocides And Their Derivatives

The types of biocides most commercially significant are:

a. Nitrogenous compounds. Carbamates, triazines, nitroaromatics and urea compounds and quaternary ammonium salts.

The carbamates have about the broadest range of biological activity known for any chemical class of compounds. The toxicity to mammals and plant growth regulating properties of some members of this family were known before 1930. The N-aryl carbamate ester, propham was commercialized in 1945. A series of thiocarbamate herbicides was introduced in 1954. The N-alkyl carbamates were patented first in 1952, but the most important today are, carbaryl, propoxur, aldicarb, methomyl, carbofuran and Bux Ten. About 32 carbamates, nine thiocarbamates and 12 dithiocarbamates, have been produced.

The first example of the triazine class of pesticides was a fungicide introduced in 1955 and now known as Dysene. The major entries in the field, however, are the herbicides introduced by the Geigy Company including: simazine, atrazine, propazine, ametryne and others nearly all of which have chlorine in the molecule.

The nitroaromatic compounds are nitrophenol herbicides and acaricides and nitroaniline herbicides.

Herbicidal activity of substituted ureas was discovered in 1946 and a series of "urons" were subsequently introduced, including monuron, dinuron, femuron, cloxuron and noruron.

About six herbicidial quaternary ammonium salts are available, of which diquat and paraquat appear to be the most popular.

b. Inorganic salts. The inorganic type of pesticides are mainly sulphur and sulphides, arsenic, copper, chromium and zinc salts, arsenates, arsenites, and chromates.

c. Botanical derivatives. The botanical type are: Pyrenthrins; rotenone and nicotine. In order to evaluate the pollution potential of pesticide, knowledge of current production volumes was needed. A serious handicap here was the unavailability of data on how much of each pesticide is produced or even on which are produced in the largest quantities. The data available is from the United States E.P.A. (Table 8), (26).

Persistence

The stability of organic compounds of this group is very low compared with organohalogen compounds or even organophosphorus compounds. The carbamate insecticides when in water, are subject to photodecomposition under the effect of ultraviolet light, (27).

TABLE 7 Toxicity bioaccumulation

Element	Toxicity LC_{50} D minimal risk	Bioaccumulation Concentration Factor	Remarks
1 Zinc	Fish 30-90	Fish 1600-2100	The lethal oral dose to mice is 57 mg/kg.
	Crustaceans 14-200	Oysters 150.000	The ermetic dose for man is 675 mg.
	Algae 0.5 - 5	290.000	No hazard for human health from sea food or seawater
	D 20 ppb	Phytoplankton 113	
		Zooplankton 1000	
2 Copper	Fish 4.5 - 6.5	Fish 130-660	The lethal oral dose is 159 mg/kg.
	Crustaceans 0,33	Oysters 24.000	The ermetic dose for man is 500 mg.
	29,5	35.000	No hazard for human health from sea food or seawater
		Phyto 38	
		Zoo 437	
3 Nickel	Fish 0.8 - 125	Fish 125	The lethal oral dose is 1g/kg.
	Crustaceans 100	Oysters 100	There is no evidence that the Ni absorbed from foods cooked in Ni or Ni-alloy containers is of hygienic significance although milligram amounts may be daily taken into the body.
	300	Phyto 41	
		Zoo 149	
	Algae		No hazard for human health from sea food or seawater
	Oysters (embryo)1.19		
	D 2 ppb		
4 Chromium	Fish 33 - 100	Fish 200	Hazard to workers producing chromates from chromite ore.
	Crustaceans 100	Oyster 500	Drinking waters standard 0.05 ppm Cr+6.
	Algae	Phyto 34	No hazard for human health from sea food or seawater
	Oysters (embryo)10,3	Zoo 65	

TABLE 7 (continued)

Element	Toxicity LC_{50} D minimal risk	Bioaccumulation Concentration Factor	Remarks
4 Chromium	D 10 ppb	Zoo 65	
5 Lead	Fish 0,34 188 D 10 ppb	Fish 6000 10.000 Oysters 7000-100.000 Phyto 2087 Zoo 15.500	Hazard to workers specially noted in certain foundry operations and in manufacturing of organic lead compounds. The continuous ingestion of molluscs from highly contaminated areas could be dangerous.
6 Selenium	Polichaete 100	Fish 500	Selenium compounds are methylated by micro-organisms and probably these compounds have antagonistic behaviour with mercury, (83). No hazard for human health from sea food or seawater
7 Arsenic	Fish 8,4 Oyster (embryo) 7.5 Polichaete 25	Fish 77-100 Oyster 432-810 Arsenic concentrations are not magnified-in food chains	Inorganic compounds are very toxic. Arsenic compounds are reduced and methylated by anaerobic micro-organisms to give dimethyl and to methylarsine, volatile products of extreme toxicity. It is proposed that a biological cycle may exist for arsenic as it does for mercury. Wood (1974)
8 Antimony		Oyster 300 Fish 100	No hazards for human health from sea food or seawater.
9 Molybdenum	Algae 54	Fish 100 Oyster 100 Phyto 10 Zoo 20	No hazards for human health from sea food or seawater.

TABLE 7 (continued)

Element	Toxicity LC_{50} ppm D Minimal risk	Bioaccumulation Concentration Factor		Remarks
10 Titanium	Algae 2	Phyto	290	The residues of titanium bioxide are noxious for acidity and iron content.
		Zoo	500	
11 Tin	Algae 2	Fish	10000	The organotin compounds are included in Table 1.
		Oyster	10000	No hazard for human health from sea food or seawater.
12 Barium	Algae 34	Phyto	62	Ba is highly toxic; the fatal dose of Ba C12 for man reported to be about 0.8 to 0.9 g. Ba was irreversibility deposited in the Skeleton.
		Zoo	100	
13 Beryllium	Fish 31			Soluble forms of Be are highly toxic by all routes of administration. Be exerts a strong inhibitory action on enzimatic activity.
14 Boron				
15 Uranium				Oral toxicity of U compounds is rather low. The farmacology and toxicology of U compounds of industrial interest are presented in four volumes comprising about 2300 pages.
16 Vanadium	Algae 10 - 20	Fish	10	The fatal dose for man has been given variously as to 120 mg. It is apparent that amounts of from 24 mg of V in daily divided doses are tolerated by man
		Oyster	200	
		Phyto	100	
		Zoo	200	
		High concentrations are found in ascidian tunicates		

TABLE 7 (continued)

Element	Toxicity LC_{50} ppm D Minimal Risk	Bioaccumulation Concentration Factor	Remarks
17 Cobalt	Algae 0.5	Fish 500 Phyto 190 Zoo 365 Mollusc 1000-5000 Crustaceans 1000-5000	The lethal oral dose for rabbits is 700 mg/kg.
18 Thalium			Thalium is one of the more toxic elements both acutely and chronically, in animals and man, regardless of the route of intake.
19 Tellurium			The actions of tellurium are similar to those of organic arsenic, specially the injurious effect on the capillaries.
20 Silver	Algae 0.05 Fish 0.01-0.04 Mollusc 0.0006 D 1	Phyto 98 Zoo 117 Fish 100 Mollusc 250	

TABLE 8 Production volumes of major pesticidal ingredients [a]

Product	Quantity	Product	Quantity	Product	Quantity	Product	Quantity	Product	Quantity
Atrazine	90	Carbaryl	55	Sulfur (inorganic)	150	Methyl bromide	22	Petroleum oil[g]	1,000
2,4 - D	45	Toxaphene[b]	50	Pentachlorophenol and salts[c]	46	Dibromochloropropane	10	Creosote	1,000
MSMA - DSMA	35	DDT	45						
Sodium chlorate	30	Methyl parathion	45	Dithiocarbamate group[d]	40	Other halogenated C_1-C_3 organics[e]	40	Coal tar Aromatic solvents	160 N.A.
Trifuralin	25	Malathion	30	Trichlorophenol and salts	20	Dichlorobenzene[f]	60	Dry carries and diluents	600
Propachlor	23	Chlordane	25	Captan	18	Naphthalene	14		
Chloramben	20	Parathion	15			Warfarin	12		
Alachlor	20	Aldrin	10						
CDAA	10	Methoxychlor	10						
		Diazinon	10						
Subtotal	298		295		274		158		-
Total all pesti pesticides	428		406		297		200		2,000

[a] Quantity produced in million pounds per year for direct pesticidal use, excludes production for other uses except as indicated.

[b] Includes Strobane-T.

[c] Includes use for termite control and as herbicide.

[d] Includes 11 products.

[e] Includes eight or more compounds.

[f] Includes moth proofing and lavatory-space deodrant usage.

[g] Includes synthetic and refined spray oils,diluents and carriers in formulated products.

TABLE 9 Characteristics and harmfulness of pesticides

Pesticide (Trade Name)	Effect	Type	Mammalian Toxicity LC_{50} (mg/kg)	M.L.C. LC_{50} Fresh w.Fish 2 g/1	M.L.C. LC_{50} Marine fish 2 ng/1	Persistence	Biaccum-ulation
Aldicarb	Insecticide	Carbamate	0-6			Low	Non
(Temik)		Nalkyl					
Carbaryl	"	Nalkyl	540	1000-4000		Low	Non
(Sevin)							
Zectran	"	"	15-63	10000-11000	1000	Low	Non
Atrazine	Herbicide	Triazine	3080	25000-130000		Low	Non
(Aatres)							
Trifluralin	"	Nitroaniline	10000	68-360		Low	Non
(Treflan)							
Alachlor	"	Amide	1200			Low	Non
(Lasso)							
11 products	Fungicide	Dithio-Carb-	1000-8000		Moderately	Low	Non
(Maneb Zineb)		amate			toxic		
Diquat	Herbicide	Quaternary	400	10000			Non
		Ammonium	112-200	5000-50000			
Paraquat	"	"					
Pyrethrins	Insecticide	Botanical	1500	50 - 70		Low	Non
Diuron (	Herbicide	Urea	3400	4000-17000	6300		
(Karmex)							

Toxicity

Most investigations into the toxic effects of pesticides on fish are carried out with organochlorine insecticides (DDT, BHC, dieldrin and endrin) and with organophosphate (methyl parathion, fenthion, malathion). Very little data exists on other pesticides in marine organisms.

In Table 9 data is given regarding toxicity to mammals, fresh water fish and marine fish, persistence and bioaccumulation taken from the E.P.A. report, (26), and H.V. Holden, (28).

Bioaccumulation

No data has been reported on residues of these compounds in birds, mammals or fish. It is considered highly unlikely that any bioaccumulation of these compounds occurs in the sea.

4.7.3 Organosilicone Compounds And Substances Which May Form Such Compounds In The Marine Environment Excluding Those Which Are Biologically Harmless Or Are Rapidly Converted Into Harmless Substances

"Organic compounds of silicone" may be defined as compounds containing at least one silicone-carbon bond per molecule. Those in general commercial use may be classified as follows:

a. Silicone chemicals. These are non-polymeric compounds, generally containing one (or two) silicone atoms per molecule and which include for example, monomers, intermediates, cross-linking agents for the silicone industry and ancillary chemicals for other industries.

b. Silicone fluids. These are siloxane polymers and copolymers for example polydimethylsiloxane, and may be used as unadulterated liquids, mixtures or emulsions for a wide variety of applications.

c. Silicone resins and elastomers. There are polysiloxanes which are rigid or electomeric substances for use as extruded or moulded materials or articles, sealants, adhesives or coating. Production figures are given in Tables 10 and 11.

Silicone Chemicals

The largest class of chemicals produced commercially in this category is that of the methyl chlorosilanes, most of which is used in the production of polysiloxanes.

Toxicity and persistence. Whilst the chlorosilanes themselves are corrosive materials, in contact with water they are rapidly converted into harmless hydrochloric acid and in sea water the acid is neutralized.

Silicone fluids

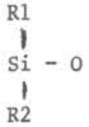
These compounds have been broadly defined as any commercial composition which contains the siloxane polymer chain:

TABLE 10 Estimated world market for organosilicone compounds

Areas	Silicones	Silicones oils	Silicone elastomers
USA	50.000	11.300	30.000
EUROPE	27.000	3.750	9.200
JAPAN	11.000	1.750	2.900
URSS	12.000		
Total	100.000	16.800	42.100

TABLE 11 Estimated European Market for silicones in 1976

Fluids and Fluid Products	Resins and Elastomers	Silanes	Total
20.000	17.000	3.000	40.000



$$\begin{array}{l} R1 \\ | \\ Si - O \\ | \\ R2 \end{array}$$

where R1 and Rs are the same or different radicals selected from H, alkyl or aryl. By far the greatest proportions by volume of silicone fluids which are in commercial production, are the poly-dimethylsiloxane (PDMS) in which $R1 = R2 = CH_3$.

Persistence. Under environmental conditions the silicones are probably both chemically and biologically stable.

Toxicity. The potential for adverse environmental effects is not at all clear. Although chronic feeding studies with mammals indicate a low order of biological activity, some of the results are doubtful. However, even assuming a negligible level of mammalian toxicity, the possibility of these compounds having no adverse effects on aquatic species is questionable. Although fish do not seem to be highly susceptible in four days exposure, such brief periods are of limited use in assessing the effects of long-term exposure. The studies on Daphnia clearly indicate the need for further testing with larger groups over longer periods of time.

Thus, the lack of monitoring data and the inadequate testing of aquatic invertebrate toxicity are the major impediments to a sound evaluation of the potential environmental hazard posed by the fluid siloxanes. Although present information in other areas does not indicate that these siloxanes do or are likely to present an appreciable hazard, the above mentioned deficiencies should be corrected before new uses involving gross environmental exposure are initiated.

Bioaccumulation. Although bioaccumulation studies of silicones in low trophic levels of the food chain have not been reported, some studies with fishes have been undertaken by Dow Corning. Bluegill sunfish were exposed to 14 C-labelled PDMS for 30 days at 1 and 10 ppm. No evidence of accumulation was observed and the tissue storage in these fish was minimal.

Silicone resins and elastomers

These are solid and stable materials insoluble in water, and with an extremely low level of toxicity. Therefore they pose no potential or hypothetical threats to the environment.

Other organosilicone compounds

There are other organosilicone compounds which are used in small quantities, being developed for commercial use or which may be developed in the future. These include products which are biologically active, some of which are being studied for pharmaceutical applications.

4.7.4 Crude Oils And Hydrocarbons Derived From Petroleum

Oil pollution is popularly regarded as an important contaminant of the sea, largely because it is visible, and is a great despoiler of coastal amenities. It also kills sea birds, particularly the diving variety.

In general, oil is lighter than water and tends to spread fairly rapidly, forming a thin layer which is moved over the surface by the influence of winds and tides.

In temperate and tropical zones oils are biodegradable and also polymerized; under the action of light and oxygen, density increases and the particles may become sufficiently dense as to sink. In very cold waters such as in the artic, the rate of biodegradation appears to be very slow. A fresh crude oil can lose up to 30% by evaporation in 30 hours. A much smaller amount can dissolve in the water, which increases the density to the sinking point. Oils with a high wax content or which are very viscous do not degrade so rapidly and are frequently found on beaches as lumps or tar balls. When highly dispersed, oil may be moderately toxic to marine life, but under normal field conditions toxicity is low.

In inland estuarine waters, enclosed bays or similar situations, the effect of the more toxic aromatic fractions together with the reduction in dissolved oxygen resulting from biodegradation may produce more marked mortality in many species.

Some oils contain carcinogens and their reported occurrence in the food chain as the result of pollution could lead to some risk to man as the ultimate consumer. Fish and shell fish become tainted in polluted areas and become unmarketable.

Persistence

The problem of the persistence of petroleum hydrocarbons is not as yet fully understood.

The aliphatic compounds. The n-alkanes are quite easily degraded in experimental tests. The iso-alkanes are more persistent but seem to be degradable, though some authors have noted that the iso-alkanes are not attacked within 2 months.

The alicyclic compounds. Only a few experiments have been carried out to determine the degradation of alicyclic compounds. Research to find organisms which are able to degrade decalin, showed no results, but earlier it was shown that decalin can be degraded by bacteria.

In motor oils exposed to freshwater and seawater sediments, almost all the alicyclic components of the oil are degraded by more than 50% within three weeks.

The aromatic compounds. The persistence of the aromatic compounds, especially the polyaromatic components, are even more doubtful. Some polyaromatic compounds, phenanthrene, 1.2-benzanthracene and perylene were degraded 37-41% within two weeks by an algae. A great variety of polyaromatic compounds were exposed to natural freshwater and seawater sediments and were almost all degraded 30-60% within three weeks, Walker et al, (29). Contrary to these results Floodgate, (30), reaches the conclusion that the polyaromatic hydrocarbons of petroleum are persistent, and Harrison et al, (31), found that polyaromatic hydrocarbons of higher molecule-weight that C 14 - showed no detectable degradation in activated sludge, but contact with river water for 21 days caused 80% oxidation of naphthalene to carbon dioxide.

Oil mixture - crude oils. Brown & Huffmann, (32), have shown that the alicyclic compounds are the most persistent, followed by the iso-alkanes, then the aromatic compounds, the n-alkanes being the least persistent ones.

In the natural environment the persistence of oils may be very lengthy, from two to ten years, but these investigations are all dealing with oils released into the water from tanker accidents, where very large amounts of oils are discharged at one time.

It is doubtful if a comparison between the high persistence of oils and hydrocarbons and the persistence of oils and hydrocarbons more constantly discharged at a low level can be made. It appears that all the hydrocarbons which are naturally present in petroleums can be degraded under certain conditions. It is questionable if any of the natural compounds in petroleums are persistent in water at low concentrations, yet many questions are still to be answered.

Complete oxidation of one mg of hydrocarbon requires between 3 and 4 mg oxygen, (33), and as water under normal conditions contains between 6 and 11 mg dissolved oxygen, this means that degradation of 1.5 - 4 ppm of hydrocarbon in water needs the total amount of dissolved oxygen. Fresh oxygen is, of course, supplied from the surface, but the oxygen content may not be lowered much before organisms are adversely affected. Furthermore, discharge of petroleum hydrocarbons and oils in many cases takes place in areas with a high organic matter content, and this competes strongly with the hydrocarbons for the available oxygen. The presence of other degradable products reduces the degradation rate, and low water temperature also has a strong reducing effect on oil degradation. The persistence of oil is therefore much higher in cold and arctic climates.

Toxicity

The toxicity of oils is to a large extent caused by the fractions with the lowest boiling points which are quite rapidly lost by evaporation, (34).

The aliphatic compounds. The acute toxicity of the aliphatic compounds is very low. Heptane, one of the lowest boiling point alkanes, is shown to be almost non toxic to mosquito fish: LC_{50} (48h) is 4924 ppm, (35).

The alicyclic compounds. The alicyclic compounds show a much higher toxicity than aliphatic ones. Results collected by EPA, (35), are summarized in Table 12.

The aromatic compounds. The highly toxic part of petroleum hydrocarbons is the

TABLE 12 Toxicity of alicyclic compounds to aquatic organisms LC_{50}, (35).

Compound	Organism	Duration	LC_{50} ppm
Cyclohexane	mosquito fish	48 h	15500
"	minnow	96 h	30
"	bluegill	96 h	31
"	goldfish	96 h	33
"	guppy	96 h	48
Naphthenic acid	bluegill	96 h	5.6
" "	Physa (algae)	96 h	6.6 - 7.5
" "	Nitzschia	96 h	43.1
" "	zebrafish eggs	96 h	3.5
" "	zebrafish adults	96 h	16.3

water soluble aromatic compounds, the toxicity of which is stated in Table 13.

TABLE 13 Estimated concentrations of soluble aromatics causing toxicity to aquatic organisms, (36).

Class of organisms	Concentration
flora	10 - 100
finfish	5 - 50
larvae (all species)	0.1 - 1.0
Pelagic crustaceans	1 - 10
gastropods (snails etc)	1 - 100
bivalves (oysters, clams etc)	5 - 50
benthic crustaceans (lobsters, crabs, etc)	1 - 10
other benthic invertebrates (worms etc)	1 - 10

The olefinic compounds. Information on toxicity of olefins is scarce and the only results from tests with isopren (2-methylbutadiene) are presented in Table 14.

These results show a somewhat lower toxicity than those of the alicyclic and soluble aromatic compounds.

Crude oil. The mixture of various hydrocarbons in crude oils have been tested on aquatic organisms. Some representative results are summarized in Tables 15 & 16.

Linden, (40), applied the toxicity of crude oil test to herring larval which showed a lethal effect at concentrations of 0,05 - 1 ppm.

TABLE 14 Toxicity of olefins to aquatic organisms, (35).

Compounds	Organisms	Durations	LC_{50} ppm
Isoprene	minnow	96 h	75
"	bluegill	96 h	39
"	goldfish	96 h	180
"	guppy	96 h	140

Pollution of seawater with oil products at concentrations of 0.1 - 0.001 ml/l produces a pronounced toxic effect upon the larval stages of crabs and shrimps, (41). On the contrary Renzoni, (42), concludes that oil is only toxic to organisms at very high concentrations, 1 part per thousand, which are seldom attained at sea. The discrepancy in results is often due to the fact that some authors refer to the amount of oil added to the test medium while others refer to the amount of oil dissolved in water, the latter being of most interest from an ecological point of view with respect to low concentrations of discharge from non accident sources.

Different crude oils vary widely in their toxic effects on intertidal organisms and toxicities vary greatly with temperature, (43).

Sublethal effects

At low concentrations of crude oil emulsions, 0.6 ppm, larvae of American lobsters did not develop beyond the 3rd stage, (44).

In plankton algae, cell division is seen to be arrested when crude oil concentrations reach 0.1 - 1000 ppm and for some species the minimum effect level is as low as 0.1 ppm, (45).

Abnormal swimming behaviour is seen in larvae of the Baltic herring at concentrations of 0.05 - 1 ppm crude oil, (40).

A special problem is the so-called pheromones, substances which are released from the organisms into the water and used as part of their communications system. Pheromones work at very low concentrations, and the effect of oil interacting with pheromones is not well known. Effects on the feeding behaviour of lobsters are seen at a concentration of 10 ppm crude oil, (46).

Small concentrations of oil may lead to an unpleasant taste in fish and shellfish destined for human consumption, (47).

To conclude, crude oils may be toxic at concentrations as low as 1 ppm, with sublethal effects at the level of 0.05 ppm or even lower. Of the main components, the water soluble aromatic compounds are the most toxic and may show effects at even lower concentrations.

Since the eggs and larvae of many varieties of pelagic fish, float on the surface or inhabit the upper layers of the sea, they are particularly exposed to the effects of oil pollution and suffer a high mortality rate.

Sea birds are perhaps the only group of marine organisms that have so far been affected by oil pollution to a sufficient extent to jeopardize local populations which in some cases constitute the total world population of the particular species.

TABLE 15 Toxicity of crude oils to aquatic organisms

Crude oil origin	Organism	Duration hours	LC_{50} ppm	Ref
S. Louisiana	Neanthes (worm)	96	12.5	a
S. Louisiana	Capitella (worm)	96	12.0	a
Kuwait	Capitella (worm)	96	9.8	a
Iran	Octocoral	96	12	b
Iran	Snail	168	17	b
Iran	Hermit crab	168	21	b
Iran	Shrimp	168	2	b
Sinai	Shrimp	168	16	b
Iran	Goatfish	48	6	b
Sinai	Goatfish	48	16	b
Iran	Rabbitfish	168	0.8	b
Sinai	Rabbitfish	168	15	b
S. Louisiana	Mysidopsis (shrimp)	48	25	c
Kuwait	Mysidopsis (shrimp)	48	18	c
S. Louisiana	Palaemonetes(shrimp)	96	62	c
Kuwait	Palaemonetas (shrimp)	96	36	c
S. Louisiana	Three fish species	96	69-78	c
Kuwait	Three fish species	96	36-200	c

a. Rossi et al, (37).

b. Several tests with other species showed no LC_{50} at 30 ppm with neither Iranian or Sinai crude oil Eisler et al, (38).

c. Anderson J.W. et al, (39).

The total mortality per year from chronic oil pollution in the North Sea and the North Atlantic has been estimated at from 150.000 to 450.000.

Accumulation in Biological Matter

Marine organisms which contain petroleum hydrocarbons have generally either been exposed to a single oil spill or to an area of chronic exposure. The amounts of petroleum hydrocarbons in marine organisms collected from oceanic sources, chronically polluted coastal area, polluted harbours and a single oil spill have been summarized in the National Academy Report, (48).

Although bio-concentration has been shown to occur, the process of biomagnification, that is the increase of a given material at successive trophic levels within an ecosystem, remains a theoretical possibility. There is no convincing evidence at this time for the food chain biomagnification of petroleum hydrocarbons.

TABLE 16 Petroleum Hydrocarbon Levels in Marine Macroorganisms, (48).

Organisms	Area Type a	Hydrocarbon Type	Estimated Hydrocarbon Amount (μg/g)
Macroalgae			
Fucus	4	Bunker C[c]	40 dry
Enteromorpha	4	No. 2 fuel oil	429 wet
Sargassum	1	C_{14}-C_{30} range	1-5 wet
Higher plants			
Spartina	4	No. 2 fuel oil	15 wet
Molluscs			
Modiolus, mussel	4	No. 2 fuel oil	218 wet
Mytilus, mussel	4	No. 2 fuel oil[c]	36 dry
Mytilus	4	Bunker C[c]	10 dry
Mytilus	4	Bunker C, aromatics	74-100 wet
Mytilus	3	n-C_{14}-C_{37}[c]	9 dry
Mya, clam	4	No. 2 fuel oil	26 wet
Pecten, scallop	4	No. 2 fuel oil	7 wet
Littorina, snail	4	Bunker C, aromatics	46-220 wet
Mercenaria, clam	3	C_{16}-C_{32} range	160 dry
Crassostrea, oyster	2	polycyclic aromatics	1 wet
Crustacea			
Hemigrapsus, crab	4	Bunker C[c]	8 dry
Mitella, barnacle	4	Bunker C[c]	8 dry
Lady crab	3	C_{14}-C_{30}	4 wet
Plankton	2	benzopyrene	0,4 wet
Sargassum shrimp	1	C_{14}-C_{30}	3 wet
Lepas, barnacle	1	C_{14}-C_{30}	6 wet
Portunus, crab	1	C_{14}-C_{30}	34 wet
Planes, crab	1	C_{14}-C_{30}	11 wet
Fish			
Fundulus, minnow	4	No. 2 fuel oil	75 wet
Angulla liver, eel	4	No. 2 fuel oil	85 wet
Smelt	3	benzopyrene	0-5 dry
Flatfish	2	C_{14}-C_{20}	4 wet
Flying fish	1	C_{14}-C_{20}	0.3 wet
Sargassum fish	1	C_{14}-C_{20}	1.6 wet
Pipefish	1	C_{14}-C_{20}	8.8 wet
Triggerfish	1	C_{14}-C_{20}	1.7 wet
Birds			
Herring gull, muscle	4	No. fuel oil	535 wet
Echinoderm			
Asterias, starfish	4	Bunker C, aromatics	10-147 wet
Luidia, starfish	2	C_{14}-C_{20}	3,5 wet

a) Area Types: (1) oceanic; (2) chronic pollution, coastal;
(3) chronic pollution, harbour; (4) single spill.

c) n-Alkanes only

Potential Impairment of Marine Ecosystem and Sea Water Use

Effects on human health by pollution of edible marine organisms

Oils contain carcinogens such as the polynuclear aromatic hydrocarbons (PNAH). It has been alleged that these PNAH's will persist in tissues of marine biota exposed to oil discharges and will be accumulated up the food chain, reaching concentrations presenting a hazard of cancer-induction in man as a consumer. It has been alleged that oil discharges have induced carcinomas in marine produce.

Compared with biosynthesis and terrestrial run-off, oil does not provide a significant proportion of the PNAH input to the marine environment on a global scale, but can be a major contributor on a local scale, particularly in sewage discharges and refinery effluents.

PNAH's in marine produce will be ingested, usually after cooking, and may or may not form a regular proportion of the daily food intake. PNAH's are poorly absorbed by the mammalian gastrointestinal tract when added to the diet.

It is still a matter for debate whether there is any dose-response relationship for chemical cancer-induction in man, or a threshold dose below which carcinogens do not induce cancer. No reports have been found of epidemiological studies which link gastro-intestinal cancers in man with the injestion of oil contaminated fish or shell fish.

There are, however, indications of higher frequencies of stomach cancer associated with consumption of smoked fish (which does contain high levels of carcinogenic PNAH's) in Iceland.

Loss of Marine Foods

The extent of proven or alleged losses due to oil pollution has been impossible to evaluate fully, due to the inadequate documentation of incidents, claims, closures, or condemnations of produce. However a few examples have been compiled which serve to indicate the probable extent of the problems. Instances have been found of produce being rendered unacceptable on the grounds of altered appearance, and of the closure of fisheries on the grounds of a government determinated health risk, but most of the existing data and documentation refers to the problem of tainting.

It was established that; (1)- crustaceans, fish and molluscs exposed to oily conditions can acquire an objectionable oily taste; (2)- the production of an oily taste is intimately associated with the presence of volatile compounds derived from oils, refined, products or dispersants; (3)- the range and quantity of odorous compounds varies with the type of oil and refining process, with the middle distillate fractions, like diesel oil, containing the greatest number.

The use of dispersants facilitates the uptake of oil and its components and their introduction to the lipid pool of the organism. The use of oil dispersants therefore increases the likelihood of tainting. The solvent fractions of older dispersants contained tainting compounds of the same nature as those found in diesel and crude oils. There are indications that the tissue lipid content and the amounts of free lipids increase the susceptibility to tainting. Fatty fishes and lipid-rich organs, such as gonads, will become more strongly tainted and perhaps for a longer period of time. Therefore, the seasonal condition of the produce will also affect the susceptibility and the strength of taint, as lipid contents and metabolic rates vary.

External contamination with oil does not necessarily mean that tainting of flesh has occurred, although visible external contamination may in itself be a reason for rejection of produce. Even ingestion of oil by marine organisms does not necessarily cause tainting of flesh, but some species of crustacea and molluscs are consumed together with their gut contents, which may lead to rejection of produce. Cooking of whole animals which have been internally or externally fouled with oil may lead to tainting of the meat. There have been too few studies on the tissue levels of oil components in tainted produce for any tainting threshold levels to be established. A threshold of 10-30 ppm in tissue spiked with a North Sea crude oil has been reported with an upper limit of 200-300 ppm, beyond which no further increases can be sensed by a trained taste panel. Threshold levels of 5 ppm gas oil in spiked mussel tissues, and 4-12 ppm extractables from diesel oil in lobsters have also been reported. Exposure to ambient water concentrations as low as 0.01-0.02 ppm oil can lead to tainting of meats.

Aesthetics

The occurrence of petroleum residues in the form of tar balls or tar lumps on beaches and on the ocean surface is well documented. They are a nuisance in many respects and both injurous and troublesome to beach users.

4.7.5 Cyanides And Fluorides

Cyanides

While cyanides are among the most toxic of all industrial chemicals, are produced in large quantities and used in many different applications, they are the cause of only a few serious accidents or deaths. This is due in part to the fact that the word "cyanide" is synonymous with a highly poisonous substance, and a certain amount of care in handling is thereby ensured.

The main sources of cyanide waste are the extraction of lead, zinc, gold and silver from ores, the heat-treating of metals, electroplating, various ionic reactions and the manufacture of adiponitrile.

For such wastes, alkaline oxidation and chemical decomposition by free chlorine or hypochlorite have been successfully applied for a long time, followed by heavy metal removal using precipitation.

Persistence. Cyanide is biodegradable and treatment methods are available which eliminate the need to discharge cyanides. The bio-degradability of cyanide and the readiness with which it forms complexes with certain metal ions, e.g. copper, means that large scale dispersion of cyanide is unlikely and that any detrimental effects would be local in nature, (49).

Toxicity. Cyanides are very toxic, and the hazards for fresh water organisms are very high. We have not found data concerning its toxicity in seawater. GESAMP rated potassium cyanide as: not known to be significantly bioaccumulated; highly toxic to living resources, TLM 1 ppm, moderately hazardous to human health, oral intake LC_{50} 5-50 mg/kg: slightly hazardous (assolution) to human health, skin contact and inhalation and no problems to reduction of amenities, (50).

Fluorides

The main sources of fluoride waste are the manufacture of fertilizer from fluorine-bearing phosphate rock, the production of aluminium, steel and enamel plant.

Chronic fluorine intoxication "fluorosis" was first described as occurring among animals, (51). Darmous, an abnormality of the teeth and bones, occurs among sheep and cattle pastured in North Africa in land where the vegetation is contaminated by fluorine-bearing dust derived from phosphate deposits. Severe cases among sheep, goats and cattle have occurred both in Europe and in the United States in the vicinity of factories that emit fluorine-containing compounds into the atmosphere.

Fluorides occur naturally in many public water supplies and, if present in excessive amounts, may possibly give rise to dental fluorosis in children. When present in much higher concentrations, they may eventually cause endemic cumulative fluorosis with resulting skeletal damage in both children and adults.

Fluorides are also regarded as an essential constituent of drinking water, particularly with regard to the prevention of dental caries in children. If the fluoride concentration in the drinking water of a community is less than 0.5 mg the incidence of dental caries is likely to be high. The recommended control limits for the concentrations of fluorides in drinking water depend on the annual average of maximum daily air temperature; for a range from 17.7°C to 26.2°C a lower limit of 0.7 mg/l is recommended and an upper limit of 1.0 mg/l.

Fluorides occur naturally in seawater, the average concentration is 1.3 mg/l. There is no evidence of accumulation of fluoride in seaweeds and grazing molluscs collected in the vicinity of a large discharge containing a low fluoride level, (52).

4.7.6 Non Biodegradable Detergents And Other Surface Active Substances

This group of substances has the property that, when added to water, small quantities significantly reduce the surface tension.

The synthetic detergents are composed of one hydrophobic group and other hydrophilic groups. The hydrophobic group consists generally of a long hydrocarbon chain and is soluble in organic products, oils and fats (lipophilic), and can be anionic, cationic or non-ionic.

The water soluble components are generally inorganic compounds e.g. sodium polyphosphates, silicates or sulphates and are common to all types of detergents.

The annual utilization of detergents is about 10 kg per inhabitant per year of which 80-90% is anionic type and the rest non-ionic.

The active substances in the majority of synthetic detergents consist of a series of alkyl benzene sulphonates (ABS).

Oil spill dispersants. Oil spill dispersants normally consist of a surface-active agent (surfactant) mixed with a hydrocarbon solvent and sometimes a stabiliser.

The earlier dispersant used in the Torrey Canyon incident contained an aromatic hydrocarbon solvent and therefore was very toxic. In 1969 Corexit 7664 was introduced of which the surface active agent is a non ionic polyhydric alcohol ester of fatty acids and the solvent is isopropyl alcohol.

The most widely used non-ionic surfactants are those that are obtained by condensing long-chain alkyl and alkyl phenols with ethylene oxide. Owing to the presence within the molecule of both hydrophilic and lipophilic characteristics, the surfactant can orient itself in the oil-water interface with the lipophilic group(s) in the oil and the hydrophilic in the water, so producing fine oil droplets when energy is provided by mixing.

Toxicity. The toxicity depends on the chemical structure of the detergents. It is generally admitted that normal ABS (alkyl benzene sulphonate) are more toxic than the branched ones. Maggi and Cossa, (53), have studied the toxicity of five household detergents, anionic type (Table 17).

Wilson, (54), has compared the toxicity of ten oil dispersants for Crangon and Cardium (Table 18).

Persistence. The persistence of detergents is dependent on their molecular structure. The alkyl benzene sulphonate is more easily biodegraded when the alkyl chain is normal (non-branched) and long and when the distance from the alkyl chain to the sulphonate group is great.

The branched ABS are found almost intact after treatment by activated sludge or wet oxidation. Therefore they are considered as non-biodegradable.

It is convenient to remember that according to the Council of Europe, 20 November 1970, the sale of detergent products for washing and cleaning with a biodegradability of lower than 80% is forbidden.

Cossa, D. and Maggi, (55), have studied the biodegradability of 5 household detergents. Their results are given in Table 19.

The pollution characteristics of detergents have been related to:

1. Non-biodegradability resulting in foaming over the water surface.
2. Phosphate content, leading to enrichment of receiving waters.
3. To a lesser degree, direct toxicity of the ingredients.

Virtually all domestic detergents on the world market today are biodegradable as a result of conversion by manufacturers from hard alkyl benzene sulphonate (ABS) to the soft linear alkyl sulphonate (LAS) form. The former however, are still widely used in industry.

Sodium polyphosphate remains a major constituent (20-60%) of most proprietary detergents. Because they perform vital functions related to cleansing efficiency and no widely acceptable substitute is available, manufacturers are reluctant to eliminate or even reduce the amounts of phosphate in detergents. The main hazards to marine waters from detergents contained in sewage are the effects on some marine species, specially on larvae, and the increment of phosphate which may produce the process of eutrophication. In some cases the presence of foam is detected, resulting in aesthetic problems and also in interference with the process of oxygen transfer. The presence of detergent films on the surface of the sea has been indicated as a possible mechanism for introducing other pollutants into it by improving the solubility of atmospheric pollutants.

The persistence of detergents depends on their molecular structure. The alkyl benzene sulphonate is more easily biodegraded when the alkyl chain is normally long (non-branched) and when the distance from the alkyl chain to the sulphonate group is considerable.

LAS is more readily degradable biologically than ABS. However, it is also two to four times more toxic. Lethal concentrations of LAS to selected fish species have been found to vary in short term, chronic toxicity studies.

It is recommended that the maximum acceptable concentrations of linear alkyl

TABLE 17 LD 50 after 48 to 96 hours exposure (the values are given in mg of active material per litre), (53).

	D_1 LD 50		D_2 LD 50		D_3 LD 50		D_4 LD 50		D_5 LD 50	
	48 h	96 h	48 h	96 h	48 h	96 h	48 h	96 h	48 h	96 h
Mytilus edulis	27.5	5.7	22	6.2	29	12.2	11	4	60	24.5
Cardium edule	20	4.3	35	15	17	14	9.4	5	13	7.3
Purpura lapillus	12	5.8	30	7.8	40	16	7.3	6.7	8.3	7.5
Gibbula umbilicalis	17	7.5	31	9	50	17.5	31	5.5	72	10
Littorina littorea	100	14	100	17.5	100	70	100	20	100	27
Patella vulgata	5	3	15	8.1	7.2	5.8	3.2	3	66	54
Artemia salina	22	13.5	7.3	5.8	4.5	2.3	3.7	3.4	100	70
Clinabarius misanthropus	100	100	100	100	100	100	100	100	100	100
Palaemonetes varians	100	40	100	100	100	100	100	100	100	100
Crangon crangon	100	50	100	100	100	100	100	100	100	100
Actinia equina	15	9.2	16.3	15	16.3	15	15	13.3	100	100
Pomatoschistus minutus	8.1	8.1	5.0	5.0	4.5	4.5	3.4	3.3	0.9	0.9
Anguilla anguilla (civelle)	9.1	9.1	3	3	2.9	2.9	2.9	2.9	2.1	2.1

D_1 - Manaxol OT

D_2 - Igepal NA

D_3 - Dobane JN

D_4 - Dobane 83

D_5 - Dobanol 25-35

TABLE 18 A Comparison of the Rank Orders of Ten Dispersants for Crangon and Cardium, (54).

Dispersant	48 h LC_{50}	Crangon Rank	Cardium Rank
Slickgone 2	(33 - 10)	1	3
BP 1002	(33 - 10)	2	5
Gamlen OSR	(33 - 10)	3	1
Cleanosol	(33 -100)	4	2
Atlas 1901	(100 - 330)	5	4
Dermol	(100 - 330)	6	6
Plycomplex A	(100 - 330)	7	7
BP 1100	(1000 -3300)	8	8
Corexit 7664	(3300-10000)	9	9
BP 1100 X	(10.000)	10	10
	r = 0.843		

TABLE 19 Time in days for biodegradation of 50% of surfaceactive agent, (55).

Household detergents	Initial conc. 20 mg/1	Initial conc . 40 mg/1
D_1 - Manaxol OT	4	5.2
D_2 - Igepal NA	7	7
D_3 - Dobane JN	7	7
D_4 - Dobane 83	6.3	6.6
D_5 - Dobanol 25-35	2.1	3.8

sulphonates (LAS) in water should be 0.05 of the 96 hour LC_{50} value determined using the receiving water in question and the most sensitive important species in the area as test organisms. It is suggested that concentrations of LAS in water in excess of 0.2 mg/1 constitute a hazard in the marine environment.

4.7.7 Inorganic Compounds Of Phosphorus And Elemental Phosphorus

Nutrients

Eutrophication and the production of toxic algal blooms (e.g. red tides) are becoming more frequent, especially in shallow closed regions such as the Oslo fiord, Baltic Adriatic and the Seto Inland Sea in Japan. More attention should be paid to this special problem. Although there is no agreement on the triggering mechanism for such blooms, nutrients clearly play an important part, and increasing pollution may be the cause in some areas.

The sources of nutrients from the viewpoint of marine pollution are many and, in most cases, very difficult to control. A large amount of nutrients reaches the marine environment in domestic sewage, from human excreta and detergents. Erosion of cultivated land also contributes some nutrients to the sea, but proper soil management can considerably reduce this runoff loss. Partially anaerobic conditions in shallow water bodies, such as lagoons, lakes and estuaries, can lead to the discharge of a large amount of phosphate ion into the receiving coastal zone. In addition to these sources, industrial wastes have a considerable nutrient input into the sea. In some areas, nutrients are intentionally applied as fertilizer for agriculture.

Phosphorus

Phosphorus is normally found in the sea in the form of phosphate, either particulate, organic or inorganic. If discharged in elemental form, however, it remains largely in that state and is potentially highly toxic. There have been some instances of elemental phosphorus being discharged to the marine environment from factories producing phosphorus from phosphate ores and from ships carrying phosphorus, both in bulk and in drums. Much of the phosphorus becomes locked in the sediments where it remains virtually unchanged for a considerable period of time; the fraction remaining in the water is slowly oxidized to phosphate. One large scale incidence of toxicity arose on the coast of Newfoundland from a factory discharge. Large numbers of herring, cod and other species were killed, in some species extensive haemolysis and reduction of haematocrits was observed.

4.7.8 Thermal Pollution

Increase in temperature due to discharges from power plants and to industrial cooling and waste water may cause two main undesirable effects; it decreases oxygen solubility in water and increases the metabolic activities of microflora and fauna, which in turn may result in higher BOD and local hypertrophication. Fluctuating water temperatures may produce changes in biological communities. The effects of this form of pollution naturally depend on the receiving sea water temperature and that of the effluent, and also the efficiency of mixing and dissipation by means of currents, tides and wind.

Special care is needed in siting power plants, employing sea water for cooling, in tropical areas where animals and plants may have a narrow range of temperature tolerance and where even a rise of a few degrees may cause severe mortality rate.

It is known that several enzyme reactions which take place in organisms are dependent on temperature. Increase in temperature may result in a significant increase in the uptake and accumulation of certain pollutants.

Ecosystem changes have been observed in the vicinity of thermal discharges.

A temperature increase may affect the marine organisms directly by changing physiological or behavioural processes, or it may affect organisms indirectly by changing some aspects of the environment on which the organisms depend.

Temperature increase leads to an increase in the rate of lethal action of cyanides.

4.7.9 Effluents Containing Radioisotopes

Introduction

Long before pollution problems in general had become matters of public concern, preventing pollution of the sea from the discharge of radioactive wastes has been recognized as an important problem. In fact, already in 1958 the UN Conference on the Law of the Sea adopted a Convention on the High Seas. art. 25 which provides that every state shall take measures to prevent pollution of the sea from the dumping of radioactive wastes, taking into account any standards and regulations which may be formulated by the competent international organizations. Since then the International Atomic Energy Agency (IAEA), Vienna, has called on several panels of experts to formulate principles and guide-lines for establishing limits for the release of radioactive materials into the environment and especially into the sea, (56, 57, 58, 59).

The effects of radiation exposure on man are based on the recommendations of the International Commission of Radiological Protection, (60). The ICRP has been functioning since 1928 and also periodically reviews new evidence and revises, if necessary, previous recommendations.

Radiation effects on marine organisms and ecosystems have been reviewed in the IAEA panel on the Effects of Ionizing Radiation on Aquatic Organism and Ecosystems, (61), and in the panel on the Radiation Effects on Population Dynamics in Ecosystems, (62). These recommendations are used as guidelines for the assessment of the safety of proposed disposal of radioactive wastes into the marine environment.

Practically without exception these guidelines and criteria have been used by national authorities to legislate for the issuing of authorizations for the discharges of wastes containing radioisotopes into the environment, including national marine waters. The authorization for release is based on an Environmental Impact Statement for each nuclear installation. This document contains data on background levels of radioactivity in the environment and also estimates the radiation dose to the public that results from normal plant operation.

The basic object of radiation protection is to prevent the occurrence of serious effects and to limit the probability of late somatic and genetic effects to levels which are deemed to be acceptable, (61).

Legislation based on ICRP recommendations is in force in France, Italy and Yugoslavia.

Persistence

Radioisotopes are only destroyed by radioactive decay. The daughter nuclide is often also radioactive. The daughter nuclide is a different chemical element with completely different chemical behaviour in the environment and may emit different forms of radiation.

As a first approximation one can assume that radioisotopes behave like their stable isotopes and that their persistence in the marine environment is influenced by their residence time in the water before settling and being adsorped onto the sediment. Residence times differ according to the individual marine environment. In general residence times are shorter in coastal waters.

Toxicity and other harmful effects

Radiation carcinogenesis in man, genetic effects of radiation, experimental radiation carcinogenesis and development effects of irradiation in utero have been recently reviewed by the UNSCEAR, (63).

Radiation may cause somatic and genetic effects. The most important somatic effects are malignant diseases and disturbances in the prenatal development. The carcinogenic effect of alpha radiation and neutrons is greater than for other types of radiation.

The quantification of somatic effects is difficult because in most cases only gross alterations can be detected. The observations made on the populations of Hiroshima and Nagasaki are also significantly different than those in the Marshall islands. In UNSCEAR, (63), the risk of fatal malignancies is estimated to be not greater than 100 E-6 per rad (= 10 E-6 per gray). Non fatal malignancies have the same risk. Thus the total risk of somatic malignancies is equal to 200 E-6 cases per rad.

Genetic effects are ever more difficult to estimate: the risk of induction of excessive mutants per gamete is estimated to be less than 60 E-6 per rad. The risk of inducing a dominant mutant per gamete is less than 20 E-6 mutants per rad exposure. The risk of serious effects in the first generation of offspring (F-1) of irradiated parents is equal to 20 to 30 E-6 defects per rad.

The total genetic damage due to gross and marked defects in each generation after prolonged exposure is estimated to be about 200 E-6 mutants per rad of exposure.

The total genetic load cannot, however, be assessed at this stage since the quantification of the minor deleterious effects caused by ionizing radiation is still uncertain. ICRP, (60), estimates the total genetic risks as follows: risk in F-1 and F-2 is equal to: 40 E-6/rad; all other Fs: 80 E-6/rad; total somatic risks: 200 E-6/rad.

The effects of ionizing radiation on aquatic organisms and ecosystems have been reviewed by an IAEA panel recently, (64).

Comparing the dose rates received by groups of marine organisms from the natural environment, fallout, the discharge from a nuclear fuel processing plant and a nuclear power reactor (Table 20), shows that natural background, fallout and the release from a nuclear reactor contribute in the same order of magnitude to the dose rates received by marine organisms. The doses from releases from the Windscale Fuel Processing plant are 2 to 3 orders of magnitude larger.

Different dose rates are received by different groups in the same environment. Although these dose rates can be estimated with a certain accuracy the effects are difficult to assess.

Few chronic exposure experiments using marine organisms or fresh water organisms have been carried out. Exposure to acute doses conducted with very high doses cannot be extrapolated to chronic low dose situations. The few chronic experiments show, however, that high external doses are necessary to obtain observable effects.

Experiments regarding irradiation from radionuclides present in the water produce conflicting results.

Russian workers reported that very low concentrations of nuclides (e.g. 10 E-12 Ci 90-Sr/ y/1) would cause malformations and increase mortality in fish embryos. However, these observations could not be confirmed by other workers (Table 21) who could observe effects only in the range of 10 E-4 Ci/1 and higher. Adverse effects on the behaviour of aquatic organisms have also been reported for low dose exposures.

Radiation effects can be modified.

Additional environmental stress will enhance radiation effects. Repair, on the other hand will reduce the radiation effects.

TABLE 20 Summary of dose rates (μrad.h^{-1}) to marine organisms from environmental radioactivity, (64).

Source	Phytoplankton	Zooplankton	Mollusca	Crustacea	Fish	
	20 m depth remote from sea bed	20 m depth remote from sea bed	20 m depth, on the sea bed	20 m depth, on the sea bed	20 m depth, remote from sea bed	20 m depth on the sea bed
NATURAL BACKGROUND						
Cosmic radiation	0.5	0.5	0.5	0.5	0.5	0.5
Internal activity	1.9-7.3	2.6-15.7	7.4-14.9	7.9-21.4	2.7-4.2	2.7-4.2
Water activity	0.4	0.2	0.1	0.1	0.1	0.1
Sediment activity,	-	-	1.5-16.0	1.5-16.0	-	1.5-16.0
	-	-	1.6-21.0	1.6-21.0	-	1.6-21.0
Total[(a)]	2.8-8.2	3.3-16.4	9.5-31.5	10.0-38.0	3.3-4.8	4.8-20.8
FALLOUT						
Internal activity,						
^{3}H, ^{14}C, ^{90}Sr, ^{137}Cs, ^{239}Pu	0.01-0.88	0.23-13.4	0.06.0.32	0.004-0.097	0.02-0.06	0.02-0.06
Other nuclides	0.25-24.6	1.2-134	0.04-7.7	0.36	0.12-1.7	0.12-1.7
Water activity	5×10^{-5}-0.016	4×10^{-5}-0.011	$(0.2-32)\times10^{-4}$	$(0.2-32)\times10^{-4}$	$(0.3-65)\times10^{-4}$	$(0.2-32)\times10^{-4}$
Total [(a)]	0.26-25.5	1.4-147	0.10-8.0	0.36-0.46	0.14-1.8	0.14-1.8
WASTE DISPOSAL						
Windscale						
Internal activity	200-2100	530-6900	15.3-58.9	6.9-67.9	0.5-1.5	0.5-1.5
Water activity	0.2-3.3	0.2-3.0	0.05-1.2	0.05-1.2	0.09-2.4	0.05-1.2
Sediment activity,	-	-	36.4-3340	36.4-3340	-	36.4-3340
	-	-	207-5380	207-5380	-	207-5380
Total [(a)]	200-2100	530-6900	51.8-3400	43.3-3410	0.6-3.9	37.0-3340

TABLE 20 (continued)

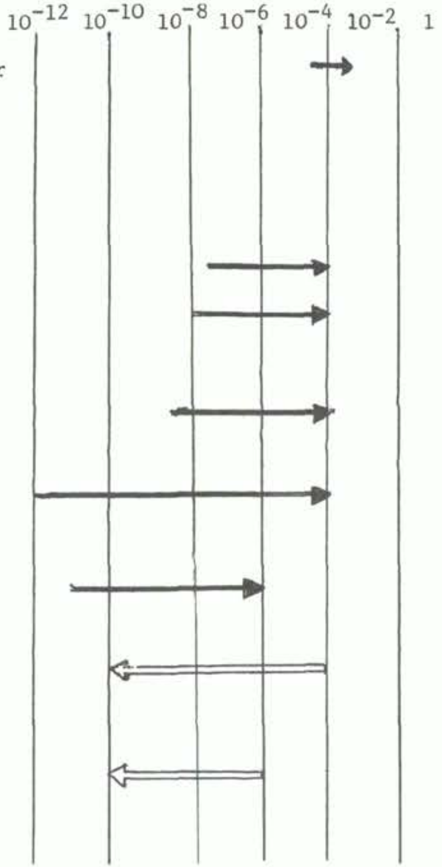
	Phytoplankton 20 m depth remote from sea bed	Zooplankton 20 m depth remote from sea bed	Mollusca 20 m depth on the sea bed	Crustacea 20 m depth, on the sea bed	Fish 20 m depth, remote from sea bed	20 m depth on the sea bed
Bradwell						
Internal activity	NDA	NDA	1.37-1.81	NDA	NDA	NDA
Sediment activity	-	-	1.69	1.69	-	1.69
	-	-	1.32	1.32	-	1.32
Total (a)	-	-	3.1-3.5	1.7	-	1.7

(a) Excluding the contribution due to β - radiation from the sediment

TABLE 21 Summary of experimental studies on the effects of radionuclides in water on aquatic organisms

(Positive effect: ● or ➞) (Negative effect: ○ or ⇦)

Concentration of radionuclides* (Ci . 1^{-1})

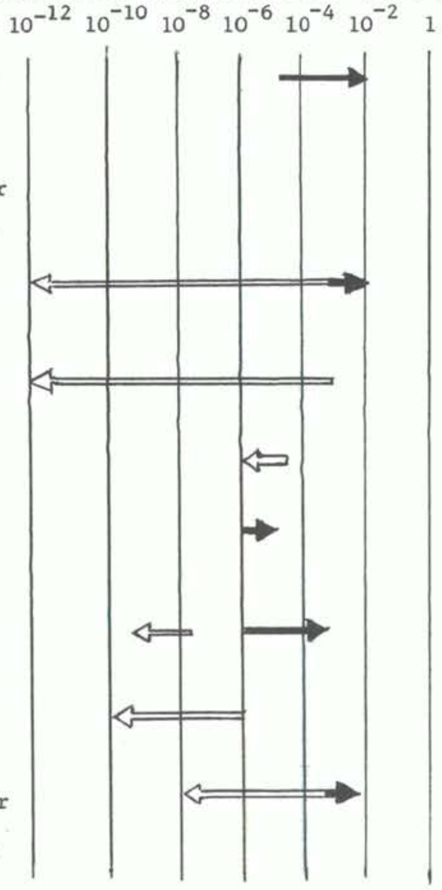


Investigators		Types of effects
Lebedeva,	^{90}Sr	Shortened the life-span of adult individuals of Daphnia magna.
Sinevid	^{90}Y	
Telichenko		
Polikarpov,		
Ivanov	"	Delay in emryonic development of fish eggs (anchovy)
"	"	Increase in the mortality rate of embryo of fish eggs and tendency to be smaller in size of young fish was observed.
"	"	Decrease in cell division in grastrula stage and chromosome aberration of fish eggs (anchovy, stone perch)
Polikarpov,	^{90}y	Increase in malformation rate of fish eggs (anchovy, mullet, green wrasse, horse mackerel)
Ivanov		
Fedorov et al	"	Increase in malformation rate of fish eggs (plaice, Pleuronectes platessa)
Brown,	"	No significant increase in mortality or in the production of abnormal larvae (brown trout, Salmo trutta),
Templeton		
Neustroev,	"	The rate of development of the egg was the same as the control up to stage of one-third development of the yolk sac (atlantic salmon, Salmo salar)
Podymakhin		

TABLE 21 (continued)

(Positive effect: ● or ➡) (Negative effect: ○ or ⇦)

Concentration of radionuclides* (Ci . 1^{-1})



Investigators		Type of effects
Kulikov et al	^{90}Y	Morphological abnormalities, delay in development, and mortality (eggs of the fresh water mollusc, (*Limnaea stagnalis*)
Shekanova, Pechkurenkov	^{90}Sr ^{90}Y	Non-developing larvae appeared in developing eggs of the loach
Hiyama, Shimizu Suyama	"	Sharp decrease in the rate of attaining the pluteus stage (see urchins, *Pseudocentrotus depressus*, *Anthocidaris carassispina*)
" "	"	Normal rate of hatching and malformation of eggs (*Mylio macrocephalus* and *Rudaris ercodes* in sea water)
Rgami et al	"	Normal rate of mortality and abnormality of the embryo (fresh water killifish, *Oryzias latipes*)
" "	"	Effect on gonad was found in fish, exposed in contaminated water, continuously 70 days after hatching (fresh water killifish, *Oryzias latipes*)
" "	"	Damage on seminal glands in fish, exposed 15-30 days (fresh killifish, *Oryzias latipes*)
Kosheleva	"	Egg mortality during the time of incubation was the control level in the Atlantic salmon (*Salmo salar*)
Nelson	^{90}Sr ^{90}Y	Significant increase in abnormal larvae (pacific oyster, *Crassostrea gigas*)

TABLE 21 (Continued)

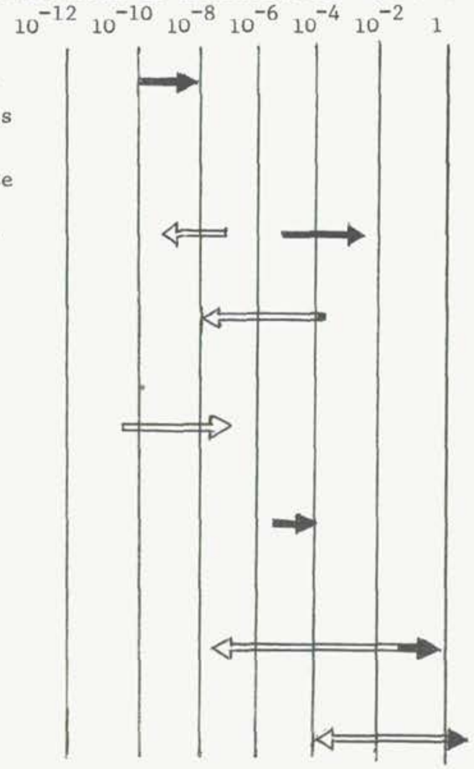
(Positive effect: ● or ➡) (Negative effect: ○ or ⇦)

Investigators		Concentration of radionuclides* (Ci . l^{-1})						Types of effects
		10^{-12}–10^{-10}	10^{-10}–10^{-8}	10^{-8}–10^{-6}	10^{-6}–10^{-4}	10^{-4}–10^{-2}	10^{-2}–1	
Tsytsugina	^{90}Y		○					Significant increase of chromosomal breakages was found in the ruff (Scorpaean porcus)
Guthrie and Brust Scott	"					➡		The testes and ovaries of adults were atrophied when larvae of Aedes aegypti and A.atropalpus were reared in radioactive water.
Strand et al	"				⇦			No significant differences on rainbow trout during embryogenesis
Migalovskaya	^{90}Sr			⇦	⇦			No decrease in the percentage of dividing cells was detected in the investigated development stages. In variants with $2x10^{-5}$ Ci.1^{-1}, there was a reliable increase in the frequency of chromosomal aberration, beginning with the epithelial blastula stage (Salmo salar)
Williams, Murdoch	^{137}Cs				○			No influence on population density in a population of a copepoda (Tigriopus califormicus) kept in radioactive water for several years.
White et al	"			⇦	⇦			No visible abnormalities on the developing eggs and larvae (mummichogs, Fundulus heteroclitus)
Hallopeau	F.P. ^{137}Cs			○	○			No effect on the reproduction of Artemia salina

TABLE 21 (Continued)

(Positive effect: ● or ➡) (Negative effect: ○ or ⇦)

Concentration of radionuclides* (Ci . 1^{-1})

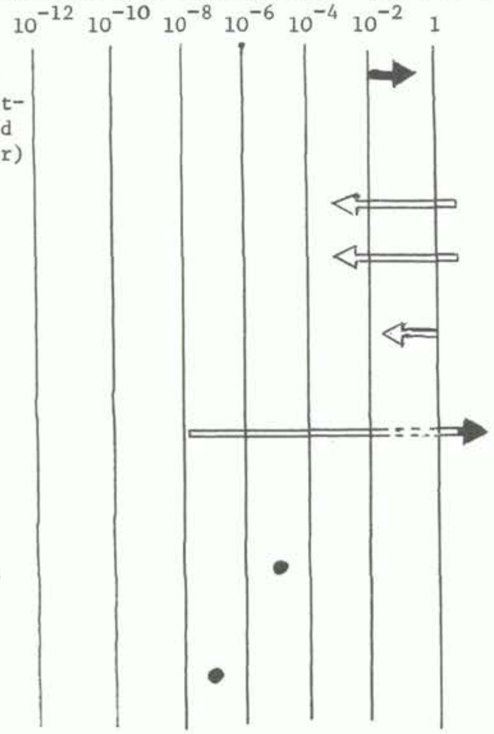


Investigators		Types of effects
Kosheleva	F.P. ^{137}Cs	Considerable number of deaths were observed in the Atlantic salmon (Salmo salar) when the eggs were exposed to radioactive water.
Migalovskij	^{144}Ce	
Mashneva	F.P.	Damage at early stages of developing eggs of carp and Coregonus peled
Nelson	^{51}Cr or ^{65}Zn	Significant increase in abnormal larvae (Pacific oyster, Crassostrea gigas)
Havlik, Robertson	^{226}Ra	Photosynthetic oxygen production in fresh-water phytoplankton was sharply reduced by 24 hours exposure to a ^{226}Ra concentration of 3×10^{-8} Ci.1^{-1}
Akita,	HTO (tritiated water)	50% attainment to pluteus (violet sea archin (red sea urchin, Pseudocentrotus depressus)
" "	"	50% attainment to pluteus (violet sea archin, Anthocidaris crassispina)
Etoh, Ueno, Ichikawa	"	Slight decrease of the rate of hatching (fresh water killifish, Oryzias latipes)

TABLE 21 (Continued)

(Positive effect: ● or ➡) (Negative effect: ○ or ⇦)

Concentration of radionuclides* (Ci . 1^{-1})



Investigators		Types of effects
Buggeln, Held	HTO (tritiated water)	Reduced percentage of germination of the asexually produced spores (Padina japonica)
Blaylock et al	"	No effects on embryo development of cyprinus carpio
Walden	"	No effects on embryo development of Gasterosteus aculeatus
Erickson	"	No significant effects on mortality, growth, male characters behaviour and thermal death of the guppy fish Lebistes reticulata
Ichikawa, Suyama	"	Decreases in hatchability were observed and 10 Ci.1^{-1} effects were noted on body shape and eye diameter of larvae of two species of marine fish (Paralichthys olivaceus and fugu niphobles)
Federowa	^{14}C	Increase of malformed larvae of Coregonus peled, when Na11 $^{14}CO_3$ was added to the water seven days after fertilization.
Tsytsugina		Significant increase of chromosomal breakages was found in the ruff (scorpaena porcus)

Note: * It is important to realise that the quoted concentrations do not directly indicate the dose, received by organisms and/or organs.

But also favourable effects, e.g.: on development and survival, have been observed at low chronic doses.

Genetic effects were observed similarly at very high concentrations (e.g. 0.1 Ci 3-H/1).

It must however be kept in mind that all exposures tested on marine organisms would never be permitted in the natural environment because the protection of human population requires lower releases of radionuclides than those which could effect marine organisms.

Chlorine discharges from seawater cooled nuclear power reactors have the same impact as chlorine discharges from conventional plants.

The temperature effect of discharges of cooling water affects marine biota only in badly sited power stations. Discharges of warm cooling waters on the open coastline should not have observable effects.

Accumulation in biological materials and sediments

Radioisotopes (as their carrier isotopes) are taken up by marine organisms, in suspension and in sediments.

For radioprotection purposes the uptake by biota is expressed as concentration factors (CF), (66), and the absorption by sediments as distribution coefficients (DC). The CF's and DC's of isotopes and stable carriers have different values depending on marine organisms and types of sediment (Table 22 and 23). The physico-chemical form of a radioisotope markedly influences its uptake and consequently its CF and DC. Under certain conditions the physico-chemical form of the radioisotopes can be different from that of the naturally occuring carrier isotope(s). Therefore, only as a first approximation can the CR and the DC of the naturally occuring carrier be used for prediction purposes.

TABLE 22 Average concentration factors for Benthic Algae, Plankton and Mollusc, Crustacean, and Fish Muscle, (24).

Chemical Group		Benthic algae	Phyto-plankton	Zoo-plankton	Mollusc Muscle or Soft Parts	Crustacean Muscle	Fish Muscle
I A	Li	-	-	-	0.28	1.2	0.47
	Na	-	-	-	0.2	0.3	0.13
	K	-	-	-	8	13	13
	Rb	-	-	-	16	13	17
	Cs	-	-	-	8	23	15
	Fr	-	-	-	-	-	-
I B	Cu	100	30,000	6,000	5,000	-	1,000
	Ag	-	23,000	9,000	7,100	7	-
	Au	470	-	-	400	400	60
II A	Be	110	1,000	15	-	-	-
	Mg	2	2	4	1	-	0.2
	Ca	2	2.5	5	0.4	120	1.5
	Sr	96	-	-	1	3	0.1
	Ba	-	17,000	900	-	-	8
	Ra	1,400	12,000	190	1,300	140	130
II B	Zn	410	15,000	8,000	11,000	2,000	500
	Cd	200	-	-	-	-	1,000
	Hg	-	-	-	-	-	-
III A	B	1	-	1.6	-	-	2
	Al	15,000	100,000	100,000	9,000	12,000	10,000
	Ga	1,300	8,000	7,000	2,000	2,000	-
	In	-	-	-	-	-	-
	Tl	-	-	-	-	-	-
III B	Sc	2,000	2,000	1,000	-	300	750
	Y	480	1,000	105	12	--	250
	La	-	-	-	-	-	-
	Ce	670	90,000[b]	1,000	360	2	0.3
	Pu	1,300	2,600	2,600	260	3	3
IV A	C	4,000	3,600	2,800	4,700	3,600	5,400
	Si	100	2,000	300	50	-	20
	Ge	50	-	-	-	-	-
	Sn	-	6,000	450	-	-	-

TABLE 22 (continued)

Chemical Group		Benthic algae	Phyto-plankton	Zoo-plankton	Mollusc Muscle or Soft Parts	Crustacean muscle	Fish Muscle
IV A	Pb	700	40,000	3,000	40	-	-
IV B	Ti	4,100	25,000	17,000	-	-	-
	Zr	2,200	60,000	25,000	2	2	1
	Hf	-	-	-	-	-	-
V A	N	-	36,000	24,000	47,500	44,000	65,000
	P	10,000	34,000	13,000	6,000	24,000	33,000
	As	2,000	-	-	650		
	Sb	-	-	-	-	-	-
	Bi	-	-	-	-	-	-
V B	V	600	600	700	1,000	330	110
	Nb	1,000	1,000	-	7	3	100
	Ta	-	-	-	-	-	-
VI A	S	1	-	-	0.3	-	1
	Se	1	-	-	-	-	-
	Te	-	-	-	-	-	-
	Po	1,000	-	-	-	-	-
VI B	Cr	1,600	2,400	1,900	400	100	70
	Mo	8	-	26	60	10	10
	W	5	-	-	20	2	3
VII A	F	1	-	-	-	-	-
	Cl	1	1	1	1	1	1
	Br	-	-	-	-	-	-
	I	5,000	-	3,000	50	30	12
	At	-	-	-	-	-	-
VIII B	Mn	2,300	4,000	1,500	12,000	1,900	80
	Tc	-	-	-	-	-	-
	Re	-	-	-	-	-	-
VIII	Fe	4,800	45,000	25,000	9,600	2,400	1,600
	Co	800	1,500	700	700	500	10
	Ni	1,000	5,000	3,000	-	-	-
	Ru	390	200,000[b]	34,000[b]	3	100	0.05
	Rh	-	-	-	-	-	-

TABLE 22 (continued)

Chemical Group		Benthic algae	Phyto-plankton	Zoo-plankton	Mollusc Muscle or Soft Parts	Crustacean muscle	Fish Muscle
VIII	Pd	-	-	-	-	-	-
	Os	-	-	-	-	-	-
	Ir	-	-	-	-	-	-
	Pt	-	-	-	-	-	-

[a] Data derived from Polikarpov, (68), Templeton, (69), Goldberg, (70), Vinogradova and Koval'skiy, (71), Fukai and Meinke, (72), Nicholls et al., (73), and from the unpublished work of Lowman.

[b] Slowey et al., (74).

TABLE 23 Distribution of Sorbed Radionuclides and Total radioactivity in Different Size Fractions in Three Types of Sediment, (75).

Sediments Origin	Size μ	Fractions % Weight	Distribution Coefficients for Each Size Fraction (value x 10^2) ^{90}Sr	^{137}Cs	^{106}Ru	^{59}Fe	^{65}Zn	^{60}Co	^{147}Pm	^{54}Mn	$^{95}Zr/Nb$	^{144}Ce
Dutch	> 64	51.1 ± 4.9	0.0	0.0	0.0	0.0	0.0	5.8	0.0	0.0	0.3	0.4
Wadden	32-64	21.7 ± 4.5	0.0	1.6	3.1	76.0	0.0	3.7	0.0	1.4	42.0	3.3
Sea[a]	16-32	9.5 ± 3.2	0.0	5.4	0.0	53.0	260.0	65.0	0.0	35.0	66.0	120.0
	8-16	5.6 ± 2.0	0.0	12.0	7.3	370.0	490.0	59.0	0.0	8.0	1,040.0	950.0
	4-8	8.4 ± 1.9	0.0	16.0	5.2	510.0	380.0	430.0	320.0	480.0	1,220.0	540.0
	4	3.7 ± 0.8	26.0	6.2	4.7	540.0	112.0	220.0	280.0	97.0	670.0	124.0
Mediterranean	> 64	0	-	-	-	-	5.2[b]	-	-	-	-	-
off	32-64	3.0 ± 1.3	15.0	2.8	41.0	15.0	68.0	380.0	24.0	19.0	117.0	32.0
Monaco[a]	16-32	15.2 ± 4.2	2.0	1.3	11.0	101.0	140.0	540.0	0.8	41.0	290.0	73.0
	8-16	36.0 ± 8.6	7.6	1.4	22.0	118.0	150.0	730.0	4.5	61.0	150.0	82.0
	4-8	39.1 ± 7.5	9.3	2.3	34.0	183.0	140.0	820.0	101.0	76.0	310.0	147.0
	4	6.2 ± 1.9	5.9	0.5	7.8	63.0	97.0	140.0	130.0	23.0	160.0	41.0

Sediments Origin	Size μ	Fractions % Weight	Radioactivity μ Ci/g dry weight
Irish Sea	100-200	26.0	2.0×10^{-4}
Pipeline	50-100	27.4	3.0×10^{-4}
outlet	20-50	22.6	9.0×10^{-4}
Sellafield[c]	10-20	14.0	2.5×10^{-3}
	4-10	6.1	4.6×10^{-3}
	< 4	4.0	6.2×10^{-3}

Specific Radioactivity = $1.3 \pm 0.4 \times 10^{-6}$ μ Ci/cm^2

[a] The Dutch Wadden Sea and Mediterranean sediments were suspended in radionuclide-enriched seawater for one month (30 g sediment in 20 litres of seawater); size fractions were separated by sedimentation techniques (Duursma and Eisma, unpublished.

[b] For ^{65}Zn, another Mediterranean sediment was used with 3.3% 64; 7.6%, 32-64 μ; 49.2% 16-32 μ; 24.9% 8-16 μ; 12.7% 4-8 μ; and 2.3%, < 4 μ. [c] The Irish Sea sediments were exposed in the field to radionuclides discharged near Sellafield, (76).

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CHAPTER 5

Characteristics of Discharge Site and Receiving Marine Environment

5.1 HYDROGRAPHIC, METEOROLOGICAL, GEOLOGICAL AND TOPOGRAPHICAL CONDITIONS OF THE COASTAL AREA

The present guide essentially deals with the problems related to the authorization of the discharge of a given effluent in a given area.

The same problem may be viewed from a different point of view. As a matter of fact, when such authorizations can be granted on rational and well-motivated grounds, it is also possible to evaluate, at territorial planning level, the different questions connected with the existence of such a discharge and its effects on the marine environment; therefore it is possible to evaluate whether an urban or industrial settlement may be located in a given spot.

No matter how it is viewed, the problem depends on different local factors.

As alréady mentioned, the first two sections (Sections 5.1 and 5.2) of chapter 5 aim at describing the physical environment (topography, bathymetry, hydrography, etc.) as well as other elements (presence of other discharges, particular use of the sea zones).

The aim of this section is to indicate what information must be obtained as to the physiographic characteristics of the zone and to give a qualitative description of the correlations between the various elements considered and the problem investigated; the quantitative definition is expressed by means of the relevant analytical formulations.

The greatest difficulty encountered in dealing with this topic is that of defining the zone to be taken into account for evaluation of the dispersion and absorption capacity of the marine environment and for the safeguarding of the different uses. No definition with a rigorous mathematical basis or based on formulations of general validity is presently possible.

As will be mentioned here-after, the discharge should include:

a) all coastal areas characterized by a given use that may be related to or derive from the discharge in question;

b) all those discharges (and discharge zones) that are interdependent with the discharge under examination. Such an interdependence or interaction is realized wherever the quality of the seawater affected by a given discharge is also affected by other discharges.

The rigorous solution of such a problem (definition of the zone affected by discharge - which in the following will be simply referred to as "discharge zone") would involve the solution of all questions related to seawater pollution originating from discharges from inland areas; a number of such questions may today be answered in a satisfactory although incomplete way.

In any case, instead of ignoring the question or referring only to "local evaluations" indispensable though they are, it is considered more opportune to outline the main components contributing to its solution and to propose a few examples of formulations that may permit an overall evaluation of the extent of the "discharge zone".

We wish to stress the great importance of a thorough evaluation of this mainly topographic aspect of the problem. As a matter of fact, it has often happened that even very expensive works have given only partial results (and sometimes even no useful results at all); for example, this has been the case when the problem of the existence of other discharges or of other uses has not been taken into consideration even at approximative evaluation level.

To give a practical example, mention can be made of an experience probably not new to many of those who have closely followed the development and realization of sanitation projects for coastal zones used for bathing.

As a matter of fact, it has often happened that, after building those treatment and disposal facilities capable of neutralizing the microbiological pollution produced by the main municipal sewer, the bathing beaches still remained polluted - at least in part - due to the presence in the vicinity of minor discharges and of rivers or streams microbiologically polluted by inland settlements.

A further possibility of error, albeit less evident, is that several major discharges may concern the same coastal area; hence the evaluation of the dilution and absorption capacities separately carried out with regard to only one discharge, may be misleading.

5.1.1 Definition Of The Coastal Area To Be Considered For Evaluation Of The Problem And For Granting Of Authorization

In order to evaluate whether a given discharge is acceptable or not, the first indication required is its geographical location. This presents no problem. It is advisable, however, that the location be established on maps of a scale sufficient to illustrate not only the local aspects but also the general context of the problem.

Hence for siting use will be made of maps of the scale of 1:100,000, 1:25,000 or even 1:10,000. Even larger scales (1:1000-1:100) may be used to evidence particular connections with the sewer system, bypasses, layout of treatment plants, sampling points, etc.

Obviously, at least one of the maps used should include bathymetric data; such maps are already available for the whole Mediterranean sea and have been accurately prepared by the hydrographic offices of the Navies of several countries both Mediterranean and other (British Admiralty Charts).

It is likewise important that such maps give all main indications concerning urban and industrial settlements, both present and foreseen, river mouths and their degree of pollution, the coastal areas destined for particular uses (shellfish-culture, recreational beaches, harbours, areas of reproduction, of fishing, marine parks, etc.).

Furthermore, all other discharges, both present and foreseen, must be indicated.

All discharges must be reported, even if of minor importance; as a matter of fact, it may happen that the microbiological quality of a coastal area be endangered near the point of discharge even by a very small discharge (e.g. from a hotel) if it flows in proximity to the bathing beaches. In fact one of the difficulties which often arises in the sanitation of coastal areas consists in the purification of a number of small discharges not served by the sewer system. Obviously, for graphic reasons, discharges of minor importance may be indicated only on larger-scale maps, whilst those of major importance will be shown in the smaller-scale ones. This has a certain logical justification, since discharges of minor importance - when of similar nature - have a more limited range of action.

As to the hydrographic, meteorologic and other characteristics, useful for characterizing the discharge zone in terms of capacity to absorb potentially polluting discharges, see paragraphs 5.1.3 and 5.1.4.

As already mentioned, a perfect solution to the problems is extremely difficult, if not impossible; hence it is here considered useful to propose a number of approximative and indicative solutions.

Actually, the very definition and determination of the limits of a discharge is open to question from a hydrographic standpoint. As a matter of fact, while microbiological pollution produced, for example, in Nice certainly does not compromise bathing at, let us say, Sanremo, some important hydrographic characteristics, which determine the environmental absorption capacity with regard to certain substances (e.g. phosphorus compounds, turbidity, density) also depend on very extensive circulation phenomena requiring study of the movements of enormous water masses, concerning large areas of the Mediterranean basin, if they are to be fully understood.

The knowledge of such large-scale hydrographic phenomena may be useful both to explain and to correlate the results obtained from purely local surveys; however it usually leads to the evaluation of the main hydrographic characteristics of the waters near the coast, which requires prolonged sampling in situ since the current, salinity and temperature conditions characterizing such areas are changeable due to the complex interaction of various factors, such as tides, winds, gradient and residual currents, etc.

The above charts should be accompanied by cards containing the data graphically represented on the charts (obviously with references to the chart content).

However, as already mentioned, the fundamental problem considered here is that of the definition of that extent of the area to be taken into account for the above-mentioned evaluation.

When considering one discharge, one must then ask how many kilometers of coastline must be examined in order to identify the various discharges and the varying uses. Furthermore, it must be established which inland settlements are to be considered, for their polluting effect, in order to judge whether the proposed sanitation project (and hence the treatment and disposal works for a given discharge) is valid or not.

At this point, since the concept of a "discharge zone" is considered useful, in spite of its limitations, one may proceed to consider some of the difficulties which arise in the definition of such a zone. Then some simplifying criteria will be formulated, capable of obviating them at least in part.

A few examples, which certainly do not represent every existing case, may give an indication of some typical situations; they may also allow a few conclusions to be drawn as to the mode of interaction between discharges and on the complexity of the analytical evaluations required for a correct appraisal of the problem.

Fig. 6a illustrates a discharge pipeline with diffuser under landward current conditions; the concentration, downstream of the initial dilution process is indicated as C_o and the concentration of the same substance in a point in proximity to the shore is indicated as C_1. C_1 is a function of C_o and of the eddy diffusion process, which follows the initial dilution process (as well as of the various assimilation and transformation phenomena affecting the substance considered).

In Fig. 6b it is assumed that two "equal" and symmetrical discharges mutually interact in a given area off the shore; the concentration in coastal waters is C_1 and not, as might be believed, $2C_1$.

The hypothesis of current considered here is exceptional and unfavourable; however, it has been chosen to clarify the example.

The purpose of such an example is to show that, in the interaction zones, the effects of separate discharges are not necessarily the sum total; however this is sometimes the case (see below).

The example illustrated in Fig. 6c is analogous to that shown in 6a; the analytical derivation of concentration C_o is indicated and the position of the sewer of Fig. 6d is represented (dashed line). Fig. 6e contemplates the hypothesis of a certain type of interaction between the two discharges, in consequence of which the sea current affecting diffuser 1d is already polluted by the discharge 1c.

The symbols have the following meanings:

S = ratio of initial dilution for discharge 1c;
S_1 = ratio of initial dilution for discharge 1d;
C_o = concentration in sea water (in respect of a given substance) downstream of the initial mixing zone of discharge 1c;
C_o' = concentration in sea water (in respect of a given substance) downstream of the initial admixing zone of discharge 1d;
C_o'' = concentration in sea water (in respect of a given substance) downstream of discharge 1d, in the hypothesis that the dilution water is not unpolluted seawater but comes from discharge 1c;
C_1 = concentration at a point situated at a given distance downstream of diffuser 1c, in the hypothesis that this is the only one in operation; the position of this point corresponds to the position of the point C_o' to which reference has been made;
C_2 = position of a point downstream of C_1 (Fig. 6c). This corresponds to the position of C_2 (Fig. 6d) and of C_o'' (Fig. 6e);
C = concentration of the substance considered in the discharged effluent (Fig. 6c);
C' = concentration of the substance considered in the discharged effluent (Fig. 6d);
C_s = concentration of the substance considered naturally present in the sea water upstream of the mixing zone.

Fig. 6e also reports the analytical expression defining the value C_o''.

When the two discharges, 1c and 1d, operate simultaneously, under the conditions assumed in Fig. 6e, concentration C_o'' does not equal the sum of concentrations C_1

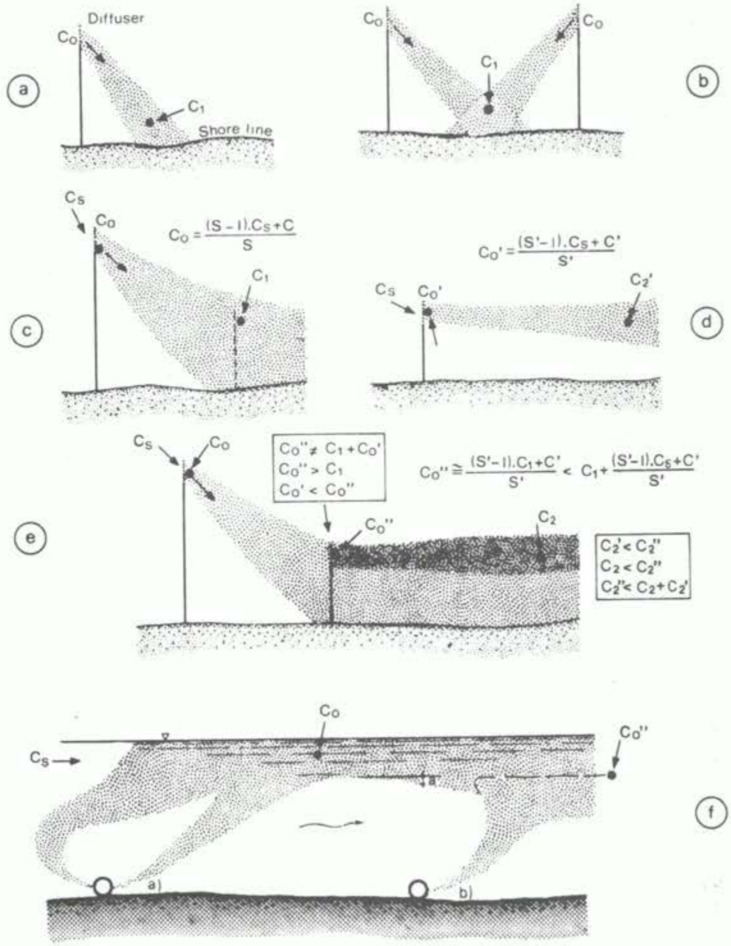


Figure 6 Interaction between discharges; some examples: open coast.

and C''_o, but is lower.

With regard to the downstream point, concentration C''_2 is higher than both C_2' and C_2, but is still lower than the sum of the two above terms.

The above reasoning is rather schematic also because it has been supposed that the mixing field downstream of discharge 1c is homogeneously distributed from the surface towards the bottom.

On the contrary, it is known when there is no sufficiently marked density gradient in relation to the diffuser characteristics, the discharge jets rise and create a surface field the thickness of which essentially depends on the direction and intensity of the sea current traversing the diffuser. After completion of the initial dilution process, the mixing field gradually deepens, thickens and broadens.

Only at relatively great distances (where as the initial dilution process is less developed in relation to the difference in density between the mixing field and the seawater beneath, and hence a greater or lesser slackening of dilution in a vertical direction), may it be assumed that the mixing field concerns the whole liquid column.

For puposes of the example, however, this is of practical importance only when the depth of the zone is limited (10-20 m).

Hence, on the whole (Fig. 6f), the jet from diffuser b) does not mix entirely, during its rise, with water already polluted by a), as it is confined to a higher level.

Fig. 7 schematically illustrates an example of interaction between two discharges, as may occur under the most usual conditions, i.e. along the axis of a river or in a somehow delimited flow.

As the diagram clearly shows, two successive discharges (with a volume insignificant compared with that of the flow volume) result in a concentration twice as great as that caused by one discharge alone; hence in these cases, the final consequence is a sum of the single effects.

Fig. 8 present some hypotheses of disposal in a semi-closed environment (such as a bay) and possible interactions.

Fig. 8a illustrates a discharge of volume Q and concentration C_o, situated in the most internal part of the bay; the average concentration in correspondence to the outlets is C, and obviously depends on the exchange rate between the bay and the open sea.

Assuming that the internal waters of the bay are well mixed, it may be presumed that the average value is approximately equal or at least comparable to the average value of the waters leaving the bay ($C_b = C$).

Fig. 8b shows how, by doubling the polluting load, the average concentration both leaving the bay and contained inside it are also doubled (hence a superimposition of effects by addition occurs) provided that the position of the second discharge is sufficiently far inside the semi-enclosed area under consideration.

The hypothesis in Fig. 8c is that the second discharge is close to the outlet into the sea; in these circumstances, whilst the average concentration in the water leaving the bay is doubled, that of the inner zones is not.

This example, though schematic, is plausible when the flow rate of the two discharges is low in relation to the exchange rate between the bay and the estuary, which is fairly common.

Another condition required for the plausibility of this example is that there is no inflow into the bay or river large enough to cause stratification phenomena and density currents. In this case, if the bay is of considerable size (e.g. a few tens of km) with fairly deep waters, the effects of the Coriolis forces might be of some importance: in our hemisphere they would induce an anti-clockwise current, which would move the discharge in proximity to the bay mouth inwards.

Where discharges are concerned, estuaries and lagoons are more complex than open coastlines; the topic will be dealt with in detail below.

The above examples may give some idea of the complexity of the physical nature of the problem which is further complicated by differences of the distances involved

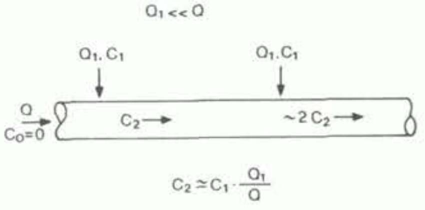


Figure 7 Interaction between discharges in a confined flow.

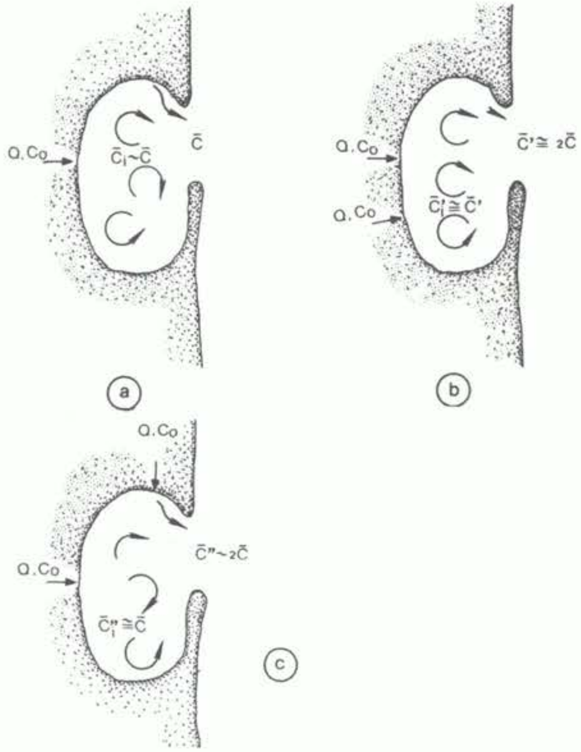


Figure 8 Discharge in a semi-confined area. Interaction of different discharges: some examples.

and their different consequences in the marine environment.

The problem of definition of scale (i.e. of the extent of the area to be taken into preliminary account for purposes of the formulation of a judgement with regard to the authorization for a given discharge) may be simplified by:

1) eliminating from the calculation parameters and types of pollution expected to be controlled through inland treatments (e.g. floatables, depositable solids, macroscopic solids, etc.), or which have no appreciable importance in relation to the uses and discharges considered;

2) distinguishing discharges into:

- municipal or assimilable discharges;
- industrial effluents;
- rivers.

With regard to the range of action of municipal discharges, it is opportune to refer to the parameter which most sensitively reflects propagation, that is colimetry.

It is known that in most cases, i.e. when the problem of municipal discharges has been tackled on the basis of respect of a suffiently low colimetric limit (without neglecting a minimum inland treatment, which may consist of simple treatment for domestic wastes or of an advanced sedimentation treatment for muncipal effluents in general), satisfactory results have been obtained with regard to marine pollution, in relation to the particular type of pollution (primary and secondary organic pollution).

This is also so from the aesthetic point of view and with regard to eutrophication of coastal waters and the protection of marine life.

These are empirical conclusions for, even though colimetry has been the most frequently investigated parameter, it has no precise correlation with the different characteristics of municipal sewage (pathogenous germs, nutrients, etc.) giving rise to typical forms of marine pollution.

In any case, with the aim of maintaining a sufficiently low coliform concentration along the shore, treatment systems on land, as well as dispersion systems favouring natural purification have been realized, their scale proportional to discharge volume (or the size of the population served and also depending on the fundamental hydrographic characteristics of the sea zone concerned).

Formulations and computing methods exist which make it possible to appraise the problem in terms sufficiently accurate to permit the designing of works which provide an adequate margin of safety at acceptable costs (as indicated by the satisfactory results obtained).

These methods will be described in the next section.

The above considerations are valid provided that the so-called sanitary protection of beaches is not achieved mainly by effluent chlorination. Intensive chlorination would appear to allow discharge of primary sewage even in proximity to zones used for bathing or mollusc-culture.

However, apart from the poor reliability of such a solution, intervention of this kind is unsatisfactory from the aesthetic point of view, and the degree of protection it seems to provide is misleading, for it may depend on a low colimetric level, achieved by means of highly chlorinated discharges subsequently subjected to insignificant dispersion processes.

However, even the direct on-shore discharge of an effluent from a biological treatment plant, highly chlorinated to comply with the above standards, is not a rational system of treatment and of disposal into the sea, and the colimetric index can be validly applied only in the context of such a system.

In fact it is known that colimetric reduction in an oxidized effluent gives rise to an increase of toxicity to a level which may be much higher than in the crude sewage. This often happens when such an effluent is discharged on the shore in close proximity to bathing zones where low colimetric standards are applied (e.g. 100 colifaecals x 100 cc, as proposed by the EEC and already applied in some Mediterranean areas).

At the same time, the inconsiderable removal of nutrients by biological treatment and, even more so, the transformation of such substances into compounds which can be rapidly assimilated by algae, constitute, as is known, an inadequate solution to the problems of coastal eutrophication. These problems may be aggravated by discharge in the zone of a treated effluent.

This may occur when a single point characterized by poor water exchange receives several discharges, originally located a certain distance apart, which would allow a more effective dispersion of nutrients and phytostimulants.

After mentioning the conditions and design criteria that enable application of a colimetric limit to give the best results for marine environment protection against municipal effluents in the broad sense, we shall consider some approximate quantitative evaluations serving as an a priori appraisal of the range of action of a given domestic - or assimilable - discharge (or even an urban effluent as far as the microbiological and organic pollution component is concerned).

It is well known that the sea area microbiologically polluted by a given sewage discharge does not depend only on the sewage volume (and a little on the water supply), but also, to a considerable extent, on the velocity and direction of the sea currents affecting the discharge point; hence the point of discharge is of great importance for defining the area concerned.

Generally speaking, wastewaters may be discharged on the shore; in this case the degree of initial dilution is almost nil (S=1). Moreover, under such circumstances, subsequent dilution and overall dispersion occur more slowly due to the fact that the polluted field generally stays in proximity to the shore and is subjected to currents of a peculiar type (longshore currents), which may also be particularly fast.

The poor initial dilution ratio often leads to the occurrence of a stratification phenomenon, which markedly slows down vertical eddy diffusion. Therefore, compared with disposal offshore, inshore discharges may be considered to have a far greater range of action.

The sewage in question being raw, sediments with a high content a pathogenous microorganisms deposit on the sea bottom near the sewer outlet and when such sediments undergo the action of in shore breakers, re-suspension and hence water pollution are more likely.

Some empirical and experimental formulas are available which have proved reliable; in fact they are more experimental than empirical in the strict sense, in that they take into account all the fundamental parameters as the basis of microbiological pollution propagation. The structure of the formulas corresponds to the mechanism of the phenomenon that one wishes to outline.

The formulas in question are those of Pomeroy, (118), developed after studying the Californian coast, and of Aubert-Desirotte, (13), the coefficients of which were derived from tests in the Mediterranean (see Appendix I after Chapter 7).

The above formulas allow an approximate evaluation of the possible extent of propagation of microbiological pollution as a function of the volume discharged, the pipeline depth, and of the sea current velocity.

The Pomeroy formula directly includes the distance from the point of discharge, while in Aubert-Desirotte's the drift time appears as a variable; this is more realistic since bacterial disappearance and dispersion phenomena predominantly depend on time.

Aubert-Desirotte's formula allows the current speed to be taken into account, whereas in Pomeroy's formula it can be taken into account by means of the adjustment of a correction coefficient to be evaluated for each zone.

Naturally, if sufficiently precautionary conditions are assumed e.g. by assuming a current speed of 20 cm/sec (a value rarely exceeded with significant frequency - over 5-20% of the time - in, for example, the Italian coastal waters), Aubert-Desirotte's formula, too, can be applied in terms of space instead of time.

For the above reasons, such empirical formulas cannot be conveniently applied to direct discharges on the shore; nor was this intended, for they were designed above all to serve for the determination of the length of discharge pipeline suitable to protect coastal waters from microbiological pollution.

However, as is well known, even with regard to shore discharges, the extent of microbiological pollution caused by effluents from large urban centres is greater than that produced by small settlements. Hence it is opportune to attempt some approximate evaluations serving to determine at least the extent of the sea area to be subjected to more detailed studies.

In the context of such approximate considerations, it may be said that the respect of a restrictive colimetric standard (e.g. 100 faecal coliforms/100 ml) requires a reduction of the bacterial load of 1:1,000,000. For average water supplies in the Mediterranean (i.e. of order of 200l/inh/day), the concentration of faecal coliforms in raw sewage is about 100,000,000 faecal coliforms/100 ml.

When discharge pipelines are used, such a result is obtained by dilution and by bacterial disappearance phenomena.

Broadly speaking, initial dilution ratios of 1:100 to 1:200 are often obtained in practice and subsequent dilution phenomena may cause the overall nearshore dilution ratio to reach values of the order of 1:1,000. Hence a three-logarithm decrease is often guaranteed in disappearance phenomena.

On the hypothesis that dilution phenomena do not occur, the extent of the disappearance phenomena should be approximately double and, in this connection, the drift time or the distance covered under certain current conditions should be doubled.

Therefore a double range of action may be attributed to sewers discharging on the shore in comparison with off-shore and sea-bottom discharges (i.e. sufficiently off-shore and at a depth at which empirical or experimental formulas guarantee adequate shore protection).

On the hypothesis that the crude sewage is subjected to biological treatment, the average reduction of the bacterial load may be assumed to be of the order of 90%; it may in actual fact be less or even as high as 99%. Therefore, as regards discharging on the shore, a decrease of the order of 10^4 to 10^5, and not of 10^6, is required i.e. of one or two logarithms instead of six.

The current velocity being the same, the proportional decrease of the range of action is of the order of 15-30% (for a discharge on the coast). For an offshore discharge it is greater since the decrease deriving from the initial dilution remains constant).

It seems reasonably precautionary to focus attention on the lowest value indicated (15%). As a matter of fact the phenomena of bacterial disappearance (i.e. all phenomena, apart from actuality phenomena, which involve a decrease in the number of bacteria still present in the liquid column after some time) occurs more slowly, especially during the first hours, when the sewage has undergone treatment e.g. the traditional biological treatment, which removes a high percentage of suspended solids.

During the first hours of drifting, in fact, flocculation and sedimentation play an important role in disappearance phenomena in general, (109).

Four main situations may indicate to which the evaluation of the scale of the phenomenon may be referred:

a) surface discharge along the coast - raw sewage (screened or primary effluent);
b) surface discharge along the coast - secondary effluent;
c) off-shore discharge - screened or primary effluent;
d) off-shore discharge - secondary effluent.

A number of schemes should be indicated and justified here.

In this respect, raw sewage discharge is not entirely comparable to a primary effluent discharge: the former contains pieces of faeces and macroscopic substances, which are carried over long distances without undergoing dilution, sedimentation or self-purification.

In fact, for a number of reasons, at least in the Mediterranean area, the problem is predominantly concerned with the discharge either of raw sewage on the shore or of secondary effluents off-shore or of secondary effluents on the shore or in the terminal stretches of water courses.

In actual fact, in the Mediterranean area, primary treatment prior to discharge of municipal and domestic sewages are rarely foreseen; as a matter of fact, if an adequately dimensioned submarine outfall is realized, a more complete treatment (even primary) than an efficient pre-treatment is not - or does not seem to be - urgent. Furthermore, once it has been decided to carry out a purification treatment, this is generally planned according to traditional concept of high BOD reduction, even though this is irrational in the case of open sea discharges.

For economic reasons, treatment and disposal of a given discharge have seldom been carried out by adequate inland treatment plants and offshore disposal systems, but in a number of cases, the construction of treatment plants, which proved adequate, was followed, a few years later by the construction of submarine outfalls.

It may also be observed that, in actual practice, although chemical precipitation allows a considerable removal of suspended solids as well as a greater phosphorus removal (which is sometimes opportune) than that obtained by the traditional biological treatments (60-80% instead of 20-30%), treatment, when adopted frequently consists of a traditional biological treatment, (98).

5.1.2 Principal Information Of Topographic Character

Following on what has been said as regards the scale of action of the various forms of pollution and of the spatial dimensions to be allotted to the area to be taken into consideration when deciding whether or not to authorize a particular discharge, and bearing in mind the elements of topographic and cartographic character which are listed in the paragraphs relating to the maps showing various uses of coastal waters in a given area and to the waste discharge inventory maps (Section 7.3.1), there is but little to add as regards the indications of topographic character which permit a definition, under a geometric aspect, so to speak, of the essential characteristics of the problem of concession of an authorization.

One can simply repeat that the cartographic representations must be of adequate scale to include the whole area to be considered with regard to the authorization in question: generally from a scale of 1:25,000, in cases of discharges of minor importance (as, for example, the isolated discharges of coastal settlements with less than 10,000 inhabitants) up to a scale of 1:100,000, generally suitable for areas characterized by many uses and large discharges which interact.

One may add that in the large-scale cartographic representations (1:10,000, 1:5,000, 1:1,000), suitable for illustrating the arrangement of sewerage, treatment and disposal works, it would be opportune to show the existing sewer system and the planned additions. The delimitations of the various urban and extra-urban zones according to the various uses, as established by the master plans, should also be indicated, with particular attention being given to those zones where new settlements are to be constructed. It is also extremely useful to give information regarding the number of rooms or m^3 built per hectare as a characteristic of the various localities, and, should the data be obtainable without excessive difficulty, the number of inhabitants served by the various sections of the sewer system, or at least of the various districts. It would be opportune to show the position of the meteorological stations and, more particularly, of the anemometric and pluviographic survey stations. The maps can be accompanied by illustrations of the principal sewer system with particular attention being given to the gradient of the main collectors parallel to the shore; in fact it is with these that problems of inadequate gradient most frequently arise. At least one of the maps must be quoted.

In order to obtain an adequate judgement concerning the suitability of a certain system of treatment and elimination, a comparison should always be made with the possibility of re-use of the treated effluents. To this end it is useful to indicate even on a separate map - the delimiting agricultural zones, also indicating the types of cultivation and their extensions, with notes as to the need and availability of water supplies. For this same reason industries or industrial zones, too - albeit not themselves falling within the study area (since, from the point of view of pollution originating from the relative discharges, the corresponding problems could be kept separate) should also be indicated, with brief comments as to the type of processing employed, size (no. of employees, quantities processed etc.) and, if possible, information concerning the adequacy of the existing water supplies.

Lastly, it could be useful to give a definition of a bay or gulf in terms of some essential geometric elements; for example, one could define "bay" as being any area of sea that was partially confined and had internal dimensions of 30-40% larger than the width of the outlet into the open sea. This definition would have some significance in that it is well-known that the discharge of more or less treated effluents in bays, estuaries and gulfs calls for greater caution from the intervention and planning point of view, in order to keep the polluting loads acceptable at origin within certain limits. It could therefore be required that, in cases of discharges in such zones, the maps show the whole bay or gulf. This criterion should be applied with a certain discretion because the whole of the Mediterranean and perhaps even the ocean could be considered a bay or gulf.

It is therefore suggested that, for purposes of the above-mentioned evaluations, bays be defined not only in geometrical terms but also in terms of a certain ratio between the maximum polluting load foreseeable in the future - upstream of purification treatments - and the dimensions of the body of water in question.

Indications as regards the depth of the marine zones affected by existing or future discharges could be included in the information amongst the data of a topographic nature. Such information is generally obtainable from the maps prepared by the Hydrographical Offices of the navies of various countries. We could at this point make a brief comment of a general character on the importance of such elements, that is to say on the greater or lesser advantage of great depths for the disposal of more or less treated effluents.

On the whole it can be said that neither sea-floors characterized by a very slight gradient (i.e. under 5%) nor steeply sloping sea-floors (i.e. with gradients over 10%) constitute a favourable factor in the elimination of the wastewaters discharged by means of a pipeline. Generally the most favourable sea-floor is the one which slopes down rapidly to below 10m and then reaches a depth of about 40-60m at a sufficient distance from the coast to enable control of the phenomena of microbiological pollution and eutrophization.

The fact that a profile which deepens rapidly to below 10m is desirable is justified by considering the cost of the work of constructing the pipeline in the zone of the breakers and, in any case, the costly works of protection or weighing-down that is necessary to ensure sufficient stability at depths where the effect of the waves on the pipeline or the undermining action induced by erosion of the sea-bed sediment might jeopardise the static behaviour of the pipeline.

Bearing in mind that the reduction of coliform concentration, so as to respect the common colimetric standards for seabathing more particularly, for mollusc-cultivation necessarily depends on the phenomena of bacteria disappearance of an order of at least 3 log and thus on a sufficiently long permanence of wastewaters in the sea before unfavourable currents take them in proximity to the shore. It is understandable that a deep discharge near the shore is likely to constitute an adequate remedy for microbiological pollution; certainly, at depths superior to 20-30m and with a suitably designed diffuser, it is often possible in the Mediterranean to keep the discharge jets submerged for the whole of the summer period. However, it is in any case advisable, to guard against the effect of possible upwelling phenomena on discharges close to the shore, for such entrapment phenomena to take place at a certain distance from the coast.

The same can be said with regard to another important question, that is, the protection of the coastal waters against enrichment and eutrophication phenomena; initial dilution alone is unlikely to provide an adequate control of the phenomena which, on the whole, requires good dispersion (eddy diffusion and conveyance) in waters which are relatively poor in nutrients, that is to say, considerably distant from the shore. The limit of 50-60m derives from the fact that below this depth the cost of diving increases exponentially.

5.1.3 General Considerations Concerning The More Significant Hydrographic Data (Currents; Rate Of Exchange Of Coastal Waters; Vertical Density Distribution; Etc.)

The particular hydrographic data of greatest significance are best illustrated in the context of those aspects (provision of initial and subsequent dilution ratios, control of microbiological pollution) of the problem with regard to which a certain knowledge of the movements of currents is important. In fact it is not a general knowledge of currents that is necessary for the solution of marine pollution so much as particular and sufficiently detailed information with regard to a particular place

A great deal of the data available of an oceanographic nature, often referring to the open sea, is not, in fact, useful for purposes of controlling coastal pollution as the location of the surveys required and the great variability, in space and time, of the data reflect conditions further off-shore; which differ considerably from those found further out to sea. Moreover, as previously mentioned, it is not possible to carry out a definite and satisfactory programme of preliminary research without the collaboration of the technicians responsible for designing the disposal works.

In fact it is usually the designer of the underwater pipeline and, in general, the technician responsible for evaluating the improvement of the quality of the sea water to be brought about by the programmed interventions, who will decide whether the most significant currentometric measurements should be made in the surface layer or in deeper layers, whether the most useful currentometric measurements would be of the Langrangian or of the Eulerian type, the precision required for data regarding salinity and temperature, and the relative frequencies, depths and positions and which characteristics of wave movement (stability of the pipeline) are of interest.

It is therefore to be recommended that currentometric investigations be carried out not only with the help of the oceanographer but also with the collaboration of the designing technician, who will ask certain questions with reference to the data he needs for his calculations.

If the regulations of a country foresee standards only with regard to effluents (and therefore exclude criteria and standards with regard to the receiving waters), it is not considered necessary, from the administrative point of view, to carry out environmental studies; it is in fact useless to know the destination of effluents discharged into the sea if there are no regulations concerning the quality of the receiving waters.

In this respect regulations based solely on the quality of the effluents have some interesting advantages from the point of view of the economy obtainable by avoiding environmental studies; on the other hand, though, it would seem that the cost of environmental investigations which are not an end in themselves but oriented to the ends of the project could be justified by the notable saving obtained in the carrying out of the work and, above all, by the success of this work in terms of the improvement of the quality of the receiving waters, improvements which, in the absence of such surveys, would depend on chance and sometimes may be negligible.

In a classic study carried out by E.A. Pearson in 1956, (108), but still up-to-date as regards the choice of treatment systems, re-use systems and systems for disposal of waste waters in coastal localities, the conclusion is reached that one of the keys to a rational system of final disposal is an adequate knowledge of the currents in the coastal zones more directly affected by the discharge.

In fact many of the factors which are frequently mentioned in this regard are important not so much in themselves as in relation to the marine currents to which they give rise; this is true, for example, of the effects of the winds and of the tides, which concern the discharge and destination of effluents almost exclusively by means of the sea currents they create.

It is considered opportune to put the accent on the risks inherent in generalized evaluations of the characteristics of currents which, in coastal zones, are above all subject to the interaction of combinations of factors that cause a great variability from place to place and also, in a given place, with time. This is particularly true of many areas of the Mediterranean, where the coastal circulation is very difficult to illustrate cartographically and adequate knowledge of it can be obtained only by means of prolonged and repeated measurements.

Generalizations to the effect that marine currents constitute a more or less favourable element compared with other seas, as regards the disposal of wastewaters, are not easily applicable to the Mediterranean.

Firstly it is necessary to avoid the confusion which sometimes exists with regard to phenomena of very limited spatial and temporal dimensions (of the order at most of a few km or days) and oceanographic events concerning the movement of large masses of water in the open sea, which are characterized by spatial and temporal scales of a different order of magnitude.

Also in the context of these general comments concerning the more significant hydrographic data - a more detailed explanation will be given when the various dispersion and dilution phenomena are considered - it should be borne in mind that, with regard to the substances of Group II, the reference to the average time for the renewal of the Mediterranean waters (which has been said to be of the order of 80 years) is of little significance.

Firstly it should not be presumed that the time taken for the renewal of a body of water is an adequate expression of its susceptibility to pollution; it indicates rather, with regard to a given pollution load, the specific inertia of the receiving body in the face of progressive pollution phenomena, and subsequently with regard to the recovery of its original quality, when the polluting action ceases. Thus to affirm that the renewal time of a body of water is very long means, above all, that once a certain level of pollution has been reached, a considerable length of time must elapse - after elimination of the source of pollution - before the waters return to an acceptable state.

It should be remembered, however, that a renewal period, which can be calculated by dividing the volume of a basin by the rate of exchange, is of mainly theoretical significance, since the Mediterranean cannot be considered a thoroughly mixed receiver; thus, while in the zones nearest to the Straits of Gibraltar renewal time may be of the order of a few years or less, in more remote parts of the Mediterranean basin the renewal time will have values considerably higher than those defined, theoretically, as average values.

At the same time generalizations as to the different origins of the currents produced in the Mediterranean, compared with other seas, can be misleading; for example, the wind currents, residual and density currents are often more important in the Mediterranean than those caused by the tides; this is neither a favourable factor as regards the elimination of more or less treated wastewaters, nor is it an unfavourable factor.

One must bear in mind that, in order to attain high ratios of initial dilution (depth, volume of discharge and diffuser characteristics being equal) a good current speed is favourable, particularly as it provides - per unit of diffuser length - a greater volume of diluting water and produces a field of pollution (or of surface mixing) which is less deep than it would have been, for reasons of continuity, in the presence of weak currents; consequently the height of rise ot the jets in pure waters is greater.

Effectively high dilution ratios are also helped by currents which do not have a to and fro oscillating movement but, instead, provide a continuous supply of new diluting water.

If, generally a good current speed favours the production of a high level of initial dilution, fast currents in a land-ward direction lessen the time available for the development of phenomena of bacteria disappearance which substantially condition the reduction of the bacterial load and allow a certain colimetric standard to be respected.

Therefore the presence of currents of variable direction and high speed, such as those caused by large tide movements, may or may not, according to the case, constitute a favourable element as regards the disposal of the effluents.

Origin of currents

It has been said that the best way to ascertain the movements of currents in coastal localities is by means of repeated measurements, above all of Lagrandian type, if possible in all four seasons and at different depths. Within certain limits, however, it is possible to correlate the trend of currents to that of certain factors that generate them, such as winds and tides; when these relationships have been established, even if in an approximative manner, it is possible to utilize the often abundant wind and tide-gauge data to give a greater statistical significance to evaluations concerning the trends of currents, and particularly with regard to certain critical current conditions, that is, slow and prolonged off-shore currents (which slow down initial dilution processes) and fast currents running towards the shore.

In some cases these correlationships are very evident, when the effect of tides is determinant and evident; this occurs when tide movements are considerable and density currents and wind-caused currents are less important. Even when tide movements are not considerable (of the order of a few tens of cm/sec), the correlationship between currents (direction and intensity) and tide can be notable; this occurs in correspondance to narrow mouths providing communication between estuaries or bays and the open sea.

The illustration of the methods serving to establish the relationship between winds and tides, on the one hand, and the marine currents, on the other, does not fall within the province of this report; it will merely be pointed out that it is possible to extract the fluctuating components from current-measurement data in an adequately satisfactory manner by means of harmonic analysis.

In general, the relationships are easier to establish when the current measurements are made in the presence of only one of the factors with which they can correlated; for example, in a zone where the currents are mainly due to the effect of wind and tide, measurements made after a long period (10-20 hours) of wind calm (or very light wind) allow the effect of the tide to be clearly revealed.

It is considered opportune to point out that, even though the relationships in question often constitute a valuable instrument permitting a greater statistical significance to be assigned to direct measurements, in general it is not advisable to formulate major sanitation plans on the basis of current-measurement data obtained prevalently by deduction (for example, from knowledge concerning winds, tides, densities). At the same time, it can be affirmed that, as an already considerable body of practical experience demonstrates, works of minor importance, such as the designing of sea discharge pipes serving population centres of a few thousand inhabitants, can be carried out with a limited knowledge of the currents; these can be estimated for purposes of calculation in accordance with abundantly precautionary criteria, since the saving which a major oceanographic survey would permit would probably not compensate for the cost of the survey and the time it would require.

In this respect, it can be affirmed that in the off-shore Mediterranean, it is extremely improbable that speeds of under 1-2 cm/sec will be maintained for a number of hours; generally current speeds are over 4-5 cm/sec; only in exceptional cases are shoreward currents of speed exceeding 30 cm/sec found in the open sea.

A brief list can be made of the various types of currents with reference to the factors that generate them.

The currents may be caused by:

- differences of density between different sea zones;
- wind;
- tide;
- mass transport;
- debouchment of rivers.

Density currents. Density currents are caused by differences of weight of liquid columns of different density; the density of sea water depends on the temperature, on the salinity and, in the case of very great depths, on the pressure. In the case of shallow depths, the influence of pressure is of little relevance to a study of discharge jet entrapment; and the effect of pressure on the density can safely be ignored.

Where waters tend to get colder or warmer or where evaporation tends to increase salinity and, finally, in marine zones with a considerable fresh-water input, the density of the waters tends to vary; the density variation obviously corresponds to a variation of specific weight and, thus, to a gradient of pressure in a horizontal direction which causes those movements of water masses known as density currents.

Density currents may reveal a fairly constant trend in relation to the regularity of occurrence of the factors giving rise to the variations of density (sweet water in-flows, evaporation, etc.).

Density currents include very large currents, characterized by the movement of enormous volumes of water and a large scale of action; in fact density currents may occur on different scales and in zones such as the Adriatic, estuaries, gulfs, etc.

It is known, for example, that in the Adriatic the sweet-water input along the Italian coast gives rise to a density current which moves in an anti-clockwise direction; this type of rotation (anti-clockwise) is due to the action of what are called Coriolis (or geostrophic) forces, which, in the northern hemisphere, tend to impart an anti-clockwise rotation to masses moving along the meridians (or in a direction close to that of the meridians).

Measurements made in various localities of the Adriatic, at a distance from the shore of between 1 and 6 km, have revealed that the speed in the currents in the coastal strip may be affected in some way by the prevalently anti-clockwise circulation of the Adriatic, but are also affected to a considerable measure by the action of the winds and tides.

The example reveals that, even where major density currents of relatively constant direction and appreciable speed exist, data relating to the open sea are often unsuitable for evaluating current conditions immediately off the coast, where large movements of water masses further off-shore sometimes give rise to currents running in the same direction and, in other cases, especially if the shape of the coastline is irregular, to counter-currents. There are also overlapping effects of other factors.

It is considered opportune to point out that the density currents, which to some extent concern the whole of the Mediterranean area and are, in their general lines, fairly well known, provide very useful indications with regard to the destination of large masses of water and to the general circulation of the Mediterranean; the extrapolation of these data for purposes of representing conditions immediately off-shore, however, generally gives rise to considerable errors.

It is known that in the Mediterranean evaporation exceeds precipitation; the Mediterranean waters are therefore saltier and heavier than ocean waters. Through the Straits of Gibraltar there is thus a considerable deep-water current of saltier, heavier water from the Mediterranean to the Atlantic; in the upper layers there is a current of lighter and less salty Atlantic water entering the Mediterranean.(*)

(*) The rate of flow has been estimated as being of the order of 10^6 m^3/sec; certain ocean density currents have much larger flow: e.g. for the Kuroshio current, 20 x 10^6 m^3/sec.

Apart from the considerable significance of this phenomenon in relation to the chronic impoverishment as regards nutrients of large areas of the Mediterranean basin (due to the fact that the deep outgoing waters are considerably richer in nutrients than the surface water), it is known that this exchange through the straits of Gibraltar is caused by differences of density.

Currents caused by the wind. The winds exert on the marine surface an action of frictional traction, as is normally the case when two fluid zones, whether heterogeneous or not, are moving at different speeds. Naturally, if the speed of the marine current for some reason (for example on account of earlier winds or for other reasons) is equal (in vectorial terms) to that of the wind, the traction is nil; in all other cases the traction effect is produced.

The wind acts directly on the surface of the sea and gives rise to surface currents which, in their turn, draw increasingly deeper layers with them; it is understandable that wind-caused currents are fastest on the surface and decrease in speed with depth, ceasing on the sea floor.

In relation to the inertia of the water masses, a certain time will elapse before a surface current achieves steady conditions; this time is of the order of a few hours; it is more than an hour or two and, in general, less than 12 hours.

Experiments have been carried out to ascertain the relationship, in steady conditions, between the wind and the speed of the current it induces. This ratio oscillates between 1:30 and 1:50; the differences between the experimental data may be due to the different depths at which the various researchers took measurements and to the different speeds of the winds. The ratios generally taken into account are of the order of 1:40 to 1:50 for the surface layer and strong winds and 1:30 for the surface layer and light winds.

As has been said, this ratio is to be considered valid in steady conditions: these conditions are of considerable practical importance because it is convenient, in order to simplify and impart a precautionary character to the verification calculation with regard to a discharge pipe, to assume that a wind of a certain speed continues to blow towards the shore for an indefinite time.

In fact, especially immediately off-shore, the wind frequently changes direction and intensity; in practice steady flow conditions do not occur frequently; onto the effects of the wind are superimposed the effects of the tides, residual currents, etc.

The relationship between the speed of a current at a certain moment (or the speed indicated by a fixed current-meter) and the speed of the wind in that same moment is thus of very limited significance, for the speed of the current will not depend on the speed of the wind at that moment but on the "history" of the winds in the preceding 5-10 hours.

For purposes of establishing a possible relationship between wind and marine currents, one can compare the speed of a marine current at a given moment to a speed "resulting" from the wind, to be calculated on the basis of the wind speed vectors in the preceding 8-10 hours; in doing this, the weight attributed to the various vectors is increased as the time of the measurements approach the moment when the effect on the marine current is evaluated. (Fig. 9) In any case, this system permits comparisons which are more reliable than a comparison between the speeds of current and wind at a given moment.

Wind-caused movements of masses of water are, naturally, also affected by the Coriolis forces; in consequence, the direction of a surface current deviates to the right at an angle (in normal flow conditions) of between 30° and 60° to the direction of the wind and this variation varies progressively with depth, according to a law expressed geometrically by a spiral (Ekman's spiral).

In the northern hemisphere, currents parallel to a coast on the right thus tend to give rise to a secondary spiral movement which results in the surface layers being pushed towards the coast, while, for reasons of continuity, the deeper layers move away from it; with the coast on the left, the opposite is the case. The deeper waters tend to rise in proximity to the shore. From the point of view of coastal pollution these two facts are of considerable interest: in the first case it occurs that winds parallel to the coast give rise to surface current with a marked tendency to run at a right angle to the coast (towards the shore). In these conditions short discharge pipelines discharging insuffiently treated effluents (if the discharge jets on termination of the process of initial dilution, arrive at the surface) may give rise to a state of shore pollution unforeseeable on the basis of aneometric data.

The second case can give rise to phenomena of up-welling, that is, the rising of deep waters, which often bring with them considerable concentrations of nutrients, contributing to the abundance of fish in the waters but at the same time making them more turbid. Up-welling phenomena are often found on the northern coasts of the Mediterranean, from Barcellona to Monte-Carlo, and in the Aegean Sea. It should be noted that the marine zones more abundant in fish, and not only in the Mediterranean, are those characterized by up-welling phenomena.

This rising of deep waters may also result in the shoreward transportation of effluents dispersed off-shore where (taking advantage of the local characteristics - depth, distribution of density, current conditions - and thanks to diffusers of adequate dimensions) the discharge jets have been trapped beneath the surface of the sea.

All these considerations serve to give an idea of the complexity of the mechanism underlying the formation of marine currents, and lead to the conclusion that the best way of acquiring a good knowledge of them is by means of direct measurements.

It is opportune to say something further about wind-caused currents.

a) Comparison between aneomometric data obtained at a land station and the corresponding data measured at sea.

Above all in cases of the planning of treatment and disposal systems for large urban or industrial centres, the localities affected by the intervention are fairly close to meteorological observatories where, among other data, wind directions and speeds are registered in a systematic manner, the data often relating to a long period of time. Sometimes these surveys are continuous, by means of monitoring equipment, in others the measurements are made by an observer at fixed intervals (e.g. every three or six hours). Generally, the data relating to the various months and years are subjected to simple statistical elaboration in order to obtain average values of frequency and intensity with regard to the various wind directions.

These data must be considered, though with due caution in view of what has been said above, a useful basis for the evaluation of the trends of marine currents in determinate situations; with particular regard to the faster currents in a shoreward direction.

The problem is often posed, or, better, should be posed, of whether, and in what measure, the wind trends observed by a land station reproduce to a satisfactory degree the wind trends in the sea zone of a discharge.

Generally, where there are low-lying coasts and observation stations close to the

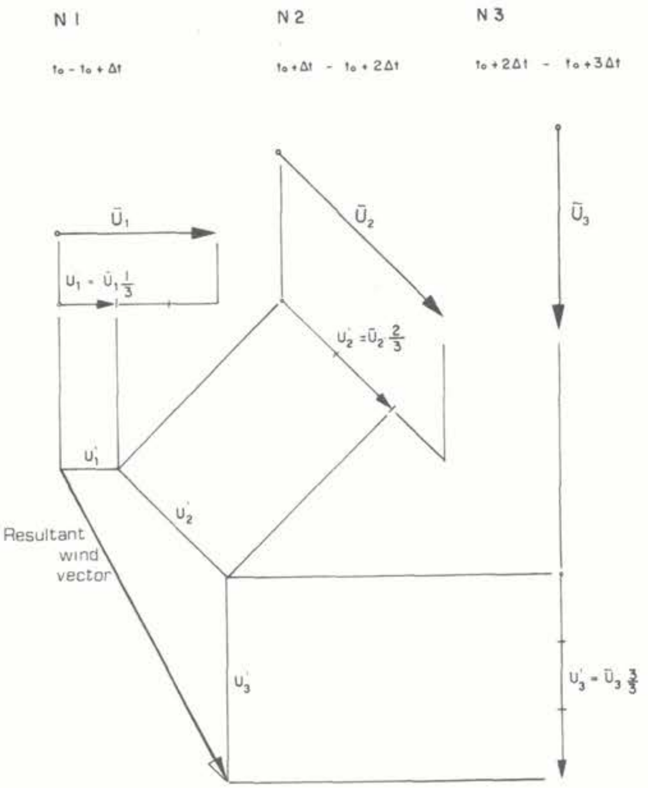


Figure 9 Simple vectorial summation of average wind measurements made at different times in order to estimate marine currents related to wind stress.

shore, this correlation exists to an adequate degree, especially with regard to winds blowing from sea to shore (which represent the most unfavourable conditions and, thus, the most interesting for calculation purposes).

When, however, the observation station is situated close to or in a hilly or mountainous zone, or on towers or buildings at a height considerably above sea level, it may happen that the data registered reflect the situation at sea in an excessively distorted manner.

It is therefore advisable to carry out some simple operations to resolve the problem, by making, at different times and on different days, simultaneous measurements, using identical instruments, in the two places, in order to evaluate the degree of correlation between the speeds observed: it is important that these tests be carried out in different wind conditions and, in particular, with high-speed winds blowing from the sea to the shore. The series of data thus obtained can be subjected to simple statistical elaboration leading to the deduction of suitable coefficients of correlation between the vectors; even a simple comparison, however, can give, fairly quickly, an idea of the suitability or otherwise of using data provided by a land station for the purposes of the study.

An interesting comparison can be made between the wind characteristics on the days that the current measurements are made and the average wind trends in previous years or in the corresponding period in previous years. The average trend may be calculated with reference to single years or to a series of years.

In localities where the activity to be protected is principally bathing; it is of particular interest, since bathing takes place almost exclusively in summer periods, to compare the wind diagrams developed during the study with the wind diagrams relating to the summer periods of previous years. Obviously, this type of comparison is possible only when the anemometric data provided by the land station correspond adequately to the sea-measured data.

As regards the preparation of synthetic diagrams providing a synoptic view of wind distribution in terms of frequency and intensity in the various directions, it is suggested that diagrams analogous to the one shown in Fig. 10 should be used; this form of representation seems to be fairly convenient since it provides indications at the same time both of frequencies and intensity of winds from the various directions; in the example considered, the type of dotting refers to a wind intensity range while the length of the dotted zone is directly proportional to the frequency of the wind in that particular direction.

Diagrams analogous to those shown in Fig. 11 result in a certain distortion of scale in that, as one moves away from the centre of the diagram, frequencies being equal, the dotted areas tend to become larger. It is by means of comparison of diagrams of the type shown in Fig. 10 that it is possible to carry out the comparison mentioned above between the wind characteristics observed in the study period and the characteristics over longer periods in previous years; this comparison has an indicative character and is fairly significant: if in the period of study (that is, when the current measurements are made) the wind blows from sea to shore with less frequency and intensity than in other years or in the summer periods of other years, it may be concluded that the current-measurement data obtained probably represented situations less favourable than the typical conditions of other years or of particular season.

b) A comment must be made with regard to the ratio (from 1:30 to 1:50) between marine current and wind in steady conditions.

The lower ratio (1:30) refers to surface layers and relatively light winds (of the order of a few knots); and the 1:50 ratio relates to winds of considerable speed (over 10-20 knots). This is on the whole a favourable circumstance in that, generally, the problem caused by light winds concerns the existence of currents sufficiently fast to ensure a good initial dilution ratio; vice versa, a critical circumstance in concomitance with strong winds blowing towards the land, is connected to the fast marine currents in a shoreward direction. The fact that the ratio varies from 1:30 to 1:50 according as to whether the winds are light or strong is thus a fortunate circumstance.

c) Wind-caused currents may give rise to the relatively rapid propagation of surface films composed of aggregations of floating particles, oils, foam; this, apart from considerable aesthetic disadvantages, also has a potential hygienic disadvantage in relation to the relatively high concentrations of micro-organisms of faecal origin included in these films.

The movement of such oily patches may be the subject of calculations in relation to particular and accidental circumstances (e.g. spreading of oil), but should not enter into the normal procedures for dimensioning sewage disposal works, in that the primary objective of the planning of systems of treatment and disposal is the elimination at source of such floating substances by means of systems of oil removal, or gravity or flotation separation.

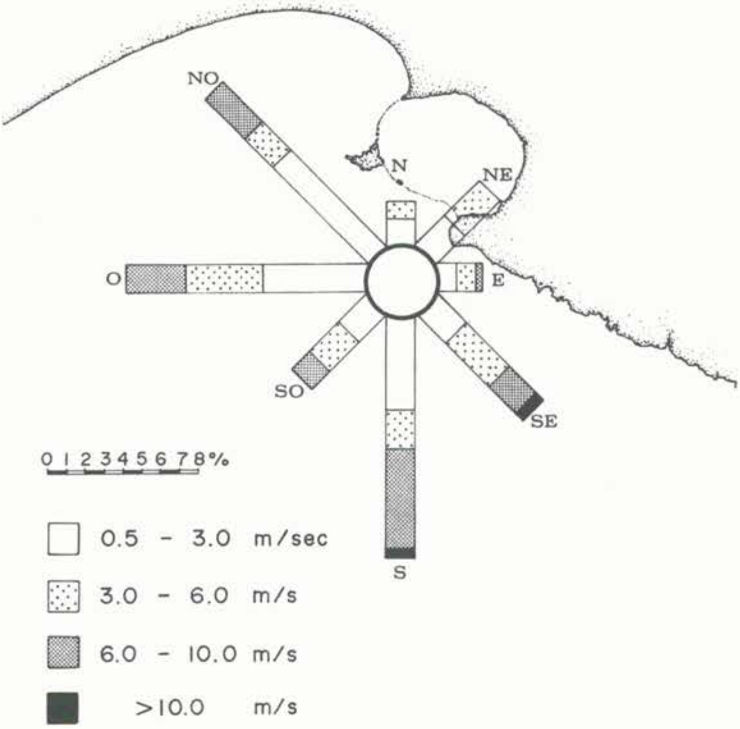


Figure 10 Example of graph showing intensity and direction of the wind.

It would appear that, where entrapment of jet occurs, the discharge of even simply pretreated sewage, provided careful oil-removal has not been omitted, does not give rise to the formation of visible oily patches.

d) In the presence of shallow bottoms, short diffusers, small density gradients, the jets reach the surface and the mixing field that is formed involves the surface layers; in these conditions, until the overall degree of dilution achieved exceeds the ratio of 1:100 to 1:200, the off-shore discharge can be distinguished from the land, especially from raised positions; in fact in these localities smooth surface zones are formed which do not reveal the slight ruffling caused by the wind. This also occurs with biologically treated sewage and is not synonymous with pollution; analogous patches called "surface slicks" are formed on sea and lake surfaces in the absence of discharges.

In the case of wind speeds of less than 6-7 knots, these patches have an elongated form, with the major axis perpendicular to the direction of the wind, and are called "internal wave surface slicks". The patches in question apparently move at a high speed; it should be pointed out, however, that this speed relates to the displacement of certain conditions of the free surface and does not involve the

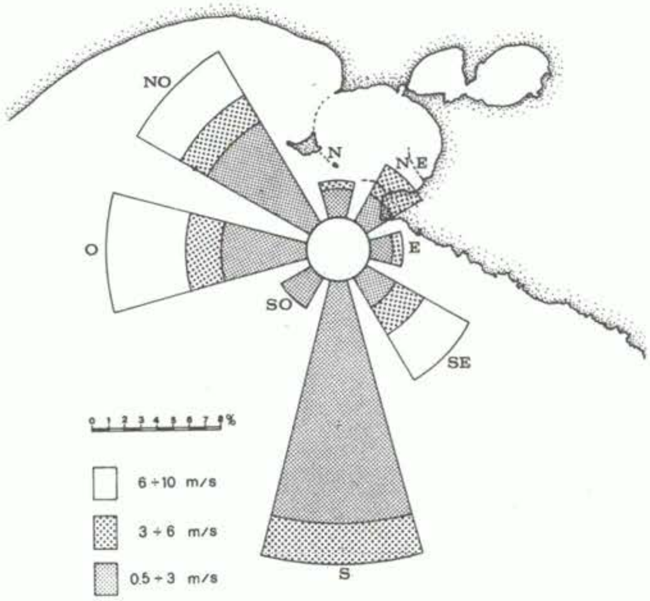


Figure 11 Further example of graph showing intensity and direction of the wind.

the transport of particles. In consequence these phenomena are not related to the more or less rapid propagation of possibly polluted masses of water. Other surface slicks which form when the wind speed exceeds 6-7 knots are of somewhat different constitution; these are called wind slicks and the corresponding calm zones have their major axis aligned with the direction of the wind. In the interior of these zones rather important mixing actions occur both in a vertical and in a horizontal direction. This mixing may involve the dispersion of contaminated water masses and is therefore important for disposal purposes.

e) As regards transport and current phenomena not caused directly by the wind but, rather, by wave movement, itself caused by the wind, more will be said later (cf Mass transport); here it can be pointed out that wave movement in itself, where the sea is said to be formed, involves little remixing of the liquid mass and a negligible transportation of the same.

In the sea zone in which, by the effect of the wind, waves are formed, wind-friction-caused marine currents are present and a certain turbulence develops which contributes to a better dispersion of effluents discharged into the sea; this turbulence becomes important at wind speeds above 7 m/sec.

f) Something should be said about currents in proximity to the sea floor. From the point of view of pollution, these currents effect above all the movement of substances deposited on the sea floor in as much as the particles in question have hydrodynamic characteristics permitting transportation by rolling or by being returned to the suspended state by the action of the deep marine currents and, in particular, by the fluctuations caused by the waves.

Just as it is a good rule to avoid the formation of floating films, so it is advisable, at least where discharges in the Mediterranean are concerned, to provide for the elimination at source of settleable solids that, particularly in rough sea conditions, could be returned to suspension and subsequently pollute the coastal waters.

In general a good way of ascertaining the final destination of certain settleable particles is that of identifying the localities in which such substances, or analogous materials, have settled.

The trends of deep currents, as regards the determination of probable paths followed from a hypothetical discharge point, can be investigated by means of seabed drifters, marked with the place and time of their launching; these drifters are recovered in the course of shore inspections, when the time and place of their finding are noted.

g) Traction action in the presence of waves. The traction effect exerted on liquid masses by the wind has been studied, experimentally and theoretically, in the presence of wave movement; contrary to what might be expected, the presence of waves does not significantly increase the speed of a wind-induced marine current.

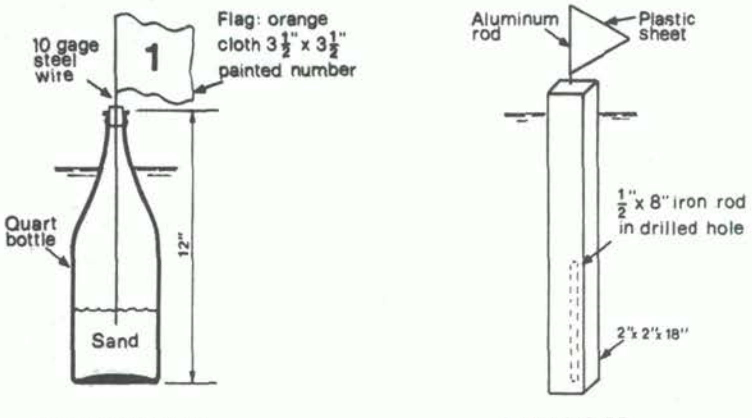
Currents caused by the tide. Tidal movements in the Mediterranean vary from zone to zone; in the northern Adriatic they frequently exceed one m/sec in certain zones of the Tyrrhenian they are no more than a few cm/sec.

In the open sea, tide-induced currents have a rotary movement which is deformed in proximity to the features of the coastline. When the coast re-enters to form an elongated and narrow bay, the tide movements cause a forward and backward movement. When the bay has a large area in comparison with the mouth providing access to the open sea, there exist, in the mouth, so-called hydraulic currents as a result of the alternate filling and emptying of the basin.

There are analytical methods of making an approximate evaluation of the speed of marine currents induced, in the presence of a particular shape of the coastline, by a certain tidal movement; the tidal movements can be ascertained by means of systematic surveys using the tide-gauges installed by the various hydrographic services or, in localities not covered by such instruments, by simple direct measurements. These can be carried out inside a tube immersed in the sea water and communicating with the exterior by means of a small opening, so as to reduce the oscillations caused by the movements of the waves (Fig. 12).

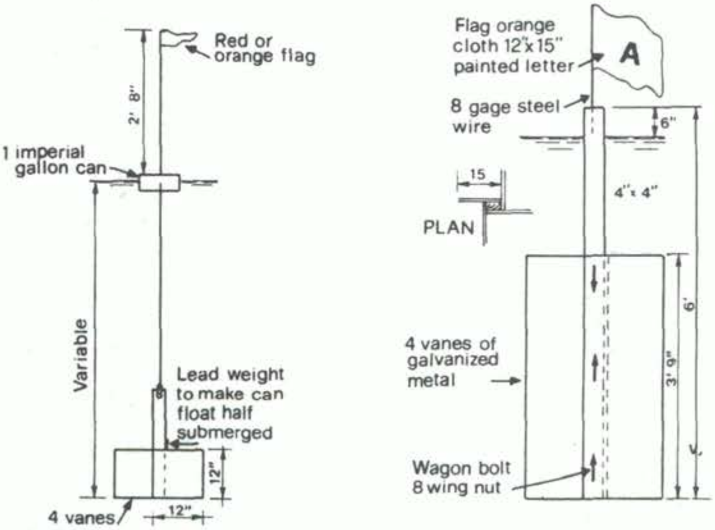
In certain localities tidal trends can be foreseen with a good degree of accuracy by means of suitable mathematical models into which the constants characteristic of the various localities are introduced. The use of such models give rise to no difficulties and in fact they are regularly adopted by the various institutes.

Mass transport. It is known that wave movement does not involve any notable transportation, except in the zone of breakers; the orbits of the liquid particles are in fact almost closed. A certain mass transport does take place owing to the fact that the orbits do not close on themselves; the appropriate calculations show that the mass transport induced by wave movement is of the order of a few mm/sec, and it is therefore not taken into account in order not to make the calculations complicated. These movements are in fact lower by some orders of magnitude to the speed of the marine currents (which range from a few centimeters to a few decimeters per second, with the exception of the tidal hydraulic currents in narrow mouths between large bays or lagoons and the sea, where the speeds may be of a few meters a second). In the proximity to the shore, the wave movement creates a certain hydraulic gradient which induces, in relation to the angle of wave-approach to the shore, the so-called longshore currents; these are determinant with regard to the transport of solid materials, and may be important under the aspect of



EAST BAY SURVEY

NANAIMO, BC



VANCOUVER SURVEY

EAST BAY SURVEY

Figure 12 Examples of free floats, (108).

dispersion of effluents, since their speed may be considerable. Polluting substances discharged directly on the shore may thus make long journeys in a relatively short time and accordingly are less subject to the action of autopurification phenomena.

It should be added that the breaking of the waves in proximity to the shore gives rise, in a homogeneous polluted field which passes beyond the zone of the breakers, to a remixing which is only apparent; in fact the remixing of liquid masses inside a homogeneous field does not provide dilution by eddy diffusion: this is possible only in the presence of charges of concentrations from point to point.

For purposes of discharge by means of an underwater pipeline, the longshore currents are of little or no importance in that one of the purposes of an adequate system of treatment and disposal is the maintenance of conditions acceptable to the marine environment even in the discharge zone, that is, at a certain distance from the shore.

The longshore currents are also of little importance from the point of view of microbiological pollution in that suitably dimensioned underwater pipelines should ensure the hygienic protection of coastal waters that might be affected by this phenomenon.

Currents caused by the flowing of rivers into the sea. The masses of fresh water poured by the rivers into the sea enter it, especially when in concomitance with a falling tide, at a certain speed and therefore are characterized by a certain inertia; the outlets of rivers are characterized, as revealed by observation from the air, by an extension of the water course in a seaward direction, floating on the marine surface, and by a final deviation depending on the other current factors. Flanking the outlets counter-current zones often come into being.

The inflow of rivers conditions the hydrology of downstream sea zones in various ways by reason not only of the inertial phenomena mentioned above, but also of others; among these mention can be made of the floating expansion on top of the sea water, as a result of which the surface waters may be characterized by a degree of salinity clearly lower than that of the lower layers. The already mentioned density currents can be caused by inflows of fresh water and may result in movements of water masses having a volume of a higher order of magnitude than that of the watercourse itself.

The debouchment of rivers also, in general, has a marked influence on the hydrological and biological conditions of the marine waters concerned, in relation to the enrichment phenomena induced by these inflows and to the modalities of dispersion and assimilation of the nutrients in the marine environment; this also depends on the formation or otherwise of considerable density gradients able to impede to a large extent eddy diffusion between the surface and underlying layers.

Under the name of inertial currents one includes also certain currents produced by any factor e.g. wind, which continue, diminishing, for a certain period even after the event giving rise to them has ceased.

It is in relation to the considerable inertia of liquid masses (in relation to the resistance to movement provided by the bottom of the surrounding liquid masses) that current conditions represented by speeds of less than 1-2 cm/sec are unlikely to continue for several hours.

The presence of tides, of regular daily winds, of large density currents and, finally of the inertial effects mentioned above, contribute to the elimination of prolonged water stagnation and, in practice, always make a certain amount of dilution water available, the amount to be evaluated in the least favourable circumstances.

Estuaries, (93). The above considerations relate principally to open coasts; bays and estuaries have characteristics that require a separate treatment, above all in relation to the greater or lesser inflows of water from the interior and to other factors.

These estuaries may be broad, shallow and characterized by a small inflow of fresh water and, at the same time, by considerable tide movements, or may be of the stratified type of elongated form, considerable depth, receiving a considerable inflow of water from the interior, and subject to small tide movements.

This differentiation of the various types of estuary is important in that the destination of the effluents discharges and the most suitable forms of dispersion of the same vary accordingly (always supposing that final discharge into an estuary is the only solution that is practically possible). In general it is better to avoid discharging into estuaries or other confined zones or into zones with limited exchange, in favour of discharging into the open sea.

The models listed below are unlikely to be realized in full in the hydraulic functioning of an estuary; this is partly because important factors such as the inflow of fresh water or the amplitude of tide movements may vary with time.

It is nevertheless considered useful, for a comprehension of the fundamental mechanism governing circulation in estuarine zones, to cite from the literature on the subject the following typical models:

a) Highly stratified type

In this type the forces of gravity, in relation to considerable depths and inflows of fresh water, prevail over the mixing effects induced by the oscillations of the tides.

In the lower part of the estuary, which in this case is elongated and deep, a wedge of salt water is formed which moves upstream or downstream in relation to the delivery of the river. Between the fresh water flowing on the surface and the salty wedge beneath there develops, in correspondence to the interface, a frictional action due to different speeds.

This friction becomes greater or less according to whether the speed of flow of the fresh water is faster or slower, with the result that the salt-water wedge is either pushed back towards the mouth of the estuary or allowed to advance even for a considerable distance in the opposite direction.

The marked difference of density between the salt-water wedge and the fresh waters above it prevents the development of eddy diffusion between the two zones; there are, however, intrusions of salt water from the wedge towards the fresh water surface currents, particularly as a result of the formation of density waves at the interface, which become unstable. These intrusions are of relatively more modest volume, and thus the exchange of deep salt water and the increase in the volume of the surface current are likewise to be considered modest.

In the circumstances described, a discharge by means of a diffuser of waste water which contain, as is usually the case, an appreciable residual quantity of polluting substances may easily give rise to a jet entrapment. This means that the mixture of effluent and deep salt waters mixes little with the surface current of lighter fresh water running rapidly towards the sea.

In such circumstances the residence time of the polluting substances in the deeper layers becomes considerably greater, making it advisable for the situation described above to be avoided. In general, it is opportune that effluent discharged into an estuary should remain there as short a time as possible before being transported into the open sea. The disadvantages described above are increased when the polluting substances discharged contain putrescible settleable substances, which may give rise to phenomena of chronic lack of oxygen in the deep layers.

b) Partially mixed type

In this type of estuary the mixing effects due to the action of the tide become of determinant importance. Even though there is a fairly accentuated vertical rise gradient this is not due to the presence of two clearly distinguishable layers but, rather of an upper layer of brackish water running over a lower layer of more salty water. There is a continuous vertical migration of material upwards from below and downwards from above in consequence of the effect of eddy diffusion. The volume of brackish water on the surface is thus considerably greater than the volume of fresh water, while the saltier layer is subjected to a continuous exchange; in fact it gives salty water to the surface layers and, for reasons of continuity, receives on average the same volume of salty water from the mouth leading to the open sea. In this type of estuary, deep discharges arrive in the surface layers fairly quickly; the deep discharge of light waters may in fact even favour the local vertical mixing processes to a considerable degree.

Whereas in the first type of estuary considered a surface discharge of fresh water does not in any way concern the deep waters of the salt-water wedge, in this case a surface discharge of fresh water, by effect of the intense vertical mixing, affects even the deeper layers; from these layers, the polluting substances, as a result of the process known as eddy diffusion, return to the surface layers even upstream of the discharge point.

c) Vertically homogeneous type

If the action of the tides and the relative mixing movements predominate over the phenomena connected with the inflow of fresh water, the liquid column may be considered fairly homogeneous, as regards salinity and density, in a vertical direction; in this, as in the preceding case, there is a certain gradient of salinity in a horizontal direction, the waters closer to the mouth being saltier.

If the dimensions of the estuary are considerable, the effects of the forces of Coriolis increase to the point of governing the circulation within the estuary.

In this case a salt-water current enters from one side of the mouth and runs through a certain stretch of the coastal zone in an anti-clockwise direction, while a current of less dense water continues this circulatory movement by running close to the shore and out through the mouth. Taking the relative proportions into account, the average circulation of the Adriatic may be considered to be of this type (even though, in proximity to the mouths of large rivers, stratification phenomena, especially in the summer period, are marked).

The method of calculation available to predict the distribution of substances discharged with sewage in the interior of estuaries will be treated briefly in Paragraph 5.3 (dispersion characteristics).

Consideration has been given so far to the main types of current found in the waters of open coastlines and to the factors which give rise to them, with particular regard to their significance in the context of the dispersion of more or less treated effluents. Something has also been said about the main circulation mechanisms in estuarine zones. Before going on to give a brief illustration of the techniques most commonly adopted for the measurement of marine currents, it is opportune to mention an important parameter which determines, in a certain sense, the ability of the marine environment to receive and disperse in an adequate manner a certain load of pollution.

This is the time of exchange that characterizes a particular sea zone, and it is correlated to the average residence time of the contaminants or substances in general that are discharged inside it.

The exchange of a sea zone is determined by its volume, by the currents that traverse it, and by the flow sections concerned.

Thus, a knowledge of the currents makes it possible to evaluate in more or less accurate terms, depending on the particular case, the exchange characteristic of a particular zone or of a particular stretch of coastal waters.

The concept of exchange is particularly useful with regard to problems of pollution which are not solved in the course of the first few hours or, at most, in the course of one day, but have a scale of action more prolonged in time and, thus, also in space.

In many cases the evaluation of the time of exchange of a particular sea zone may be facilitated by the fact that the zone in question receives considerable inflows of fresh water.

It is thus possible, by measurement of natural tracers (salinity, specific alkalinity, silicates...) to evaluate experimentally the amount of exchange characteristic of the zone and the average residence time of the various substances discharged into it.

In the absence of such natural tracers, it is necessary to resort to artificial tracers (fluorescent or radioactive) and to the measurement, generally continuous or repetitive, of the relative concentrations in the zone.

Some difficulties are created by phenomena of absorption and extinction of certain tracers, in particular of fluorescent tracers.

At present it is possible, by means of these techniques, to obtain fairly reliable information with regard to zones of about 100 km in width; in view of the present limits of sensitivity of the instruments used to detect the presence of the tracers, surveys on a larger scale would be prohibitively expensive and might give rise to collateral effects owing to the enormous quantity of tracers that would have to be used.

With reference to the preceding paragraph and, in particular, to the substances of Group II, it can be affirmed that, at least in the vast majority of cases, the spatial dimensions of pollution phenomena associated with the type of discharge considered in this report are lower than the above limit (about 100 km) by at least one order of magnitude.

Using a "natural" tracer present in abundance, the task is simpler, provided that the measurements are made with sufficient care and precision, using instruments of adequate sensitivity, and refer to an adequate extension of space and time (that is, it is necessary to make measurements in many points and at different times).

Taking as an example one of the tracers most useful in practice for the purposes in question, that is, salinity, the average time of residence, with regard to a particular sea zone, can be calculated by dividing the volume of fresh water present by the total volume of inflow from the land.

The volume of fresh water contained in the zone considered can be evaluated by integration, assigning to the various points of the sea-water mass a reductive coefficient "F" calculated as follows:

$$F = \frac{Sm - S}{Sm}$$

where: S = salinity measured on the spot

Sm = the salinity of the off-shore waters (or upstream, in the case of a current), where the effects of the inflow of fresh water which directly concern the zone are not appreciably felt.

For example: supposing the salinity Sm = 38% and the measured salinity S = 19% = 0.5. Thus, a content of 500 litres of fresh water is assigned to each 1 m^3 of volume. In the hypothesis that the salinity of the whole zone was 38%, the quantity of fresh water contained would be nil and the exchange time very brief. Conversely, the lower the salinity of the waters of a zone, the longer, in relation to a determinate inflow of fresh water, will be the average residence time (and the exchange time).

Measurement of marine currents

The measurement of marine currents is carried out in various ways which can be distinguished into two groups, (147).

a) measurement of flow, or the Euler method;

b) measurement of path, or the Lagrange method.

The second method essentially consists of placing a floating body in a particular point of the sea zone considered; this floating body essentially consists of two parts, a submerged part, or drifter, which is subject to the pushing action of the marine current at that given depth, and an above-surface part - body - which supports the drifter and, furthermore, permits identification of the position of the device at different times.

The path followed by the device is followed by a boat for a number of hours; At night a light is used. At more or less regular intervals in time the position of the device is noted; in this way it is possible to trace a path along which the points corresponding to the various moments are identifiable.

As will be explained in Appendix II, the movement of the drifter can also be followed from the land, or from a stationary boat, by means of radar, provided a suitable radar reflector is installed on the drifter.

The first group of measurements is associated with the use of current-gauges, or similar devices, which permit an observer stationary in a particular point - in relation to the sea floor - to observe the speed and direction of the marine current at the various depths.

As far as forecasting the destination of contaminants introduced into the sea by a discharge is concerned, the path, or Lagrangian, method perhaps gives the more useful and more immediately interpretable information. On the other hand, the Euler method provides numerous measurements of current speed at a particular point, at various depths, and at intervals.

It is important to note that the deduction of current paths from a number of measurements of the Euler type (made in several points of the zone considered) has difficult aspects and is possible, in theory, only in cases of non-turbulent motion and in the presence of relatively simple contours.

It is recommended that both systems of measurement be employed or, when this is impossible, or inconvenient, in relation to the financial resources and the importance of the project, that a series of measurements according to the Lagrandian system should not be omitted.

In any case, in view of the degree of variability of the currents, which sometimes can be correlated to the various seasons, the measurements should relate to a period of time sufficiently long to make it possible to distinguish the components of periodic currents from the components of non-periodic currents.

There exists a certain difference of view among the various researchers as to which type of measurement is more suitable for an adequate description of the circulation in a particular sea zone.

It has already been pointed out that this evaluation should be made in the light of the purposes of the survey; in this case, which is concerned above all with the ascertainment of the destination of effluents discharged into the sea, the information obtained by means of the Lagrandian system is particularly clear and easy to use.

This type of measurement, however, if a system of radar surveying is not available, requires a considerable use of manpower; the Eulerian measurements, on the other hand, if recording current-gauges are available, can be made with limited manpower.

In some cases the availability of certain types of instruments or trained personnel may induce a research team to favour one method rather than the other.

Whichever technique is adopted, the persons responsible for a survey should provide guarantees with regard to certain aspects of the coastal circulation and, in particular, with regar d to the frequency with which a time referring to the return of contaminants to the shore is, in reality, reduced (unfavourable conditions correspond to situations in which the return-to-shore times are shorter).

To sum up a number of concepts relating to the hydrological characteristics of the Mediterranean, one can refer to Lacombe's statement, cited by Sournia, (128), "the Mediterranean is a reduced model of the ocean that evinced, in a relatively restricted area, a great variety of hydrological mechanisms, currents, phenomena of upwelling, convergence and divergence".

The calculation of balances is closely linked to the obligatory passage of water through the Straits of Gibraltar.

The Mediterranean is characterized by an often unstable vertical equilibrium of the water masses, in consequence of which, in the winter period, homogeneous conditions down to a depth of 2500 m may be found in some zones.

The Mediterranean is a concentration basin, in which evaporation prevails over the inflow of fresh water and creates an annual deficit balance of about 1 m; this deficit is made good by the inflow of Atlantic waters through the Straits of Gibraltar (and, in a smaller measure, by waters from the Black Sea passing through the Dardanelles).

The Mediterranean is a sea poor in nutrient salts: this is because the inflowing Atlantic waters are not rich in nutrient salts, while the removal of these substances by the deep currents flowing out through the Straits of Gibraltar results in a continuous and considerable loss. This is because the deeper waters tend to acquire nutrient salts as a result of the processes of death and sedimentation of living substances created in the upper layers. This lack of nutrient salts increase with the distance from Gibraltar, except in particular zones (e.g. coastal zones characterized by urban agglomerations of considerable size and the mouths of rivers), even of considerable dimensions, where the concentrations of these nutrients and activity may reach levels considerably above the average values of the Mediterranean.

Figures 13 to 16, give indications, taken from existing technical literature, concerning the trend of off-shore currents and salinity, temperature and density distributions in the Mediterranean basin. As has already been pointed out a number of times, the usefulness of such information for the characterization of the hydrographic conditions immediately off-shore is very limited and extensive local surveys are necessary.

Density of marine waters

The density of the marine waters and, more precisely, the vertical distribution of density in the zone foreseen for a discharge, is, together with the current characteristics, the most important element determining the physical destination of effluents discharged into the sea.

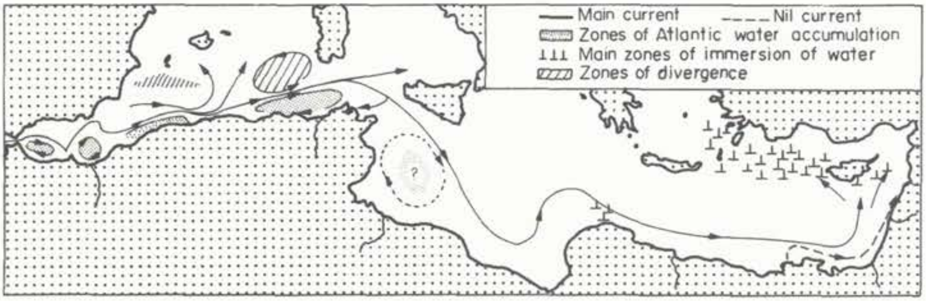


Figure 13 The Atlantic current during winter along the African coast of the Mediterranean (The outline of the main current in the eastern basin and the secondary features along the Tripoli coast are hypothetically deduced from hydrology, (128).

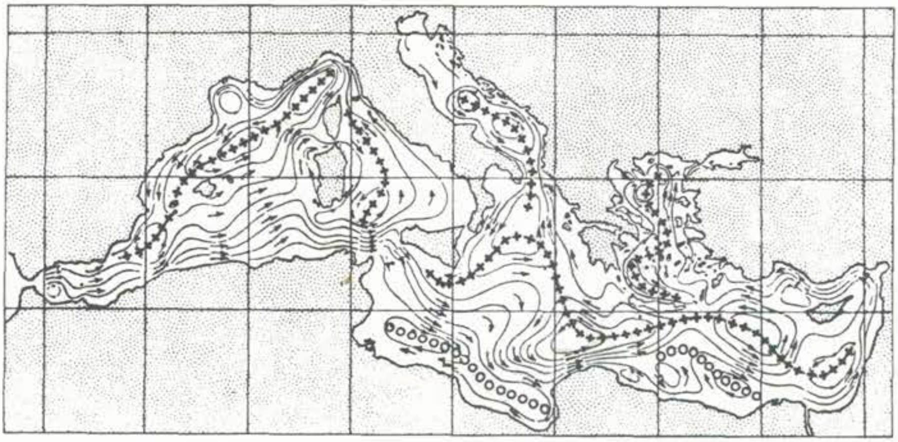


Figure 14 Geostrophic components of surface currents during winter (xxx divergences, ooo convergences), (128).

In the case of a surface discharge, the vertical distribution of density of the marine waters is of little or no importance. However, when the discharge is at a distance from the shore and, thus, at a certain depth, by means of a suitable diffuser, (advisable in the case of a sea discharge), the vertical distribution of density conditions affects both the initial dilution ratios that can be achieved and the level to which the jets will rise. This level is associated, obviously, with the occurrence, or otherwise, of the phenomenon of entrapment (when a field of pollution is not on the surface).

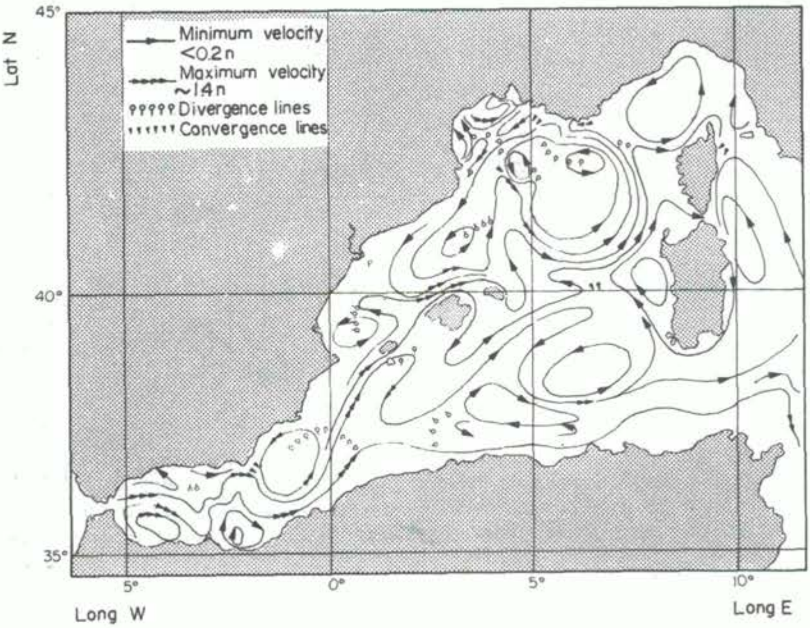


Figure 15 Diagrammatic map of surface currents during summer in the western part of the western basin, (128).

In oceanography, density measurements constitute a determinant element of the knowledge of the hydrographic characteristics and movements of large masses of marine water. For these purposes the density measurements, that is, measurements of temperature and salinity, must be made with great precision, generally to two figures of decimals. As regards the forecasting of dilution and dispersion mechanisms, less precise measurements and simpler instruments are acceptable, provided that the surveys are repeated with a frequency sufficient to take into account the variable conditions typical of coastal waters.

The density of sea water is expressed in kg/m^3 and depends on the temperature, the salinity and, to a certain degree, also on the pressure.

For purposes of calculation of dilution and dispersion, the variations of density caused by pressure may be ignored because in the surface waters they are very slight, and because they affect the sewage/sea water mixture and sea water to virtually the same extent. (*).

Table 24 gives coefficients "h" of correction of sea water density at the various depths which take into account the compressibility of the water. As can be seen, at a depth of 100 m this effect accounts for 0.5% and is thus, for the purposes considered here, completely negligible.

(*) In oceanography, however, the question of pressure is of considerable importance; it should be borne in mind that, were sea water incompressible and the whole mass of sea water to assume the volume of sea water at atmospheric pressure, the level of the seas would rise by 30 m and 5 million km^2 of land would be submerged.

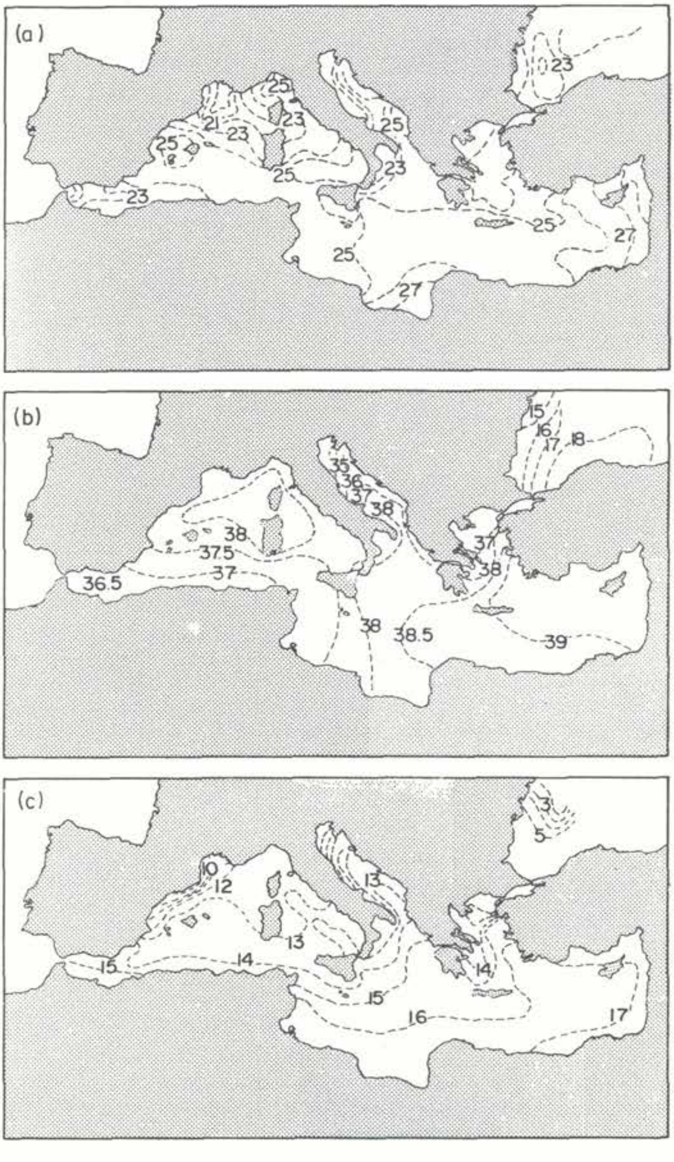


Figure 16 a) Summer isotherms in the Mediterranean sea
b) Winter isotherms in the Mediterranean sea
c) Salinity in the Mediterranean sea (average values), (128).

Formulas and diagrams for the calculation of density as a function of the salinity and temperature are given in Appendix III.

It is noticeable that the influence of salinity is considerably greater than that of temperature corresponding to 1 unit of salinity; in other words, to pass from a density of 1027 to 1028 kg/m^3, at a temperature of 20°, the salinity must increase from a little under 38% to a little over 39%; with 38% salinity, a density change from 1028 to 1027 will require a temperature increase from 16.3° to 20.2°.

It has already been said that density measurements are useful above all in discharge zones; in particular, they can be made at various levels in correspondence to the point of release of drifters and current drogues, or in proximity to the stations where a current-gauge is installed.

Table 24 - Coefficient of correction of the density of sea water at various depths

DEPTH (m)	COEFFICIENT
0	1
10	1.00004
100	1.00047
1000	1.00666

For discontinuous measurements, from 5 to 10 measurements in a vertical line seem, in general, to be sufficient; there are devices for the continuous measurement of depth, temperature, conductivity (salinity is deduced from the conductivity and the temperature and the density is deduced from the salinity and the temperature) or for the direct measurement of depth, temperature, salinity (computed automatically by the instruments).

If the measurements are carried out by means of sampling with bottles, it is appropriate to take from these same bottle samples for other analyses e.g. dissolved oxygen.

The results of the various measurements of temperature, salinity and density are usually shown in a graphic form (Figure 17) which reveals the existence of large gradients (pyknoclines).

A rapid variation of water density between zones at different levels is an element which facilitates the phenomenon of entrapment of the jets; this phenomenon may occur even in the absence of pyknoclines if there is a sufficient density difference (between the water at the bottom and the water on the surface - at least 0.5 kg/m^3).

If the salinity is constant, the pyknocline coincides with the thermocline.

A comparison is sometimes made between phenomena of entrapment of jets of deep sea discharges and phenomena of thermal inversion in the context of air pollution, where gaseous discharges do not rise above a certain level and form a hood. This comparison, although it is instructive, is scientifically somewhat inappropriate since the phenomena of air pollution and the rise of gaseous effluents are considerably conditioned by the variation of pressure and diminution of temperature due to adiabatic transformation. In marine waters such variations of pressure and temperature are negligible and the phenomenon of entrapment occurs only because a sufficiently intense mixture of light and fresh water with deep and dense sea waters leads to the formation of a mixture denser than the surface water layers.

Even in this respect it is impossible to generalize as far as the Mediterranean is concerned, not only because vertical density gradients are variable from zone to zone, but also because in the same zone they vary with the seasons; in a certain season they may even vary from day to day (e.g. as a result of strong wind that completely remixes the water column in the surface layers - a few tens of meters - that are concerned with the dispersion of effluents).

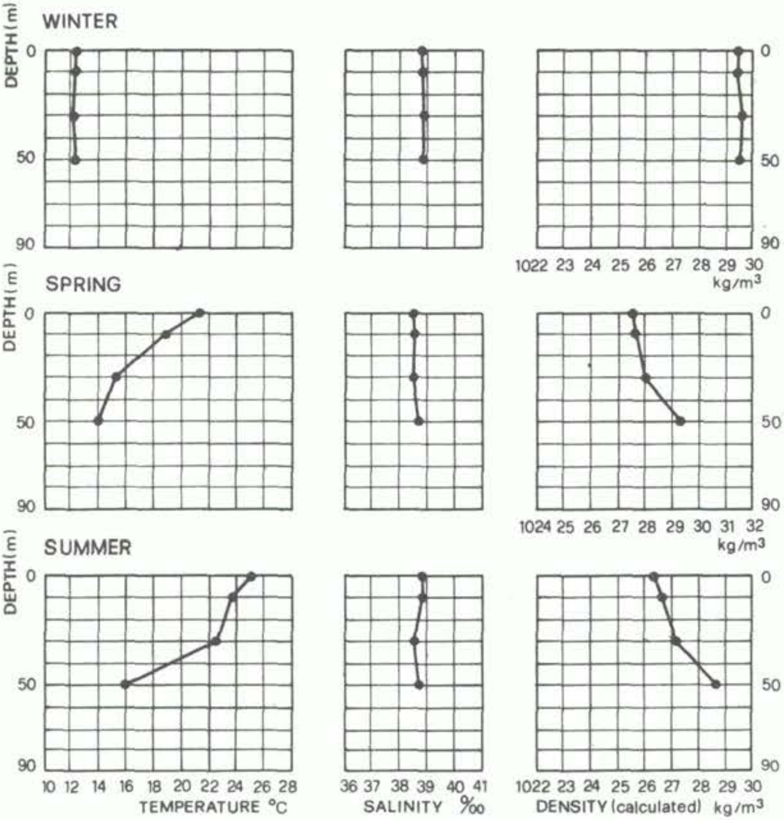


Figure 17 Temperature and salinity profiles; calculation of density

Along the Italian coast, for example, it has been proved in practice that, during the summer period, adequately dimensioned diffusers can bring about the entrapment of jets at discharge depths exceeding 20-30 m; this is of a certain interest in view of the extreme variability of situations by which the Italian coast is characterized. This does not mean that phenomenon cannot occur at smaller depths, nor that it necessarily occurs at greater depths.

For one thing, in particular circumstances it happens that, even in shallow waters (10-20 m), a clear separation is formed between the surface layers directly influenced by the inflow of large rivers (and in these layers the turbidity and primary productivity are notable greater) and the deeper layers (in which photosynthetic activity is reduced on account of the turbidity characteristics of the upper layers). In the deeper layers there may occur phenomena of sedimentation and decomposition of the organic substance created in the upper layers, which leads to a reduction of dissolved oxygen to below saturation point.

In such situations the entrapment of the discharge jets may be considered undesirable; moreover, the limited vertical diffusion between the surface and deeper layers makes the nutrient salts (which influence the trend of dissolved oxygen) less rapidly available, and they thus remain confined to layers in which the scarcity of light energy slows down their utilization. An observation of a fairly general character with regard to the Mediterranean can be made concerning the minimum ratios of initial dilution required in order to avoid the formation of masses of insufficiently diluted surface waters, which tend to expand by floating and which, because of the action of unfavourable winds, may lead to the pollution of the coastal waters.

The density of the waters of the Mediterranean may reach 1029 kg/m^3. In the North Sea waters, where the density is considerably less (about 1025), the initial dilution ratio required to guard against these effects is evaluated at 1:50.

The phenomenon is linked to the density of the sea water in the sense that a mechanism would not exist in the case of discharge into a mass of water of the same density as the discharge (and its importance increases with the difference between the density of the effluent and that of the receiving waters). The appropriate calculations indicate that in the Mediterranean this ratio should be at least 1:60 (Figure 18 and relative calculations). This does not constitute a problem since, for other reasons, it is both technically and economically possible, in most cases, to achieve an initial dilution ratio of more than 1:100.

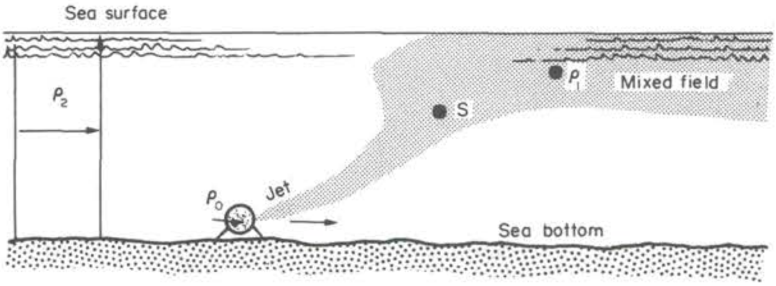
As to the frequency of density measurements, it is considered that, generally speaking, a few measurements a week are sufficient. From time to time, it could be opportune to make further measurements, close together in time, so as to obtain information concerning the degree of variability of the data with time; this will be useful for the definition of a program suitable for the acquisition of an adequate knowledge of the situation without unnecessary expenditure.

5.1.4 Data Of Meteorological, Geological And Other Types Concerning The Characterization Of An Area Of Discharge, For An Evaluation Of The Capacity Of The Marine Environment To Absorb Potential Pollutants

Although it can be affirmed that the problem of the treatment and dispersion at sea of sewage is pertinent, even as regards the granting of authorization for a discharge, to a variety of other problems and themes, it seems to be right and opportune to acknowledge that, whereas certain factors are under this aspect, of determinant importance (and they are specifically listed in Appendix III), others are of indirect importance or acquire importance in the context of the executive planning of the sanitation works, and others again are fairly superfluous under every aspect.

It has happened in the past that, in localities in which the problems were faced in a more active and timely manner, environmental surveys, even of a routine nature, were carried out which provided a body of data only part of which was essential to understand the problem and the preparation of the solution, while the remaining part, despite the high cost of obtaining it, was useless for practical purposes.

It is therefore opportune that surveys, rather than being carried out in approximate and fragmentary manner in order to cover every possible element, should be carried out in a precise and adequately frequent manner with regard not to every possible element but to the most important parameters.



$$\rho_1 = \frac{\rho_0 + (S-1)\,\rho_2}{S}; \qquad S = \frac{\rho_2 - \rho_0}{\rho_2 - \rho_1}$$

$$\text{for } \rho_2 - \rho_0 \sim 29\ \text{kg/m}^3,\ (\rho_2 - \rho_1)_{CR} < 0.5\ \text{kg/m}^3,\ S > 58 \sim 60$$

Figure 18 Horizontal discharge of waste water in vertically homogenous sea water

$\rho 2$ = sea water density
ρo = waste water density
$\rho 1$ = density of the mixed field
S = initial dilution ratio

As regards the hygienic protection of the coastal waters, this was the main guideline provided by the study carried out under the auspices of UNEP and WHO with regard to the sanitation plan for the Mediterranean.

This section is prevalently concerned with some aspects, which could be considered physical, of the problem, that is, with the hydrographical and topographical characteristics of a zone, with particular regard to the regulation of uses and discharges. For this purpose, the study of the currents and a knowledge of the vertical distribution of density are by far the most important elements and ample space has therefore been dedicated to them, it having been considered opportune to treat briefly questions of a geological and meteorological nature that may have some bearing on the theme considered.

Meteorological data

The importance of the winds has been considered in relation to the influence they exert on masses of marine water in producing currents; apart from this influence, a knowledge of the wind does not appear to have any significant bearing on the dispersion at sea of effluents.

Knowledge of the winds may, however, have a certain importance under another aspect. It would be opportune to install treatment plants down-wind of and at a certain distance from centres of habitation because certain treatment phases, particularly in concomitance with organizational difficulties, planning inadequacies or transitory phases of operation, may generate unpleasant smells affecting the residential zones and also the recreational zones it is wished to protect. Sources of unpleasant smells may, for example, be the sludge dispersion lines, where the fresh-sludge system is used; the sludge drying beds, when there is trouble with the digestors or primary sedimentation tanks which are too large or which are provisionally treating only a fraction of the design flow. Likewise trickling filters of inappropriate dimensions or faulty design may give rise to unpleasant smells and insects; the latter may be transported by the wind in the direction of the inhabitated zones, though they tend to remain in the proximity of the plant.

Aerosol formation, too, which can be correlated to certain forms of aeration (surface aeration), has been the subject of studies and discussions in relation to the possibility that winds of a certain intensity will carry liquid particles loaded with pathogenic bacteria and viruses into inhabited areas.

Among the questions of a topographical nature, apart from those concerning the location of a sea outlet (in relation to the position of other outlets and particular uses), there is the no less important problem of determining the land zone in which the treatment plant is to be installed; it is necessary to take into consideration the characteristics and uses of the limitrophe zones and also the possible sanitary, touristic and aesthetic disadvantages that the location of the plant in a particular zone may entail.

In view of the often disorderly process of urbanization, which, unfortunately, has already compromised, in a manner difficult to redeem, large stretches of the Mediterranean coast, this problem is of considerable importance, for the areas destined for treatment plants and their future extensions tend, also for reasons of an economic nature, to be in the few green zones that remain behind the residential areas.

From the point of view of the adequately broad scope appropriate to Integrated Planning (the usefulness or, better the necessity of which appears to be further confirmed by these observations), it would seem to be essential to plan sewage treatment and disposal systems taking into consideration not only the characteristics and uses of the marine waters that may be concerned, but also the characteristics and uses of the hinterland. In some cases the convenience of using treated sewage for the irrigation of suitable cultivations or for certain industrial purposes may be further confirmed by the shortage of zones available, in proximity to the coast, for the installation of treatment plants. It is not superfluous to point out that, in the delimitation of the areas destined for these purposes, it is necessary to foresee not only possible future extensions of the plants in consequence of increases of the load to be handled (or of the formulation of stricter standards with regard to the effluent), but also the advisability - which can be expected to become increasingly urgent in many arid zones - of re-using such waters before discharging them, and therefore, of providing, for this purpose, suitable treatments which serve to improve the quality of the effluent.

Meteorological - marine data more relevant to field investigations

It is a good rule, on the various days of sampling or surveying, to register the following meteorological-marine conditions, if possible several times in the course of a day:

- wind direction and intensity;
- temperature of the water (and possibly also of the air, since it is easy to measure, though for practical purposes it is not very significant);
- cloud coverage;
- state of the sea;
- precipitation in preceding hours.

It would be opportune to register these data at the beginning or at the end of the various measurements.

Information concerning wind direction and speed and precipitation are useful also with regard to the night, since marine currents in the early hours of the morning are influenced by winds blowing during the night.

Many of these data will not in fact be useful for purposes of authorization of a discharge or of interpretation of the environmental data collected in the course of surveys. However, in certain situations, it may not be possible, if data concerning the concomitant meteorological-marine conditions are not available, to explain the results of experiments (which do not always enable the mechanism by which they are determined to be ascertained).

With regard to precipitations it is known that they give rise to a considerable increase of rate of flow, by comparison with the typical values of dry weather (an increase of the order ot 100 times and more); it is also known that the conditions of marine pollution and the environmental situation in general depend, particularly in the immediate off-shore area, on the precipitation.

A knowledge of the precipitation is particularly important for planning with regard to sewage networks, emergency discharges, pre-treatments, flood runoffs and, finally the sea zones that may be affected by these discharges.

As regards the geological aspect, it can be said that this relates more to the supporting of the works than to the evaluation of the capacity or otherwise of the marine environment to receive a particular discharge. It often happens, in coastal zones, that the land on which treatment plants are to be installed has very unfavourable characteristics as regards the execution of the foundation works, which may also be very expensive (use of piles, etc.) and thus condition technical choices.

A certain knowledge of the geological and, in particular, the sedimentological characteristics of a zone is necessary for the laying of an underwater pipeline, in that it makes it possible to forecast with a certain reliability possible action of erosion of the sea floor, which may compromise the stability of the pipeline, or movements of sand banks, which may bury the diffuser.

Furthermore, a knowledge of the zones in which particles of a certain size or particular hydrodynamic characteristics naturally tend to settle and accumulate provides useful indications concerning the destination of any sludge formations to which the discharges may give rise.

5.2 INITIAL DILUTION ACHIEVED AT THE POINT OF WASTE RELEASE

5.2.1 General Remarks About The Benefits Related To Good Mixing Of Waste Waters With Ambient Waters At The Point Of Discharge

Section 5.2 and 5.3 are concerned with the main physical processes affecting the destination of the various discharges and, thus, any pollution to which they may give rise in the receiving waters (the degree of initial dilution of surface discharges is not considered because these discharges, by reason of their lower density, float on the sea water right from the start, with no, or negligible, dilution).

Rather than seeking to carry further the theoretical discussion of the mechanisms governing these phenomena, it is the purpose of these paragraphs to set forth the theoretical and experimental conclusions of greatest practical usefulness also with regard to the criteria to be considered in granting authorization for a discharge. In particular, the purpose is to make clear the significance of these phenomena with regard to eventual standard criteria and the way in which these phenomena can be taken into account in that context. This section is concerned in particular with the process of dilution of discharge waters released beneath the surface of the sea during their upward movement.

It is opportune, first of all, to distinguish between the various processes which contribute to the dilution and dispersion of discharge waters.

Discharges on the sea bottom or at certain depth can take place in the form of a single jet or, more conveniently, in the form of several jets distributed along a special stretch of piping (diffuser).

In any case, the jet, or jets, once they have emerged from the outlet, begin an upward movement following a trajectory which is more or less straight depending on the diameter of the jet and its initial speeds.

The jet, lighter than sea water, moves upward just as a stone (heavier than sea water) thrown from the land, follows a downward trajectory which is longer and straighter if the initial speed of the stone is greater.

During the upward movement, a certain mixing of the discharge jet and the surrounding sea water occur, according to a mechanism which will be described in greater detail subsequently; the upward movement may stop in proximity to the surface, when the "sewage field" (or "mixing field") is on the surface, or at an even considerable depth, in cases of the phenomenon of entrapment of the jet.

In any case, the first-phase, or initial, dilution may be considered to start when the jet emerges from the diffuser and to end when the jet reaches the sewage field that has been formed above it; in the interior of this mass - the sewage field - the jet mixes not with clean sea water but with a mixture of sea water and sewage which has approximately the same composition as the jet itself at the end of its upward movement (Figure 19).

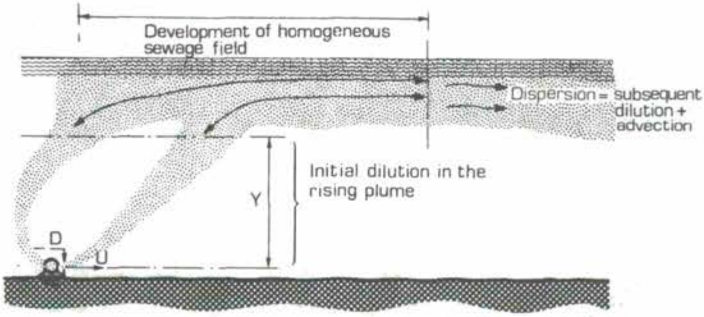


Figure 19 A distinction between various stages of dilution and dispersion phenomena

D = diameter of jet at point of discharge

U = nominal mean velocity of discharge

On completion of the process of initial dilution, the phenomenon of dispersion proper begins; this concerns the sewage field, that is, the mass of water which consists of a mixture of sewage and sea water.

The process of dispersion may be sub-divided according to the two mechanisms concerned (*):

- the transport, or movement away from the discharge point;
- the process of eddy diffusion, which involves the progressive dilution of the sewage field as it moves away.

The distinction between transport and eddy diffusion is in a certain sense conventional; the circulation of the liquid masses may in fact be seen as a superimposition of turbulent motions of very different scale.

Generally, the phenomena of transport are attributed to movements on a large scale, which cause an evident movement of the sewage field away from the discharge point, albeit following a sinuous course.

Eddy diffusion is attributed to vorticose movements of extension by or comparable to the transversal dimension of the sewage field, which in time give rise to a progressive dilution from the centre of the field to the outskirts.

Strictly speaking, it is permissible to compare eddy diffusion to dispersion only when the distribution of the average speeds in the receiving water is uniform, that is, when there is no variation of the average speed in the various points of the receiving water.

The importance and limits of dilution and dispersion have long been debated; on the one hand,it is possible to point to the considerable environmental improvements achieved, with regard to certain forms of pollution, by taking appropriate advantage of these phenomena; in other cases it has been affirmed, no less reasonably, that, where highly toxic substances, characterized by considerable persistence and bioaccumulability, are concerned, the benefit is merely apparent.

It is, thus, very important to make clear right from the start the usefulness and the limits of the physical processes in question, with particular regard to the various forms of pollution of the marine waters and to the types of substances with which such forms of pollution are associated.

Such a clarification will make it easier to introduce the technical terms relating to the phenomena in question into the criteria that may condition the granting of authorization to discharge the substances of Group II.

It can be said that a rational system of disposal of sewage in the sea concerns, from the point of view of the physical processes, two orders of mechanisms:

a. a mechanism by which the substances discharged reach in the sea a point different from their original point and are then transported by the currents into zones different from those previously concerned;

b. a mechanism by which the concentration of substances in the receiving environment is reduced as a result of the more intense processes of dilution affecting discharge waters.

(*) Strictly speaking, between these two phases - initial dilution and subsequent dilution - there is an intermediate phase denominated by various authors as zone of homogenization or zone of stabilization. This is a zone in which the mixture of sea water and sewage (considerably non-homogeneous especially in conditions of small depths and low Froude numbers) tends to assume a fairly uniform composition in a spatial sense, as a result of the residual turbulence of the upward movement and the turbulence caused by the deviation of the jet in correspondence to the zone of stabilization.

As to the first aspect, it can be said that the change of point of discharge and of zones affected by the same give rise to the following benefits:

1. Certain substances are discharged not where their concentrations are excessive but in zones where, in relation to their much smaller concentrations, their effect is not harmful but beneficial.

   This is the case of some substances of Group II and, in particular, of nutrients, which, discharged immediately off-shore or in confined waters, may give rise to grave eutrophication phenomena, whereas, if they are discharged further out to sea, in the generally oligotrophic Mediterranean waters, they bring about a useful increase of productivity. In an analogous manner, the effluent of a treatment plant containing ammonia, nitrates and phosphates may be harmful if it is discharged into a lake, whereas the same effluent dispersed in irrigation waters would have a beneficial effect.

2. Some substances which are harmful if present in one zone are discharged in zones in which they are neither harmful nor beneficial; this is the case of pathogenic germs, included in Group II, which are harmful in certain zones e.g. mussels cultivation beds and undesirable in others e.g. bathing zones where the existence of certain standards makes a particular level of microbiological pollution inadmissible.

   This type of benefit is confined to substances characterized by a rapid extinction in the marine environment, so that the presence of these substances in undesirable concentrations is confined to certain area round the discharge point.

3. Even the disposal of substances which are in any case harmful to the marine environment by means of the by-passing of a body of water particularly delicate as regards hydrological conditions (poor exchange), uses (mussel cultivation) or protection of the aquatic environment (marine parks, protected zones, reproduction zones) constitutes an appreciable benefit, which should not be under estimated, for the residual toxicity of effluents, however treated, especially in the presence of large industrial centres, is destined, as far as practical aspects are concerned, to retain an appreciable value.

To make a comparison with analogous situations that may occur in the case of a river, it can be affirmed that it is desirable that treatment plant effluents be discharged, if possible, downstream of drinking water intakes (provided, naturally, that the distance is reasonable and the flow of drinking water does not depend to a determinant degree on the flow of the discharge waters).

Even if a rational system of disposal and dispersion at sea is beneficial under the various aspects considered, care should be taken that the diminution of the pollution level achieved by means of systems of disposal and dispersion is not, for the most part, merely apparent. This consideration regards, for example, the presence of floating substances, which, since they are spread over a large surface, are present in lower concentration (mg/m^2); however, the relative benefit is mainly apparent because the lower level of pollution achieved extends over an area which is proportionally larger.

Furthermore, all floating substances tend to collect, in certain conditions of wind-caused conditions, along the beaches or, off-shore, along the lines of convergence.

As already mentioned, the same can be said with regard to a variety of substances the harmful effects of which decrease very slowly with the diminution of concentration; for example, a discharge into the sea of an effluent containing 0.05 ppm of mercury, supposing the initial dilution ration to be 1:10, would give rise in the receiving waters to a concentration of about 0.005 ppm. This result could be compared to that of a treatment plant with a performance of 90% (in terms of removal of that substance). In this case, however, the comparison is not valid since the reduction of 90% would be accompanied by a tenfold increase of the flow. Despite the increase of inflow, the problem could be considered solved if the reduction of 90% resulted in an effluent substantially harmless as regards the marine environment and not susceptible to phenomena of accumulation and persistence which could, sooner or later, cause an initially acceptable situation to deteriorate. This is not in fact the case in the example given.

On the other hand, the comparison is valid with regard to such parameters as BOD. A 1:100 dilution of sewage containing 200 ppm of BOD, would give rise to an effluent of volume 100 times greater but nonetheless harmless, with a BOD level of about 2.5 to 3 ppm, generally saturated with oxygen. By definition, this parameter does not give rise to persistence or accumulation phenomena; it is therefore not to be expected that, with the passing of months or years, the situation would deteriorate as a result of the discharge. This can be confirmed by DO and BOD measurements in the vicinity of coastal discharges that have been functioning for hundreds of years.

An efficacious system of standards (while leaving the regional or local administrations free to choose case by case the most suitable technical means of achieving a particular result, that is, a certain level of protection of the receiving waters), should ensure that the phenomena of dilution and dispersion in the marine environment are not exploited beyond their limits. At the same time, such a system of standards should favour the best utilization of such processes, in the sense of ensuring that the cash available, often insufficient, to be spent for purposes of protection of the marine environment is spent in the best possible way, in relation to the local conditions, that is, in the way leading to the greatest environmental benefit.

In view of the complexity assumed by the problem when absolutely perfect solutions are sought, there is the risk that standards or criteria that are too ambitious in this respect will prove difficult to put into effect, and this will discourage their application (thus leaving room for wholly arbitrary standards and solutions). An efficacious system of standards should have as its purpose the achievement of the objects previously described, without neglecting fundamental requisites of clarity and simplicity with regard to the concept of the standards and the type of controls; it is in relation to these last two considerations, the result that can be achieved by this process in proximity to the discharge point, and the controls foreseen by the regulations in that zone, that the process of initial dilution acquires a major practical importance.

Figures 20 to 23 illustrate the concepts set out above.

Figure 20 is a schematic representation of a city which discharges the treatment-plant effluent (not disinfected) either in proximity to the beaches (where there are mussel cultivation beds and bathing activities) or further off-shore, by means of a diffuser.

In the first case a certain proportion of the pathogenic germs discharged into the sea return to the inhabitants through the consumption of mussels; the coliform concentration is very high close to the shore and decreases with distance. There are also very high concentrations of nutrients close to the shore which may give rise to eutrophication phenomena.

In the second case there is a high coliform concentration round the discharge point, but the protection of the waters used for bathing and mussel cultivations is assured.

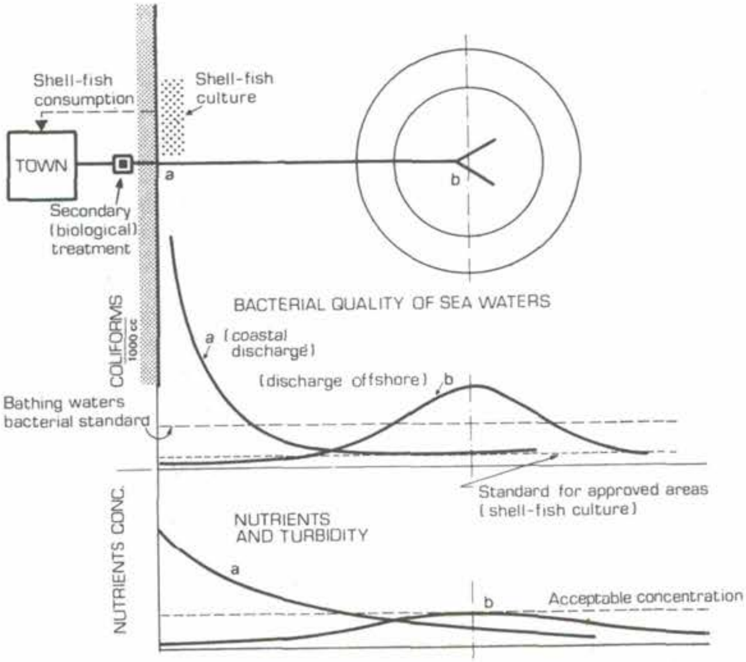


Figure 20 Bacterial quality of sea water and nutrient concentrations in various hypotheses about the point of final disposal: detrimental effects on water uses.

a) point of discharge near the coast

b) point of discharge off-shore

The distribution of nutrients has its highest concentrations in proximity to the discharge point. However, these concentrations are considerably lower than the maximum concentrations in the case of a discharge on the shore. In particular, the coastal waters, which have a poor rate of exchange, are characterized, in the case of an off-shore discharge, by concentrations of nutrients smaller by several orders of magnitude than they would be in the case of discharge on the shore.

Figure 21 represents a parallel case e.g. a city which can discharge its treatment-plant effluent into a lake or transport it a reasonable distance for the irrigation of suitable cultivations.

In the first case the pathogenic germs return to the inhabitants through the drinking water (just as in the case of the shore discharge they returned through mussel consumption), whereas in the case of discharge for irrigation (though the place of discharge would be characterized by a high concentration of pathogenic germs and pollution indicator organisms) the ground waters feeding the lake, during the passage through porous media, undergo a purification phenomenon which makes them acceptable on entry to the lake.

The same can be said with regard to nutrients which, discharged into the lake, would give rise to eutrophication phenomena, whereas if they were dispersed where they could be beneficial, for purposes of irrigation (Figure 20, or off-shore, in oligo-

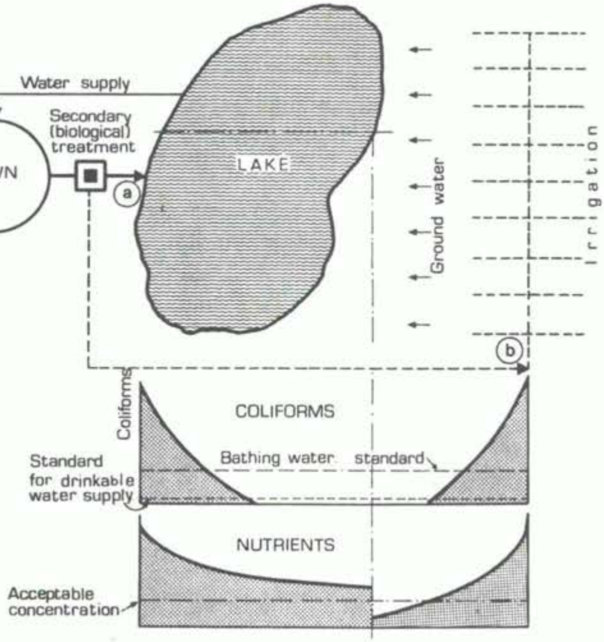


Figure 21 Quality of inland waters in various hypotheses about the final disposal and detrimental effect on uses of water.

a) final disposal in the lake coastal area

b) disposal for irrigation.

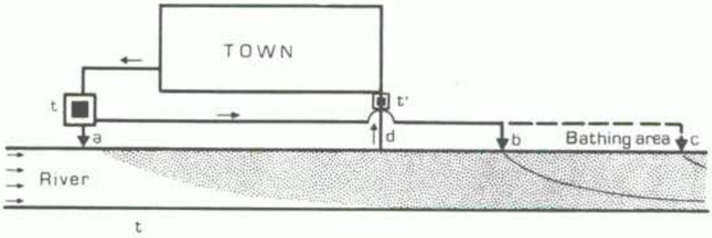


Figure 22 Inland waters: detrimental effect on water supply quality in different hypotheses about the point of final disposal of treated waste waters:

t - waste water treatment plant

t' - water supply treatment plant

d - water supply intake works

a,b,c - alternative points of final disposal of waste water treatment plant's effluent.

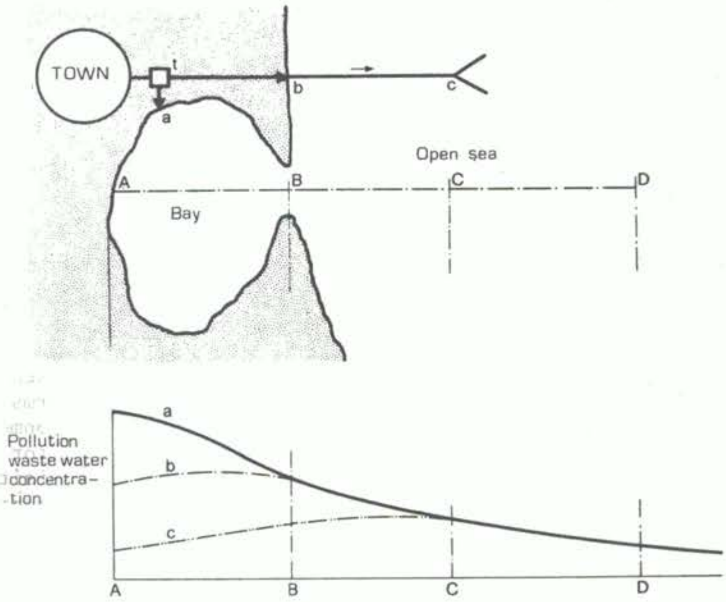


Figure 23 Detrimental effects on marine environment due to residual toxicity or biostimulant effects of treated waste waters, in various hypotheses about the point (a, b, c) of final disposal.

trophic waters), the greater part of them would be consumed in those zones, and they would thus reach the lake in considerably reduced quantities (as they return to the coastal waters in reduced quantities in hypothesis "b" of Figure 20).

Figures 22 and 23 represent the terms of a comparison between a typical river discharge situation and a sea discharge situation. In the hypothesis of discharge a) (see Figure 22) the treatment-plant effluent (t) is discharged upstream of the drinking water intake, thereby rendering the water supplies less suitable for use. It would be convenient, therefore, to discharge the effluent downstream of the intake positions b) and c).

In Figure 23 the treatment-plant effluent (characterized by a certain residual toxicity still harmful to aquatic life) can be discharged into a bay, on the shore outside the bay or, better, off-shore; as regards the persistent toxic substances, it can be affirmed that, on average, the quantities discharged into the bay move out of it and affect the off-shore waters as well.

The transfer of the discharge from position a) to position b) and from position b) to position c) provide the same type of benefit obtained, in the case of Figure 22, by transferring the discharges from "a" to "b" and "c".

In fact, even though the total quantity of toxic substances discharged and the concentration induced off-shore remain unchanged, the changing of the point of discharge brings about a notable reduction of the toxic effects inside the bay (hypothesis of discharge b) and c)) and in the immediately off-shore waters, (hypothesis "c").

5.2.2 Reasons Why And When It Is Important To Take Into Account The Degree Of Initial Dilution

It is considered possible to control pollution caused by the discharge of the substances Group II in an adequate manner by means of three types of standards:

a. Standards relating to effluents, to limit the quantities (rather than the concentrations) of substances on which it is considered opportune to impose such a limitation by reason of their toxicity, persistence and accumulability and the relative inefficacy in their regard of phenomena of dispersion, transformation or extinction.

b. Microbiological standards in mussel cultivation and bathing zones, to maintain the microbiological quality of the waters in accordance with the limits foreseen by criteria or standards serving to safeguard the health of the population and, indirectly, the aesthetic qualities of the receiving waters.

c. Standards concerning the marine waters in the vicinity of the discharge point, serving to maintain, with regard to substances less dangerous in terms of persistence, toxicity and accumulability and with a smaller range of environmental effects (i.e. the substances of Group II), a qualitative level appropriate for the protection of aquatic life in its more delicate forms, and to respect requisites of an aesthetic nature adequate to permit every sort of aquatic sport or recreational activity.

This brings one to the importance, already justified by the final considerations set forth in the preceding paragraph, of the phenomenon of initial dilution in relation to rational systems of waste disposal and, above all, for purposes of a system of standards, at the same time efficacious and simple, with regard to the disposal of the substances of Group II.

It can be objected that, after the process of initial dilution has taken place, other phenomena have the effect of reducing by a number of orders of magnitude not only the concentrations but also the total quantities concerned and that a standard referring to the quality of the marine waters in the proximity of the discharge point, and requiring of those particular waters a quality sufficient to safeguard the marine environment, would often give rise to excessive expenditure and excessive investment in treatment works on land (and, to a certain extent, in the construction of diffusers) in comparison with what would be the case if the same limits were applied with regard to the zones where uses would be affected if they were not respected. In this way the possibilities of dispersion in the marine environment could be fully and rationally exploited for the purpose, as indicated above, of deriving the maximum benefit from the money spent.

Without wishing to deny the scientific grounds of such objections, it is nevertheless considered opportune (and in particular for the reason given at the end of the preceding paragraph) to propose the adoption of standards that, in relation to the disposal of the substances of Group II (with the exception of pathogenic germs) serve to protect the marine waters even in proximity to the discharge points and this at least from the medium and long-term point of view, since, in the transitory conditions imposed by lack of financial resources, it would be possible to tolerate considerably worse conditions in the receiving waters in proximity to the discharge point, provided always that they remained within certain limits which precluded the coming into existence of effectively intolerable situations.

The type of standard proposed takes its place at an intermediate level between criteria concerned only with control of the quality of the discharge waters or the quantities discharged - and the criteria of a control based on the uses of the receiving waters.

Despite the fact that this last criterion, applied by properly trained teams and by means of adequately efficient administrative structures, makes it possible to follow more closely the criteria of optimization that have been outlined (for which reason these possibilities should in any case be left open, each individual country acting as it deems opportune), it would appear, however, that, in general, the application of standards for the protection of the sea waters in the proximity of the discharges, apart from the merit of revealing in a considerable measure the capacity of dilution and dispersion characteristic of the zone and the system of disposal, also has the advantage of sufficient simplicity and clarity to render its widespread application probable.

With regard to the term "dispersion" used above, it may seem inappropriate in the context of standards and criteria concerning the quality of the sea waters immediately downstream of the process of initial dilution; it should be pointed out however, that the quality of the waters round the discharge point reflects not only the quality of the effluent discharged and the degree of initial dilution achieved, but also, and in a measure which in the long term could be determinant, the quality of the dilution waters. These may be affected by the presence of the discharge itself and also by other discharges, depending on the processes of dispersion and evolution occurring in the zone, and on the size and positions of the discharges.

Even in the presence of only one discharge, in fact, if a phenomenon of dispersion did not occur downstream of the process of initial dilution, the quality of the sea waters of the zone would tend to deteriorate progressively towards the original quality of the effluent (though naturally a phenomenon of convection or transport, even in the absence of marine currents of other origin, could be generated by the difference or density between the sewage field and the sea water below.)

Thus, where the quality of the receiving water is checked in the vicinity of the discharge point, even though this quality essentially depends on the characteristics of the discharge waters and on the dimensions of the phenomenon of initial dilution, the phenomena of dispersion and evolution concerning that and other discharges will also, though indirectly and to a limited extent, be taken into account.

It can also be affirmed that, among the physical phenomena that govern the destination of the discharges, the process of initial dilution can be controlled by means of the project calculations (and thus by the planning of a suitable disposal unit) more easily than the phenomena of dispersion that occur subsequently; these, despite their determinant importance, are subject in a greater measure to natural circumstances over which the planner has no control. To a certain extent this is also true with regard to the process of initial dilution, which depends not only on the characteristics of the diffuser, the volumes discharged and the depth, but also on the marine currents at the various depths and on the vertical distribution of density.

However, as will be seen, even in conditions of total absence of current lasting for a few hours (a highly improbable situation), the diffuser is able to draw towards itself from nearby zones a certain quantity of dilution water and to form a zone of sufficient density to avoid phenomena of floating (and the possibility, in the event of a shore-ward wind, of polluting the shore).

It should also be borne in mind that while by means of the process of initial dilution it is not difficult to obtain dilutions of the order of 1:100 - 1:400, the process of dilution by eddy diffusion downstream of a diffuser of suitable length increases the total dilution ratio considerably (generally 3-6 times over, 10 times being the maximum), and this at a distance comparable to the length of the pipeline, and thus in proximity to the coastal zones to be protected. This increase of the dilution ratio is not without interest; it is greater, however, when, in certain respects, the initial dilution ratio is less.

A shorter diffuser, in fact, gives rise to a smaller sewage field. In this field the concentration gradient, in a direction transversal to the axis of movement, is greater, and the phenomena of eddy diffusion in a horizontal direction are accordingly more intense.

A sewage field which is initially very large will thus undergo, in its central part, a process of subsequent dilution which is slow, for volumes of water contaminated to a certain degree are mixed with volumes of water with a degree of pollution which is only slightly smaller.

Some calculation procedures with regard to discharge pipelines and diffusers in fact take into account a certain range of solutions and a certain field of hypotheses with regard to the direction and speed of the "critical" marine current; conditions more favourable to an efficacious process of initial dilution may be less favourable as regards the phenomena of subsequent dilution and the extinction of certain parameters (in the first place the bacterial load).

Other optimization procedures seek to establish, for purposes of respecting a certain colimetric standard in the coastal waters, the best combination of purification treatment, length of pipeline and length of diffuser; developed in particular in Denmark, these procedures will be referred to later.

Whereas, on the one hand, the increase of the process of initial dilution by the use of long diffusers and the formation of a very large sewage field, makes the phenomena of subsequent dilution less rapid, on the other hand it happens that too low a ratio of initial dilution gives rise to particularly light surface masses of sea water and sewage (that is, of density over 0.5 kg/m^3 less than that of the surface sea water) which may impede eddy diffusion in a vertical direction (on account of the large density gradient which hinders these turbulent exchanges between the upper and the lower layers).

This outline of the importance and the limits of the phenomena of initial dilution (in the context of dispersion phenomena and dilution) as regards the process of sanitation of a particular sea zone induces a certain preference for standards which refer to the sea water downstream of the process of initial dilution.

The advantage of applying controls in the discharge zone are:

a. greater simplicity and clarity of verification operations, and freedom, in the context of such operations, from problems caused by the possible interaction of several discharges. If the sea waters are acceptable in the proximity of a particular discharge, it cannot be held responsible, at least as far as the substances of Group II are concerned, for a situation of pollution that has come into being elsewhere;

b. possibility of prevention and control in the planning and execution phases, in that a certain degree of initial dilution can be more easily ensured;

c. the prudential character of the criterion, in that the effluents are discharged in zones at a certain distance from the localities that are more delicate from a hydrological and environmental point of view (this is implicit in the need to ensure, by means of an adequate depth of discharge and a sufficient supply of pure water, the desired development of the process of initial dilution). Thus, by maintaining in the proximity of the discharge point a quality of water satisfactory for aquatic life, it follows that, as the distance from the discharge point increases, so will the degree of protection against pollution be greater.

A policy of maintaining a quality of water in the discharge zone that is satisfactory both from the aesthetic point of view and as regards the protection of aquatic life also has a certain favourable aspect of a psychological nature that should not be overlooked.

It could be assumed in non-scientific circles (which, however, have so far carried considerable weight with regard to public opinion, and, in effect, to the interventions carried out) that the polluted zones will in any case expand progressively with time, or that, in concomitance with unfavourable currents, they will move and pollute even zones at a considerable distance.

Although from a scientific point of view whether this is so or not can be ascertained case by case by means of experiments, the fact remains that such demonstrations lack the character of accessibility and immediacy that would be achieved by maintaining in a satisfactory and aesthetically unexceptionable condition the sea waters in the immediate proximity of the discharge.

Moreover, it would be possible in this way to solve also another problem which often arises, in practice, with regard to the formulation of the requisites of quality of the receiving waters or to the granting of authorization for the discharge of a particular effluent.

It may be objected, in fact, that if the calculations presented by the designer foresee a satisfactory situation, in proximity to the point of discharge, in virtue of the continuous supply of clean sea water, this guarantee can be invalidated by the action of more or less distant discharges which pollute the dilution water beforehand or, as has been already hypothesized, by a progressive increase of the level of basic pollution caused by the discharge in question.

Wishing to proceed with the example by referring to a parameter of little significance as regards sea pollution but which is, nevertheless, frequently the subject of attention (also in relation to its debated, but in any case fundamental, significance with regard to fresh water pollution and purification treatment), namely, BOD, it could be objected that the evaluation of BOD in the receiving waters as a function of the characteristics of the effluent and the initial dilution ratio could be invalidated by the progressive increase of BOD and the progressive reduction of oxygen in the whole of the sea zone.

The discharge of an effluent characterized by a BOD level of 200 ppm with a dilution of 1:10 will give rise to a sewage field characterized by a BOD level of about 20 ppm.

In these circumstances the standards of quality with regard to the marine waters should be referred to positions considerably distant from the discharge and possibly susceptible to the influence of other discharges, without there being an immediate distinction between the effect of one discharge and that of another. It is still not made clear by the control system whether the 20 ppm of BOD in the discharge zone is or is not to be attributed to a slight increase (resulting from a high initial dilution ratio) of a relatively high basic level (which would be an unfavourable situation). In this case the BOD value of the receiving waters could pass from a value of say 15 ppm upstream of the discharge to 20 ppm downstream of it.

However, if 4-5 ppm were established as the maximum concentration of BOD permissible in the receiving waters in proximity to the diffuser, such questions (which could certainly be answered by suitable ad hoc surveys) would no longer have any cause to be posed: if downstream of the initial dilution process the concentration of a certain substance is clearly below the acceptable limits for the receiving waters, this level will be all the more acceptable in the dilution waters reaching the diffuser.

5.2.3 Short Explanatory Notes About The Mechanism Of Initial Dilution

The process of initial dilution is essentially a process of eddy diffusion.

One can consider the case of a horizontal jet. The case of a vertical jet is of considerable theoretical importance in that it simplifies certain aspects and permits the reliability of certain schematization in representing the phenomenon to be verified.

But, in fact, the discharge jet is always horizontal because in this way the path followed by the jet on its upward journey is longer and a greater measure of dilution is obtained than would be in the case of an upward discharge.

Moreover, discharge through holes or mouths located in the sides of the diffuser has the advantage of facilitating the discharge of particles of sediment transported in turbulent suspension in the diffuser.

Generally the discharge jets are given a slight downward inclination in order to lengthen the path followed by the jets, while not imparing the stability of the pipeline; this downward inclination is of the order of 4^{o}. In these conditions there is a certain removal of the lighter sediments deposited round the diffuser without, however, the creation of large holes tending, above all when the jets are close together, to cause the diffuser to sink into the sea bottom.

The discharge waters, whether treated or not, have substantially the same specific weight as the supply waters. The increase of dissolved solids occurring in the course of the normal uses of an urban network does not exceed 1 gr/l; in fact the classic attribution of a contribution of about 100 gr/inhab x day of dissolved substances (about half of which are organic) to a sewage contribution of 200 l/inhab x day corresponds to a maximum increase of 500 ppm.

The dissolved solid content of the Mediterranean waters oscillates between 37 and 39 gr/l. Sea water thus weighs about 27-29 kg/m^3 more than sewage. The discharge jets proceed forwards, by virtue of the kinetic energy they possess on issuing from the diffuser, and upwards, on account of their different specific weight.

The geometry of the upward movement thus depends on the contrasting effects of the inertial forces (essentially correlative to the speed of outflow, the initial density of the jet being more or less constant) and the buoyancy, which depends on the difference of density (likewise constant at the beginning of the process) and on the volumes of mixture concerned, which are correlative to the dimensions of the jet.

Just as the form of a rectangle, more or less elongated, depends not on its length or width, but on the adimensional number expressed by the length width ratio, so does the phenomenon of initial dilution in its various aspects, from the geometrical characteristics of its course to the degree of dilution achieved, depend not so much on the value of the diameter D or the speed of the jet V, as on a relationship between these terms which is called the Froude number:

$$\frac{V}{\sqrt{g' D}}, \quad \text{where } g' = g \frac{\gamma_1 - \gamma_0}{\gamma_0}$$

This number expresses the ratio between inertial forces and gravity forces that governs the mechanism of the phenomenon.

By attributing a value to the Froude number, it is possible to determine the degree of dilution, the dimensions of the jet and the co-ordinates of the same as a function of another dimensional parameter, which is the distance Y above the jet divided by the diameter of the jet Y/D. It is not the absolute value of the distance Y that is important, so much as the ratio between this distance and the diameter of the jet.

The formulas and tables presented below are based on these parameters.

The mechanism of the phenomenon of initial dilution depends, as has been said, on a phenomenon of eddy diffusion, as a result of which properties or substances which are more concentrated in the centre of the jet than in the ambient field, undergo, as the rising movement proceeds, a process of homogenization which tends to reduce the concentrations in the centres in favour of the peripheral zones.

The movements which produce the homogenization are vorticose mixing movements that involve a transport of matter.

Between fluid zones moving at different speeds, these vorticose movements naturally tend to be more intense when the velocity gradient (in this case between the jet and the ambient fluid) is larger and the density of the fluid is greater.

These vorticose movements tend to be attenuated by the viscosity of the fluid.

Whether the movement is regular (or laminar) or turbulent thus depends on whether or not the forces causing instability (connected, as has been said, with the inertia and the speed gradient) prevail over the forces due to viscosity.

The intensity of the mixing-movements - turbulence - is closely connected with another adimensional parameter, that is, with the ratio between the two types of forces concerned; this ratio is called the Reynolds' number.

$$R_e = \frac{\rho V d}{\mu}$$

where: ρ = density of fluid
V = velocity
d = dimension
μ = viscosity of the fluid

It is reasonable to expect the value of the Reynolds' number to be of a certain importance with regard to the mechanism of diffusion of a jet; this is certainly true where Reynolds' number values below a certain threshold are concerned. Above this level, that is, in fully turbulent conditions, a variation of the Reynolds' number does not significantly affect the phenomenon and, as this is the case in practice, this aspect of the problem may practically be ignored.

It is opportune, in view of the importance of the subject, to say something further about the mechanism by which the process of eddy diffusion gives rise to a transport of substances from richer (higher concentration) zones to less rich (lower concentration) zones.

It is obvious that the mixing together of two volumes of water, one fresh and the other salty, gives rise to a mixture of intermediate salinity, volumes initially lacking salt will gain salt and volumes initially rich in salt will lose it. Figure 26 illustrates the phenomenon: the vorticose movement transports a certain volume from zone A into zone B and corresponding volume from zone B into zone A. The result of this exchange is that, if zone A were initially richer in a certain substance than zone B, zone A would be impoverished and zone B enriched. It is understandable that the variation induced by this exchange, that is, the migration of substance from zone A to zone B, will more more intense when the difference between the concentrations of the two zones is greater and the mixing movements are move intense. If the concentrations in A and B were equal, the mixing motion would not give rise to transport of substances, while, even if the concentrations in A and B were different, there would be no transport of substance in the absence of mixing (apart from molecular diffusion). For this reason, the process of eddy diffusion is more intense in the first part of the jet, where the gradient of concentrations in a transversal direction is larger. Again, a large difference in speed between the jet and the ambient fluid favours an efficacious process of eddy diffusion; this could not occur if the speed of the jet were low in relation to the ambient fluid (this hypothesis naturally refers to a non-turbulent environment of equal density to the discharge.

5.2.4 Formulas Of Practical Use And Graphs For The Calculation Of The Degree Of Initial Dilution: Single Jet And Several Jets In A Row

It is intended here to present an exhaustive summary of the technical literature pertinent to the forecasting of phenomena of initial dilution. A number of formulations and tables which are particularly easy to use are given for the purpose of permitting a preliminary evaluation of the phenomenon and to make clear the most important questions concerning the phenomenon and the possibilities of forecasting it.

On the occasion of the granting of authorization for a discharge, the authority concerned should make the applicant responsible for the effective degree of initial dilution obtainable, reserving the final authorization until the works have been carried out and tested.

In any case, it would be appropriate to submit the applications for authorization to a preliminary technical examination to ascertain whether, in general, the calculations submitted by the applicant were adequately plausible; in particular, use could be made of tables indicating (in relation to the depth of the discharge, the length of the diffuser and the volume of the discharge) the maximum ratio of initial dilution obtainable in certain conditions of typical currents.

In this paragraph the case is considered of a motionless non-stratified fluid; it is a hypothetical case, especially with regard to the first hypothesis, in that the marine environment is normally affected by currents of greater or lesser dimensions. However the tables and the formulas introduced in the case of these hypothesis constitute the basis for the development of more complex calculations which take into account the vertical distribution of density and the direction and speed of the marine current.

When speaking of the mechanism of the phenomenon of initial dilution, mention was made of the significance of the Froude number and of the relative depth in a description of the phenomenon.

In Figure 24 the degree of initial dilution obtainable is expressed as a function of the Froude number and the relative depth. In Figure 25 the trajectory of the jet and its transversal dimension (the diameter of the jet is D=2w) are indicated as functions of these parameters. These figures are taken from Brooks, (25).

Among the various formulas allowing the numerical calculation of the degree of initial dilution, the following can be cited, presented by Cederwall, (34).

$$S = 0.54\,F\,\left(\frac{Y}{DF}\right)^{7/16} \qquad \text{if } Y/D < 0.5\,F$$

$$S = 0.54\,F\,\left(0.38\,\frac{Y}{DF} + 0.66\right)^{5/3} \qquad \text{if } Y/D \geq 0.5\,F$$

For isolated jets at considerable depth ($Y/D > 200$)

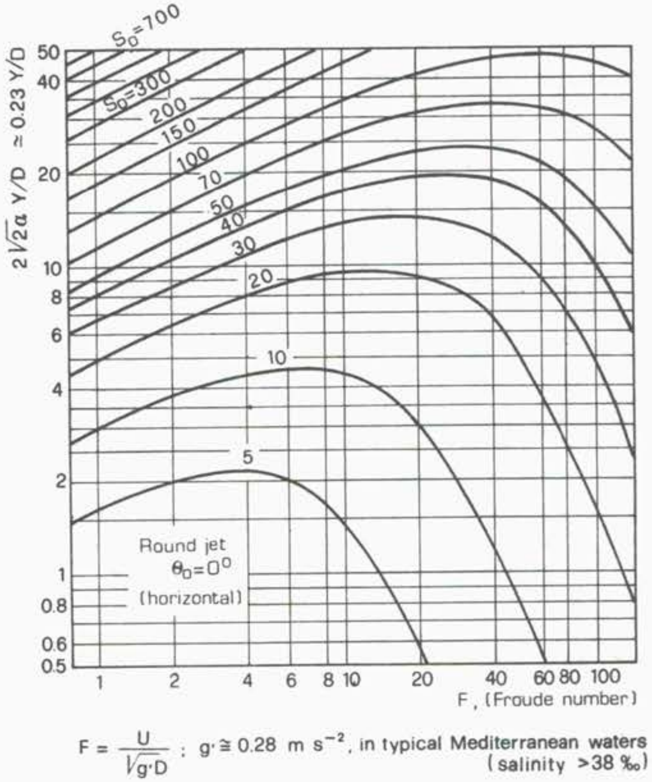


Figure 24 Centreline initial dilution as function of the Froude number and depth, (25), (For symbols see also Figure 96).

Brooks proposes the following expression:

$$S = \frac{0.078\ g'^{\ 2/3}\ .\ Y^{5/3}}{Q^{\ 2/3}}$$

where:

Q = volume of the jet;

$g' = g \cdot \frac{\Delta\gamma}{\gamma}$ ($g' \sim 9.81 \cdot 0.028 \sim 0.27$

The case of an isolated jet, though important for purposes of establishing certain bases of calculation, is in practice of limited importance, in that the more rational types of diffuser have a relatively large number of outlet openings of small dimensions, placed close together.

Figure 26 gives a schematic representation of the hypothesis of two non-merging jets.

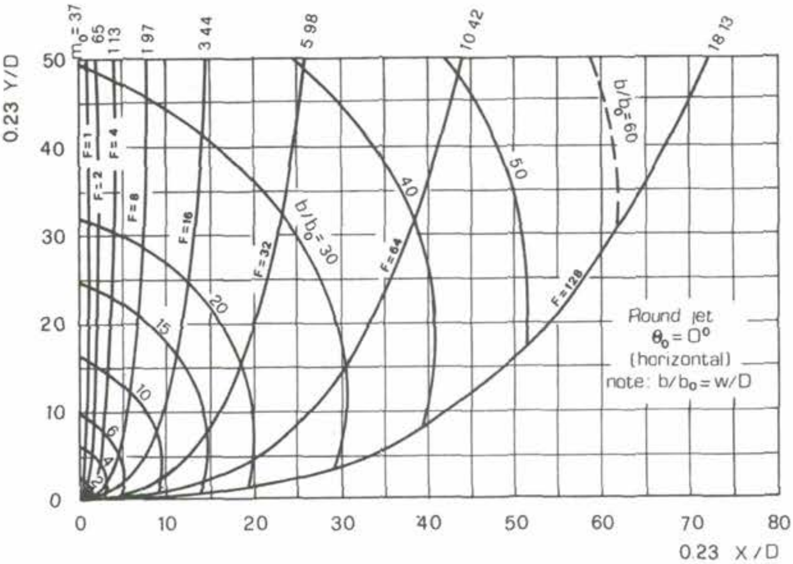


Figure 25 Trajectory and jet width for horizontal round jets, (25).

2w = jet width (two standard deviations of concentration distribution curve across the plume)

D = diameter of jet at point of discharge

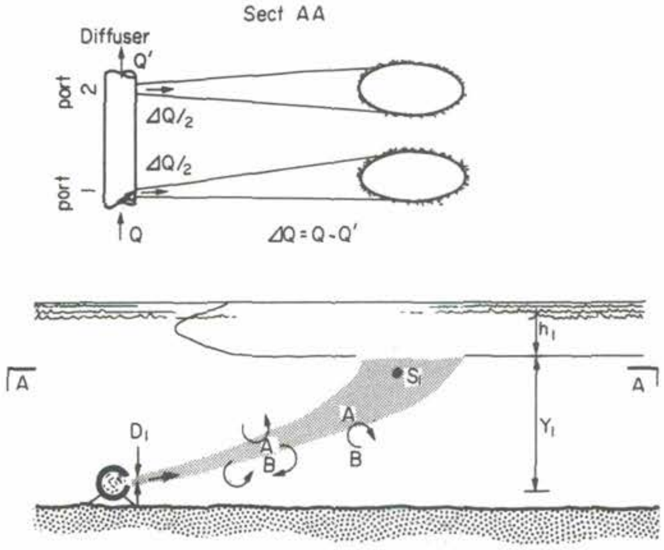


Figure 26 Jets not merging

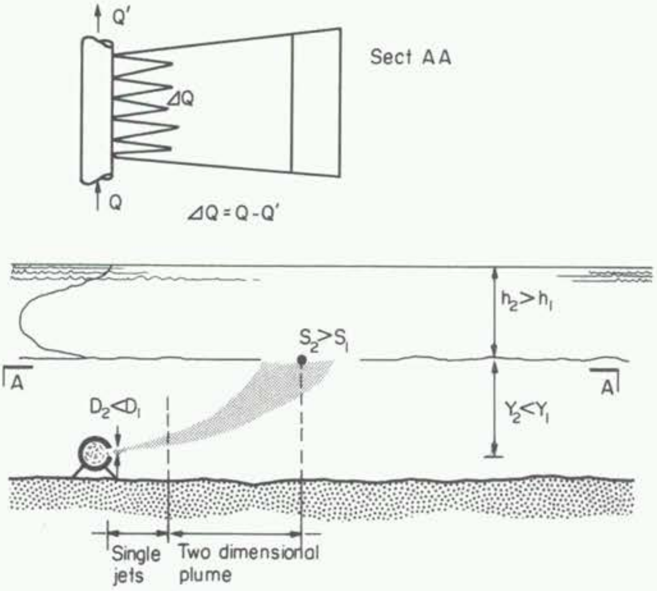


Figure 27 Jets merging together to form a two dimensional plume.

In Figure 27, to be compared with Figure 26, the same volume is discharged by several jets close together and of smaller diameter: compared with the conditions illustrated in Figure 26, there is a considerable increase in the degree of initial dilution achieved. The jets interact with each other and, after a first stretch of trajectory that could be called free, form a continuous field which may be likened to a jet of certain dimensions, speed, original density.

The precise evaluation of phenomena of interference between several jets is still the subject of experimental research, but from the line of interference onwards, it can be evaluated with reasonable approximation by means of numerical procedures of calculation with regard to a bi-dimensional plume.

For jets at a considerable depth, Brooks proposes the following simple formula

$$S = 0{,}38 \frac{g'^{\,1/3} \cdot Y}{q^{\,2/3}}$$

where q is the volume per unit of length of the diffuser (e.g. $m^3/ s \times m$).

This formula is applicable to diffusers with small (a few cm) outlet openings in proximity to each other (at intervals of a few meters) and at an adequate depth (20 m or over).

If the current is in the direction of the axis of the diffuser, $\alpha = 90^\circ$ and $b \cos \alpha = 0$.

This does not correspond to reality. Amongst other things in the hypothesis of a "point" discharge or an isolated jet, the quantity of dilution water available would be constantly equal to zero. In reality, even in the case of marine currents running in the direction of the axis of the diffuser, a certain quantity of dilution water is intercepted in any case, not only because the jet itself has a certain dimension in a transversal direction and, moreover, draws towards itself waters from the surrounding zones, but also because the jets follow a more or less straight trajectory, depending on the Froude number, which leads to the interception of a certain volume of dilution water, along a certain front.

In the case of jets situated on both sides of the diffusers, and taking into account the dimensions of the jet, this front may be assumed as 2-3 times the depth of the discharges; for purposes of the various calculations, it would thus seem to be opportune to replace the length of the diffuser "b" by the modified length "b + 2h" or "b + 3h", where "h" is the depth of the discharge. This modification makes little difference where currents in a transversal direction and long diffusers are concerned, and excludes unrealistic results in the case of currents in the direction of the axis.

5.2.5 Influence Of Marine Currents On The Obtainable Degree Of Initial Dilution

If one considers the type of discharge which in practice is most important, that is, discharge by means of a diffuser of a certain length, one finds that the degree of initial dilution obtainable is related not only to the characteristics of the jets, but also to the quantity of marine diluting waters that the diffuser traverses.

If the discharge zone were not affected by any current, a layer of considerable thickness composed of a mixture of sea water and sewage would be formed above the diffuser; in reality, however, even in the absence of marine currents of another type, the thickness this layer acquires is limited by the fact that the mixture is continuously moving away because its density is different from that of the sea water. It is clear, in any case, that, when a marine current passing over the diffuser is characterized by a considerable speed, the sewage field above the diffuser is less thick than it would be if the speed of the current were low. The degree of initial dilution is greater when the thickness of the sewage field is smaller on account of the greater distance that the jet rises through "clean" waters. In normal conditions the volume of the sea water/ effluent mixture, created by means of the process of initial dilution, must be equal to the volume me Qd:

$$Q_d = v \cdot b \ \cos\alpha \cdot h$$

where: b = the length of the diffuser;

α = the angle between the axis of the diffuser and the direction of the marine current;

h = the depth of the sewage field;

v = the speed of the marine current.

The effective degree of dilution achieved may thus be calculated graphically by means if the intersection of two curves (Figure 28), which express, in relation to the depth, the volume of diluting water available and the degree of initial dilution obtained.

At the point of intersection the volume of the mixture created at a certain depth by effect of the process of initial dilution (SQ) is equal to the volume provided by the marine current that permits the removal of the said volume ($SQ = v \cdot \cos\alpha \cdot h$).

For the sake of greater precision, it should be pointed out that, if the thickness "h" of the sewage field is temporarily smaller ($h' < h$), the degree of initial dilution obtained (S') will be, for the moment, greater and would give rise to a flow (S'Q) greater than that removable ($Q'd = v \cdot b \cdot \cos\alpha \ h' < S'Q$) by the action of the current; the sewage field thus tends to get deeper as long as the equality in question is not respected.

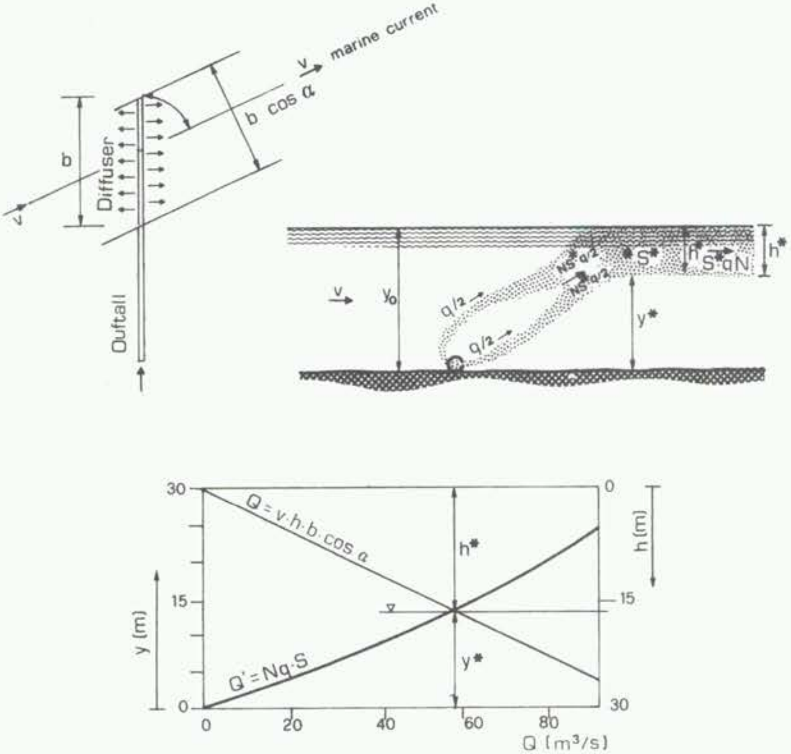


Figure 28 Evaluation of initial dilution for a multiport diffuser, taking into account also the thickness (h) of the mixed field and the rate of flow of dilution water, $Q = v \cdot h \cdot b \cos\alpha$. (S = initial dilution ratio; N = number of ports)

5.2.6 Mechanism, Effects, Forecasting And Desirability Of Jet Trapping Phenomena

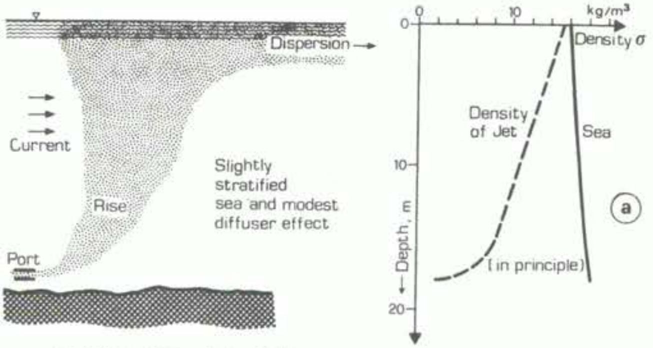
The phenomenon of entrapment of the discharge jets essentially consists of the formation of a sewage field of density greater than the density of the surface layers of sea water. With reference to Figure 29, (58), two conditions are considered (a and b).

a. In the first condition (or hypothesis) the intensity of the phenomenon of initial dilution is modest and the vertical density distribution of the receiving waters is fairly uniform.

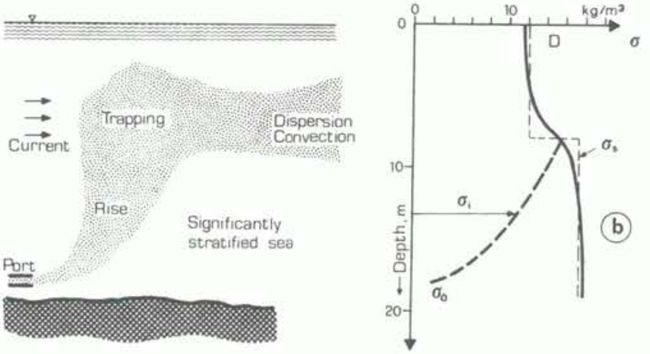
The density of the jet increases as it rises but always remains less than the density of the sea water; in this case the sewage field remains on the surface.

b. Case of a jet of initially small dimensions (greater initial dilution) and a vertical density distribution of the sea water characterized by a rapid diminution a certain distance from the bottom.

In this case there is a mixing of the jet and the deep and dense sea waters sufficient to produce a mixture of greater density than that of the surface layers. In



Formation of a surfacing field



Typical subsurface trapping

Figure 29 Definition of marine disposal phenomena, (58, 112)

σ_s = density of sea water

σ_o = density of jet at the point of discharge

σ_i = density of jet.

the graph on the right of Figure 29(b) the vertical density distribution of the marine environment is schematically represented by means of a dotted line in order to illustrate the parameter in a clearer manner and also to suggest certain schematization useful for calculation purposes.

The ascending jet is endowed with a certain kinetic energy the vertical component of which is due to the action of the buoyancy forces acting on the mixture, which is less dense than the surrounding water.

Thus, in the zone where the movement changes direction (from a direction prevalently vertical to one prevalently horizontal) there is a local extension of rise (generally of the order of 20% of the distance of rise) due to the inertia of the jet.

As to the effects of subsurface trapping, it can be said that, generally, they are beneficial and therefore desirable, in that the mixing field, polluted, for instance, by bacteria, is withheld from wind-induced surface current running towards the shore (which often cause critical situations of pollution).

In these circumstances, too, if it were wished to apply the standards relating to bathing in the discharge zones, even the proximity of the discharge point would be found free from bacterial contamination.

The phenomenon of trapping may acquire a certain importance in zones where it is not wished to increase the primary productivity (by means of nutrients and biostimulant substances contained in the discharge); these substances are confined for a more or less long period of time (thus having a better chance of dispersion) in the deeper layers, where the light energy available for the processes of photosynthesis is less than in the surface layers.

From the aesthetic point of view, too, the trapping of the jets is a favourable factor for, in this way, there is no alteration of the liquid surface, an alteration which is always noticeable when jets reach the surface, whatever their nature (and thus irrespective of the degree of treatment of the sewage), owing to the different degree of salinity and power of refraction of the liquid.

The formulas which allow the height of rise and, thus, the occurrence, or otherwise, of the phenomena of entrapment to be forecast also permit an evaluation of the degree of initial dilution obtainable.

It is obvious that verifications should be carried out even with regard to this aspect, in the sense that, once the phenomenon of initial dilution has occurred, the quality of the sea waters should be such as to safeguard the aquatic life in an adequate manner.

With regard to major current-measurement surveys, it is natural to require that, when entrapment phenomena are foreseeable, not only the surface currents should be investigated, but also those in the deeper layers, and not only the speeds of the currents in proximity to the diffuser, but also the routes of the currents downstream of the diffuser.

It is possible to take into account the conditions of discharge in a stratified ambient fluid (in which, that is, the vertical density distribution is significantly variable) by means of calculation procedures which proceed by successive stages, taking advantage of the formulations developed with regard to jets discharged into a homogeneous ambient fluid. In this case the characteristics of the ambient fluid can conveniently be represented by means of a series of strata internally characterized by a constant density (Figure 30), (58, 112). The height of rise of the jets is thus foreseen to correspond to the level at which the density of the jet is equal to that of the ambient fluid at that depth.

In this way various levels of the sewage field are determined, in particular the median zone (MIDI), situated at the level at which the average density of the jet is equal to that of the receiving waters; the upper level of the sewage field (MAXI) is that at which the density of the centre of the jet is equal to that of the receiving waters. Other levels are also determined in correspondence to the zone where the rising movement ends, which for reasons already mentioned (the inertia of the jet) are considerably higher than the levels of the sewage field proper.

By carrying out these calculations in relation to various discharge conditions and various typical density distributions (the data, obviously, being chosen so as to provide a statistically significant representation of the effective functioning conditions) it is possible to formulate certain forecasts, summarizable as, for

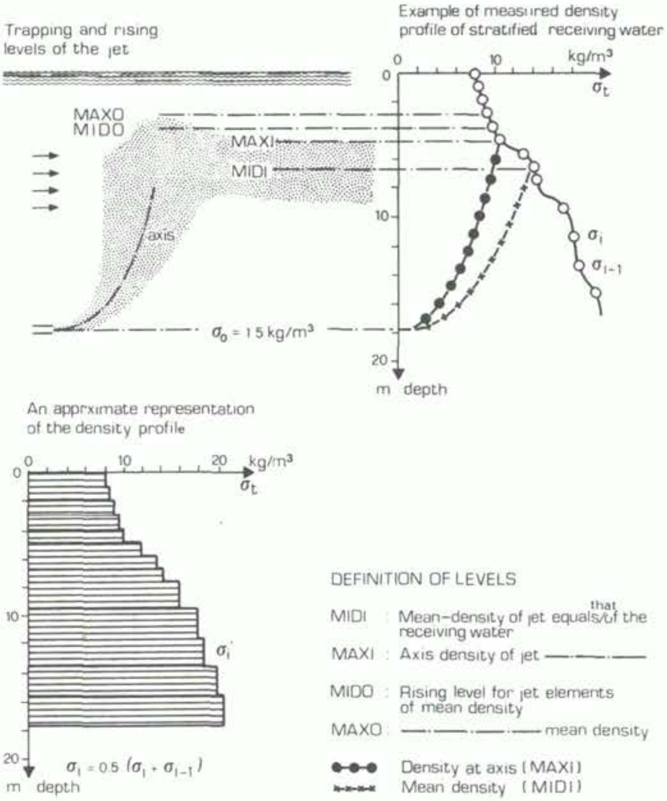


Figure 30 Rising and trapping of sewage in stratified sea, (58, (112).

example, in Figure 30 with regard to the foreseeable frequency with which the sewage field will be situated approximately at a certain depth.

In view of the laboriousness of these calculations, the use of a computer is advantageous. Some block schemes (Figure 31), (57), are given with regard to these developments.

Allowing a few approximations, the height of rise of a jet or spring can be calculated by means of some formulas developed by Brooks, (25), if:

Q_o = the volume of an isolated jet;

q_o = the discharge volume per unit of length;

σ_d = the density of the discharge jet;

σ_1 = the density of the receiving water in proximity to the bottom (discharge level);

σ_o = the density of the ambient fluid at the level "y" measured above the discharge;

$\frac{d\sigma_o}{dy}$, $\frac{d\sigma_o}{dy}$ = the density gradient;

g = gravity acceleration;
y max = maximum height of rise of the jet
$\sigma_d{}'\sigma_1{}'\sigma_o$ = reduced densities of the jet, of the ambient fluid at discharge level and at the level "y" respectively.

In the case of an isolated jet, the maximum height of rise, y max, can be evaluated as follows:

$$Y^4 \max = 6340 \; \frac{Q_o \; (\sigma_1 - \sigma_d)}{g \; {\frac{d\sigma_o}{dy}}^{3/2}}$$

In correspondence, the value of final dilution in the centre of the jet (minimum value) is expressed by:

$$S = 0{,}28 \; \frac{g^{1/8} \; (\sigma_1 - \sigma_d)^{3/4}}{Q_o^{1/4} \; {\frac{d\sigma_o}{dy}}^{5/8}}$$

In the case of discharge by means of a number of proximate jets (which, at a certain distance from the outlets, come to constitute a continuous scource), the expression relating to the height of rise is, according to Brooks, the following:

$$Y^3 \max = \frac{610 \cdot 90 \; (\sigma_1 - \sigma_d)}{g \; {\frac{d\sigma_o}{dy}}^{3/2}}$$

while the final dilution is expressed by:

$$S = 0{,}41 \; \frac{g^{1/6} \; (\sigma_1 - \sigma_d)^{2/3}}{q_o^{1/3} \; {\frac{d\sigma_o}{dy}}^{1/2}}$$

It will be noted that the above formulations do not take the intensity and the direction of the marine current traversing the diffuser into account in any way; the thickness, of sewage field and, finally, the degree of initial dilution obtainable, as well as the height of rise of the jets, are closely linked to these parameters.

It would appear that an adequate theoretical solution to the problem has not yet been found; a method of approximate calculation has been proposed by Olivotti (Olivotti 1977, unpublished). This procedure is rather cumbersome and requires the use of a computer. The procedure is of the trial and error type. As a first step it is hypothesized that the free height of the jet is, for example, 1 m above the level of the discharge; known procedures are then used to determine the degree of dilution obtained in this hypothesis, the thickness of the sewage field (obtained by a knowledge of the speed of the marine current) and the average density inside the sewage field. If the average density of the sea waters in correspondence to the sewage field is greater than the average density of the sewage field, it means that the hypothesis does not correspond to the real conditions, and a further hypothesis is accordingly formulated, increasing the height of rise by 1m.

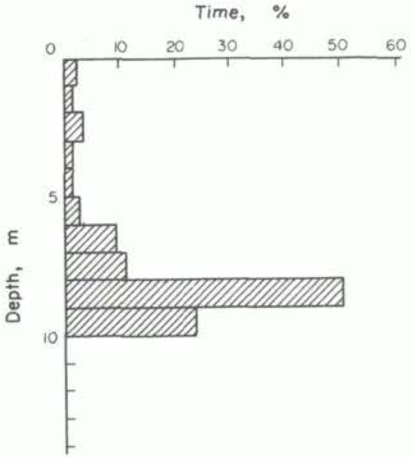


Figure 31 Frequency of trapping (MIDI) (see Figure 30) in % of time at different levels, (58, 112).

Proceeding in this manner, in the end one of the following results is obtained:

a. the upper level of the sewage field as calculated is higher, theoretically, than the level of the sea surface;

b. the average density of the sewage field is greater than the average density of the sea waters at the corresponding depths.

In both cases the calculation stops and the degree of initial dilution and the height of rise of the jet have been determined at the same time.

5.2.7 Oceanographic And Other Data Needed For An Evaluation Of The Degree Of Initial Dilution Obtainable

The characteristics of the preliminary oceanographic surveys serving to provide the data necessary for calculations with regard to the degree of initial dilution obtainable and the height of rise of the jets can be deduced from the preceding paragraphs in which the main variables are mentioned in relation to their relevance to the various calculations.

These parameters can be summarized as follows:

1. depth of the discharge point;
2. form and length of the diffuser, dimensions of the outlets and intervals between them, volume of discharge;
3. marine currents: directions and speed on the surface, on the sea floor, and at least at one intermediate level;
4. vertical density distribution.

5.2.8 Some Proposals Of Administrative Regulation For The Definition And The Standard Measurement Of Initial Dilution

As has already been indicated, and will be explained more thoroughly in the paragraphs that follow, the measurement of the initial dilution of a particular discharge constitutes an important means of control of the quality of the marine waters.

In this way, knowing the basic level of the various substances and also the characteristics of the effluent, it is possible to determine whether or not the standards, with regard to the receiving waters, are being respected, without having to carry out laborious analytical determinations with regard to the receiving waters themselves, analyses which would have to be repeated at various times (owing to the high degree of variability of the situation) and with regard to all the various pollution parameters.

An efficacious system of regulations should, therefore, establish certain standards relating to the experimental determination of the degree of initial dilution obtained.

Such regulations should take into account the real mechanism of the phenomenon but also the practical need to operate according to standardized, and therefore in a certain measure conventional, methods.

Four elements to be specified:

1. the tracer to be considered;
2. the method of making random measurements or taking samples;
3. the place where such measurements or samples are to be taken;
4. *the definition in statistical terms of the dilution value assigned.*

1. As to the tracer, use can be made of natural tracers (inner tracers) such as salinity, phosphates, ammonia and silicates. The advantage of natural tracers is that, as in any control relating to sea pollution, a method favouring frequency of controls, that is, one which is simple and inexpensive, is to be preferred.

Natural tracers allow the determination with adequate reliability of dilutions of the order of 1:200 - 1:300, thus covering a large part of the range of values of the initial dilution process that is of practical interest.

More accurate results can be obtained by using radioactive tracers, but this requires expert personnel and special instruments; such methods have been used for some time in, for example, Denmark. The use of fluorescent tracers for these purposes has disadvantages relating to the high absorption of the tracers by the suspended particles generally contained in discharge waters.

2. Since the sewage field immediately downstream of the initial dilution process does not have characteristics of absolute homogeneity, it is opportune that the sampling should not be instantaneous but continuous over a period which could be conventionally established as being of the order of 30-120 sec.

This problem does not relate to salinity measurements by means of a salinometer since the response time of that instrument is of the order of some tens of seconds.

3. It would be opportune for the measurement of the degree of initial dilution to be made, for precautionary reasons, in the most unfavourable conditions. These conditions are found in the liquid zone downstream of the diffuser in the direction of the current. When the sewage field is on the surface (which can be ascertained by inserting coloured tracers into the pipeline), the sampling could be made on the surface, at a certain distance from the diffuser (to ensure that the rise of the jet has occurred) and, as has been said, downstream of the diffuser in the direction of the current.

In the case of submerged jets, the depth of the sewage field can be investigated by means of salinity - measurement probes, which also serve to establish directly the degree of initial dilution achieved.

The sampling distance should be such as to fall outside the initial mixing zone; it could be established conventionally as a function of the depth of the discharge, a multiple of the same. For example, the regulations could establish that measurements and samples serving to establish the minimum degree of initial dilution be taken downstream of the diffuser (in the direction of the marine current) at different depths and at a distance from it of 2-4 times the depth of the diffuser.

4. The regulations could establish a necessary degree of initial dilution without establishing an absolute value but by means of an indication in statistical terms.

The use of average values is recommended because, if samples are taken outside the zones of maximum concentration or outside the area of the jet, it is possible to obtain values apparently referring to the initial dilution (ratios of 1:1000 and over) which do not correspond to the real situation and which also unduly affect the average. It would seem more opportune to require that the minimum degree of dilution be, for example, in 95% of the cases over 1:80 (this value is given as an example, but it also has a certain practical importance in that it is often possible, in an economic sense, to achieve this value). The percentage specified (95%) takes into account the possibility of errors in the determination of the concentration of the tracer.

5.2.9 Relevance Of Initial Dilution Phenomena In The Laws And In The Practices Of Various Countries

This subject will, naturally, be treated in a following section (concerned with the capacity of the marine environment to absorb discharges without harmful effects); it may nonetheless be of some interest, in the final part of this chapter, to refer to the role played by the phenomenon of initial dilution in the practices and regulations concerning protection of the marine environment of the various countries which have for some time occupied themselves with the problem of marine pollution.

In some Mediterranean countries (France, Yugoslavia, Israel) directives (which in some cases establish standard values) have been formulated with regard to the quality of the receiving waters in relation to the uses made of them; one can mention the French "guide numbers" with regard to waters used for bathing or mussel cultivations, and the criteria introduced in Israel and Yugoslavia with regard to the various uses that may be made of the receiving waters.

Many of these "guide numbers" or criteria can be achieved even in proximity to the discharge point by means of adequate diffusers or treatment (or pretreatment) on land.

In France a number of authoritative directives establish that, in view of the limitation of purification treatment, the processes of dilution and dispersion (resulting from the use of long discharge pipelines) should be exploited in order to safeguard the coastal waters in an adequate manner; these directives, at the same time, point out that it is opportune to subject sewage, before discharge, to suitable forms of treatment.

In Yugoslavia, in addition to protection of the marine waters in terms of respect of criteria of quality in relation to the various uses, the sanitation of the coastal zones is very suitably provided for not in terms of the single discharges, but on the basis of regional sanitation plans which foresee the construction of long collectors, the carrying out of primary treatments, the construction of underwater pipelines and, in addition to these aspects particularly relevant to the disposal of sewage, various other solutions of the town-planning type which reflect a careful system of territorial planning.

In Israel the criteria as regards standards and intervention are very similar to the Yugoslavian; with regard, in particular, to the exploitation of phenomena of dilution. Apart from having as their purpose, in a manner appropriate to the various cases, the respect of certain standards with regard to the receiving waters, they also furnish particular numerical specifications. For example, in certain zones used for recreational purposes, it is required that the minimum degree of total dilution of all used waters must be at least 1:1000 (a dilution including initial dilution and also subsequent, or second-phase dilution).

In Spain some regulations of considerable practical interest relate precisely to the characteristics of works for off-shore disposal and dispersion; various hypotheses with regard to treatment on land (simple pre-treatment, primary treatment, biological-chemical treatment) are taken into consideration and, in relation to these hypotheses, various minimum values of initial dilution (from 1:40 to 1:80) are required.

In Venezuela, too, detailed technical standards have been developed which relate to the modalities of construction of the diffusers and the degree of dilution to be obtained, in relation to the characteristics of the discharge waters and the uses of the coastal waters.

In Norway the Government Commission for Resources entrusted the Institute for Research for Norwegian Waters with the task of preparing a guide or "Code of Practice" with regard to the disposal of waste waters; this text contains indications concerning the physical and engineering aspects of the problem, and also concerning the appropriate analytical formulations and environmental data necessary for the development of the various calculations. Suggestions are also provided concerning the most suitable modalities for construction of underwater pipelines and diffusers.

A reference can also be made to the USSR, where the objectives of the policy of protection of the coastal waters are to ensure the particular quality of the waters in accordance with the characteristic uses in the various zones. To achieve these objectives, the evaluation, case by case, of the most suitable degree of treatment of sewage, length of discharge pipeline and diffuser, are foreseen. The final choice is guided by an optimization procedure which has as its objective a certain level of environmental quality and a minimum cost.

In general it can be said that even a respect of a colimetric limit requires, as far as rational solutions are concerned (and the massive chlorination of effluent discharged on the shore cannot be considered one of them), the utilization of the process of initial dilution.

In fact, respect of a certain colimetric standard in the coastal waters can be achieved by means of a suitable combination of treatment on land and utilization of the phenomena of dilution, dispersion and extinction at sea; this combination may be established by means of certain optimization procedures which, for example, have repeatedly been adopted in Denmark.

A procedure developed by the "Danish Isotope Centre" makes it possible to choose, with a certain logical justification, an optimum combination of purification treatment, length of pipeline and length of diffuser; this is a graphic procedure which will be referred to again later.

Nearly all the countries bordering on to the sea have adopted colimetric standards with regard to their coastal waters; it can therefore be said that in all these cases the respect of the limit implies a certain utilization of the phenomena of initial dilution and dispersion (as well of the phenomenon of extinction and removal by means of purification treatments on land).

In fact this possibility becomes purely theoretical where the standards concerning the effluent are so extreme as to prohibit in practice, for economic reasons, even the realization of an underwater pipeline; in that case the respect of the colimetric standard can be achieved only by means of purification processes of the chlorination type (and, it is to be hoped, dechlorination of the effluent), and the phenomena of dilution and dispersion are not even considered.

A region where the problem of marine pollution has been faced with a certain seriousness is California. The discharge waters, apart from having to respect certain standards as to the effluent, must be subject to a minimum ratio of initial dilution of 1:50 or, in any case, to a dilution ratio such as to permit respect of the restrictive standards applied with regard to the receiving waters in order to safeguard aquatic life.

Great Britain represents a particular case; the problem of marine pollution has received a great deal of attention and has long been dealt with in a rational manner, in accordance with the careful policy with regard to the protection of waters which has been characteristic of that country for many years.

In practice, urban sewage in Great Britain is disposed of, in most cases, by discharge, after appropriate pre-treatment, by means of a diffuser and at a suitable distance from the shore. The most suitable degree of initial dilution is determined with regard primarily to requisites of an aesthetic nature, in the sense that, the closer the discharge is to the shore, the greater is the degree of initial dilution required to maintain the water used for bathing or recreation in general in a satisfactory aesthetic condition.

In addition to other requisites of a chemical nature, it would appear, in any case, that this objective (to render the sea waters unexceptional from an aesthetic point of view) merits some priority in the context of the Mediterranean, where, in most localities, the high degree of transparency of the waters is one of the most important tourist attractions.

5.3 DISPERSION CHARACTERISTICS

5.3.1 General Remarks Concerning Dispersion Of Wastes In The Sea: (a. Initial Dilution - Subsequent Dilution; b. Dispersion Models)

The preceding paragraphs indicate that the focal point of the control of marine pollution, as far as the quality of the receiving waters and the protection of aquatic life are concerned, corresponds to the zone surrounding the discharge points, excluding the zone of initial mixing.

The reasons for favouring this solution, which is adequately suitable for representing the characteristics of the environment in terms of capacity to absorb a certain load of pollution, and at the same time sufficiently simple for widespread application, have already been set forth; nevertheless, both under the aspect of environmental effects and under that of practical application of systems of regulation, due importance should be attributed to the processes of dispersion of the effluent outside the initial mixing zone.

It is, in fact, important to know what further measure of protection can be assigned to certain marine zones which are particularly delicate as regards environmental requirements (reproduction zones, marine parks, mussel cultivations, coastal zones in general). This further measure of protection is provided by the phenomena of transformation of various substances in the marine environment.

At the same time the respect of a certain level of quality in the proximity of a discharge point depends on a knowledge of the basic level of the contaminants; this knowledge is acquired most efficaciously by means of direct measurement, where it is wished to ascertain the effects of already existing discharges, or, where it is a question of forecasting the effect of future discharges, by applying more or less approximative prediction methods. The techniques of foreseeing phenomena of transport and subsequent dilution are thus strictly relevant to the theme considered (regulatory aspects), quite apart from their fundamental importance under the aspect of environmental effects.

The question has been the subject of extensive technical literature and treatment in some cases of great complexity, but often the hypotheses assumed have shown a poor capacity to represent the practical manifestation of the phenomenon to enable the use of certain algorithms.

It can therefore be affirmed right from the start that, when it is not considered opportune to rely on approximative evaluation of a strongly precautionary character, probably the most suitable way of predicting the phenomenon is by simulating it with the use of tracers (and seeking to reproduce conditions as similar as possible to the real future conditions: these could be governed, among other factors, by an appreciable difference of density between the mixing field and the surrounding sea waters).

It can be said that the methods of prediction of dispersion phenomena develop along two fundamental lines:

a. by means of a knowledge of the process of initial dilution, the depth and dimensions of the sewage field formed outside the zone of diffusion is evaluated; the trend of the concentrations inside this field is expressed as a function of the drifting time (or of the distance, given a certain speed), of the initial dimensions and depth of the sewage field, of the value of the coefficients of eddy diffusion and, in particular, of their trend as a function of the spatial scale of the phenomenon.

To this type of schematization belong also those methods of prediction that involve the creation of patches (volumes of sea water marked with fluorescent or radioactive tracers) whose movements are followed over a period of time and the concentrations within the patches continuously recorded.

b. Dispersion models. Where a fairly large scale study is to be made of the simultaneous effects of several discharges, a prediction procedure based on mathematical dispersion models may be applied.

These models also make it possible to predict the average distributions of the various contaminants in the long term. As in the preceding scheme, use is made, as parameters controlling the phenomenon, of the coefficients of eddy diffusion and current-gauge data, as well as of suitable expressions that take into account certain biochemical and biological phenomena relating to the extinction of certain parameters (bacteria) or the absorption of others (e.g. nutrients).

Although, in the future, great efforts should be made to render such models more widely applicable, their practical use today is impeded by the laboriousness of the oceanographic surveys necessary to obtain the basic physical data; usually predictions of the effects of a sea discharge have been formulated using the first of the two systems indicated, that is, by supposing that a marine current of particular intensity is running from the discharge point to the zone under study. In addition to its great simplicity, this system of prediction generally leads to the evaluation of the maximum pollution conditions and thus provides a more precautionary criterion than a more complex system serving to determine the average conditions.

5.3.2 Mechanism Of Advection And Subsequent Dilution

The phenomena of transport and subsequent dilution are sometimes given the comprehensive name of dispersion. It has already been pointed out that there is a certain arbitrariness in the distinction between the two types of phenomenon owing to the fact that the circulation of sea waters may be considered as deriving from the superimposition of various vorticose movements of different scales; generally, movements on a relatively large scale compared with the dimensions of the sewage field are considered as transport, while turbulent movements comparable to or smaller than the size of the field are considered as phenomena of eddy diffusion, which bring about the progressive dilution of the field in a vertical and horizontal direction.

The coefficient of eddy diffusion is expressed as a length squared divided by the time. The coefficient of eddy diffusion essentially expresses the intensity of the mixing processes in a certain sea zone; the more intense these natural mixing processes, the faster is the dispersion of substances or properties initially more concentrated in a certain volume.

In studying the phenomena of eddy diffusion that affect the sewage field during its movement away from the discharge point, it is possible to formulate various hypotheses concerning the trend of the coefficient of eddy diffusion: it may be considered constant, or increasing in a linear manner with the increase of the dimensions of the sewage field, or increasing at a greater speed (the dimensions elevated to the power of 4/3).

The various hypotheses considered may be verified in one sea zone and not in another; they imply, in any case, a different speed of expansion of the sewage field, which is greatest in the last hypothesis (proportional to the size of the sewage field elevated to the power of 4/3), and slowest in the case of the first hypotheses.

It is not the intention here to recapitulate the extensive technical literature available, but to draw attention to the salient aspects of the phenomenon and to methods of calculation of particular relevance.

However, it is considered useful to give in Tables 25 and 26 a summary of the information presently available (and of what is required of future surveys) relating to the prediction of phenomena of dispersion in the sea; this summary was prepared eight years ago for the National Academy of Engineering on the proposal of the Federal Water Quality Administration of the United States.

As can be seen, though some technical data of considerable importance for purposes of prediction are available, there is much that still remains to be ascertained, which makes it advisable, where systems of regulation and verification are concerned, to proceed with a certain caution, and even to give preference, with regard to methods of calculation, to those which may be more approximative but offer more assurance of being on the safe side.

5.3.3 Influence Of Advection And Subsequent Dilution On The Spreading Of Pollutants

The subject has already been considered in the more general context of the benefits and limitations of utilization of the phenomena of dilution and dispersion for protection of sea water against polluting discharges.

It can be said that the main interest of the phenomena of dispersion and subsequent dilution lies in the fact that they make it possible to provide zones, according to their distance from the discharge zone, with a measure of protection greater than in the discharge zone; this occurs by means of the two typical processes denominated by the term "dispersion". The process of transport essentially depends on the trend

Table 25 Priorities and estimated initial minimum effort for research and investigation of physical processes and interaction, (93).

Recommended research and investigation	Estimated minimum total effort (*) (man-years)	Priority	Completion Time
Initial dilution and diffuser design	37		
Buoyant jet diffusion		B	S
Waste fields		B	S
Barge dumping of sludge		A	S
Thermal waste		B	S
Flow patterns		A	L
Physical processes in estuaries	185		
Quantitative prediction models		A	L
Hydrodynamics		B	L
Estuary transitions		A	S
Biological and chemical processes		A	L
Turbulence processes		A	S
Turbulent (eddy)flux studies	72		
Observational studies		A	S
Prediction models		A	S
Subsurface tracer experiments		B	S
Physical processes in coastal areas	360		
Data collection		A	L
Intermediate-scale current patterns		A	S
Large-scale exchange processes		B	S
Decay of non-conservative constituents as related to physical factors	20	A	S
Interactions between floatable and settleable components of wastes and physical factors	46		
Character of floatables		A	S
Mechanisms of transport		B	S
Reduction of surface concentration		B	S
Case studies		A	L

(*) Total effort for this programme area is 720 man-years.

"S" is short term (less than 5 years).

"L" is long term (less than 10 years).

Table 26 Status of information on jet and plume mixing, (93).

Type of discharge and environment	Point source	Line or slot source or multiport diffuser
Continuous discharge in uniform environment	A	A
Simple buoyant plume	A	A
Submerged buoyant jet, horizontal (or sinking jet)	A	B
Submerged buoyant jet, directed upward (or sinking jet directed downward)	A	B
Submerged sinking jet directed upward (or buoyant jet downward)	B	B
Surface buoyant jet (e.g. hot water)	B	-
Continuous discharge in stratified environment		
Simple buoyant plume in linearly stratified environment	A	B
Simple buoyant plume is irregularly stratified environment	C	C
Horizontal, inclined, or vertical (upward) buoyant jet in linearly stratified environment	A	B
Horizontal, inclined, or vertical (upward) buoyant jet in irregularly stratified environment	B	C
Downward (inclined or vertical) buoyant jet in linear or irregularly stratified environment	C	C
Continuous discharge in ambient currents		
Buoyant jet, vertical into uniform current	A	C
Buoyant jet, transverse into a current (uniform or stratified) (surface or subsurface discharge)	C	C
Sudden and unsteady release (as from barges)		
All cases	C	C

"A" indicates that good hydrodynamic models have been developed for gross behaviour, and have been checked by experiments; future research is needed only to clarify details of velocity and concentration profiles and to determine more reliable entrainment or spreading coefficients.

"B" indicates that hydrodynamic models have been proposed but not checked adequately by experiment; future research should include such laboratory experiments and revision of models as required.

"C" indicates that both theory and experiments are lacking. In all cases, good field observations have been extremely sparse and are vitally needed.

(Lagrandian) of the marine currents in a zone: the exposure of a certain zone to a discharge made in a certain place may be greater or lesser according to whether the trend of the currents is more or less favourable.

In any case, in comparison with the conditions considered in the classic verification calculations (which assume a continuous transport from the discharge point to a similar zone in particularly fast and constant conditions of current), the average conditions (or, better, the integral which most appropriately expresses the exposure to the discharge) are considerably inferior, owing to the fact that the currents do not always run in the same direction and, as a rule, do not follow a rectilinear course.

It often happens that the trend of the currents is prevalently parallel to the shore; in this case the direct action of the discharge on the coastal localities is not very frequent and it is in this that the main benefit of the phenomena of mass transport lies.

As to the importance of phenomena of eddy diffusion, as has already been said and will be more specifically illustrated later in this chapter, these phenomena cause an increase, generally not more than two- to five-fold, of the total dilution, compared with the initial value in the zone proximate to the discharge.

Despite the relative modesty of this increase, it is nevertheless important because it increases initial concentrations of the order of 1:100 - 300 to values of 1:1000 and over in distances comparable to the length of the pipeline; such values are practically impossible to achieve by means of simple initial dilution.

As to the limitations of the dispersion phenomena, it should be pointed out that, were it not for the contemporaneous phenomena of assimilation, phase transfer (particularly from the liquid phase to particles in suspension), and sedimentation, the body of physical processes mentioned above, dispersion included, would not protect the Mediterranean waters in any manner against their progressive pollution, and would merely retard the increase of pollution in the coastal zones. These prospects (even though not in absolute terms, for all contaminants, apart from possible accumulation phenomena, are also subject to phenomena of progressive extinction in the marine environment) must be borne in mind not only with regard to the substances of Group I but also, in some degree, with regard to the removal of the total quantity discharged of certain substances of Group II; for example, some heavy metals, listed in Group II, though they do not affect the contamination of the Mediterranean as a whole, may pollute coastal zones on a larger scale than is the case of e.g. phenomena of bacterial pollution, and with much greater characteristics of persistence. In this respect, and with regard to such substances, the adoption of standards with regard to the receiving waters should be appropriately accompanied by measures (among which that of control at source is of fundamental importance) serving to reduce the total quantities discharged.

For these reasons it is advisable that, where substances of Group II with characteristics of greater persistence are concerned, a systematic survey of the quality of the sea water in the various discharge zones should be carried out in order to ascertain experimentally that the capacity of disposal and dispersion of those substances is not exceeded.

Such surveys could be more frequent when considerable changes occur in the discharge situation and subsequently could be carried out at certain intervals.

5.3.4 Dependence Of Advection And Subsequent Dilution Phenomena On Initial Dilution

The process of initial dilution has a greater influence on the trend of the phenomena of subsequent dilution than on the phenomena of transport proper (which are determined by the trend of the marine currents in the zone).

In fact, the occurrence, or otherwise, of phenomena of entrapment of the jet depends on the degree of initial dilution and the vertical density distribution of the sea waters; since the trend of the surface currents is generally considerably different from that of the currents in the deeper layers, even the transport phenomena that determine the movement of the sewage field away from the discharge zone are somehow correlative to the level of entrapment and thus to the particular process of initial dilution.

With regard to the development of the phenomena of subsequent dilution, connected, as has been said, with the turbulence naturally present in the marine environment, the modalities of the process of initial dilution have an important influence in relation to two fundamental factors:

- the dimension of the diffuser, and thus of the sewage field
- the density of the mixture that constitutes the sewage field.

In fact, the larger the sewage field, the slower is the phenomenon of eddy diffusion: a low degree of initial dilution (below 1:60 - 1:80 in the case of the Mediterranean) leads to the formation of a sewage field which is markedly stratified in comparison with the sea waters below and is therefore subject to a retarded process of turbulent dilution in a vertical direction. The vorticose movements on which it should depend are in fact attenuated as a result of the need to transport heavier waters upwards and lighter waters downwards, which leads to the loss of much turbulent energy.

In the following paragraphs are set forth a number of analytical formulations that correlate the extent of the process of eddy diffusion to the dimensions of the sewage field and to the vertical and horizontal coefficient of eddy diffusion.

In general it can be said that a high degree of initial dilution along an open coastline is in itself a favourable factor also with regard to the degree of total dilution (turbulent dilution + subsequent dilution) of the sewage field as its distances from the discharge point progressively increases.

With regard to transport movements in the deeper layers, it can be said that, especially where movements towards the shore are concerned, in general they constitute situations less critical than those of surface currents, in that they are less fast. However, the coefficients of eddy diffusion relating to the deeper layers would be lower than those of the surface layers.

The phenomenon of entrapment of the jets, to which a high degree of initial dilution thus contributes, is in some ways favourable and in others unfavourable to the development of subsequent dilution.

However, when the main problem concerns the respect of a certain colimetric standard in the coastal waters, a considerable increase of the drifting time (with which the dimensions of the phenomena of bacterial extinction is associated) is certainly much more important than a reduction of the extent of the process of subsequent dilution. Under this aspect, therefore, a high degree of initial dilution is still advantageous.

5.3.5 Evaluation And Relevance Of Subsequent Dilution

A very simple prediction technique is proposed by Fischer, (42). With reference to the scheme in Figure 32:

b = width of the diffuser;

b_1 = the projection of the diffuser from the perpendicular of the direction of the speed of the marine current;

l = the distance between the diffuser and a certain section down stream of the same where it is wished to evaluate the degree of subsequent (and thus of total) dilution obtained.

In the hypotheses that the field widens at an angle of 5° on either side (a total of 10°), the width of the sewage field at the distance "l" will be:

$$b'_l = b_l + 0.15\ l$$

This evaluation takes into account the dispersion only in a horizontal direction (which tends to widen the sewage field) and ignores dilution in vertical direction, which is important especially when the discharge is made in deep waters, in the presence of a high speed of current above a long diffuser. In this case the thickness of the initial sewage field is smaller (1/3, 1/4 or even less) in comparison with the total depth: at the same time, the high degree of initial dilution achieved permits, in the absence of natural density stratifications, a good development of eddy diffusion in a vertical direction.

In any case the expression in question is of interest not only on account of its simplicity and precautionary character, but also because, as the author pointed out, the final results do not differ much from theoretical and/or experimental results obtained in a more accurate or complicated way by other authors, (26; 28; 60).

A method of calculation traditionally used in engineering calculations utilizes some of the developments introduced by Brooks, (26), which are briefly illustrated.

The schematic diagram given in Figure 33 also corresponds to a sewage field expanding in a horizontal direction and once again the phenomenon of eddy diffusion in a vertical direction, with the limitations pointed out above, is ignored.

The fundamental hypotheses on which Brooks' developments are founded are, in fact, that mixing in a vertical direction is negligible, as also is mixing in a longitudal direction (this mixing tends to concern volumes discharged at different times and which, at a given moment, are accordingly at different distances from the diffuser).

Other hypotheses concern the applicability of a law of diffusion with a variable coefficient of eddy diffusion that essentially depends on the width of the sewage field (which, in turn, depends in the distance from the source).

In the scheme in Figure 33:

b and bl are coincidents (the initial width of the sewage field coincides with the length of the diffuser);

u = speed of marine currents;

L = width of the sewage field at the distance "x";

x = the distance, measured along the axis, of the source (diffuser);

$t = \frac{x}{U}$ = the drifting time

Brooks provides some expressions which permit the calculation both of the width of the sewage field (as a function either of the co-ordinate or of the drifting time t (t = x/U) and of the degree of dilution along the axis outside the field; these expressions differ according to the various hypotheses that can be formulated with regard to the trend of the transversal coefficient of eddy diffusion "e". This last may in fact, be considered constant,

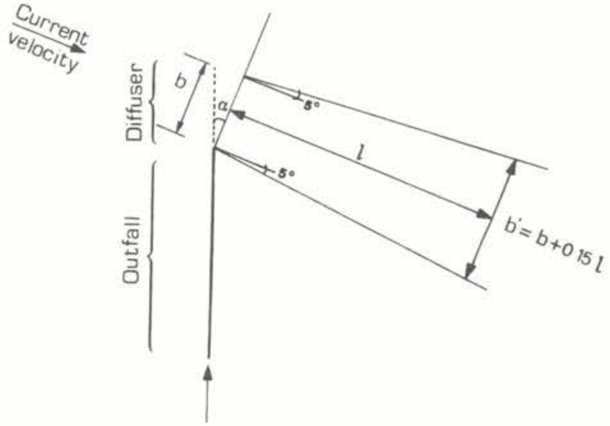


Figure 32 Effective width (b') of the sewage field or plume formed by a multiport diffuser; a simple evaluation, (42).

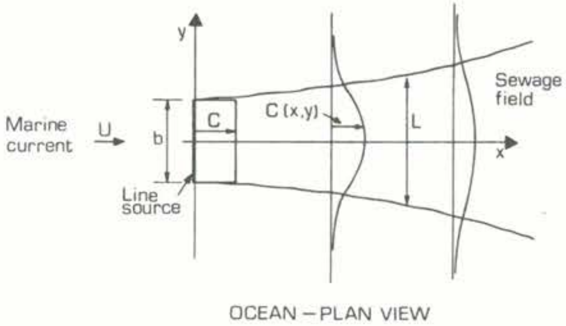


Figure 33 Schematic diagram of sewage field diffusing laterally in an ocean current (die-off not considered, (26).

b = length of diffuser

a) $\varepsilon = \varepsilon_o$ initial value (downstream of the diffuser) for L = b

b $\varepsilon / \varepsilon_o = \frac{L}{b}$

c) $\varepsilon / \varepsilon_o = \left(\frac{L}{b}\right)^{4/3}$

or may be considered variable in linear proportion to the width L, or, as suggested by Pearson, variable as a function of the width elevated to the 4/3rd power.

As regards the trend of maximum concentrations along the axis, the following expressions therefore apply:

a) $\varepsilon = \varepsilon_o$

$$C_{max}(x) = Co \cdot \text{erf} \sqrt{\frac{3}{4\,\beta\,\,x/b}}$$

b) $\varepsilon / \varepsilon_o = L/b$

$$C_{max}(x) = Co \cdot \text{erf} \sqrt{\frac{3/2}{(1+\beta\,\frac{x}{b})^2 - 1}}$$

c) $\varepsilon / \varepsilon_o = (L/b)^{4/3}$

$$C_{max}(x) = Co \cdot \text{erf} \sqrt{\frac{3/2}{(1+\,2/3\,\beta\,\,x/b)^3 - 1}}$$

where:

$$\text{erf}\ x = \frac{2}{\sqrt{\pi}} \int_o^x e^{-}\,v^2\ .\ dv$$

$$\beta = \frac{12\ \varepsilon_o}{U\ b}$$

The symbol erf represents the classic Gaussian function (the Standard Error Function); the term β can be obtained from the speed of the current, the initial width of the sewage field "b", and the initial value of the coefficient of eddy diffusion; the initial value of the coefficient of eddy diffusion in the hypotheses of proportionality to the scale of the phenomenon elevated to the 4/3rd power may be obtained from Figure 34. For example, for an initial width of the sewage field (b=L) of 10^4 cm, one obtains $\varepsilon_o=2 \times 10^3\ cm^2/s$.

Even without applying these formulas, the graph in Figure 35 permits a direct evaluation in function of the parameter $\beta\ \frac{x}{b}$ since

$$\beta = \frac{12\ \varepsilon o}{Ub}\ \ ;\ \ \beta = \frac{x}{b} = \frac{12\ \varepsilon o\ \cdot\ x}{Ub\ \cdot\ b} = \frac{12\ \varepsilon o}{b^2}\ .\ t$$

and, as a function of the drifting time "t", the degree of subsequent dilution predictable by applying Brooks's expression.

An applicable graph substantially equivalent to the one in Figure 35, and even simpler, is shown in Figure 37, which provides directly, as a function of the initial width of the sewage field (bl), the predictable degree of subsequent dilution, on the hypotheses that the coefficient of eddy diffusion is proportional to the scale of the width. This graph was proposed by Lawrence, (144).

As has already been said, Brooks, (26), has provided a number of expressions permitting the evaluation of the width acquired by the sewage field with progressively increasing distance from the source; these expressions are given below and are represented in Figure 36, which allows an immediate evaluation of the width "L" as a function of the distance from the source "x" or of the drifting time "t".

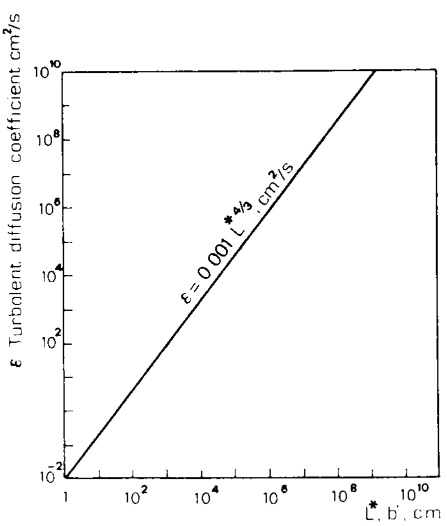


Figure 34 Variation in eddy diffusivity ε , and scale of diffusion phenomena, (108).

L* = effective width of the sewage field

b' = effective width of the sewage field at the point of discharge (b' = b = length of diffuser for current velocity normal to diffuser axis)

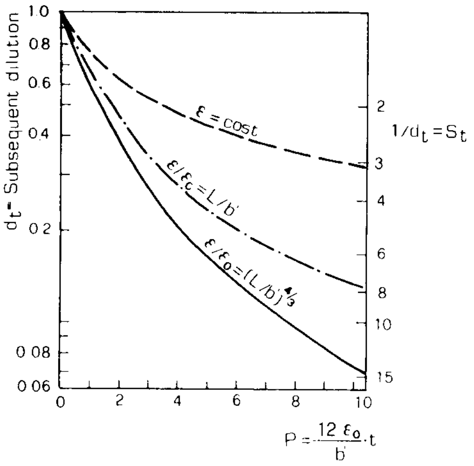


Figure 35 Evaluation of subsequent dilution as function of time "t" (following the development of sewage field) in different hypotheses about ε (turbulent diffusion coefficient, (26).

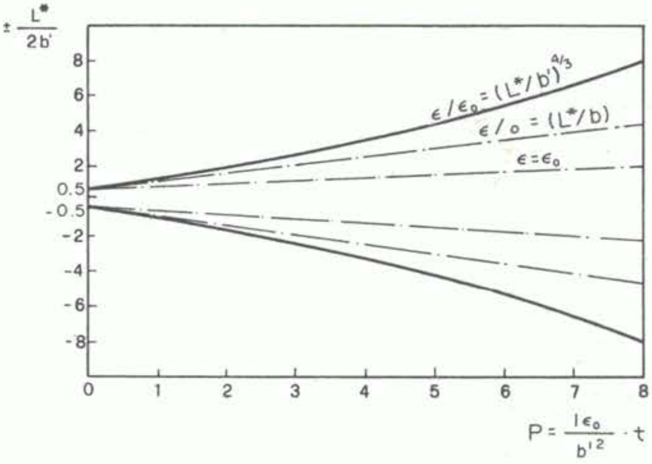


Figure 36 Relative half-width of the sewage field (L*/2b') in different hypotheses about ε (diffusion coefficient) and as function of time, (26).

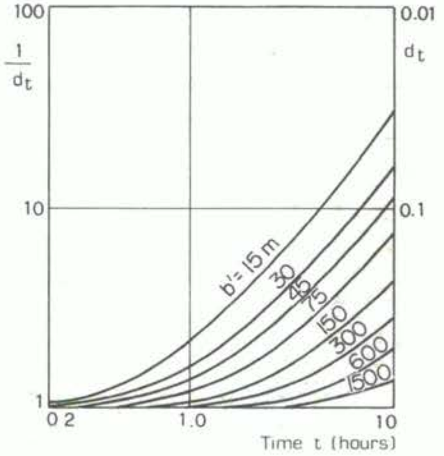


Figure 37 Graph for an approximate evaluation of subsequent dilution as function of time "t" (following the development of the sewage field) in the $\varepsilon \propto L^{4/3}$ hypotheses (prudential evaluation), (144).

a) $\varepsilon = \varepsilon_o$; $L/b = (1 + 2 \beta x/b)^{1/2}$

b) $\varepsilon / \varepsilon_o = L/b$; $L/b = 1 + \beta x/b$

c) $\varepsilon / \varepsilon_o = (L/b)^{4/3}$; $L/b = (1+2/3 \beta x/b)^{3/2}$

where

$$= \frac{12\ \varepsilon\ o}{U\ b}; \quad x = U\ t$$

A treatment which takes into account the diffusion process in a vertical as well as in a horizontal direction have been developed by a number of authors; here some expressions developed by Foxworthy are illustrated.

According to this author if:

C_o = the initial concentration, in correspondence the central axis of the sewage field (or plume);

x = the distance from the diffuser, measured in the direction of the marine current and along the central axis of the field;

σ_{yo} = the lateral variance of the waste concentration distribution at the origin of the plume (the initial standard deviation of the concentrations of the substances considered, in the initial part of the sewage field, along a transversal section);

σ_{zo} = the vertical variance of the waste concentration distribution at the origin of the plume;

ε_y = the coefficient of horizontal eddy diffusion;

ε_z = the coefficient of vertical eddy diffusion;

U = the speed of the current.

$$C = \frac{C_o}{\left(\frac{2\,\varepsilon y \cdot x}{\mu\,\sigma^2_{yo}} + 1\right)^{1/2} \cdot \left(\frac{2\,\varepsilon\,z \cdot x}{\mu \cdot \sigma^2_{zo}}\right)^{1/2}}$$

σ_{yo} and σ_{zo} are correlated by Foxworthy with the initial dimensions of the sewage field, deducing from the continuity equation:

$$\sigma_{zo} = \frac{So \cdot Q}{4\,\pi\,U \cdot \sigma_{yo}}$$

where:

Q = volume of the discharge;

So = degree of initial dilution;

σ_{yo}, is deduced from $\sigma_{yo} = 0{,}16\ b.U^{-1{,}29}$ (in feet);

$\varepsilon\ y$, can be expressed as a function of the horizontal scale (width of the sewage field, equal to $4 \cdot \sigma_y$) as already said: $\varepsilon_y \sigma (4\sigma_y)^{4/3}$

$\varepsilon\ z$, is correlated by Foxworthy with the action of the wind:

$\varepsilon_{zo} = 3{,}6 \cdot 10^{-6} . w^{2{,}48}$ (in feet), for w (speed of wind) between 3 and 30 feet/sec (0,91 - 9,1 m/s)

Using the same expression but starting from experimental data obtained by measuring the concentrations inside a sewage field produced by a diffuser or temporary source, it is possible to deduct the horizontal and vertical coefficients of eddy diffusion.

Thus, analagous formula are available for predicting subsequent dilution in volumes of water created by discontinuous discharges; the dimensions progressively acquired by the patch in time, the values of S, the progressive diminution of concentration in the centre, are here again expressed as function of the coefficient of horizontal, and possibly also vertical, eddy diffusion. This opens the possibility of carrying out experiments with regard to this coefficient using discontinuous discharges instead of a continuous source. Costs being equal, the results of experiments with patches of considerable dimensions are more reliable than those obtained with regard to plumes of dimensions much smaller than those of discharge it is wished to simulate.

Diackisin, (79), Neuman and Pearson (1966) have carried out an extensive examination of methods, even of practical applications, permitting the experimental evaluation of these coefficients.

It has been said that the vertical coefficient of eddy diffusion seems to depend to a considerable degree, at least in the surface layers, on the action of the wind; it is therefore understandable that measurements made in different wind conditions give rise to different results.

Even the coefficient of horizontal eddy diffusion generally varies according to the moment of the measurement, and the marine currents are likewise variable.

It is therefore considered opportune, in the event of having to choose between a few accurate measurements and numerous more approximative measurements, to opt for the second alternative as the one providing a more adequate representation of the phenomenon.

In this regard, it will be remembered that, from the degree of dispersion of drift cards, it is possible to arrive at an evaluation of the coefficients of eddy diffusion (horizontal, obviously); this is naturally an average value referring to the path followed by the drift card from the moment of introduction till their arrival at the shore.

It has already been said that the speed of expansion of a path or of a field (or plume) created by continuous discharge depends on the intensity of the horizontal mixing movement, that is, on the magnitude of the coefficient of horizontal eddy diffusion.

According to an expression which it would appear was first resolved by Einstein:

$$\frac{d\sigma^2}{dt} = 2\,\varepsilon$$

therefore:

$$\sigma = \sqrt{2\,\varepsilon\,t}$$

where:

ε = the coefficient of horizontal diffusion;

σ = the standard deviation characteristic of the distribution of concentration in a direction transversal to the plume.

With reference to Figure 38, the sections A and B of the sewage field, or plume, downstream of a diffuser are considered.

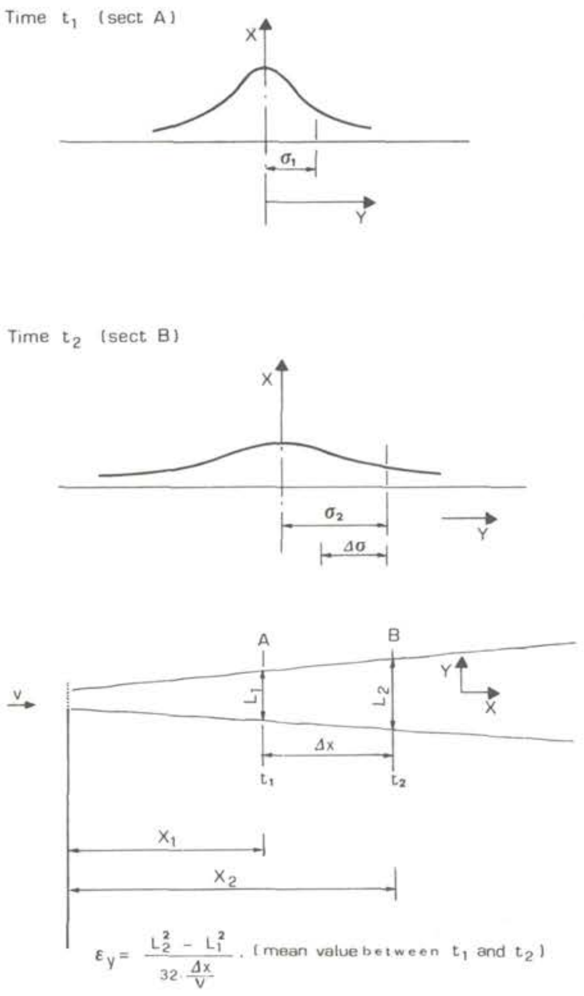


Figure 38 A simple evaluation of horizontal eddy diffusivity from the width of the sewage field at different times, (108).

In the section closer to the source (section A), the distribution of the concentrations of the various substances discharged can be represented by a Gaussian curve characterized by a small value of σ , σ_1 (in fact experimental findings reveal that the trend of the concentrations in the interior of that zone is rather irregular, even though, in its major features, it is comparable to the scheme presented). In the section B, which is at a distance of Δx from section A, the distribution of concentrations is flatter than in the other section in consequence of horizontal mixing; σ_1 is thus greater than σ_2. Knowing that the speed V of the marine current links the time $t_2 - t_1$ to the distance $x_2 - x_1$, it is possible to obtain a very simple expression of the coefficient of eddy diffusion:

$$\varepsilon = \frac{\sigma_2^2 - \sigma_1^2}{2\,(t_2 - t_1)}\ ) ;$$

An equivalent and more intuitive expression was proposed by Gunnerson:

$$\varepsilon = \frac{L_2^2 - L_1^2}{32 \cdot \triangle x/v}$$

(the width of the sewage field is assumed to be equal to 4 times the value of the standard deviation).

A particularly interesting possibility with regard to the prediction of dispersion phenomena affecting future effluents consists of the formation of considerable volumes of sea water marked with a radioactive (or fluorescent) tracer (*) without, however, seeking from the trend in time of the concentrations in these volumes, to arrive at the evaluation of the coefficients of eddy diffusion, which are used to predict the rapidity of mixing phenomena concerning a field deriving from a future continuous source. In a more direct manner one imagines that a continuous discharge is the result of an uninterrupted succession of discontinuous discharge, similar to the one used for experimental purposes.

As has been mentioned, the method has been adopted in numerous practical cases by the Danish Isotope Centre.

An advantage of this technique lies in the fact that the movement of duly marked volumes of considerable size provides a better representation of the trend of the currents than a single patch (this on account of the natural turbulence present in the sea waters, in consequence of which, for example, three drogues crosses introduced into the water at the same time and in the same point will not follow the same course).

It is necessary, however, that such experimental tests using tracers be carried out a sufficient number of times and over a period sufficiently long to be statistically representative of the various current conditions characteristic of the zone. For this purpose, as will be explained later, the results of these tests with tracers can also be extrapolated in the various directions, in relation to the transport phenomena investigated, over an adequately long period of time and by means of a large number of tests (using simple Lagrangian measurements) with current drogues.

Brief description of the method. Graphically the discharge is represented in Figure 39c of the rectangular diagram (QCo = cost) between the times t_o (start of discharge) and $t_o + \triangle t$ (end of discharge).

It is supposed that a boat equipped with automatic equipment for analysis and recording follows the volume of water introduced measuring the concentrations C (t,x,y) in the various points of the polluted patch, in continuous expansion, transported by the current.

It will be possible in this way to learn the distribution of the concentrations at the times t_1, t_2 ... t_n and also to plot the curve C_B (t) (Figure 39b); this curve represents the trend of the detectable concentrations as time passes, at a fixed point B chosen from the various positions occupied at successive moments by the centre of the moving path (the centre of the patch corresponds to the least diluted zone).

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* The use of the radio-active tracers is more reliable and, if carried out in the appropriate manner, without appreciable risk.

An observer stationary at B* would therefore see the concentration of the tracing substance first increase and then diminish, as indicated by the curve CB (t); this curve obviously does not have a rectangular form, but it is straighter and rounded - by reasons of the phenomenon of longitudinal diffusion as the distance between B* and the position where the trial discharge took place increases.

It will now be asked what concentration C_{BR} there would be in normal conditions at the point B* if the discharge, instead of being confined to the interval of time Δt, had been carried out continuously.

A continuous discharge can be imagined as an uninterrupted succession (of discontinuous discharges, each of the duration of Δt. Each of these discharges gives rise to a patch that, it is admitted, is affected by the same dilution phenomena and therefore their C_B (t) diagrams at the point B* are the same and "staggered" in time by an interval of Δt. The point B* is thus trasversed at the same time by patches deriving from two or more of the elementary discharges that, it is imagined, compose the continuous discharge; the concentration C_{BR} is thus the result of the concomitant effect - or, more precisely, of the sum - of all the $C_{BR}(t)$ diagrams that concern the point B* at the same time.

Thus, by repeated drawing of the diagram $C_B(t)$ shifting it each time by a time of Δt along the time axis, it is possible to proceed directly to add up the ordinates read on the various diagrams in correspondence to an identical time t* in order to obtain C_{BR} (the value of C_{BR} must be, approximately, constant in time).

The same calculation can be carried out more rapidly by the following method: considering the instant t_1, $C_B(t_1)$ is the concentration induced, at the instant t_1 by the discharge between the times t_o and $t_o + \Delta t$; the concentration $C_B(t_1 + \Delta t)$ can be imagined as the concentration $C'_B(t_1)$ induced, always in the instant t_1, by a discharge between the times t_o and $t_o - \Delta t$. In the same way the concentration $C_B(t_1 - \Delta t)$ is equivalent to the concentration $C''_B(t_1)$ induced by a discharge between the times $t_o + \Delta t$ and $t_o + 2\Delta t$; the concentration $C_{BR}(t_1)$ is thus obtained b adding:

$$\bar{C}_{BR} = C_B(t_1) + C'_B(t_1) + C''_B(t_1) + C'''_B(t_1) + \dots$$

$$= C_B(t_1) + C_B(t_1 + \Delta t) + C_B(t_1 + 2\Delta t) + \dots$$

$$+ C_B(t_1 - \Delta t) + C_B(t_1 - 2\Delta t) + \dots$$

In other words, by sub-dividing the diagram $C_B(t)$ into Δt intervals and adding the average concentrations of the various intervals, one obtains the concentrations C_{BR} in normal conditions. More correctly

$$C_{BR} = \int_{-\infty}^{+\infty} C_B(t)\, d(t/\Delta t)$$

The criterion of elaboration set forth is certainly not above criticism; for example, it has been pointed out (Frankel 1966) that the hypothesis according to which each "stretch" or "polluted patch" would follow the same course is not always reliable, if one considers the often meandering, tortuous and unstable course of the marine currents. In consequence even the criterion of the superimposition of the effects described above would not always be equally valid. The errors thus made, however, are probably on the safe side, and this method, currently adopted for numerous routine surveys and not only off the coast of Denmark, would seem to be of great interest for applicative purposes.

It should be pointed out, finally, that as these discontinuous discharge tests

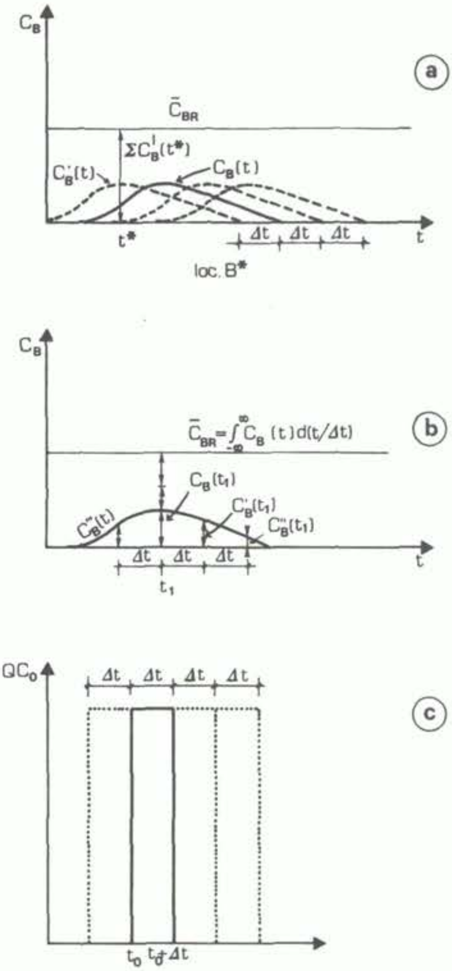

Figure 39 Time concentration curves for a steady discharge derived from experimental curves for single injections of tracer, (60).

cannot usually be continued over long periods, a certain extension of the results is required; this can be done by simply correlating the degree of dilution (that is the ratio C_{BR}/Co to the time t taken by the current to cover the distance between the discharge point p* and B*. In consequence a certain level of pollution induced, in normal conditions, at the distance x from p* (supposing the average speed of the current running from p* to B* to be V), would be reached at the distance 2x if the speed of the current were 2V.

5.3.6 Dispersion Models

Despite the observation above concerning the possibility of systematic application of mathematical dispersion models (*) in the various countries, it is nevertheless

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(*) It is sufficient to ask oneself how many projects concerning systems of sanitation of coastal zones (sewerage, treatment plants, underwater pipelines) have effectively been based on the use of such models.

considered useful to indicate briefly the nature of these models, the type of information they can provide and the type of environmental data needed for their satisfactory functioning. It is clear that if use is made of essential data deduced from hypotheses which do not reflect sufficiently well the reality of a particular zone, the results given by even a refined mathematical model will not be very reliable.

A dispersion model established for a certain coastal zone can provide an abundance of information concerning the modalities of renovation of the waters in the zone (and exchanges between the zone and the open sea), the influence of the various discharges, and the trend of concentration of the various substances discharged throughout the zone.

It can be said that an accurate mathematical model based on environmental data corresponding to reality should provide an almost complete representation of the effective situation with regard to the distribution of the various contaminating substances discharged into the sea, taking into account the results of appropriate experiments with regard to their characteristics of persistence. However, the real effect on the environment and on the composition of the ecosystems, even in the most ambitious view, can merely be approximated. This lack of precision calls for the application of very precautionary criteria.

Referring, for the sake of simplicity, to a bi-dimensional model (in which variations in a vertical direction are ignored), the zone studied is sub-divided by lines (orthogonal to each other in Figure 40) which form a set of finished elements or continuous cells; the distribution of the various substances in these elements or cells is governed by the phenomena of transport, eddy diffusion between element and element, discharges or absorption inside the various cells. In bi-dimensional models of this type eddy diffusion in a vertical direction is ignored, with the consequent limitation of the degree of conformity of the model to the real situation.

If Cij is the concentration of a certain substance (in a certain moment) in a certain cell "ij", the variation of Cij in time may be expressed in the following manner, where the indices "a", "d", "So" and "Si" refer respectively to the processes of advection, diffusion, source and sink:

$$\frac{\delta C_{i,j}}{\delta t} = \left.\frac{\delta C_{i,j}}{\delta t}\right)_a + \left.\frac{\delta C_{i,j}}{\delta t}\right)_d + \left.\frac{\delta C_{i,j}}{\delta t}\right)_{S_o} + \left.\frac{\delta C_{i,j}}{\delta t}\right)_{S_i}$$

The significance of the expression is the following:

$\frac{\delta C_{i,j}}{\delta t}$: represents the speed with which the concentration inside a cell tends to vary with the passage of time (and in consequence of the various phenomena considered below);

${\frac{\delta C_{i,j}}{\delta t}}_{a}$: represents the contribution to this variation made by the phenomena of transport; this refers to the increase (or diminution) of the concentration induced in a certain place in consequence of the tendency of an arriving current to replace the volumes contained in that space with volumes which are richer (or poorer) in that substance.

The phenomenon can be illustrated by the image of a patch which reaches a certain point (or element) and then passes it. The variations in time of the concentration in that point, induced by the passage of the patch, are attributable to transport

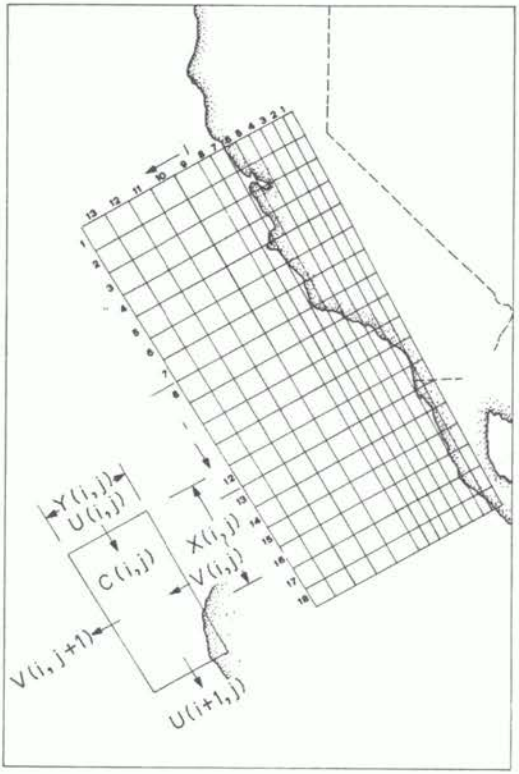

Figure 40 Definition of cells of a broad-scale dispersion model for evaluating flushing rates of the area and influence of waste discharges, (215).

phenomena.

This type of variation occurs only if there exist a) a spatial variation of the concentration (according to the direction of the average current), and b) an advective flow, which must therefore be known as regards its intensity and direction throughout the zone covered by the model and in relation to the time.

The contribution of advection phenomena may thus be expressed as follows:

$$\left.\frac{\delta C_{i,j}}{\delta t}\right)_a = \frac{1}{V} \cdot \left.\frac{\delta S_{i,j}}{\delta t}\right)_a$$

where:

V = the volume of the element ij (if all the elements are equal V does not depend on the particular element considered);

Sij = the quantity of substance present in the element (ij) at the instant considered.

Thus $$\left.\frac{\varepsilon\, Si,j}{\delta t}\right)_a = d \cdot y \cdot (i-1,j) \cdot \mu\ (i-1,j) \cdot \left[GC\ (i-1,j) + (1-G)\ c\ (i,j)\right]$$

expresses the transport of substance from the element (i - 1,j) to the element (i,j) across the surface of separation between the two elements.

This surface has the following dimensions:

$$d \cdot y\ (i - 1,j)$$

where:

d = the given depth

y (i - 1,j) = width of the surface that separates the two elements.

The component of the speed orthogonal to this surface is (average value in the time Δ t considered) u (i - 1,j), while C(i,j) and C (i - 1,j) are the concentrations in the two elements (i,j) and (i - 1,j) at the time t.

The parameter G has a value equal to 1 if the direction "u" is towards the element (i,j); G = 0 if "u" is towards the element (i - 1,j).

The effects of eddy diffusion (due to those fluctuations of speed that have an average value equal to 0, and which accordingly do not give rise to transport of the type just considered, but to a phenomenon of transport by eddy diffusion) can be represented by the expression:

$$\left.\frac{\delta Ci,j}{\delta t}\right)_a = \frac{1}{V} \cdot d \cdot y\ (i-1,j) \cdot V_D \left[C\ (i-1,j) - C\ (i,j)\right]$$

The phenomenon of eddy diffusion across the surface d·y (i - 1,j) is represented by the term:

$$V_D \left[C\ (i-1,j) - C\ (i,j)\right]$$

where C (i - 1,j) - C (i,j) expresses the difference between the concentrations in the two elements considered and V_D has the dimensions of a speed (the so-called "speed of diffusion") and depends on the intensity of the mixing movements between the element (i - 1,j) and the element (i,j).

The term $\left.\frac{\delta Ci,j}{\delta t}\right)_{So}$: represents the variation - in time - induced by the entry into the element (i,j) of new substance; this may result from a discharge situated within the element (i,j) of substance produced on the spot e.g. oxygen, or transmitted by the atmosphere (aerial fallout).

If m_s (i,j) is the volume introduced (in terms, for example, of g/sec), one has:

$$\left.\frac{\delta Ci,j}{\delta t}\right)_{So} = \frac{1}{V} \cdot m_s\ (i,j)$$

A phenomenon opposite to the one considered is represented by absorption occuring inside the element; this absorption leads to a reduction of the substance present and, thus, of the concentration of the element not due to transfer to other cells. For example, the consumption of oxygen and nutrients, the extinction of bacteria, the flocculation and sedimentation of particles, can be included in this type of effect.

Generally the speed of these phenomena of absorption (or utilization or extinction) is correlated to the concentration. The greater the concentration, the greater is the speed. The curve that describes the phenomenon is thus asympotic of the type:

$$\frac{C}{Co} = e^{-xt}$$

The absorption effect is thus expressed by:

$$\left.\frac{\delta\, Ci,j}{\delta\, t}\right)_{Si} = - \lambda\, C\ (i,j)$$

where λ is a coefficient that takes into account the speed with which the phenomenon occurs in nature.

The above seems to be an adequate account, albeit simplified and reduced to the essentials, of the content of a dispersion model and of some of the numerous data necessary for its satisfactory functioning: apart from the difficulty of expressing local discharges and absorptions due to phenomena of a biological or chemical-physical nature in an analytically satisfactory manner and the approximations deriving from the bi-dimensional character of the model, it is difficult to obtain the necessary data with regard to the currents without prolonged and expensive ad hoc surveys. It is reported that an analogous model was used in a coastal zone of California to predict the intensity of water exchange and the distribution of relatively persistent substances over a large zone. In that case, despite the eminent qualifications of the researchers concerned, the results were on the whole unsatisfactory; a considerable difficulty, overcome only in part, was constituted by the formulation of correct data with regard to the currents (these were derived, in a first approximation, in relation to the horizontal density gradients and the effects of the Coriolis forces).

5.4 AN APPROACH FOR ESTIMATING THE CAPACITY OF THE MARINE ENVIRONMENT TO RECEIVE WASTE DISCHARGES WITHOUT UNDUE EFFECTS

The criteria which lead to a discharge authorization depend on the evaluation of the condition under which a given effluent can be discharged in a given marine area without diverse effects.

In previous sections of this chapter, as well as in other chapters of the report, information and details can be found which form the basis of the following section and of the guidelines suggested; it is not necessary to reiterate them here.

Following the spirit of this Guide, specific criteria or standards are not put forward; instead general principles and guidelines are proposed which could be utilized to develop specific regulations.

It has been considered that various hypotheses should be put forward in order to allow the decisions to be made by the local authorities.

In fact different methods are adopted by which, in different areas, it is possible to make regulations which are at the same time adequately simple, efficient and consistent with economic planning.

In any case an approach should be avoided which promulgates regulations that, while pleasing public opinion, are obviously impossible to put into practice for technical and economical reasons.

A more modest programme, strictly applied, should be looked at more favourably than ambitious programmes and strict regulations which have little relevance to the practical design of treatment and disposal works.

It is suggested that regulations should be laid down for the protection of coastal waters against pollution in order to avoid qualitative statements and arbitrary interpretations, e.g. regulations such as: "Damage to marine environments must be avoided" are of no practical use; biological indices would be better (e.g. diversity index) and should be quantified.

Furthermore it is considered useful to add some technical guidelines, regarding the design of treatment and disposal works; these technical guidelines could be developed as a common code of practice to which various countries could adhere in accordance with local needs. This code of practice would be useful to the authorities and to designers as it would favour the practical application of regulations, and show their technical implications more clearly.

Of course coastal waters belonging to different countries do show up relevant differences between solutions which are applicable to different specific conditions. This is not an obstacle to the development of a code of practice because the aim of such a code is not to put forward a solution applicable to all cases; on the contrary it should make it possible to define which kinds of re-use treatment and disposal works are more suitable to comply with certain regulations under different circumstances. These circumstances can differ widely in different regions of the same country, to an equal or greater extent than the way in which they differ between other countries.

5.4.1 Common Remarks For All Kinds Of Waste Water Discharges

In order to give an authorization for a discharge it is advisable to consider the following items:

a) Is the sewerage system conceived within the framework of an adequate integrated plan. Does it take into consideration an adequate zone of influence of the pollutants related to the discharge and, as a consequence, of various uses which could be impaired and also of other discharges which may interact?

b) Have techniques of control at source, which may allow a more efficient removal of certain pollutants than subsequent treatment of diluted effluents, been studied?

c) Was a possible re-use of effluent considered prior to the discharge?

d) Does the sewerage system allow for possible extension of the treatment and/or disposal works in the future at an acceptable cost?

e) Does the final point of discharge occur away from coasts or inside estuaries or confined marine waters? (These waters should be defined as a function of geometric parameters, hydraulic parameters pertaining to the rate of exchange and according to the value of the pollution load per unit of surface).

f) Each standard should be conceived in statistical terms; the term "absence of" may be used in a few cases, for instance coarse solids, visible floatables (however it is not advised even in these cases).

g) Regulations may be revised from time to time, but contradictory new regulations should not be promulgated after only a short time as this procedure may discourage further investment and induce financial losses.

5.4.2 Where To Set Objectives, Requirements And Standards

Generally speaking, standards and criteria which concern the protection of marine waters against pollution are of the following types (Figure 41):

- Standards (a_i) concern the quality of waste waters to be treated. Such standards are substantially inherent to source control, action or in-plant treatment. In extreme cases, where very strict effluent standards are enforced, these standards may require change in the water supply origins (location) or even drastic changes in the distribution network.
- Standards (b_i) concern the quality of the effluent from the treatment plant.
- Standards (c_i) concern the quality of effluent required for certain re-uses.
- Standards (d_i) concern the water quality which must be achieved after re-use, e.g. high concentrations of nitrates in the ground water induced by irrigation with treated sewage might preclude later use as drinking water.
- Standards (e_i) valid for coastal waters are substantially microbiological standards (mostly standards for coliforms) inherent to the protection of bathing waters and shellfish growing areas (some physical standards have sometimes been foreseen, e.g. transparency and suspended solids).
- Standards (f_i) concern the quality of marine receiving waters near to the point of discharge but outside the mixing zone. These standards aim to provide a satisfactory protection of the marine environment and a satisfactory appearance of the waters themselves from an aesthetic point of view.

Other limits concern the quality of sediments and of benthic fauna (as concentrations of pollutants or variations of biotic indexes may be monitored with the object of continually controlling and evaluating the impact on the environment).

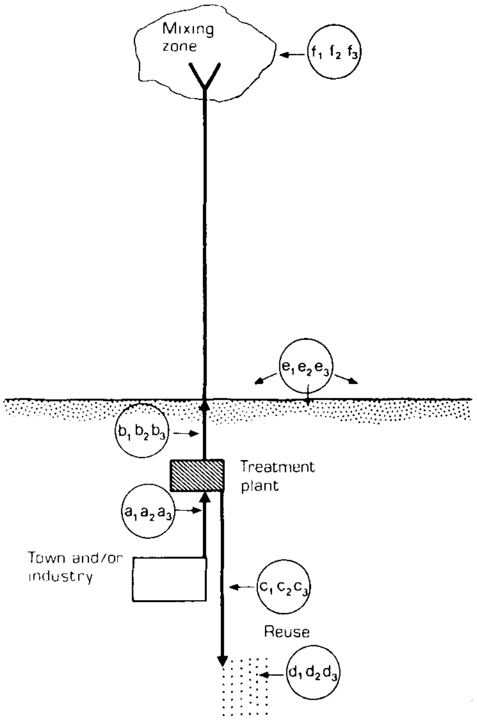

Figure 41 Application of criteria and standards inherent to the control of marine pollution from substances of Group II.

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CHAPTER 6

Availability of Waste Treatment Technology

In this chapter, the available methods of treatment for the removal of the substances, families and groups of substances or other forms of pollution dealt with in this report, will be examined.

The considerations set out here are meant to provide a basic knowledge and to assist in answering the complex question of which treatment to choose. Above all, attention is drawn to those processes which are most widely used nowadays, whilst not neglecting to mention alternative processes which can be adopted in particular circumstances or which can be put forward as innovatory solutions.

Knowledge of the unit operations which make up the processes described is assumed.

6.1 INORGANIC POLLUTION

6.1.1 Zinc

Zinc removal is generally obtained by precipitation, in the form of hydroxide. By the use of either sodium carbonate or lime as an alkalizing agent, the minimum metal solubility is reached at pH values of about 8,5 - 9 (Figure 42); at higher pH values, zinc hydroxide undergoes resolubilization, and also the precipitation of other heavy metals (e.g. nickel) may be affected.

In the plating industry, the presence of zinc is generally associated with that of cyanides. The latter must be previously removed by oxidation; an incomplete cyanide removal may adversely affect the efficiency of the subsequent zinc hydroxide precipitation, because of the formation of complexes. Similar problems may arise when using baths without cyanides, but containing other complexing agents.

Separation of precipitated hydroxide is carried out by sedimentation which, to be satisfactory, must avoid floc carry-over into the effluent; should this occur, the effluent quality would deteriorate considerably. Better results and in particular greater operating safety may be achieved by carrying out a final sand filtration. This stage is seldom applied because it is expensive and causes operating difficulties. With careful adjustment of pH, followed by sand filtration, the zinc concentration in the effluent can be lowered below 1 mg/l.

Zinc recovery from sludge by acid regeneration is economically profitable only when the element is highly concentrated and other metals are absent, as is sometimes the case in rayon production. An alternative method of recovery involves the use of ion-exchange resins. If the calcium concentration ion is low, non-selective acid resins of the

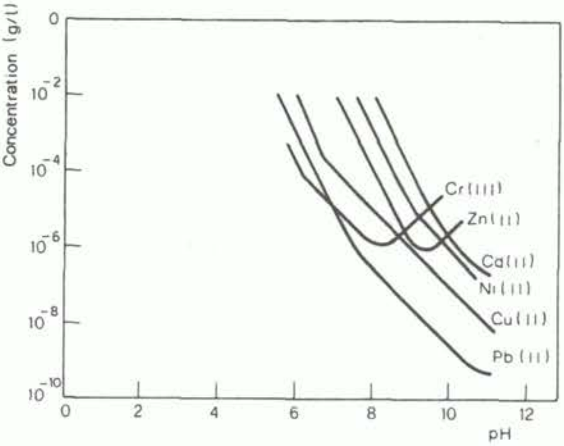

Figure 42 Solubility curves for various metals as function of pH (assumes isolated precipitation).

sulphonated acid styrene type, can be used. In the electro-plating industry, zinc is generally associated with other metals; the use of ion exchange resins may thus be foreseen for water re-use and for the concentration of the pollutant into small volumes. These must be later subjected to a conventional precipitation process, which may be thus carried out on a much reduced scale, generally as batch treatment, which is easier to control and requires simpler instrumentation. This also offers the advantage of a decrease in the chemical reagent consumption and in the over-all amount of discharged zinc and other metals.

The recovery of the zinc in wash waters (from plating baths and pickling processes) is also possible by concentration obtained by evaporation, provided that the flow rates to be treated are limited by the adoption of appropriate rinsing techniques. Concentrates may thus be re-used for bath topping up, while condensates have zinc contents that are low enough to allow their discharge without any further treatment.

However, the economic convenience of such systems always depends on the rationalization of the production cycles and usually only exists in large scale operations, even then varying widely with location, nature of product and the concern for eventual re-circulation of the waters.

6.1.2 Copper

Like the other heavy metals, copper may be removed by precipitation as a hydroxide through pH adjustment in an alkaline range; to this purpose, lime is especially used for economic reasons, even if, in the presence of high sulphate concentrations, it can cause a considerable precipitation of calcium sulphate. This is an inconvenience when metal recovery from sludges is desired, but it may be obviated by the use of other alkalizing agents, e.g. sodium hydroxide. Removal efficiency is reduced by cyanides (which should be removed by preliminary treatment) and by ammonia.

The minimum solubility of copper hydroxide occurs in the pH range 9 and 10.3. Under this condition, theoretically, very low copper concentrations can be obtained (even to 0.01 mg/l). In actual practice the results are decidedly worse because of the difficulty of controlling the reactions, the influence of other ions in solution and the carry-overs in the sedimentation phase. For these reasons the copper concentration in the treated effluent is rarely below 1 mg/l unless a final sand filtration is carried out, in which case 0,2-0,5 mg/l can be obtained. A precipitation plant with subsequent solids separation by simple sedimentations is shown in Figure 43.

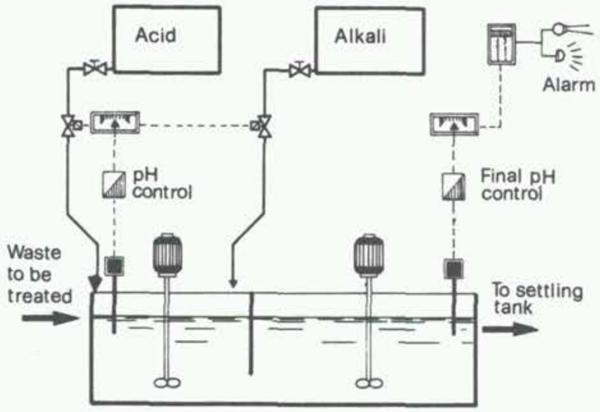

Figure 43 Scheme for pH control and metal hydroxide precipitation

An alternative precipitation process involves the use, along with sodium hydroxide, of a reducing agent such as hydrazine, which allows the separation of the metal in the cuprous, rather than cupric, form (such a system may be operated at pH 7-8); hence the advantage offered is of obtaining a much denser sludge, which may be more conveniently subjected to recovery processes. Precipitation as sulphide has sometimes been adopted, principally on mining and ore extraction wastes.

The above precipitation processes may be properly applied to fairly low copper concentrations that are typical, for example, of rinse waters from the pickling and electroplating industries. However, because of the high commercial value of copper, it is advisable to adopt other recovery systems, especially from concentrated baths.

One of the possible techniques involves crystallization, which, however, cannot be achieved by simple cooling because the metal solubility does not vary greatly with temperature. For example, in the case of nitric and sulphuric pickling baths which cannot be reactivated by the simple addition of fresh acid, crystallization may be obtained by evaporation prior to neutralization. In order to reduce the heat requirement, the process is sometimes carried out under vacuum.

Often however the evaporation is also used to obtain water suitable for re-use in the plating bath. The progressive increase of impurities limits this method of direct recovery. In any case, the possible application of the evaporation processes is subordinated, for economic reasons, to a rationalization of the use of water in the cycle, which allows the quantities to be treated to be contained.

The direct recovery of copper metal from concentrated baths may be achieved by cementation through contact with scrap iron. The copper deposit is obtained, by oxidation-reduction while iron is dissolved with a consumption of 2-3 kg/kg copper recovered. The process may also be carried out under static conditions for relatively low metal concentrations. Although the process may be speeded up by blowing in air, for higher copper contents it is better to operate by slowly stirring the bath so as to remove the copper deposits from the iron surface, which is thus kept free and available for a more rapid reaction. Copper metal is later separated from the treated solution by simple sedimentation. The cementation process may be conveniently applied to slightly acid solutions in order to avoid possible copper dissolution as well as the formation of hydroxide which, by coating the metals, might retard the process. Such a recovery technique may be easily realized and operated, but it does not allow the re-use of the acids contained in the bath and involves the dissolution of large amounts of iron, which must be removed later.

Such inconveniences are eliminated with electrolytic treatment especially in sulphuric acid pickling baths. By using an electrolytic copper cathode and an anode of lead, magnetite or graphite, it is possible to obtain a metal recovery down to a residual concentration in the bath of a few g/l, below which the process becomes uneconomic. Under such conditions the bath may be re-used and the acid recovered without the production of wastes. In any case, direct electrolytic treatment is not convenient for initial concentrations lower than 2 g/l, as it requires preliminary concentration by evaporation or ion exchange.

The use of ion exchange resins in the case of effluents with a low initial copper concentration, leads to excellent removal efficiences, often to an undetectable level, but it is only economically justified by the subsequent recovery of the metal. It is necessary, however, that the regeneration of the resin is carried out with small quantities of regenerant in order to recover a concentrated copper solution. To this end, counter-current processes of regeneration are also available to yield concentrated eluate. The process may also be applied in the case of cuprous-ammoniacal wastes, and allows the removal of both copper and ammonia.

Satisfactory results have been obtained by electrodialysis and reverse osmosis. In both cases, however, problems and limitations arise connected with the membrane selection.

6.1.3 Nickel

As for other heavy metals the treatment commonly adopted involves its precipitation as hydroxide after pH adjustment to a highly alkaline range by lime addition. The nickel hydroxide has a minimum theoretical solubility of 0.01 mg/l at pH 10; little benefit is gained by operating at higher pH values. In actual practice, nickel concentration in the treated effluent can be expected to be in the range of 0,5 - 1 mg/l.

Some problems may arise due to the fact that the optimum precipitation range of nickel occurs at pH values at which other metals may become soluble again. In such cases, in order to obtain a good removal, separation of the effluents containing metals with different precipitation ranges should be practised. Alternatively, a two-stage removal process might be adopted: the first stage at a high pH and the second at a lower pH.

The process removal efficiency is considerably affected by the physical treatment for precipitate separation; as a general rule, sedimentation is enough, especially when improved by the addition of coagulant aids. More complete removals may be achieved by a final sand filtration; the presence of complexing agents, such as cyanides, hinders the hydroxide precipitation and may cause a considerable decrease in the removal efficiency.

A possible alternative, though seldom adopted, consists of the precipitation of insoluble sulphides by the addition of sodium sulphide.

Satisfactory results may also be obtained using ion-exchange resin; nickel may be recovered from eluates by precipitation. However, recovery is impossible when nickel is mixed with other metals in the effluents.

Recovery by evaporation is also feasible, though it requires a rational use of water leading to decreased consumptions. Hence it might be convenient to perform a further concentration by evaporation of washing waters with recovery of a concentrated phase to be directly used for topping up the baths; condensates may possibly be re-circulated to the rinse water system.

The spent plating bath solutions containing nickel (and other heavy metals like copper), can also be treated directly by the Lancy process, without dilution by rinse water (Figure 44). The plated metal, with dragout adhering to it, after a static rinsing, is directly submerged in a vat containing a concentrated solution of lime - or other alkalizing agent - used to precipitate the nickel. This solution is continuously recycled to a reservoir where sedimentation of metal hydroxides occurs and where make-up chemicals are added in proportion to the amount of precipitate formed.

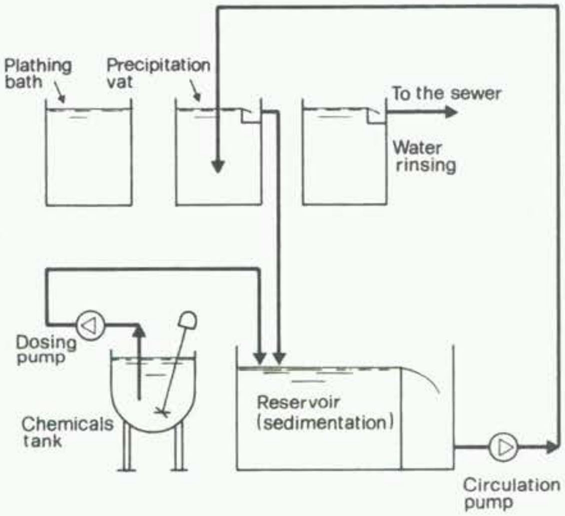

Figure 44 The Lancy Process in metal plating industry.

A final rinse with water eliminates the last traces of hydroxide from the plated metal. Because most of the pollutants have been removed in the precipitation vat, the rinse water does not need treatment, except possibly sedimentation or filtration to eliminate the small amounts of precipitate still present.

6.1.4 Chromium

Chromium is present in wastewaters as trivalent and hexavalent ion. The hexavalent form consists of chromate (CrO_4^{--}) and dichromate ($Cr_2O_7^{--}$) ions.

Chemical precipitation is widely used for chromium removal. It may be directly achieved by simple alkalization in the case of trivalent chromium. Otherwise the process may only be carried out after reduction of the hexavalent form ion to the trivalent one which, at the correct pH, leads to the formation of insoluble trivalent chromium hydroxide.

For reduction, use is often made of sulphur dioxide, which operates according to the following reaction:

$$2\,CrO_4^{--} + 3\,SO_2 + 4H^+ \rightarrow 2\,Cr^{+++} + SO_4^{--} + 2H_2O$$

Reduction is carried out at pH below 3, by sulphuric acid dosed to favour the reaction rate. The importance of an accurate control of the pH is shown in Figure 45, in which the reduction of hexavalent chromium is related to the reaction time and to the pH of the waste-waters.

Instead of sulphur dioxide, other reduction agents are frequently used, e.g. sodium bisulphite or meta-sulphite. Even ferrous sulphate is used occasionally.

Once reduction to trivalent chromium has been completed, this may be precipitated as hydroxide in the lower solubility pH range, i.e. from 8.5 to 9.5, by alkalizing with sodium hydroxide (Figure 42). Experience shows that by alkalizing with calcium hydroxide, the optimum precipitation, can be extended to values over 12. Filtration after sedimentation allows removal of fine hydroxide floc.

If ferrous sulphate is used as a reducing agent, chromium hydroxide precipitation is accompanied by the simultaneous precipitation of iron hydroxide. The considerable production of sludge usually limits the use of ferrous sulphate as a reduction agent.

Figure 46 shows an example of chemical treatment of wastewaters polluted by hexavalent chromium. Sodium bisulphite is added to the wastewater acidified to a pH of 2,5 with sulphuric acid, to reduce the hexavalent chrome to trivalent. By raising the pH, with lime, to 8.5, precipitation of trivalent chromium hydroxide takes place. It is separated from the wastewaters by settling. The supernatant then undergoes neutralization with sulphuric acid, before disposal. The hydroxide chromium sludge is dewatered on a pressure filter to obtain a solid product which can be disposed of to a controlled tipping site.

Where there are only small quantities of wastewater containing high concentrations of chromium (and other heavy metals) direct treatment on a pressure filter is often preferred thus avoiding sedimentation.

Ion exchange plants are equally widely used for chromium removal. Chromium, as well as the other ions removed from wastewaters, is concentrated in the regeneration eluate, from which it is later separated by the chemical precipitation treatment described above. The effluent of ion exchange plants exhibits characteristics that make it fit for recycling to industrial processes. Figure 47 shows the scheme of a classic ionic exchange plant for the treatment of rinsing waters from plating baths with recycle of the purified effluent. The plant includes chemical treatment units for eluate regeneration, together with spent baths. Trivalent chromium is fixed on the cationic resin, while the hexavalent ion, in the form of chromate, is fixed on the anionic one.

The ion exchange methods seems interesting because, in addition to water recirculation, it offers the possibility of partial chromate recovery. Recovery consists of feeding the regeneration (with sodium hydroxide) eluate of the chromate rich anionic resin to an acid-cycle cationic resin, so as to exchange sodium with hydrogen ions. In this way a chromic acid rich effluent is obtained, which therefore may be possibly reused. Obviously the method is effective when effluents do not contain other anions. A scheme of this processes is illustrated in Figure 48.

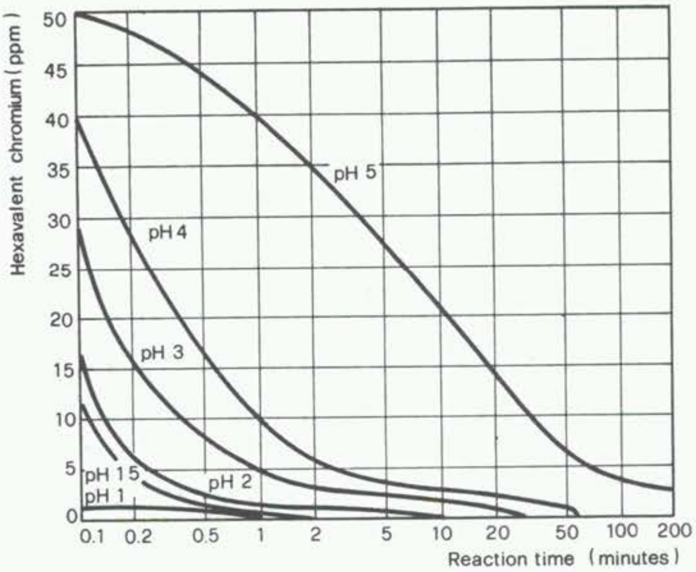

Figure 45 Reduction of hexavalent chromium with SO_2, as a function of the pH and the reaction time.

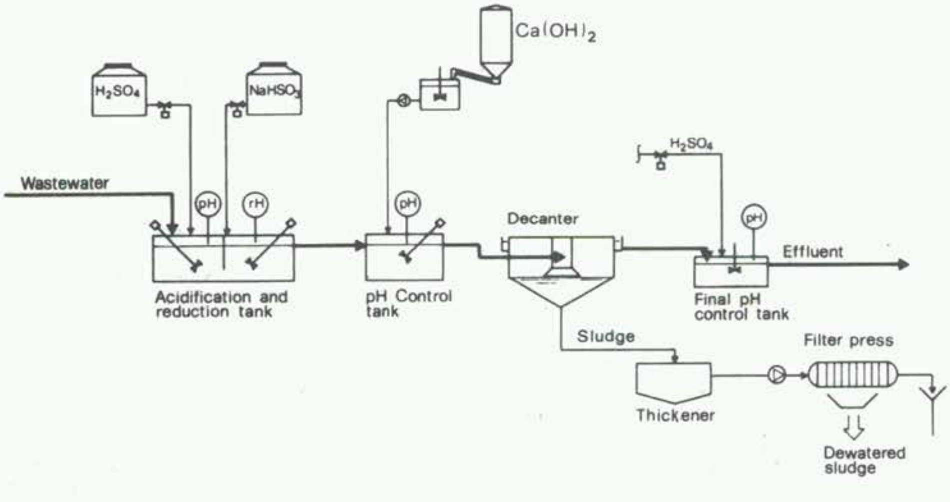

Figure 46 Chemical treatment of wastewaters polluted by hexavalent chromium.

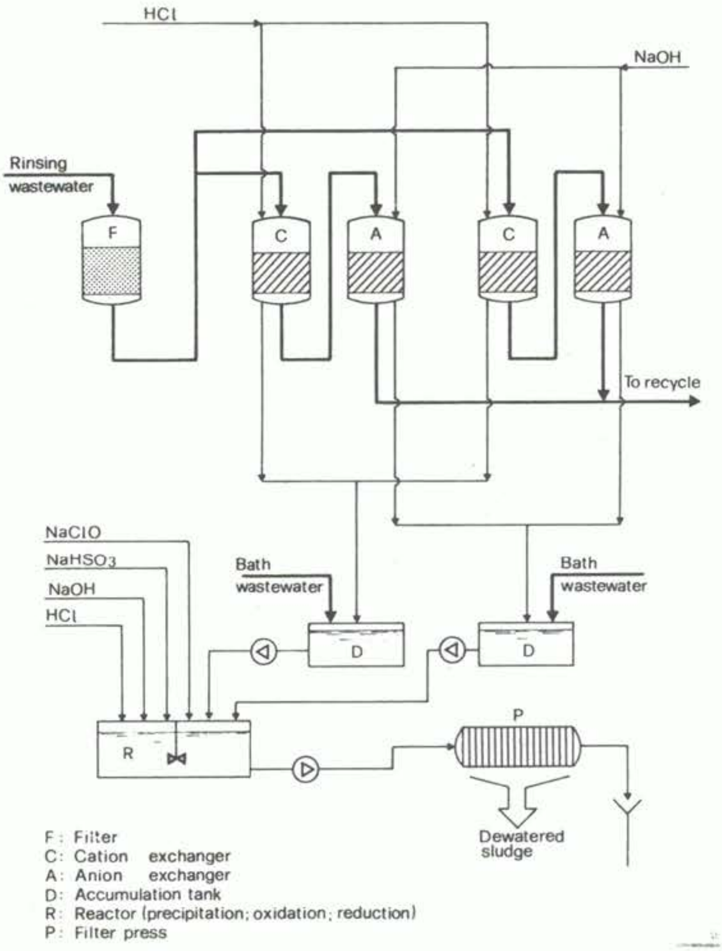

Figure 47 Ion exchange plant for the treatment of rinsing waters from plating processes, complete with chemical treatment of the regeneration eluates and concentrated bath wastewaters.

Among the techniques less widely adopted for hexavalent chromium removal, mention is made of other processes of chemical precipitation with barium and lead salts, which with chromate directly form insoluble salts. Such processes are not often adopted essentially because of the high toxicity of hexavalent chromium with sludges and of the chromium left as residue in the treatment effluent. The technique of trivalent chromium reduction and precipitation is preferred even from the economic point of view.

Among alternative techniques, mention is made of evaporation processes giving a distillate, which can be recirculated, and a concentrated end product rich in chromic acid, and different metal salts which, therefore, are potentially fit for product recovery.

Finally, mention is made of the activated-carbon adsorption process investigated by

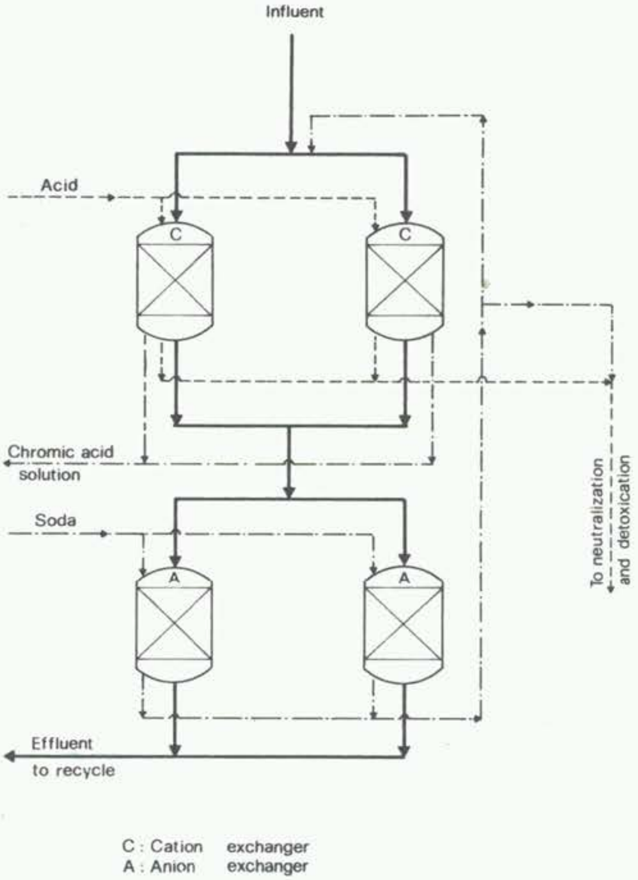

Figure 48 Ion exchange process with partial recovery of chromic acid.

E.P.A. It has been found that hexavalent chromium is easily adsorbed by passing solutions with chromium concentration of several hundreds ppm, to filters of activated carbon in granular form. Removal efficiencies of properly dimensioned columns are higher than 99%. Regeneration is conveniently carried out with sodium hydroxide, which leads to the formation of a sodium chromate solution which will be subjected to detoxication treatment. Experience has shown, however, that gradual loss of adsorption properties occurs when the number of regeneration cycles is augmented, probably due to the partial reduction of hexavalent chromium on carbon to Cr_2O_3. After 100 regenerations, the adsorption capacity is noted to be lowered from an initial value of 0.08 Kg of hexavalent chrome per Kg of activated carbon to the value of 0.04.

6.1.5 Lead

When lead is present, in colloidal form, as an organic compound, as a chelate from other organic substances, or simply in suspension, it can be removed by coagulation with iron and aluminium salts. This process can also be applied to wastes from tetraethyl lead production where the metal is partly dissolved in the mineral oils also present, both in free and emulsioned forms. The elimination of these oils, with the usual separation techniques, amongst which most important is coagulation does not however allow the concentration of lead to be reduced to values which are generally compatible with direct discharge. In fact, for the lead present in the free ion state or in the form of a soluble complex, such electrolytes are completely ineffective: hence precipitation processes are required which lead to the formation of hydroxide, carbonate or, less often, of other insoluble salts, which may be removed by the usual physical processes. For hydroxide precipitation, a treatment with lime (or, less often, with sodium carbonate) is generally preferred at highly alkaline pH values (pH 9-10), although literature reports processes carried out at lower pH. The presence of complexing agents, e.g. of ammonia, can cause a considerable decrease in the removal efficiency. Precipitation as carbonate may be achieved by the addition of sodium carbonate (examples of filtration on calcareous beds, e.g. dolomite, are also reported). Separation of lead hydroxide or carbonate precipitates is often not very feasible and always requires long sedimentation times. Separation may be favoured by a further addition of flocculation agents or by a final sand filtration stage. With careful attention during the treatment, it is possible to reduce the lead concentration to 0,02 - 0,03 ppm, almost one order of magnitude lower than that often obtained by simple sedimentation.

An alternative precipitation consists of the use of ortho phosphoric acid to form lead phosphate which has a very low solubility at pH values close to 7. For good efficiency, the process requires a large excess of the acid, which, however, may create possible problems of excessive phosphate content in the effluent.

Different possibilities are open in the use of sodium sulphide as a precipitation agent, with the formation of lead sulphide which is black and insoluble. The toxicity of this product, however, makes rigid control of the process necessary in order to avoid carry-over which can also be caused by the bad settling characteristics of the precipitate; it is therefore advisable to provide filtration downstream of the sedimentation which can effect an adequate removal of the suspended material.

As to the removal of organic lead compounds, in particular of lead tetraethyl, satisfactory results may also be obtained by ion exchange, with the use of acid cationic resins. The eluates containing high lead concentrations may be subjected to an oxidation process for organic lead mineralization; this may then be removed by the physico-chemical treatment already described.

6.1.6 Arsenic

Coagulation processes with polyvalent metals (especially iron and aluminium) can remove arsenic, even in the soluble form. This is a consequence of complexation with metals and of a subsequent co-precipitation with hydroxide flocs which form under convenient pH conditions. A simultaneous adsorption onto the flocs may also occur. The same flocculants commonly used for the treatment of primary waters and effluents can be used, in particular ferric sulphate and chloride as well as aluminium sulphate. Efficiency levels are high when arsenic is present as arsenate, much lower when it is arsenite. In the latter case, a preliminary chemical oxidation is generally advisable, which may be carried out by chlorination. Arsenic removal requires different pH conditions depending on the flocculant used: from 5.5 to 8.5 with ferric sulphate, from 7 to 8 with aluminium sulphate, 8-9 with ferric chloride.

Therefore the treatment to be adopted does not differ from the usual physico-chemical processes for the removal of suspended matter from waters, i.e.: coagulation-flocculation, sedimentation; filtration on sand; if arsenites are present, pre-chlorination is required. If a particularly high removal is necessary, an additional adsorption treatment may be provided using activated carbon. Lime is generally used for pH adjustment.

Flocculant addition is no longer required for arsenic removal from waste waters that contain heavy metals; in fact complexation takes place with the metal ions already present in the wastewaters to be treated. It is therefore enough to adjust the pH according to the technique commonly used for metal hydroxide precipitation. The high removal levels sometimes achieved by using lime alone may probably be attributed to the described phenomenon; in the absence of heavy metals, lime addition generally leads to poor results.

An alternative process - applied very limitedly so far - consists of arsenic precipitation as sulphide (or possibly as ferric sulphide should iron be present in the waters) by the addition of hydrogen sulphide or sodium sulphide, in small amounts ($S^{=}/As^{=} = 0.4$) and at a pH close to neutral. Arsenate removal efficiency may be fairly high (effluent arsenic levls of 0.05 mg/l are reported) but it is nil in respect of arsenites, which anyhow require a preliminary oxidation.

6.1.7 Barium

Barium removal is generally carried out by chemical precipitation. Owing to the low solubility of the barium sulphate produced, one of the most widely adopted treatment techniques is the addition of excess sulphate ions (e.g. sodium sulphate) to wastewaters. The use of ferric or aluminium sulphate also involves precipitation of barium sulphate and ferric or aluminium hydroxide, which exhibit such flocculation power that it helps the removal of the lighest barium sulphate particles with consequent increase in purification efficiency.

Barium may even be precipitated as a carbonate in sufficiently alkaline waters, by operating at pH 10.5. At a higher pH, reduction of purification efficiency is observed, because of the preferential formation of the more soluble barium hydroxide.

Very interesting results, with regard to treatment efficiency, may be obtained by the ion exchange process. Chemical precipitation has always been adopted for barium removal from regeneration eluates.

Although the ion exchange process leads to better final results in terms of residual barium content, direct chemical precipitation is preferred from the economic point of view. In any case, both processes allow residual barium concentrations below 0.5-1 ppm to be obtained.

6.1.8 Boron

This is usually found in wastewater as borate ion. Although it is extensively used in industry and in the formulation of commercial detergents, the information available on its presence in wastewater is scarce. The experience acquired so far concerning its removal are also few and not very convincing.

For boron removal, the conventional biological treatment and chemical coagulation with lime and ferrous and aluminium salts proved to be ineffective.

Results of some interest have been obtained by distillation and ion exchange on selective resins, by means of which boron contents below 1 ppm may be obtained.

Experimental studies on reverse osmosis and on extraction with chemical reagents have been published.

6.1.9 Silver

Silver may be removed by chemical precipitation. For this purpose, it is made to react with hydrogen chloride or with chloride, to precipitate silver chloride. This product, originally white, turns violet on light exposure and decomposes into chlorine and silver. Excess chlorides must be controlled in order to avoid the formation of silver chloride soluble complexes. In the hypothesis of a simultaneous precipitation of the hydroxides of other metals, silver chloride recovery from mixed sludge may be carried out by acidification which, by redissolving the hydroxides, leaves the insoluble silver chloride unaltered. In the case of presence of cyanides in the effluent, this ion interferes with the described precipitation process; that is why previous removal of this anion is strictly necessary. Oxidation with chlorine or related derivatives not only removes cyanides, but also supplies those chloride ions that are necessary for silver chloride precipitation.

The effluent quality may be improved by addition of flocculation and coagulation agents, as well as by filtration after sedimentation.

Results obtained from experimental treatment appear to prove that ion adsorption occurs on the chemical precipitates of coagulation agents, e.g. ferric chloride; the final values found in the effluent are lower than 0,1 ppm.

Chemical precipitation as black silver sulphide is not very suitable as the sludge separation and its subsequent treatment are not very feasible.

Of some interest is the use of ion exchange systems, which allow the recovery of silver in the cationic phase. Anionic exchangers may conveniently be used to remove complex ions of the $Ag\ (S_2O_3)^{---}$ type, which are present in the effluents from photographic and radiographic industries. The economic feasibility of the ion exchange process depends on the concentration of the other ions present in solution in the effluent.

Finally, mention is made of the possibility of electrolytic recovery with cathodic deposition of the silver present in particularly concentrated baths.

6.1.10 Other Elements, (Tin, Cobalt, Antimony, Titanium, Vanadium, Thallium, Tellurium, Beryllium, Molybdenum, Uranium, Selenium)

The above elements are seldom found in wastewaters. That is why the information available concerning their possible treatment is limited.

For them, as also for the examined metals, chemical precipitation, co-precipitation, extraction with solvents, ion exchange and adsorption treatment may be foreseen. The last process, together with chemical precipitation is of particular interest from the application point of view. In particular, in addition to the adsorptive capacity of the various chemical precipitates, which differ depending on the element involved, on its concentration and on the concentration of the other elements contained in the sewage, it is also important to stress the interesting results obtained from a number of adsorption tests on activated carbon.

Obviously, the activated carbon treatment may be conveniently used for effluents with low concentrations of the elements to be adsorbed. The numerous results reported in the literature for the various elements bear witness to the efficiency of the method for achieving barely measurable residual concentrations.

As far as chemical precipitation is concerned, mention is made of the sulphide-aided treatment for the precipitation of tellurium, selenium (reduction of the selenite ion to elementary selenium), molybdenum, antimony, cobalt and tin.

The last three of these elements can also be precipitated as hydroxides, under alkaline conditions. Considering their amphoteric character, antimony and tin are nevertheless soluble in an excess of alkalizing reagent. Especially as regards cobalt, the capacity to form complex ions can produce notable interference in the precipitation phenomena. As regards tin, the application is also known of an ion exchange process to recover the element present in the waste as stannate ion. The process consists of the exhaustion of a weak anionic resin having chloride ion as a functional group which is exchanged with the stannate ion. On regeneration with sodium hydroxide, an eluate rich in sodium stannate is obtained which may be reused in electrolytic baths.

Molybdenum may be removed by using iron and aluminium salts, through the possible co-precipitation and adsorption mechanisms. The process takes place in a weakly acid solution. Vanadium may be removed by precipitation with ferrous sulphate under neutral pH or weakly alkaline conditions. The precipitates consists of $Fe(VO_3)_2$ and FeV_4O_9 in respect of the vanadium present in the penta - and tetravalent forms. With quantities of iron ten times as large as the stoichimetric one, values of 1-2 ppm may be obtained with regard to the pentavalent form and of 5 ppm for the tetravalent one.

6.2 BIOCIDES AND THEIR DERIVATIVES
(other than organo-halogenated and organo-phosphorus compounds)

Biocides comprise a large series of chemical compounds generally used for example as insecticides, algaecides, herbicides, fungicides, and water and sewage disinfectants.

The nature of such compounds can be organic or inorganic and their origin can be natural or synthetic. Examples of inorganic biocides are given by some compounds of lead, arsenic, mercury, copper, zinc, chromium, chlorine and their derivatives. Examples of organic biocides are several organo-halogenated compounds, such as DDT (Dichloro-Diphenyl-Trichloroethane), BHC (Benzene-Hexachloride), Aldrin, Dieldrin, Chlordane, Heptachlor, Lindane, Toxaphene, Strobane, Methoxychlor, Endrin, several organophosphorus compounds, such as Demeton, Diazinon, EPN, Methyl Parathion, Malathion, Parathion, Phenoxyalkanoic compounds, Triazines, Carbamates, Phenyoxyalkanoic acids, Urea substituted compounds, Amine compounds.

It is practically impossible to describe all feasible treatments and their relative results concerning each type of biocide. Therefore a survey is given of the general applicability of a series of techniques which may constitute a useful basis for a further examination of details. A preliminary consideration concerns the possibility of minimizing pollution from biocide factories, by setting up techniques to reduce the leakage of raw materials, finished products and solvents. To this purpose, automatic monitoring systems fitted with alarms may be situated along the sewerage system, these are capable of bringing to evidence highly polluted flows, of diverting them to dumping systems and simultaneously of indicating which plant is responsible for the polluted effluents. Another device consists of isolating the areas where biocide production is carried out, so that highly polluted waters may be collected separately. In other cases, the dry collection of powders has been carried out by systems under vacuum and also by systems involving separation with cyclones.

Effluents from biocide-producing factories are generally acid. Hence neutralization, generally with lime and sometimes with limestone or dolomite beds, takes place frequently. The use of this reagent almost always involves the precipitation of chemical compounds.

Inorganic biocides may be removed through the treatment systems already considered for different elements, copper, lead, arsenic, zinc, etc.

For organic biocides the possibility exists of detoxication of some compounds by alkalization with soda or lime at high pH. The treatment leads to the hydrolytic decomposition of biocides, generally favoured by temperature. For the other compounds, e.g. Aldrin, Dieldrin (chlorinated hydrocarbons) the rapid dehydrochlorination at pH lower than 3 is known as also is their stability in an alkaline medium. On the other hand, alkaline decomposition has been ascertained for IPC compounds (Isopropyl-Phenylcarbamate), for some Phenyoxyl herbicides and Carbaril. The hydrolysis rate may be considerably increased by the use of catalysts, such as iron chloride.

A number of methods are known of chemical oxidation with chlorine, chlorine dioxide, potassium permanganate, peroxides and ozone. The results obtained differ considerably from case to case. Chlorine and peroxides generally exhibit a quite poor effect. Ozone in particularly large doses gives the best results. Oxidation with ozone is more effective on unsaturated compounds than on the saturated ones.

Chemical coagulation with the classical aluminium and iron salts does not have any significant effects on biocide removal; therefore it is of little interest for such applications.

The treatments based on adsorption phenomena are among the most effective ones. For the purpose, the use of bentonite, saturated clay, hydrous aluminium silicate, activated carbon and other substances is known. Activated carbon is however of the most interesting from the point of view of application. Such a treatment, suitably dimensioned, generally allows particularly high removal levels and the achievement of low residual concentrations.

Biological treatment may often be applied provided that microorganisms are protected against shock load, rapid pH variations and accidental biocide leakages from the production departments. The results obtained by biological treatment are not only a function of the selected process and of its dimensioning, but they are also connected with the biodegradability characteristics of biocides. Some compounds, such as tertiary aliphatic alcohols, ethers, benzene, halogenated aromatic compounds, are not very biodegradable.

Some satisfactory examples have been achieved using activated sludge treatments, percolating beds and oxidation ponds. These last are considered of particular interest both as a direct treatment and for polishing. In order to function correctly, the discharge of highly coloured effluents and emulsions which make the water turbid, should be limited so as to avoid negative effects on algal growth, a factor of major importance for such a treatment. Much care must be taken with regard to sulphides; actually, at high concentrations, they cause the growth of dark bacterial colonies which can hinder light transmission through the water.

One of the most widely adopted techniques is incineration. The operating temperature for an efficient combustion of organic compounds is 750-1000°C with minimum residence times of 0.3-0.5 seconds. At higher temperatures, oxidation is better guaranteed, but some problems arise, concerning the thermal resistance of the materials, and the greater facility with which flue gases are formed of nitrogen oxides and of aerosols containing sodium chloride and phosphorus pentoxide which can produce persistent white fogs when the atmospheric humidity is high.

The use of scrubbers for flue gas purification is almost always required. In any case, particular care must be taken for the control of atmospheric pollution derived from sulphur dioxide, hydrogen chloride, heavy metals and organic byproducts. Heavy metals can be found following the combustion of biocides containing such elements in their chemical formulation; the serious environmental pollution that may occur in such cases discourages the adoption of this technique.

Further treatments that may be evaluated at an experimental scale are photochemical degradation, liquid-liquid extraction and foam fractionation.

For inorganic biocides having the characteristics of chemical oxidizers, such as chlorine and its derivatives, potassium permanganate and peroxides, removal from water is carried out by reduction, using inorganic compounds, such as sodium bisulphite, sodium meta-bisulphite and sulphur dioxide to quote the more frequently employed reagents. Water dechlorination is often carried out by activated carbon treatment; its action is not exactly an adsorption mechanism, but rather a catalytic activity of reduction to chloride. Activated carbon exhibits an analogous action toward chloramines.

In the case of potassium permanganate reduction, the violet colour changes to brown because of the precipitation of tetravalent manganese hydroxide which, in its turn - by excess of the reducing agent - may be reduced to divalent manganous hydroxide, which is white and more soluble.

6.3 ORGANOSILICON COMPOUNDS

Although their presence in effluents is not common, organo-silicones are widely used for the production of silicone resins, elastomers, surfactants, coupling agents, fluoro-silicones. For example, mention is made of chlorosilanes (methyltrichlorosilane CH_3SiCl_3; dimethyl-dichlorosilane $(CH_3)_2SiCl_2$), cyclic siloxane, silane monomer $(CH_3)_2\,Si(OH)_2$ and linear polymer $OH(Si(CH_3)_2O)_nH$. Such compounds are generally present in wastewaters with heavy metals, especially used as catalysts in chlorosilane production. Any forecast concerning the removal treatments of such compounds from wastewaters can hardly be made because very little information is to be found even in specialised literature. However, being organic compounds, the present trends are mostly directed to the adoption of biological and activated carbon adsorption processes.

For activated carbon adsorption, the process suitability must be checked each time by pilot or laboratory scale tests; furthermore, precautions must be taken to avoid the adsorbed silicone products causing low carbon regeneration yields, which would make the process particularly expensive.

For the treatment of effluents from those industries producing organosilicones, the biological processes generally are the most attractive. Effluent pre-treatment is almost always necessary for pH neutralization. Pre-treatment may often include flotation and sedimentation because of the presence in suspended form of other polluting compounds.

With regard to the use of other processes, e.g. chemical oxidation, the greatest drawbacks derive from economic factors. However, a patented process is known for the purification of effluents from silicone-polymer-producing plants. It consists of an initial flotation stage, followed by alkalization at pH 12 and subsequent decantation. Finally, ozonization is carried out in packed columns.

6.4 CRUDE OIL AND PETROLEUM-DERIVED HYDROCARBONS

As is known, this class of pollutants includes numerous chemical compounds of substantially different structural characteristics. In any case, they are hydrocarbon compounds (light and heavy hydrocarbons, lubricant oils, fats) which may be singled out by chemical analysis according to common methods, by organic solvent extraction.

A classification based on the different physical state in which such compounds may be associated with water, leads to the following general distinction:

i) soluble oil

ii) emulsified oil

iii) free oil.

The above distinction acquires a particular meaning in view of the selection of the possible treatment for the removal of such pollutants from wastewaters.

The simplest separation technique consists of gravity separators, i.e. exploiting the difference in the specific gravity of water and oil. Hence it is a process of natural flotation and therefore it is aimed at free fraction removal only. Air flotation, which is also widely used, achieves a higher separation rate and allows a greater efficiency and hence smaller-sized units. In general, the two processes form a primary purification stage, which must be integrated with subsequent treatment.

The emulsified oil and fat fraction may be separated from the sewage by a process which causes emulsion destabilization. Breaking up of emulsion may be achieved by chemical, physical, electrical or thermal methods. The chemical methods, which are most widely used, consist of adding to the sewage the classical coagulents (iron or aluminium salts, polyelectrolytes). The chemical sludge, enriched with destabilized oily compounds, may be separated from the water either by sedimentation or by flotation.

A similar destabilizing effect may be achieved by acidification. The method offers the advantage of no additional production of sludge, but it is generally expensive and requires a more complex control, because of the double control of the pH, both upstream and downstream of the treatment. Destabilization techniques that are mainly adopted for highly concentrated oil emulsion consist of heating or of the application of a strong electric field. Among the physical methods, mention is made of centrifugation, pre-coat filtration and filtration on coalescing beds.

No generalization is possible as to the results expected from the treatments considered, the quality of the effluents polluted by such substances being extremely variable. As an indication, the results obtained from several full-scale and experimental treatments suggest that, after the examined treatments including emulsion break-up, the residual oil content is of the order of 10-30 ppm, and that this is due to both dissolved and emulsified residual fractions.

Biological treatment may be adopted either as an alternative or integrated with the above processes. As a matter of fact, activated sludge plants, percolating beds, and in particular oxidation ponds have been widely applied for the treatment of refinery discharges and discharges from the petro-chemical industry.

When choosing a treatment for effluents from the latter industry, particular attention must be paid to the variability of composition in relation to the result obtained. However, among those organic compounds most commonly found are various hydrocarbons, their oxidation products (alcohol and aldehydes), phenolic compounds esters and oily impurities. Biological systems can remove oils and mineral fats from wastewaters because of adsorption on bacterial flocs and biodegradation. This last phenomenon, and consequently the overall purification efficiency, is particularly related to the biodegradability of hydrocarbons.

With regard to the feasibility of biological treatment, apart from biodegradability, the initial concentration of the substance itself plays an important role. As a matter of fact, because of the known interferences with bacterial activity and the oxygen transfer process in aerobic treatment, in the case of high initial concentrations it is generally advisable to perform biological treatments after the previously discussed physico-chemical ones.

The preliminary treatments are aimed at the removal of other inhibiting compounds such as, sulphides and sulphur-based organic compounds. To this end oxidation processes are normally used or, in the case of sulphides, precipitation of iron sulphide.

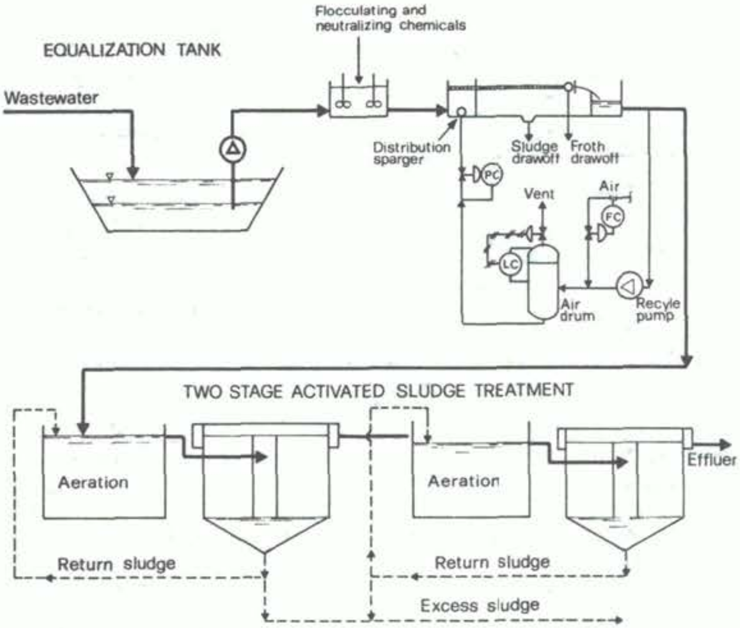

Figure 49 Chemical - biological treatment of wastewaters from the petrochemical industry.

Figure 49 is a schematic diagram giving an example of a chemical-biological plant for the treatment of the discharges from the petrol-chemistry. The plant consists of an homogenisation basin for the balancing of the pollution load, of a stage for the separation of the oily contents by means of pressurized flotation, and the addition of demulsifying reagents, and finally a 2-stage biological treatment with activated sludge.

The dissolved fraction may be removed not only by biological treatments, but also by adsorption processes, amongst which adsorption on activated carbon is certainly the most interesting. Obviously, for this treatment too, the degree of reliability is different and depends on the quality and concentration of the oily and fatty fractions present in the effluent. However, the wide experimentation done proves the great importance of the application of activated carbon in this particular field. Two types of consideration must be taken into account when considering the possibility of using the above process: one concerns the final quality of the purified effluent, the other is strictly connected with the economic aspect of the treatment. Adsorption on activated carbon is profitably applied when particular quality characteristics are required or whenever sound reasons against the application of biological treatments exist. Due to its operating costs, the process is especially applied as a finishing treatment downstream of the purification methods previously considered.

Another treatment for removal of oils worth mentioning, is ultrafiltration. It provides the separation from the purified effluent of concentrated oily phase, which is generally incinerated.

6.5 CYANIDES

Cyanides present in wastewaters may be removed by chemical oxidation, e.g. with chlorine which, in an alkaline medium (pH = 10,5-11), causes cyanide conversion to carbon dioxide and nitrogen, according to the reaction:

$$2\ CN^{--} + 5Cl_2 + 12\ OH^{--} \rightarrow N_2 + 2\ CO_3^{--} + 10\ Cl^{--} + 6H_2O$$

Transformation actually occurs in subsequent steps involving the formation of cyanogen chloride (CNCl), which is later oxidized to cyanate ion (CNO^{--}). The alkaline medium in which the reaction occurs, besides favouring the kinetics of the oxidation process, maintains those conditions which prevent volatilization of the poisonous cyanogen chloride.

Figure 50 shows the importance of the accurate control of the pH for the conversion of the cyanogen chloride to cyanate. One sees that at a pH lower than 10, reaction times of approximately 30 minutes are sufficient in order to achieve about 90% decomposition of the cyanogen chloride, whilst at a pH of 9.2 a minimum of two hours is needed; it has been noted that the dosage of chlorine has a certain influence on the rate of decomposition. It must be dosed in excess of the stoichiometric requirements.

Concerning the kinetics of the cyanide oxidation reaction one often finds opposing data in the relative literature. This presumably is due to catalytic action exercised on those ions present in the wastewater. This is particularly valid in the oxidation of the complex cyanides.

The complete oxidation of cyanides, although undoubtedly offering the best guarantee for environmental protection, is not always considered convenient to achieve. In fact, oxidative conversion is sometimes limited to cyanate formation, being a rapid reaction that involves a lower chlorine dose:

$$CN^{--} + Cl_2 + 2OH^{--} \rightarrow CNO^{-} + 2Cl^{-} + H_2O$$

Furthermore, the cyanate ion toxicity is one thousandth of that of cyanide ion; hence an oxidation limited to such an intermediate step may be justified.

Particular problems can come to light when the oxidation refers to complex cyanides; for example in the cyanide complex of potassium and copper $K_3Cu(CN)_4$, three cyanogenic groups are destroyed very rapidly, whilst the fourth group is very resistent; in the detoxication of the complex cyanides of copper and silver, after the oxidation of some cyanogen groups the insoluble copper cyanide can precipitate and the oxidation of this is extremely difficult. Finally, the complex iron cyanides can only be oxidized by extremely high amounts of chlorine at high temperature.

Cyanides may be removed by treatment with ferrous salts. This treatment has been applied to effluents in which cyanides are present in complex forms, i.e. ferrocyanides and ferricyanides. By reaction with ferrous sulphate, both compounds precipitate according to the reactions:

$$K_4Fe(CN)_6 \xrightarrow{+\ FeSO_4} K_2SO_4 + K_2Fe(CN)_6$$

$$K_3Fe(CN)_6 \xrightarrow{+\ FeSO_4} K_2SO_4 + Fe_4\left[Fe(CN)_{6\ \ 3}\right]$$

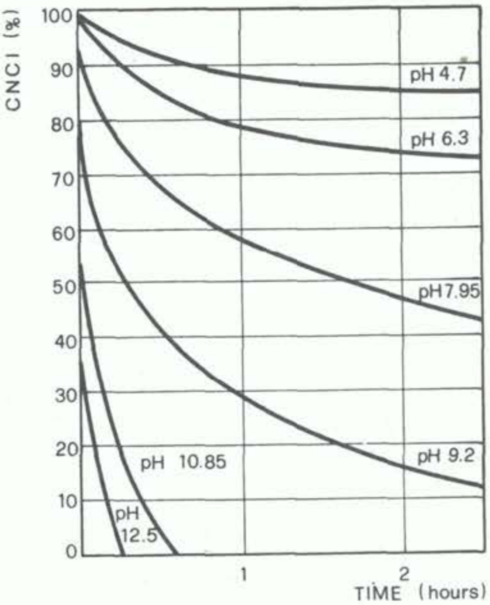

Figure 50 Decomposition of the cyanogen chloride with time and pH.

The ferropotassium-ferrocyanide precipitate is transformed by the excess ferrous sulphate into ferrous ferrocyanide $Fe_2(Fe(CN)_6)$ which, by spontaneous oxidation with the oxygen present in air, is transformed into the intense blue ferric ferrocyanide. The above reactions are accompanied by precipitation of greenish ferrous hydroxide.

Since cyanide-containing effluents are often polluted by heavy metals too, the oxidation and alkalization process is accompanied by the formation of chemical precipitates which essentially consist of the heavy metal hydroxides, of calcium carbonate and sometimes even of calcium sulphate, if hydrated lime is used as an alkalizing compound.

The results obtained with chlorine are comparable with those obtained with chloroderivatives, e.g. hypochlorites of sodium and calcium. The former, in particular, is extensively used, it being simple to store and dose.

Actually it does not require all the precautions which are rigorously needed for chlorine, which as is known, is extremely toxic. The quoted reagents being basic, the need for an alkalizing agent may be limited and sometimes even obviated. Hence, sodium hypochlorite is used in low - and medium - capacity treatment plants.

Other oxidizing agents such as potassium permanganate, ozone, chlorine dioxide and hydrogen peroxide have rarely been applied. The reason for this is to be found in the higher costs involved in such treatments and in the little information available as to the results which may be obtained under different operating conditions.

Oxidation with atmospheric oxygen, using additional catalysts, is also of a certain interest. Various patented processes are known: one method makes use of the catalytic action of the active powdered carbon, another employs a coal-like product derived from slow distillation of fossil coal.

At present, ion exchange plants are widely used for treatment and subsequent recirculation of the rinsing waters used for plating processes and generally from surface treatment of metals. Cyanides are fixed, with other anions, on anionic resins and are subsequently recovered from them in the alkaline regeneration phase. The cyanides that are present in regeneration eluates must be subsequently removed by other methods described.

Among the used alternative techniques, mention is made of stripping either with air or with air-steam mixtures. Cyanide-polluted effluent is subjected acidification to pH=2-3, to release hydrogen cyanide in the gas phase:

$$2\ CN^- + H_2SO_4 \rightleftarrows SO_4^{--} + 2\ HCN$$

Separation of the hydrogen cyanide is carried out by air or air-steam blowing into the acidified effluent. In order to obtain satisfactory results, the interphase contact occurs in packed columns preferentially operating under vacuum. A further parameter useful for increasing process efficiency is the temperature. As it is impossible to release hydrogen cyanide into the atmosphere, it may be eliminated by combustion in the presence of excess oxygen:

$$4\ HCN + 5\ O_2 \rightarrow 4CO_2 + 2N_2 + 2H_2O$$

The process may be carried out at relatively low temperature (about 300°C) in the presence of combustion catalysts (Figure 51). Instead of combustion, it is also possible to recover cyanide in the gaseous form by adsorption in sodium hydroxide solution producing sodium cyanide solution.

Finally, mention is made of electrolytic decomposition processes, which may be carried out by different methods; in all cases, they cause the anodic oxidation of cyanides.

Both stripping and electrolytic decomposition may be profitably applied to wastewaters containing high cyanide concentrations.

6.6 FLUORIDES

Fluorides are usually removed from wastewaters by chemical precipitation with calcium compounds.

Fluoride is generally found in wastewaters either in the form of fluoride ions or as hexafluosilicic acid. This last, by reaction with alkali, under neutral conditions is transformed into the fluoride ion according to the reaction:

$$H_2SiF_6 + 6\ NaOH \rightarrow 6\ NaF + Si(OH)_4 + 2\ H_2O$$

Lime is the most used reagent for fluoride precipitation as calcium fluoride, a white crystalline precipitate. Results obtained at both experimental and full scale prove that, in order to obtain optimum results, 100% excess calcium over the stoichiometric amount is required.

In any case, the use of lime produces some problems because of the low solubility of the reagent, and hence the lower availability of the calcium ion in the solution. Much better results are obtained by performing the simultaneous acidification of wastewaters to pH of 7-8.

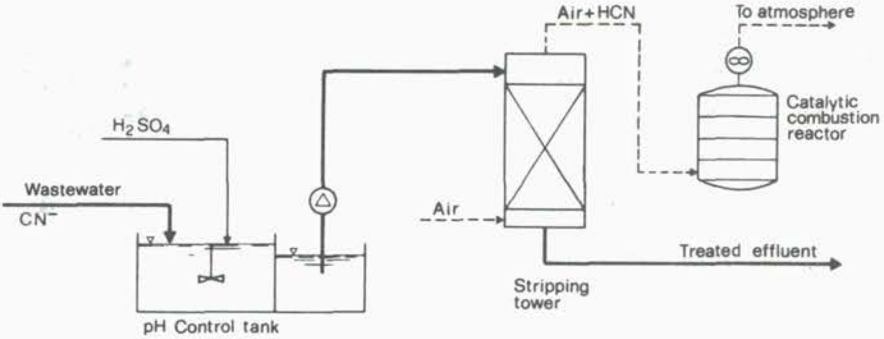

Figure 51 Stripping and catalytic combustion process of cyanidric acid.

Alternatively the use of calcium chloride can be foreseen, possibly in addition to the lime used as a neutralizing agent.

By chemical precipitation alone, residual concentrations of 8 ppm may be achieved at best, even if in full-scale plants they generally exceed 10-15 ppm. Better results may be achieved by exploiting the adsorption power of calcium fluoride precipitate. To this end, sludge recirculation must be carried out to maintain the highest possible concentrations and the reactor must be dimensioned with sufficiently high contact times, i.e. of the order of 50-60 min. For the above reasons, better final results are generally obtained with wastewater containing higher fluoride concentrations. By exploiting such conditions, residual fluoride concentrations below 5 ppm are achieved in the settled effluent.

The process may be further improved by addition of inorganic coagulents based on aluminium, iron and magnesium. These not only cause a better clarification, but further contribute to the fluoride adsorption on hydroxide flocs.

A 2-stage process was also proposed for the reduction of fluorides from 90-135 ppm to 1-2 ppm. The outline of the treatment is shown in Figure 52. The wastewaters are treated in the first stage with a high dose of lime to raise the pH to approximately 12, and then settled. The effluent is neutralized by the addition of acid and then undergoes chemical coagulation with alum and polyelectrolyte. In order to obtain good removal efficiency, an excess of lime and accurate control of pH during the coagulation stage (the influence of which is illustrated in the graph in Figure 53) are determining factors.

In addition to chemical precipitation, fluorides may be removed by adsorption. However, the process has seldom been applied at full scale and may be convenient only for very low strength wastewaters. In this sense, it may be considered as a possible integrative treatment to chemical precipitation.

The adsorbent which shows the greatest possibilities is activated alumina, which may be regenerated by sodium hydroxide, with subsequent neutralization of the eluate with sulphuric acid. Furthermore, the use as regenerant of an aluminium sulphate solution has been investigated. With a regeneration level of 183 g alum per l activated alumina, the exchange capacity has been found to be about 71 g F/l alumina. As an alternative to activated alumina, hydroxyapatite has been proposed, which may be regenerated with phosphoric acid and caustic soda. By use of the quoted reagents, final fluoride concentrations lower than 1,5 ppm may be obtained.

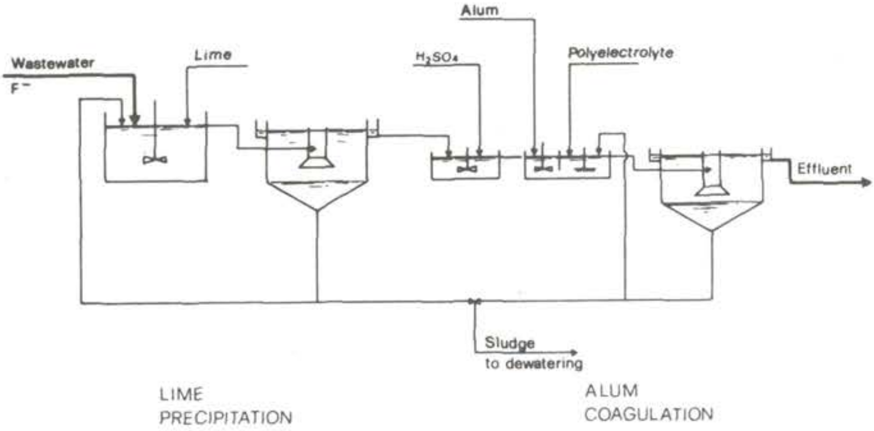

Figure 52 2-stage process for chemical precipitation of fluorides

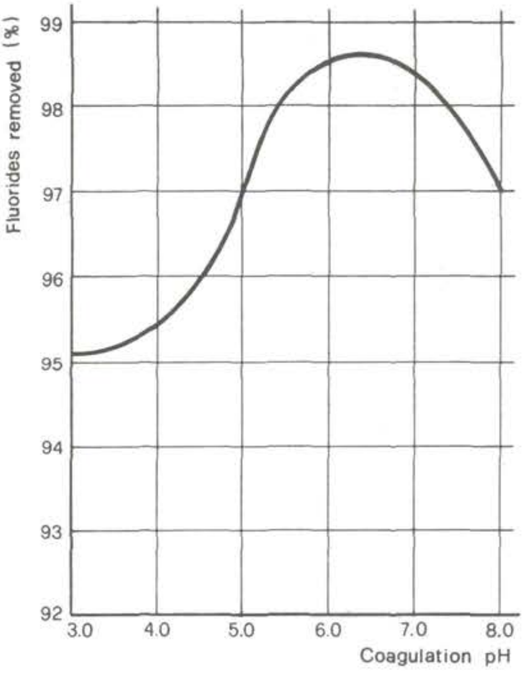

Figure 53 Percentage fluoride removal in two stage plant (see Figure 52) for constant pH in lime precipitation stage (11, 8-12, 1) and variable pH in coagulation stage (fluoride concentration in raw wastewater: 90-135 ppm).

Other adsorbents are described in the literature, e.g. bentonite, diatomaceous earth, particular activated carbons.

Ion exchange on highly selective anionic resins is a further possible means of intervention for fluoride removal.

6.7 NON BIODEGRADABLE DETERGENTS AND OTHER SURFACE-ACTIVE SUBSTANCES

The above compounds are removed by physicochemical treatments. For effluents containing average concentrations, chemical coagulation with the conventional iron and aluminium salts is extensively used. The treatment efficiency obviously depends on the effluent characteristics and on the reagent type and dose. Tests carried out on alkyl benzene sulphonate polluted effluents at concentrations above 100 ppm show the possibility of obtaining residual concentrations lower than 20 ppm. The drawback of this method is the high production of sludge containing the removed surfactants.

In order to achieve an improved quality, chemical coagulation may be conveniently integrated with a subsequent adsorption on activated carbon. The surfactants removal is comparable with the adsorption of other organic compounds; in fact, in agreement with theoretical forecasts, surface-active substances are better adsorbed from pure solutions than from effluents containing other pollutants, e.g. as is the case of laundry effluents.

Activated carbon may be used for wastewater treatment in powdered form or in the granular form as a fixed bed. As is known, the latter allows a greater flexibility and the possibility of obtaining lower residual concentrations. The determination of the adsorption isotherms allows an evaluation of the adsorption efficiency of the different activated carbons available on the market. Other useful information for the design of the adsorption system is the relationship between removal efficiency and contact time.

When the detergent concentration is particularly high, foaming may be advisable; this process is carried out by air dispersion in the form of very fine bubbles into the wastewater to be treated. Surfactants accumulate as foams, which are continuously removed from the column, and later disposed of usually by incineration. Like chemical coagulation, foaming seldom allows the achievement of residual concentrations lower than 5-10 ppm. The process efficiency is affected by temperature, pH, air flow-rate, bubble size and obviously by the surfactant characteristics.

The addition of inorganic compounds capable of complexing surface-active substances was found to exert a favourable effect on foaming efficiency. To this end, iron and aluminium hydroxides are suitable for anionic surfactants; for cationic ones, satisfactory results have been obtained with copper and iron hexacyanoferrates.

The possibility of using surface-active substances of opposite charge to bring about the formation of an insoluble complex is proved by the use of alkyl-dimethyl-benzyl-ammonium chloride for alkyl benzene sulphonate. The precipitate may be removed either by chemical coagulation or by filtration. Dosing of quaternary ammonium salt must be calculated at the ratio of 1 mg QAS to 1 mg alkyl benzene sulphonate.

Use of the process of ultrafiltration has been experimented with on different effluents containing detergents, in particular laundry wastes polluted by anionic and non-ionic detergents. Cellulose acetate membranes have shown a low grade of rejection of the non-anionic tensides and also of anionic tensides when polyphosphates are present. On the contrary, using PSAL-type membranes (non-cellulosic skin on cellulosic backing), rejection grades of over 90% have been obtained.

Tests are in progress on other treatments, such as reverse osmosis and the use of adsorption resins.

6.8 INORGANIC PHOSPHORUS COMPOUNDS

The most likely inorganic forms of phosphorus present in wastewaters are phosphates (orthophosphate, metaphosphate and pyrophosphate) and polyphosphates. Phosphites, which are seldom found, may easily be oxidized to phosphate.

The classical method of phosphorus removal is chemical precipitation. For this purpose, iron and aluminium salts as well as hydrated lime have been widely used. The first two cause precipitation of the corresponding phosphates; by reacting with orthophosphates, lime causes precipitation of hydroxyapatite: $Ca_5(OH)(PO_4)_3$. Precipitation of polyphosphates is only partial while that of phosphates, when sufficient amounts of reagent are added, is almost total. In the case of domestic sewage with a total phosphorus concentration of about 10-20 ppm (about 30% orthophosphate, 60% polyphosphates and 10% organic phosphorus,) the chemical treatment leads to residual phosphorus concentrations of 0.7-1.2 ppm.

Better results can be achieved by performing the chemical treatment downstream of the biological process, because the latter causes polyphosphate hydrolysis to orthophosphates. Therefore residual phosphorus contents below 0.5 ppm may be obtained. Chemical precipitation may be carried out by dosing the reagents in the activated sludge tank. Such a technique allows the use of ferrous sulphate, which is cheaper than ferric and aluminium salts, and which, in an aerated environment, is transformed into the ferric form. The results achieved by simultaneous precipitation are generally worse than those obtained by post-precipitation, due to the solids carry-over into the secondary sedimentation effluent. Residual phosphorus contents ranging from 0.8 to 2 ppm have normally been obtained in full scale plants.

Dosing the precipitation reagents is carried out on the basis of 1.5 - 2 mole Al (or Fe)/mole phosphorus. For lime aided precipitation the reagent is dosed to give a pH 10.5-11. In this case, consumption is strictly dependent on sewage alkalinity (Figure 54).

Phosphorus removal may also be achieved by the biological processes that are mainly used to remove biodegradable organic pollutants. A typical example is given by biological plants for domestic sewage.

The total phosphorus removal that may be obtained in the primary sedimentation stage of such plants averages 5-15% and the BOD removal 25-30%. The phosphorus removal efficiency in the subsequent biological treatment process has been evaluated at about 30% of residual phosphorus. Hence an overall efficiency of between 33-41% has been calculated. Such a result has often appeared insufficient to protect semi-enclosed water bodies from the occurrence of eutrophic conditions.

The low efficiency levels of phosphorus removal during the biological process depend exclusively on the fact that the biodegradable organic matter present is low compared with the amount needed by the bacterial population to metabolize the phosphorus contained in the sewage. As a matter of fact, the calculated ratio of BOD_5 to P in domestic sewages is 25, whereas BOD and P removal by metabolic processes occurs at a BOD_5/P ratio = 90. In other words, sewage contains a 260% excess phosphorus over the amount needed for bacterial growth.

The phosphorus removal efficiency by the biological treatment is certainly also affected by the operating load of the biological treatment plant (sludge loading). As is known, the conditions allowing the endogenous respiration of bacteria (extended aeration activated sludge plants) cause a decrease in biomass growth as well as the release to the sewage of nutrients which would otherwise be adsorbed by the sludge.

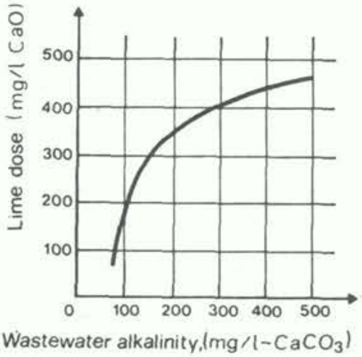

Figure 54 Lime dose to obtain pH = 10,5 - 11, as a function of the alkalinity of the wastewater.

In the conventional biological plants operated at average sludge loadings, the phosphorus content in the biomass may be evaluated at 2.5% (as PO_4 with respect to volatile solids). However, several experimental studies have shown the possibility for the biomass to adsorb phosphorus, under defined conditions, in higher concentrations (phosphorus luxury uptake), and achieve removal efficiencies over 90%. The application of this process at full scale, is at present under examination in many countries.

Another process of which a few applications are known, is illustrated in Figure 55. The raw wastewaters undergo primary sedimentation, biological oxidation with activated sludge and secondary sedimentation. The re-cycled sludge is fed to a thickener in which there are anaerobic conditions which allow the release of the phosphorus from the sludge. The supernatant is treated with lime to reduce the elevated phosphorus content. The chemical sludge is separated in the primary sedimentation basin. The interest in this kind of process rather than those chemical treatments previously described is due to the notable saving of reagent, which results.

On the subject of treatment for the removal of inorganic phosphorus, the use of algal suspensions (blue-green algae) with retention times of approximately 15-20 hours can be mentioned. Only a fraction of the phosphorus contained in the sludge is incorporated in the algal cells whilst generally a more significant fraction precipitates as calcium phosphate, if this element is present in the wastewaters. The precipitation is aided by the elevation of the pH following the photosynthetic removal of carbon dioxide.

This technique is interesting for the reduced production of sludge and for the low working costs. The more evident disadvantages are the considerable area required and, in some cases, the unfavourable climatic conditions.

A comment should also be made regarding the ion exchange system, based on resins which are selective towards phosphate ion. Experimental results confirm the possibility of obtaining residual concentrations of 0.1 - 0.2 ppm. However, the method has disadvantages of an economic nature.

6.9 PATHOGENIC MICRO ORGANISMS

The commonly used processes for removal of biodegradable organic matter (as expressed by BOD) also reduce the concentration of pathogens and thus render disinfection of

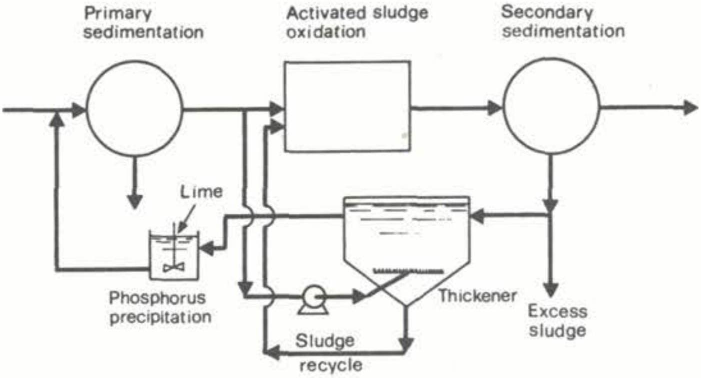

Figure 55 Activated sludge plant with chemical precipitation of phosphorus released by the recirculated sludge maintained in anaerobic conditions.

the final effluent more effective.

Removal of coliform bacteria (which is an indicator organism for pathogens) of approximately a half to one order of magnitude can be accomplished by primary treatment, while another order of magnitude is usually accomplished by secondary biological treatment. Thus full conventional biological treatment can reduce coliform bacteria by between 95 to 99 percent (lime treatment can remove coliforms by to 4 orders of magnitude). Virus removal by conventional treatment is less efficient than bacteria removal. Primary treatment removes only 10 to 30% viruses, while full biological treatment can remove between 70 and 95 percent.

The various types of wastewater treatment processes aimed at removing biodegradable substances (as expressed by BOD) are described in paragraph 6.12.

Disinfection of wastewater can be effective and economically feasible when performed on well-treated effluent. Chlorination is the most common disinfection method, although other halogens and oxidants can be used as well.

Chlorination dosage of between 15 and 50 mg/l free chlorine have been used on raw sewage and primary effluent with inconsistent results as far as coliform removal is concerned and with a danger of bacterial regrowth. Dosages of between 5 and 12 mg/l of free chlorine have been successfully used on secondary effluent.

Free chlorine and chlorine derivates combine rapidly with the ammonia present in the effluent and give rise to the formation of chloramines which, although having a weaker bacteriacidal effect than hypochlorite ions and hypochlorous acid, are more stable under solar radiation. Break point chlorination is almost impossible in sewage effluents unless they are fully nitrified and all reducing agents and most organic matter have been removed.

The use of gaseous chlorine requires somewhat complex plant and also careful operation with regard to safety. This is due to the characteristics of chlorine which can cause varying degrees of irritation to the skin, mucous membranes and the respiratory system, depending on the concentration and the duration of the exposure. It is for these reasons that gaseous chlorine is generally used in medium and large plants, because of its lower cost; in small plants hypochlorites, which are much easier to handle, are preferred, as is also the case when disinfection is foreseen only as a seasonal treatment or in emergencies.

Chlorination, as traditionally practised, does not provide virus-free effluent, sometimes an essential requirement, particularly when total reuse of effluent is to be achieved. The possibility of obtaining complete removal of viruses depends on the quality of the effluent undergoing chlorination and therefore of the type of treatment process which has been employed upstream. It is, in fact, important to obtain the complete removal of suspended solids in which the viruses can become enmeshed, thus avoiding the disinfecting action. For this reason the turbidity of the waters to be chlorinated should certainly not exceed 1,0 Jackson Turbidity Unit (JTU) and should, preferably be less than 0,2 JTU. This necessity requires the insertion of a tertiary treatment phase upstream of the chlorination (Figure 56) with coagulation and filtration.

Due to the poor virucidal properties of the chloramines, it is necessary that chlorination is pushed to break-point, so as to achieve a free chlorine residual. Therefore, in order to reduce the consumption of chlorine, it is important that the concentration of ammonia in the discharge is limited, by means of good nitrification during the biological phase.

The toxicity of the residual chlorine, both free and combined, with respect to aquatic life, has recently raised the problem of the de-chlorination of effluents. The most common process nowadays uses sulphur dioxide which reacts with both free and combined chlorine as follows:

$$SO_2 + H_2O + HOCl \longrightarrow H_2SO_4 + HCl$$

$$SO_2 + 2H_2O + NH_2Cl \longrightarrow NH_4HSO_4 + HCl$$

with a consumption of approximately 1 mg SO_2 per mg of Cl reduced. The reaction is immediate with free chlorine and slightly slower with chloramine, in any case exhausting itself within a few minutes. However, in contact with free oxygen, the sulphur dioxide has a marked tendency to oxidize, with a subsequent increase in the necessary doses and with risk of deoxygenation of the effluent. This can make an ultimate reaeration phase necessary.

A major advantage of using sulphur dioxide is that the necessary fittings for the feeding equipment are the same as those for dosing gaseous chlorine. There are also other reducing compounds of sulphur (for example bisulphite and thiosulphate) which, although having a slower reaction when compared with sulphur dioxide, are easier to dose and more adaptable to the needs of small plants.

As an alternative to these reducing processes, use may also be made of activated carbon, particularly because of the simultaneous action which is achieved in the removal of any undesirable chlororganics; the presence of free chlorine, although reducing it, is not capable of totally negating the adsorption capacity of the carbon for such compounds. This treatment however is considerably more expensive than the use of sulphur dioxide, and therefore cannot be justified if the only desired effect is the removal of residual chlorine.

As an alternative to the traditional processes of chlorination of wastewaters, other techniques of disinfection have been developed in recent years. Amongst these the most interesting appears to be the use of chlorine dioxide, ClO_2, because this oxidant does not give rise to the formation of chloramines or chlororganics such as chloroform thus avoiding the problems already stated regarding disinfection with chlorine. Chlorine dioxide is only used in aqueous solution, being generated by chlorine-chlorite or by chlorite-hydrochloric acid processes. Disinfection with

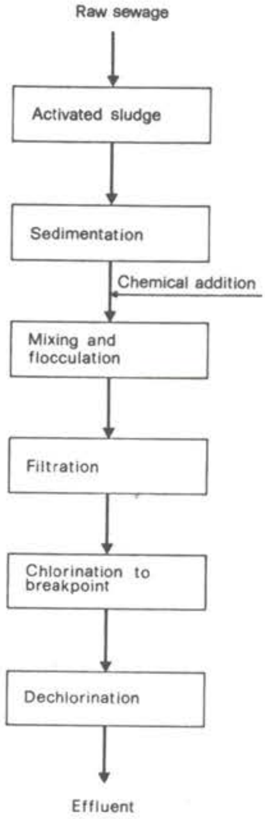

Figure 56 Disinfection scheme for virus removal, including coagulation and filtration.

ozone, too, until now almost exclusively used for the treatment of the water for supply purposes, is receiving renewed attention in the wastewater treatment field. Despite some disadvantages due fundamentally to the selective action which does not permit the oxidation of some substances, for example ethanol, and to the poor flexibility of the treatment as regards variations of load and flow, the use of ozone appears interesting for its high germicidal effectiveness, even against resistant organisms such as viruses and cysts. This disinfection technique is, however, considerably more expensive than those in which chlorine and chlorine derivatives are used.

6.10 THERMAL POLLUTION

The control of thermal discharges - mainly produced by cooling operations - is often associated with the possibility of heat recovery; its applications, so far predominantly at the experimental stage only, are conditioned by the low intensity of available heat and are direct especially towards agriculture and aquaculture. In the former case, applications concern the direct irrigation of crops (rice, maize, fodder) as well as the conditioning of green-houses and sometimes of soils, in order to lengthen the growing season. On the basis of the results obtained, the use of hot water for fish culture or crustacean breeding is of particular interest, since the metabolic and growth rates of cold blooded aquatic organisms increase greatly with temperature. There is, however, still the necessity to carry out further research in order to find more ideal temperatures for particular species, especially as regards the consumption of foodstuff and conversion ratios.

Direct cooling of wastewaters may be achieved in storage basins where heat dispersion occurs by evaporation and, to a lesser extent, by conduction and radiation. This is a very simple system, which involves low operating and maintenance costs; its drawback is the high land demand: in fact, in the case of power generation stations, it requires 0.5 - 1 ha/MW, depending on the meteorological characteristics of the areas involved.

However, space requirements may be considerably reduced by fitting the basins with sprays or with other devices which increase both the exchange surface area and the relative velocity between water and atmosphere. This makes the operation more difficult, particularly because of the possibility of obstruction to the sprays. An alternative system is to operate the basins naturally in the winter months and to put sprays into operation only when heat dispersion must be greater. Compared with natural basins, if sprays are employed, the basin surface may be reduced to 5-10%.

Another possibility uses wet cooling towers in which heat exchange between water and air is facilitated by the large contact surface, available in the inner packing. In the case of natural draft towers (Figure 57), air circulation is produced by the difference in density between the inside of the tower and the outside; two solutions are possible, i.e. with cross-currents or countercurrent, depending on the methods of feeding of the air and water to be cooled. Heat is mainly dispersed by evaporation of a fraction of the flow and, to a lesser extent, by heat convection from water to air. The tower performance is affected by weather conditions: evaporation in fact decreases on decreasing the temperature of air and on increasing its humidity.

Mechanical draft towers (Figure 58) operate according to similar principles: air is circulated by means of fans situated above the inlet of the water to be cooled. Hence towers may be more compact and lower in height, which makes their siting easier. A further advantage is greater operating flexibility, the air circulation being adjusted as a function of weather conditions. Compared with natural draft towers, the mechanical types involve lower initial investment costs but higher operating costs, especially due to the high energy-consuming fans.

If towers are used, the possibility exists of close-circuit re-use of the cooling water; in this case, the quantity of evaporated water must be restored and the salt content constantly checked.

Wet towers may give rise to environmental problems, especially due to the formation of persistent plumes, caused by condensation as moist air comes into contact with the external air. A further problem is the conveyance of water drops in the upward stream, which may be reduced, though not completely eliminated, by drop separators. The microclimate may thus be affected and persistent humidity may arise, especially in the case of forced draft towers which are lower.

In theory, such inconveniences may be avoided by using dry cooling towers. In this case, heat dispersion takes place through an exchanger consisting of finned pipes, by conduction through the metal thickness and subsequent convection, without any direct contact conveyance of droplets is eliminated; however, it being impossible to use the latent evaporation heat for cooling, as is the case with wet towers, and higher air flows and larger air temperature increases are required. This system has seldom been applied so far, due to the higher costs involved and to the tower sizing; its adoption may presently be justified only when availability is severely

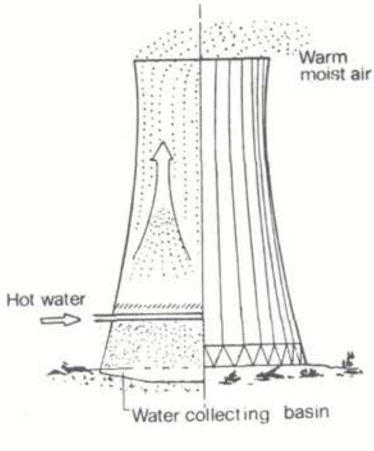

Figure 57 Natural draft counter-flow cooling tower.

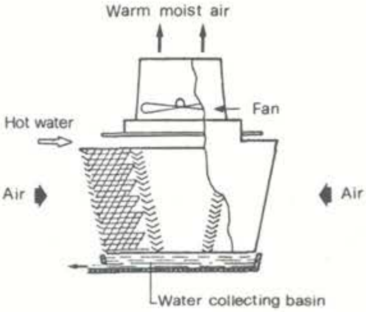

Figure 58 Mechanical draft cooling tower.

limited and significant net power generation losses can be accepted.

6.11 SUBSTANCES WITH A DELETERIOUS EFFECT ON THE TASTE AND SMELL OF PRODUCTS FOR HUMAN CONSUMPTION (Phenols and aromatic compounds)

Biological treatment can be used to remove these polluting compounds when the concentrations are not so great as to cause toxic phenomena in bacterial flora. A high degree of biodegradability, up to 200 ppm, has been seen, in particular for phenols, whilst at higher concentrations inhibition occurs. This information however is only indicative since the kind of plant involved, and also the simultaneous presence of other organic compounds, plays a decisive part in the application of biological treatment. Whenever possible, it is advisable to treat these discharges in combination with domestic wastewaters, in conventional installations either of activated sludges or trickling filters. Should industrial discharges be consistently present, it is appropriate to make use of low loaded plants such as oxidation ditches, or lagoons, or else multi-stage plants.

Biological treatability obviously cannot be assumed for all the aromatic compounds, nor for all kinds of phenols, since the characteristics of biodegradability are connected to both the complexity of the molecular structures and to the characteristics of the substances linked to the aromatic rings.

Amongst the methods of greatest interest as regards the removal of non-biodegradable aromatic pollutants is adsorption on activated carbon. The effectiveness of this process is high for polyaromatic compounds and generally for substances which have a low solubility in water, that is to say for compounds which normally show greater characteristics of bioresistance. In this sense, adsorption is proposed as a complementary treatment to biological degradation. However, phenols show good characteristics of adsorption on activated carbon, to the extent that this technique can be applied directly to those discharges with low concentrations, where conditions would render biological treatment inefficient from the technical point of view.

As regards other treatment techniques, chemical oxidation by means of strong oxidants such as chlorine dioxide and ozone, and wet combustion may be quoted. Chemical oxidation can be used when the concentrations of pollutants to be oxidised are relatively low, such as the circumstances in which adsorption on activated carbons is conveniently applied. Wet combustion has very high specific costs and can therefore only be used for particularly concentrated discharges, or for those with very low volume.

When the concentration of phenolic compounds is high, up to 1000-2000 ppm, recovery processes based on extraction, stripping, and adsorption are often used. However, these processes need to be integrated as a subsequent stage to the treatments dealt with previously.

Extraction methods are based on the use of solvents which can then be recovered by thermal or chemical methods. For example, amongst these is benzene which, after having absorbed the phenolic compounds, can be recovered by steam stripping or - alternatively - by washing with sodium hydroxide. In this latter case, sodium phenolate is formed which in the subsequent treatment with carbon dioxide gives rise to the formation of sodium carbonate and of phenols which can then be recovered. By treating the sodium carbonate with lime, sodium hydroxide can be removed for recycling to the process. The scheme of the benzene sodium hydroxide process is shown in Figure 59.

The residual phenol concentration in the effluent from the extraction treatment depends considerably on the nature of the phenolic compounds. However, residual concentrations of 100-300 ppm can generally be achieved.

Isopropyl-acetate, tricresyl phosphate, butyl alcohol, ethyl ether, and phenosolvan are amongst other solvents which can be used for this kind of process. The last, phenosolvan, can be used in practice in accordance with the scheme shown in Figure 60.

The removal of phenols from wastewaters by means of steam stripping allows the recovery of phenols in the pure state, and at the same time does not cause any secondary pollution of the wastewater with the solvent, as happens during extraction processes. The phenols contained in the distillate are recovered during washing with sodium hydroxide. Hot gas (or even hot air) can be used instead of steam, as shown in the design scheme in Figure 61.

In Figure 62 a recovery plant based on adsorption on activated carbon is shown.

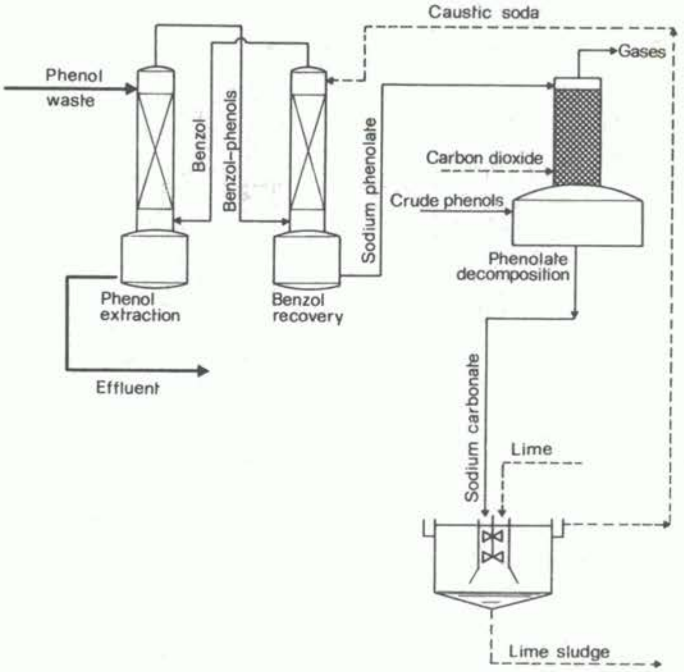

Figure 59 Phenol removal process using benzene, with solvent recovery by scrubbing with sodium hydroxide.

The phenols are adsorbed onto columns of granular activated carbon which are successively regenerated with steam and benzene. The separation of recovered phenols from the solvent is carried out in distillation columns.

6.12 SUBSTANCES HAVING AN ADVERSE EFFECT ON OXYGEN BALANCE

The risk of deoxygenation of the receiving water is generally connected with the discharge of biodegradable organic matter and with the consequent action of bacterial self-purification. Inorganic pollutants in the reduced form which, in a natural environment, can undergo reoxidation (e.g. sulphides, sulphites, reduced metals) are of minor importance. Purification of biodegradable organic effluents is almost always achieved by biological treatment (mostly aerobic and sometimes anaerobic). Only under exceptional circumstances is the biodegradable organic matter removed by physicochemical (flocculation and adsorption) or simply chemical (oxidation) processes. Deoxygenation can be also indirectly produced by the enrichment of the aquatic life due to nutrient discharge. Phosphorus removal has already been discussed in paragraph 6.8. The main nitrogen control techniques are described in this section.

6.12.1 Activated Sludge

The activated sludge process presently constitutes the most widely used form of aerobic biological treatment; it is based on the aeration of effluent in contact with an established bacterial population which, due to bioflocculation phenomena, tends to form flocs which are readily separable by sedimentation. The biodegradable

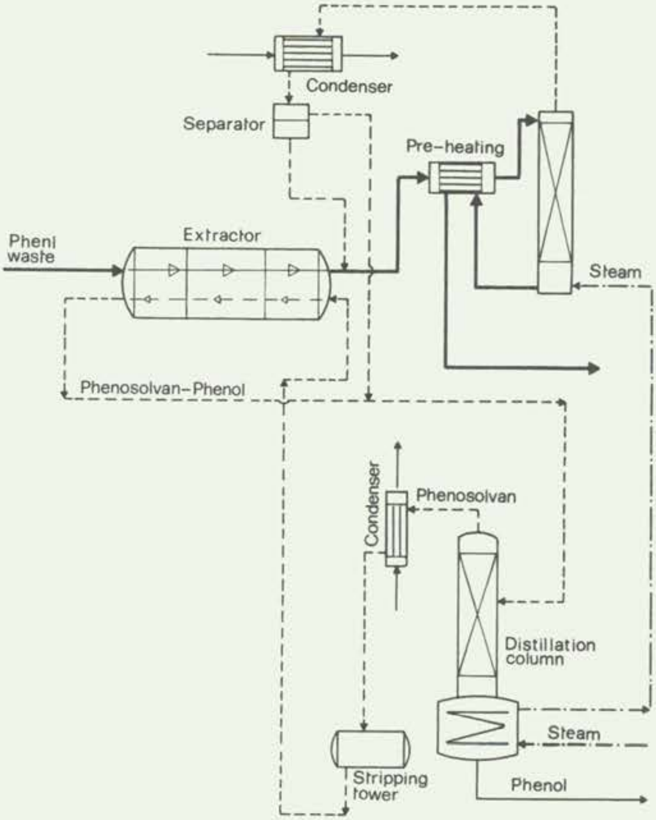

Figure 60 Phenol removal process using phenosolvan.

organic matter in the effluent constitutes the substratum that bacteria use as an energy and material source for the production of new cells. It is thus separated from the effluent and biochemically transformed partly into living organic matter, or at any rate adsorbed onto the floc, and partly into stable final products.

Activated sludge processes are especially governed by the ratio between the biodegradable organic substrate introduced in the influent and the bacterial mass present in the system. Such a ratio conditions the system efficiency (Figure 63), the process oxygen demand and the production of new cellular mass that, under steady-state conditions, must be removed, since it constitutes surplus sludge. At high ratios, although still in the range which allows a satisfactorily efficient removal of organic pollutant, surplus sludge exhibits a marked putrescibility. Subsequent stabilization processes are therefore required, which are almost always carried out by biological means. Instead, by decreasing the surplus sludge, production may also be decreased and sufficient stabilization may then be guaranteed within the process itself.

This last technique, known as extended aeration, is a practice applied only to small plants: it is evident that with low loadings and consequent long detention times, large volumes are required for the aeration tanks. On the other hand, the process

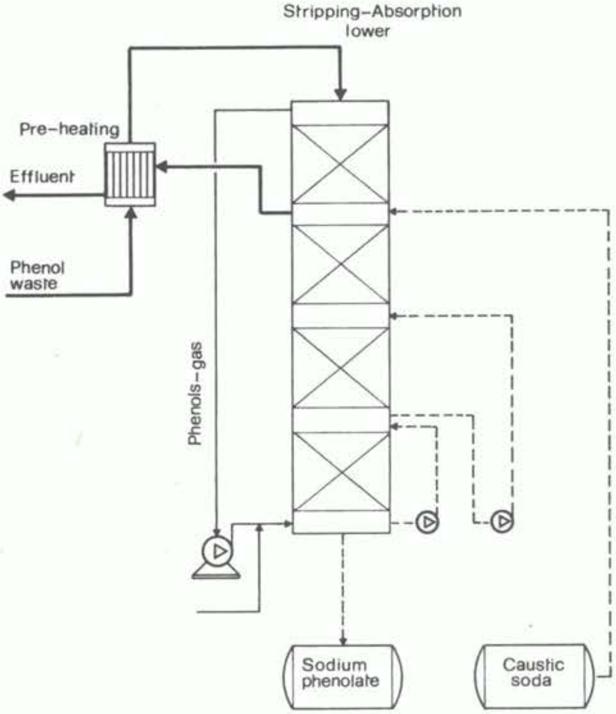

Figure 61 Phenol removal process using hot gas with recovery of sodium phenolate by absorption with sodium hydroxide.

is very simple as regards plant and operational requirements and therefore is preferable whenever complex management would present problems.

Due to high sludge age values which are maintained in the system, an extended aeration process is also capable of accomplishing complete nitrification (except perhaps when working under very severe weather conditions), thus allowing the nitrogenous oxygen demand to be satisfied without necessarily having to provide a 2-stage oxidation treatment. This latter is shown in Figure 64. The first stage is made up of a high rate activated sludge process, during which little nitrification occurs, due to the short solids retention time, but where a large part of the normal BOD is removed. The wastewater then enters the nitrification unit operated with a high sludge age value, compatible with the correct development of the nitrifying bacteria.

Activated sludge processes are carried out in basins where aerobic conditions are constantly maintained by artificial aeration provided either by surface mechanical aerators or by the direct diffusion of air into the liquid mass. Despite the fact that the removal of BOD generally follows a first order kinetic reaction, completely mixed reactors are generally to be preferred to those of the plug flow type. Apart from greater plant simplicity, completely mixed systems are, in fact, able to ensure a major dilution of the incoming wastewater into the entire basin volume; this allows less variation in organic loading and reduced shock effects, whether organic or toxic in nature. These advantages are particularly important as regards indus-

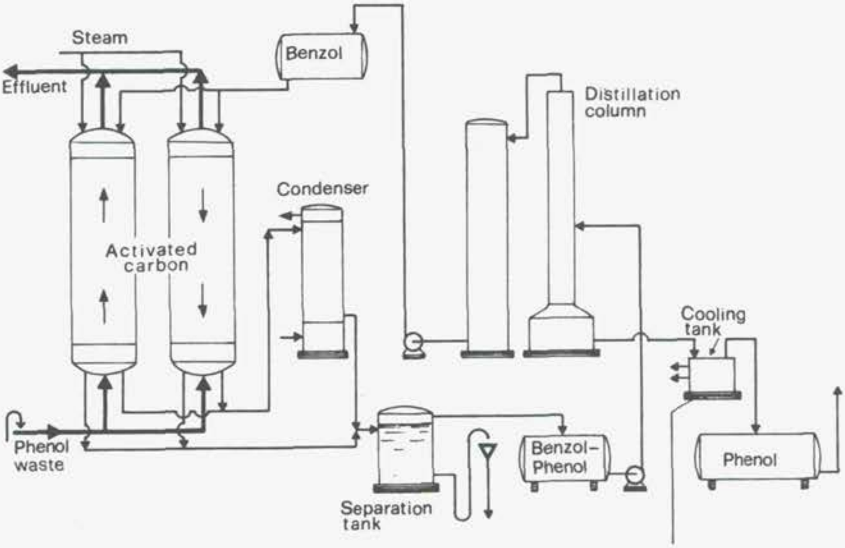

Figure 62 Phenol removal by adsorption on activated carbon and recovery with benzene.

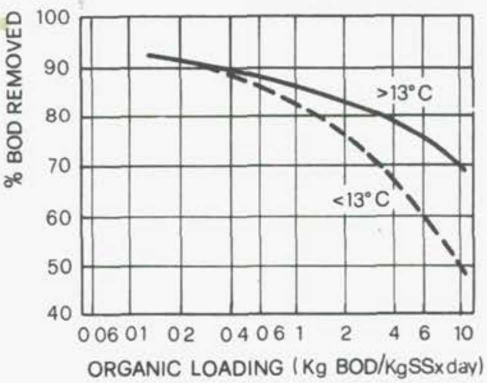

Figure 63 BOD removal efficiency versus organic loading for activated sludge treatment of municipal wastewater.

trial or combined wastewater treatment, where variations in influent conditions can often occur.

As regards wastes with a high BOD concentration, the activated sludge process can be implemented more conveniently in 2 or more successive stages, each having a sedimentation phase; in this way concentrations of substrate and bacterial population are different from stage to stage, and thus removal rate - which for first

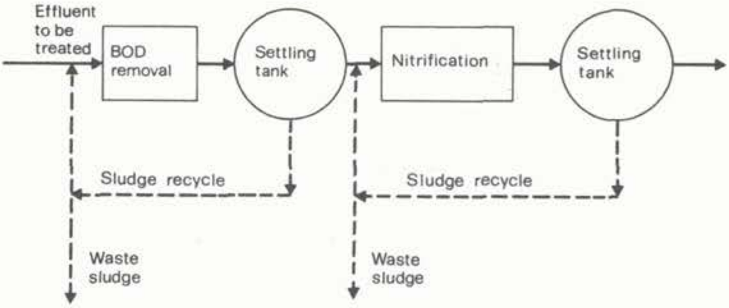

Figure 64 Activated sludge treatment plant, with separate nitrification stage.

order kinetics is in proportion to the concentrations themselves - is on an average higher than for a single-stage reactor.

Recently there has been a renewed interest in the use of pure oxygen, rather than air, in activated sludge systems and a relatively high number of plants of this kind have been built in recent years. A schematic diagram of the most commonly used pure oxygen activated sludge process is shown in Figure 65. It comprises a series of completely mixed reactors, covered so as to allow recirculation of the oxygen. Due to the higher partial pressure of oxygen above the liquid, there is the advantage of an increase in the oxygen concentration gradient between the gas and the liquid phase.

It is then possible to maintain higher cell concentrations (generally above 5.000 mg/l) and consequently a better substratum removal rate and thus shorter hydraulic residence times, with reduced aeration capacity, can be achieved. Considerable improvements are also reported as regards sludge settleability and lower surplus sludge production.

6.12.2 Lagooning

This form of biological treatment also employs bacterial suspensions; however it is far more extensive than the activated sludge process. In its simplest form, it does not require an artificial oxygen supply, obtaining it by atmospheric molecular diffusion and more especially by the photosynthetic action of the algae, which develop in the lagoon upper layers. In very shallow aerobic ponds, the presence of oxygen is guaranteed at all levels; in faculatative ponds, which are most frequently used, it is limited to the upper layers; on the bottom and in particular in the settled matter level, transformations occur under anaerobic conditions. In this treatment, no cell recirculation is practised; therefore it is impossible to artificially control the bacterial concentration at the same levels established by the kinetics of biological reactions. Therefore, in comparison with intensive processes, the volumetric loads that may be applied to lagooning are considerably lower; consequently large surface areas are needed. This is the main drawback of the system, which does however offer two advantages: a great simplicity and complete energy saving, made possible because no aeration is needed.

Aerated lagoons, in which aerobic conditions are maintained by surface aerators, are in more frequent use due principally to the fact that they require much less space; wastewater is treated on a flow-through basis, generally without any recirculation of cellular matter. When aerobic conditions are homogeneous throughout the whole

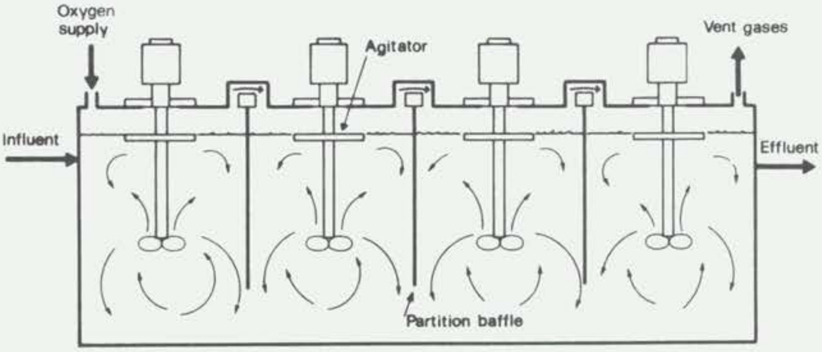

Figure 65 Schematic diagram of pure oxygen activated sludge reactor.

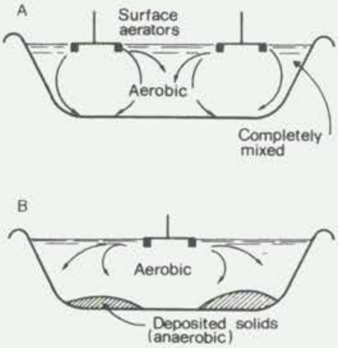

Figure 66 Two types of aerated lagoons: completely mixed (above) and with anaerobic decomposition of deposited solids (below).

system, which then operates as a completely mixed reactor, it is impossible to achieve any solids sedimentation. The essential function of this type of lagoon is waste conversion; in general the effluent may contain more than one-third of the value of the incoming BOD in the form of cell tissue and it is therefore necessary to include a final phase of sedimentation in order to limit the suspended solids contained in the effluent.

Frequent use is also made of aerated lagoons which are maintained in a state of incomplete mixing so as to allow a large portion of both the incoming solids and the biological solids produced from waste conversion to settle onto the bottom; there, they undergo anaerobic decomposition, being deprived of oxygen in this zone. This form of aerated lagoon allows a considerable saving of energy (Figure 66).

6.12.3 Trickling Filters

This system of biological treatment carried out by bacterial colonies attached to supports, has the advantage of allowing the development of a high bacterial concentration in the reactor without requiring biological sludge recirculation. Operation is relatively simple when compared to the case of systems with suspended colonies and cellular recirculation and, for this reason in the past it has had a vast field of application, particularly in the case of small and medium-sized plants where such simplicity of operation is important. In its traditional form, with stones or similar material as filter media, it is less and less used in comparison with the activated sludge process due to considerably higher space requirements. Larger problems also exist over the possible presence of odours and insects and there is some disadvantage also concerning operational elasticity. The recent introduction of plastic media with higher surface areas per unit volume and higher voidage ratios, which allows high resistance to clogging, has aroused renewed interest in this kind of treatment, especially in the case of strong industrial wastes in which the trickling filter can act as a primary high load biological phase, with relatively low efficiency, upstream from the main activated sludge process; the graphs in Figure 67 in fact give an example of those results obtainable for some industrial waste waters.

In the domestic field, again referring to plants of moderate dimensions, other techniques using biological films attached to supports have recently been developed with the introduction of rotating discs that, although having the positive aspects mentioned above as regards trickling filters, also have limited space requirements and head losses which are comparable with those of activated sludge systems.

6.12.4 Anaerobic Process

The convenience of applying an anaerobic treatment for the partial removal of organic pollutants is connected with possible energy saving, since it avoids the adoption of aeration devices; energy-saving may be very significant in the case of effluents with strong organic pollution (a BOD of at least several grams per litre). To obtain a high rate of removal the process can be carried out following a technique (anaerobic contact process) which is substantially similar to the activated sludge process. It includes a totally mixed anaerobic reactor, followed by a phase of separation and recovery of the suspended anaerobic colonies which are recycled to maintain the necessary bacterial concentration. To obtain higher removal rates, the effluent is heated to the range of mesophilic digestion using methane produced by the anaerobic transformations. The treatment does not achieve the common effluent discharge standards and therefore the process can only be included as a primary phase before a successive aerobic phase.

6.12.5 Chemical-Physical Treatment

The use of chemical-physical treatment (Figure 68) for the removal of organic pollutants from wastewaters, by means of floculation followed by adsorption on activated carbon, is generally only applicable under particular conditions in connection with those pollutants which are only poorly biodegradable, or with regard to intermittent effluents which do not allow proper functioning of biological processes. Even in the case of municipal wastewater, they could nonetheless add considerable advantage when compared with simple biological techniques, particularly due to the regularity with which they can be operated (which is insensitive to the ever-possible presence of toxic agents), the greater flexibility and, in many cases, the greater treatment efficiency, particularly for the removal of a long list of organic compounds which are not biodegradable and which therefore can be found, unaltered, in biologically treated effluents (ABS, pesticides, phenols, pyridine, acridine, various hydrocarbons, etc.).

The chemical-physical processes, if complete with adsorption phases, do not compete economically with the biological ones, for which reason their practical application in municipal plants is limited to the first stage of floculation, which only allows the removal of the suspended component, with a limited influence as regards dissolved solids. However, for some industrial discharges, activated carbon is widely used for the removal of those organic components which cannot be eliminated

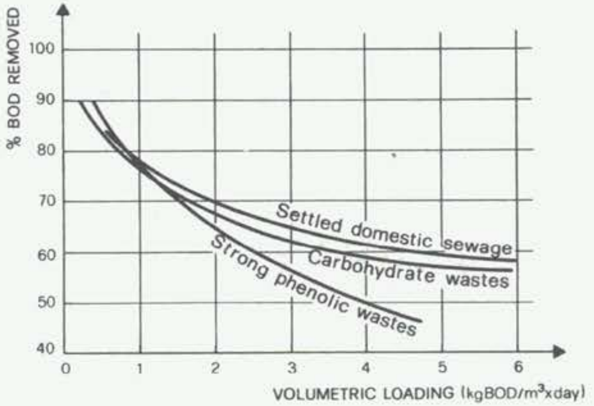

Figure 67 Performance of plastic media tricking filters, in treating different types of wastes.

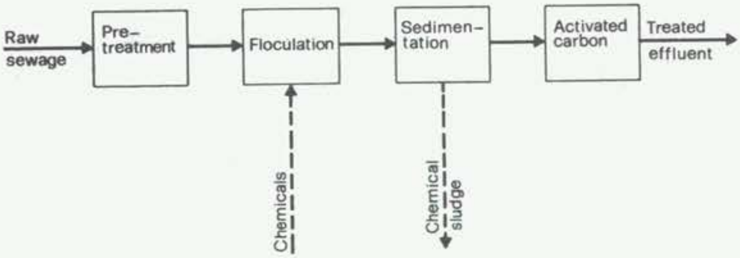

Figure 68 Physico-chemical treatment plant for municipal wastewater.

by other means.

6.12.6 Nitrogen Removal

When present as ammonia, nitrogen can be removed by chemical/physical methods. Stripping can be achieved using steam when the ammonia is present in considerable concentrations, in the region of some g/l, in view of its recovery as ammonium sulphate. More frequently stripping with air is adopted, which however requires alkaline conditions in order to transform the ammoniacal ions into free ammonia, as in the reaction:

$$NH_4^+ + OH^- \rightleftarrows NH_3 + H_2O$$

The equilibrium is completely towards the right for pH values over 11; it is necessary to operate under these conditions to obtain high level removals with residual ammonia concentrations of the order of 5-10 mg/l. The limitations in the application of this process are essentially derived from the serious problems of scaling met with when lime is used as an alkalizing agent, and from the transfer of the pollution into the gas phase. This could however be avoided by means of acid absorption and eventual recovery, but this is little used nowadays for economical reasons.

A possible alternative is the use of chlorination processes taken up to breakpoint or limited to the formation of chloramine which can possibly later be removed by means of activated carbon. The field of application of this method is limited to wastes having low concentrations of ammonia, because of the high operations costs involved with the consumption of large amounts of chlorine which almost always necessitates further dechlorination treatment, with a reducing agent. A final limitation in applying this process is the presence of organic substances or compounds which constitute an additional chlorine-demand.

The recovery of the ammonia present in industrial wastes can be achieved by ion exchange. A recovery process is available in which the ammonia from the regeneration eluate is treated with sulphuric acid followed by evaporation and crystallization of ammonium sulphate.

The predominant tendency nowadays in the removal of ammonia, as with other forms of nitrogen, is the use of biological processes with the formation of gaseous nitrogen as the final product. As regards domestic wastewater or, at any rate, discharges in which there is an internal source of carbon, the process scheme is as shown in Figure 69. The biological oxidation stage is carried out according to extended aeration techniques, so as to obtain nitrification of the organic nitrogen and ammonia. The effluent so oxidized is partly recycled to a primary anoxic biological phase in which the action of facultative denitrifying bacteria contained in the recycled biomass determine the reduction of nitrates to molecular nitrogen. The removal efficiency is related to the rate of recycle (mixed liquor plus sludge return). The second anoxic stage can be included for the complete biological removal of the nitrogen to residuals below 1 ppm. The source of carbon in this phase is almost completely made up of endogeneous carbon. In plant only having pre-denitrification stage nitrogen removals of 80-90% can be achieved with an overall recycle rate of 500-600%.

In all those cases in which it is necessary to achieve high removal efficiencies it is essential to verify that the availability of BOD in the influent is sufficient to meet the demand. In the case of domestic sewage a ratio of available BOD_5/N of 3,5-4 is necessary; thus it follows that in order to produce high de-nitrification efficiencies it is essential to avoid primary sedimentation. The final stage, shown in Figure 69 consists solely in the stripping of the nitrogen formed, by means of mechanical agitation or air diffusion.

In the denitrification of those industrial wastes lacking in BOD, the process can only be maintained by supplying supplementary organic carbon. Use is often made of methanol to this end.

For industrial wastes polluted by nitrates, biological denitrification processes with anaerobic submerged beds may be utilized. This process allows high concentrations of bacteria to be maintained, and thus high volumetric loadings, without the necessity of recirculating the biomass which is attached to the media. However there are limitations which relate to the risk of clogging, due partly to possible suspended matter in the waste water, but particularly because of the bacterial growth in the bed.

Finally, among the other possible removal processes, ion exchange on selective resins may be cited. For economical reasons interest in this method is limited to discharges with relatively low concentrations of pollutants.

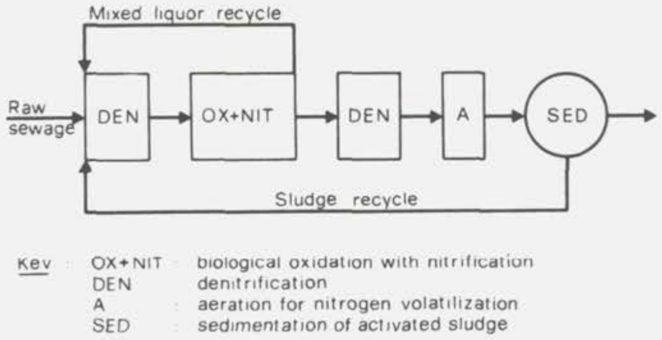

Figure 69 Process scheme for the removal of ammonia using biological process with the formation of gaseous nitrogen.

6.13 TREATMENT AND DISPOSAL OF WASTEWATER SLUDGES

Almost all the forms of treatment described produce sludges for which adequate treatment and disposal must be provided in order to remove any risks of contamination of the environment.

It is useful to make a general distinction between organic sludges and sludges which are prevalently made up of inorganic compounds, the so-called chemical sludges.

6.13.1 Organic Sludges

Essentially these come from biological treatment plants and from primary sedimentation of organically polluted wastewater.

The principal problem as regards these sludges is stabilization, in order to prevent phenomena of unchecked biodegradation in the ultimate disposal phases. Except in exceptional cases, plants generally provide stabilization by means of biological digestion.

The process consists of the reduction, in a controlled environment, of the volatile suspended solids content (VSS) by an anaerobic (or alternatively aerobic) flora.

Anaerobic sludge digestion is used in medium-high capacity plants; that is to say for more than 40,000-60,000 inhabitants served, in the case of treatment of domestic wastewater. For small capacity plants, aerobic sludge digestion is generally adopted due to the greater simplicity of operation, even if unit operating costs are considerably greater. However, various cases are known in which aerobic stabilization of sludges is carried out in plants with a capacity of more than 50,000 equivalent inhabitants. As is known, stabilization can be carried out in an oxidation basin separate from the main biological oxidation system, or else in the same oxidation basin in which the sludge loading is maintained very low so to produce an extended aeration system (see 6.12.1).

Interest in the use of anaerobic digestion for large capacity plants is being centred on the possibility of recovering the digestion gas and making use of its heating power for the production of steam and electricity. The steam is generally used for heating the sludge digestion plant and the buildings in which plant operation personnel are housed. The digested sludge then undergoes dewatering, either mechanical or on drying beds, before disposal by controlled tipping or by incineration.

It is useful to observe that in those cases in which incineration is envisaged, digestion of the sludges can be avoided, thus achieving considerable savings on both investment cost and running costs of the incinerator, since the heating power of the digested sludge is up to 50% less than that of fresh sludge (3,500 - 4,000 Kcal/kg SS for fresh sludge; 1800 - 2500 Kcal/kg SS for well digested sludge). Elimination of the digestion stage, however, presents disadvantages of a different nature: a) a larger dimensioning of the dewatering risk and incineration units, the undigested sludge containing a larger amount of solids; b) the greater risk of objectionable odours if the plant is not well run; c) the need of a reserve incinerator in case of breakdown.

Figure 70 shows the components of the most widely used treatment processes.

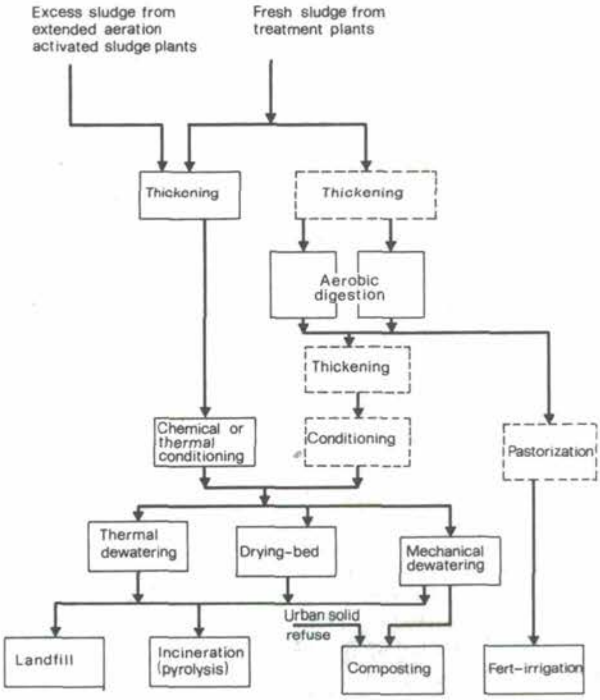

Figure 70 Components of the most widely used processes for the treatment and the disposal of wastewater sludges.

Among the systems for sludge disposal, mention must be made of discharge to sea by means of underwater pipelines. However, the use of this form of disposal must be subject to an examination of the receiving capacity of the sea area concerned and the relative sea bed, in order to avoid serious consequences of both ecological and economical nature. Amongst the major difficulties as regards discharging into the sea is the frequent presence in the sludge of persistant compounds such as, for example, chlorinated hydrocarbons and more particularly heavy metals. The difficulty of exercising an efficient control over the pollution which can be caused by this form of discharge is understandable.

The risk to human health and animal life is determined by the persistant toxic compounds, which must be carefully evaluated in relation to the use of this sludge in agriculture.

6.13.2 Inorganic Sludge

Controlled tipping is the method most usually adopted for the disposal of inorganic sludges.

In practising this form of disposal, care must be taken in the choice of the area, in order, to ensure that no leachate reaches either the surface waters or the subsoil waters, polluting them. These basic considerations are also applicable to the discharge of organic sludges. However, for inorganic sludges derived from the treatment processes under consideration, the problem is usually considerably more complex due to the greater risks of contamination of the environment. In particular, the toxic characteristics of sludges containing heavy metals, oily residues, chlorinated hydrocarbons and pesticides can be cited as examples.

In order to avoid leakage of leachate, both the bottom of the tipping site and the side walls should be essentially water-proof. When the protection constitutes natural clay layers it is necessary that the bulk permeability is such as to produce very long times for the leachate to reach the aquifera. Some organisations suggest a time of 250 years. When this geological condition is not present, it is essential to provide other means of waterproofing such as covering with plastic or cement or with bituminous materials. The water-proofing of the top of the tipping site, to totally contain the sludge, greatly helps to limit this risk factor, in that it prevents the entry of rain water. In any case it is advisable to provide the tipping sites with both bottom and lateral drainage for surface water. On the assumption that the tipping site is totally waterproofed, drainage of the bottom has the sole function of showing up accidental infiltration. However, during the operation of the tipping site, the drainage also collects rain water which washes away those sludges which are not protected on top. In this case the tipping site must be equipped with systems for the collection and treatment of drainage waters.

Amongst other alternatives to the system of direct discharge on tipping sites, mention can be made to the system of polymerization or chemical fixing, which is based on the addition of chemical compounds to sludge, capable of producing a polymerization, and thus the consolidation, of the sludge mass. This method, albeit interesting, does not however completely eliminate the problem of leachate and has a limited range of application to sludges of well-defined characteristics. The method is economically burdensome, as is also the high temperature roasting method used for the transformation of the heavy metal hydroxides into associated oxides of extremely low solubility. In future it is to be hoped that processes to recover metals and other valuable compounds can be further developed. In fact, there are rare applications of recalcination systems for sludge rich in calcium carbonate, for recovery of quick lime, and of acid recovery of aluminium sulphate from sludges rich in aluminium hydroxide.

6.14 EFFLUENTS CONTAINING RADIOISOTOPES

Except in accidents, radioactive wastes will never be discharged directly into the environment without some treatment which separates the hazardous radioisotopes from the bulk of the waste volume. In fact the scope of waste treatment consists in separating those constituents of the waste which possess a low activity and hence may be safely discharged into the environment (radioactive effluents) from radioactive components too dangerous to discharge (radioactive wastes). These wastes are, in general, concentrated to a small volume prior to permanent storage (28, 72, 73).

Gaseous wastes are filtered and bubbled through washing solutions in order to retain the fission products and radioactive particles. The retaining of the noble and hence non-reactive gases krypton and xenon is much more difficult and, therefore, in the long run the long-life 85 Kr will become one of the most critical gaseous radioisotopes.

Liquid wastes may be treated in various ways in order to separate the radioactive material from the non-active or very low level solutions.

Coagulation and sedimentation is used in many instances. As coagulants clay, alum, iron salts, and calcium may be used. Coagulation is effective for the removal of Sc, Y, Zr/Nb, PO_4 and the rare earths Pr, Ce, Pm, Sm, etc. (Figure 71). However, different physical-chemical forms can change the effectiveness of the removal process considerably, as the often wide ranges in removal efficiencies indicate.

Clay addition increases the removal efficiency in the cases where the ion exchange capacity of the clay may be utilized. Caesium and strontium are not easily removed under these conditions. The removal can be increased by the addition of iron and by raising the pH to 11.

Sand filtration removes radioisotopes which are present in the particulate form or which are adsorbed to particles. If slow sand filters are used the first to appear in the effluent is ruthenium, followed by 90-Sr, 131-I, 239-Pu and 144 Ce. Cerium is retained most effectively, since after 14 days only 8% of the initial activity leaves the filter.

PO_4 may be about 86% removed by either settling, or filtration. A combination of both settling and filtration may achieve 97% PO_4 removal.

Iodine is removed to only a small extent. Here again the physico-chemical state plays an important role, since under certain conditions less than 0.4% may be removed, while in another 11 to 25% can be eliminated.

In Figure 72 and 73 the data obtained from two different wastes containing fission products (FPs) are given. Although the overall decontamination is practically identical, the individual isotopes are removed by different methods to different extents from the solutions.

Lime and soda-ash softening was reasonably successful in eliminating up to 90% of 140-Ba/La, 89-Sr, 115-Cd, 46-Sc, 91-Y and 95-Zr/Nb, using relatively small quantities of lime (up to 0.2 g/l) and soda (up to 0.15 g/l). High concentrations (up to 0.34 g/l) may remove 95% of 89-Sr, 91-Y and 95-Zr/95-Nb. Probably the most important result is the removal of strontium. The efficiency of strontium removal varied from 60 to 90%.

Combined processes are often used for waste treatment. An example is a scavenging-precipitation-ion exchange process in which the ion exchange eluate is recycled to the precipitation system. In this way the sludge from the precipitation step contains practically all the radioisotopes which were removed from the waste.

Table 27 shows the decontamination factors (DF) achieved by the single processes and for the overall treatment. The lowest DFs are obtained for ruthenium and cobalt, which are about 10 to 1000 times less than the DFs for the rare earths, strontium and caesium.

Future nuclear plants may prefer to recycle water in order to economize on fresh-water consumption and to minimize discharge of radioactive effluents (Table 28). A clarification with alum and activated silica removed principally colloids, ion-exchanger anions and cations and the activated carbon step removed mainly cobalt and organic materials. The overall decontamination factors for individual ions was from 160 to 12,000.

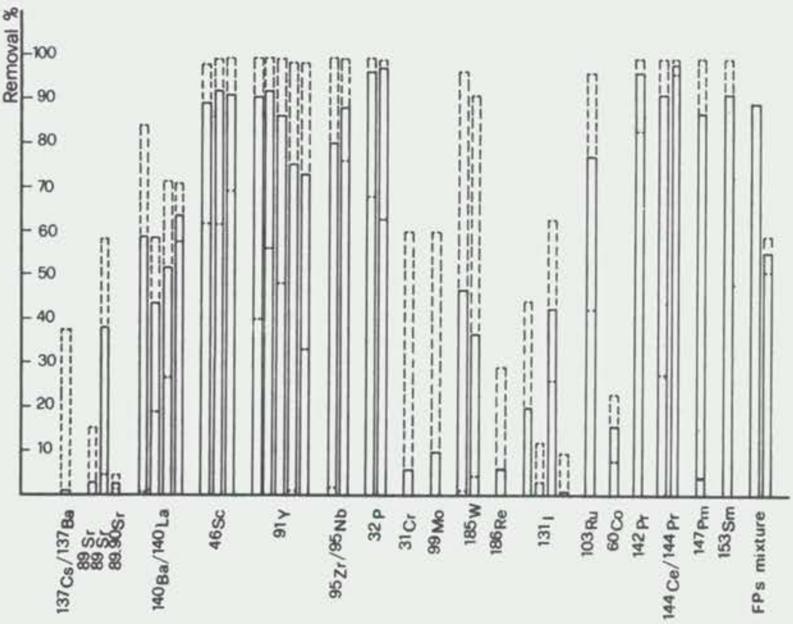

Figure 71 Removal of soluble radioactivity by chemical coagulation, (70), (Solid column corresponds to average value, intermitted column indicates the range).

Especially interesting are the DFs obtained for ruthenium, since both acidic and alkaline ruthenium wastes had been added to the original wastes in order to obtain higher counting rates and provide a variety of different physico-chemical states of ruthenium.

Foam separation may be considered in future, since it offers the following advantages: low cost chemicals (air and detergents) and equipment (simple air-sparge column). The process allows the separation of colloids by flotation and an enrichment of cations in the foam of anionic surfactants such as dodecylbenzene, Alipal LO 436, Naccol 40 FX etc. The foam separation process may be preceeded by a scavenging precipitation.

The DFs for the single processes and for the overall decontamination are smallest for cobalt and ruthenium followed by caesium and zirconium/niobium. Strontium decontamination is highest of all (Table 29).

A further example of decontamination is given by the waste of the condensate from alkaline high-level waste-storage, (12).

This waste from a Purex fuel processing is characterised by containing only ammonia and FPs in addition to residues from the solvent extraction methods employed (Table 30). Since ion exchange treatment was unsuccessful, this waste was treated by a process combining (i) steam stripping, to remove the ammonia and the organic matter, with (ii) filtration for clarification and (iii) ion exchange. Also here ruthenium had by far the lowest DF, furthermore, the two runs gave quite different results (Table 31). The authors attribute the lower DFs in either runs to effects

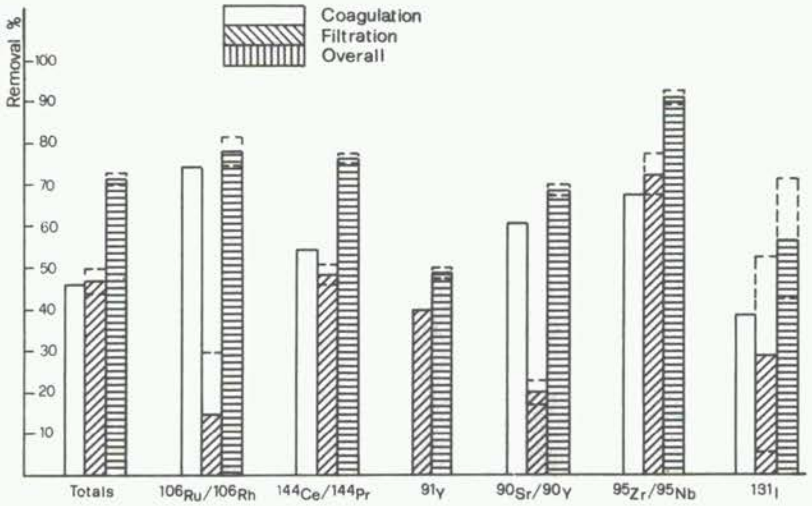

Figure 72 Removal of mixed fission products by conventional water-treatment processes, (70).

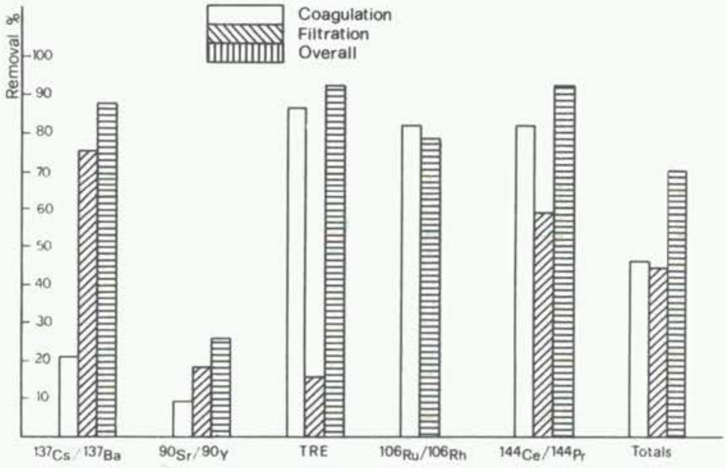

Figure 73 Removal of fission-product activity by coagulation, settling and filtration, (70) - Initial concentration of radioactive material 22 500 counts/ (min) (ml).
TRE = Trivalent rare earths other than cerium

TABLE 27 Average contamination factors (DFs) for pilot-plant tests of the recycle scavenging precipitation, ion-exchange process, (12).

Run	Gross Beta	Gross gamma	Total rare earths	90-Sr	137-Cs	106-Ru	95-Zr/Nb	69-Co
HR - 17								
Feed (2000 resin-bed volumes, (dpm/ml)	29[a]	7[a]	11.5[a]	49	7.2	0.45	2.7	1.4
Recycled eluate,[b] (dpm/ml)								
DF of scavenging-precipitation	4.3	2.3	7.2	4.9	1.41			
DF of ion exchange	2.6	~ 3	~ 53.3	~ 250	> 510			
DF over-all	11.2	~ 7	~383.3	~ 1225	> 720			
HR - 18								
Feed (2000 resin-bed volumes, (dpm/ml)	42[a]	5[a]	12[a]	42	5.9	0.42	1.4	1.7
Recycled eluate,[b] (dpm/ml)	5.12[a]	1.25[a]	2.09[a]	11.16	6.56	0.01		2.67
DF of scavenging-precipitation	1.8	2.08	4.27	3.54	2.71	1.9		6.2
DF of ion exchange	1.18	6	165	500	230	1.2		1.2
DF over-all	2.14	12.5	705	1772	623	2.1		7.3
(DF using anion exchange, 300 bed volumes						(5)[c]		(1.5)[d]
(DF over-all using anion exchange						(14)[c]		(11)[d]

TABLE 27 (continued)

Run	Gross Beta	Gross gamma	Total rare earths	90-Sr	137-Cs	106-Ru	95-Zr/Nb	69-Co
HR - 19								
Feed (2000 resin-bed volumes), dpm/ml)	18.6[a]	3[a]	8[a]	29	4.6	0.4	0.9	1.3
Recycled eluate,[b] (dpm/ml)	10.68[a]	1.13[a]	5.14[a]	13.2	5.93	0.008	0.01	0.08
DF of scavenging-precipitation	4.35	2.1	5.3	3.8	2.5			
DF of ion exchange	5.0	6.7	125	367	840			
DF over-all	22.5	13.8	657	1407	2106			

[a] cpm/ml

[b] Calculated from eluate analysis - no recycle during HR - 17

[c] Anion exchange DF = 1.5 at 1500 bed volumes

[d] Anion exchange DF = 1.0 at 1500 bed volumes

TABLE 28 Over-all decontamination factors for the water-recycle process, (12).

Clarification : Alum-activated silica coagulation

Ion exchange : Separate columns of Dowex 50W X-8 cation resin (390 ml, 3.3-min contact time) and Dowex 1 X-8 (655 ml, 5.5-min contact time).

Activated carbon sorption: Bituminous coal-based material (100 ml, 8.3-min contact time).

	144-Ce	69-Co	137-Cs	131-I	106-Ru	125-Sb	99-Sr	95-Zr/Nb	Total rare earths	Gross gamma	Gross beta	Bulk ions specific conductance
Raw-waste analysis dmp or cpm/ml	10.1	70.9	23.6	126.2	44.2	3.5	52.0	0.4	32.0	52	85	290[a]
Decontamination factors												
Over-all	330	12000	2600	430	610	300	6300	160	11000	140	1100	500
Clarification step	1.4	1.4	1.0	1.0	2.0	1.0	1.0	2.1	1.1	1.3	1.1	--
Ion-exchange step	85	72	510	270	440	100	6300	8.6	6000	110	240	--
Activated-carbon step	2.8	120	5.0	1.6	1.4	3.0	1.0	8.6	1.7	1.0	4.3	--

[a] In mho/cm

TABLE 29 Typical decontamination factors for the scavenging-precipitation - foam-separation process, (12).

	Foam height	V/LD^d (cm^{-1})	Grundite clay (lb/1000 gal)	Time (h)
Conditions:				
- Laboratory	22 in.	202	0.5	10
- Pilot plant	8 ft.	140	0.7	91

	Scavenging-precipitation		Foam column		Over-all	
	Laboratory	ppc	Laboratory	ppc	Laboratory	ppc
Liquid flow (gal ft^{-2}h^{-1})	12	24	39	15		
			Decontamination factors			
Ca	50	60	~ 2	--	~ 100	--
Sr	16	10	220	36	$> 3500^a$	1080^b
Cs	21	8	1	1	18	8.0
Co	2.3	--	1	--	2	1.3
Ru	1.8	--	4	--	$> 7^a$	4.2^a
Ce	24	--	4	--	100	$> 20^a$
Zr/Nb	--	--	--	--	--	$> 50^a$

[a] Close to lower limit of analytical determination

[b] Includes a decontamination factor of 3.0 obtained in foam recovery columns

[c] Pilot-plant

[d] V/LD: V and L are gas and liquid flow-rates and D is the effective bubble diameter.

of biological growth which had occurred in the condensate collection tanks, and assumed that the following DFs should be considered.

Sr	280
Cs	380
Ru	42

Ruthenium and other isotopes which may exist in different physico-chemical states (e.g. cobalt, zinc, cerium, etc.) present special problems for decontamination.

106-Ru especially is very important because of its relatively high fission yield and the many different physico-chemical states in which it may occur.

Electrodialysis (ion transport through permeable membranes caused by an electrical field) may achieve high DFs, (12), and is economically competitive with ion exchange resins and the evaporation processes (Table 32).

TABLE 30 Average composition of alkaline and acid condensates from Purex wastes at Hanford, (12).

Waste constituents or property	Alkaline condensate (μCi/ml)	Acid condensate (μCi/ml)
C 8 144-Pr	10^{-3}	10^{-3}
98-Sr	10^{-4}	10^{-7}
106-Ru	10^{-3}	$.10^{-2}$
137-Cs	10^{-2}	10^{-4}
95-Zr/Nb	10^{-3}	10^{-2}
Butyl phosphate	30-200 mg/l	--
Hydrocarbons	10-70 mg/l	--
NH_4^+	35-200 mg/l	--
Na^+	1 -2 mg/l	--
NO_3^-	1 -5 mg/l	--
NO_2^-	5-10 mg/l	--
HNO_3	--	1-3 x 10^{-2} M
pH	9-10	2

TABLE 31 Average decontamination factors for pilot plant. Tests for the stripping - Ion-exchange process, (12).

	Decontamination factors				
	137-Cs	30-Sr	106-Ru	95/-Zr/Nb	144-Ce/Pr
Run No. 1[a]					
Filter	1.0	1.2	1.1	2.7	2.4
Anion column[c]	-	1.0	3.0	2.2	2.0
Cation column[d]	130	550	1.7	15	7.7
Over-all	130	875	5.7	85	37
Run No. 2[b]					
Filter	49	8.9	2.8	2.9	3.8
Anion column[c]	-	-	4.1	3.3	3.2
Cation column[d]	7.8	32	3.6	> 23	> 27
Over-all	380	280	42	> 230	> 330

[a] With diatomaceous earth filter aid

[b] With diatomaceous earth and clinoptilolite filter aid

[c] Strong base IRA - 900 (Antrachite)

[d] Strong acid IR - 200 (Antrachite)

TABLE 32 Electrodialysis cell comparison, (12).

Seven-cell unit
Total effective membrane: 110 cm^2
Cell cross-section: 36.67 cm^2
Cell width: 1.9 cm

Twenty-cell pair unit
Total effective membrane: 4400 cm^2
Cell cross-section: 220 cm^2
Cell width: 0.16 cm

Seven-cell unit		Twenty-cell pair unit	
% Removed		% Removed	
Nitrate	Ruthenium	Nitrate	Ruthenium
30	13	30	12
50	23	50	22
70	37	70	34
90	58	90	56

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137-Cs	10^{-2}	10^{-4}
95-Zr/Nb	10^{-3}	10^{-2}
Butyl phosphate	30-200 mg/1	--
Hydrocarbons	10-70 mg/1	--
NH_4^+	35-200 mg/1	--
Na^+	1 -2 mg/1	--
NO_3^-	1 -5 mg/1	--
NO_2^-	5-10 mg/1	--
HNO_3	--	1-3 x 10^{-2} M
pH	9-10	2

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CHAPTER 7

Potential Impairment of Marine Ecosystems and Sea-water Uses

7.1 WATER CHARACTERISTICS WITH RESPECT TO PHYSICAL, CHEMICAL, BIOCHEMICAL AND ECOLOGICAL CONDITIONS IN THE DISCHARGE AREA

The subject of this paragraph can be treated from many different points of view; but certainly, it would not be very useful to give a general description that recapitulated the ample literature existing with regard to all the various aspects relating to the chemical, physical, bio-chemical, biological and ecological characteristics of sea waters.

It is considered necessary, instead, to bear in mind the purposes of this report, which consist of the indication of a number of guidelines common to the various countries that wish to introduce (or improve or standardize) their respective systems of regulations for the control of marine pollution.

This control (according to consensus reached in the context of the sanitation programme for the Mediterranean sea and with the approval of the principal international scientific organizations) should take the form of a policy of evaluating in each individual case the acceptability, or otherwise, of a discharge in a certain sea zone. It should be emphasised that this dependence on local conditions does not necessarily imply that the Control Body has to carry out prolonged and complex studies with regard to each discharge; the problem can be solved automatically, in the case of certain categories of discharges and substances, by respecting standards relating to the receiving waters in the most unfavourable zones (that is, in proximity to the discharges).

Naturally, in the case of a certain number of the substances in question, suitable limits on the quantities discharged should also be imposed.

The granting of an authorization and the determination of the standards themselves require evaluations concerning the physical modalities of dispersion and the chemical, bio-chemical, biological and ecological characteristics that condition the capacity of a certain sea zone to absorb a given load of pollution (and also the consideration of practical aspects which condition the effective application of such standards).

The phenomena of a physical character (dilution, dispersion) and the hydrographic and topographic characteristics of the zone have been treated in the earlier paragraphs of Chapter 5.

In this Chapter, bearing in mind the purposes of the report and, thus, the requisites of simplicity and essentially which must characterize the formulation of a system of regulation that is effectively applicable, some characteristics of the receiving waters that condition, under the chemical, biological, ecological, etc. aspects, the capacity of a certain sea zone to absorb a certain potentially contaminating load, are discussed and illustrated. The term potentially contaminating is used deliberately, since, in accordance with a criterion indicated previously, it is considered that, by means of a suitable combination of interventions at source, purification treatments, and systems of disposal and dispersion, it is possible today, at least along open coasts, to maintain in satisfactory condition, that is, not subject to pollution, even the sea waters in proximity to the discharge point.

These possibilities are limited when large urban-industrial discharges are made inside estuaries or bays: in this case more than in others, regional sanitation systems, that permit on the one hand, the disposal of effluents in hydrologically more suitable sea zones and, on the other, the planning and limitation of urban-industrial installations in relations to the effective absorption capacity of the environment, reveal their great usefulness. It can be said that this theme concerns above all three fundamental aspects:

- aspects of a hygienic nature;
- eutrophication problems;
- problems associated with the toxic effects directly caused by various substances.

At the same time, the examination of the various parameters involved should concern one or more of the following "spheres":

1) the receiving waters;
2) the sediments;
3) the marine organisms.

Such evaluations concern the description of the environmental situation before intervention for the purpose of:

a) determining the basic level of certain contaminants and predicting the future situation when the discharge is in action;
b) comparing the two situations both within the discharge zone and in the surrounding zone.

It is very important, for this purpose, to establish the criteria by means of which the variation of the environmental situation, by comparison with a certain initial and, it is to be hoped, unpolluted condition, can be ascertained.

The questions involved are extremely complex and the views of the various authors who have studied the problem, sometimes under very particular aspects, rarely agree and are often in contrast; it is clear therefore, that any proposal made in terms sufficiently clear and simple to be practically useful will not be above criticism. An attitude more inclined to find defects in every solution than to devise a better solution has sometimes, understandably, led legislative bodies to ignore the characteristics and problems in question until such a time as scientific circles can provide sufficiently homogeneous information or orientation.

It is in any case considered that one of the principal, and certainly less easy, tasks of the Mediterranean Action Plan is that of applying a certain scientific rigour to the task of satisfying the urgent need for the formulation of precise guidelines (which can only be achieved by means of the contribution of researchers, legislators and engineers with practical experience of this type of problem).

Nor should it be forgotten that the granting of an authorization of this type ought to have a certain provisional character in the sense that the final responsibility with regard to the reliability of the environmental data and of the dimensions of the processes of dilution and dispersion foreseen by the project should in any case be borne by the applicant for authorization.

The function of the Control Body should be to ascertain, in a general sense, that the calculations made do not depend on excessively optimistic hypotheses, and that the results foreseen by the project, as far as the efficacy of the purification treatments and the dispersion and disposal possibilities of certain zones are concerned, are feasible.

The controls systematically carried out on completion of the works will provide an adequate confirmation of the same as regards the hygienic and environmental aspects, and will condition the granting of final authorization.

In this regard it should be mentioned that the possibility of ascertaining whether or not pollution phenomena caused by discharges are distinguishable from variations or fluctuations of a natural character has sometimes been called into question; however, it seems reasonable to affirm that a fairly good result will already have been achieved, considering the drastic conditions that afflict a large part of the Mediterranean coasts, when the conditions of pollution have been reduced to a level low enough to render its attribution problematical. In any case, even such justifiable perplexities cannot justify the formulation of regulations that make conditions of pollution, that are both evident and intolerable, legally acceptable.

7.2 POTENTIAL IMPAIRMENT OF MARINE ECOSYSTEMS

The ecosystem is the basic functional unit in ecology, since it includes both organism (biotic communities) and abiotic environment, each influencing properties of the other and both necessary for the maintenance of life as we know it on earth. For descriptive purposes it is convenient to recognize the following components as comprising the ecosystem: 1-inorganic substances (C, N, CO_2, H_2O, etc.) involved in the material cycles; 2-organic compounds (proteins, carbohydrates, lipids, humic substances, etc.) that link biotic and abiotic; 3-climate regime (temperature and other physical factors); 4-producers, autotrophic organisms, largely green plants, which are able to manufacture food from simple inorganic substances; 5-macroconsumers or phagotrophs, heterotrophic organisms, chiefly animals, which ingest other organisms or particular organic matter; 6-microconsumer, sofrotrophs or osmotrophs, heterotrophic organisms, chiefly bacteria and fungi, which break down the complex compounds of dead protoplasms, absorb some of the decomposition products and release inorganic nutrients which can be utilized by the producers, together with organic substances; these may provide energy sources or may be inhibitory or stimulatory to other biotic components of the ecosystem.

Not merely are the substances themselves to be considered damaging for the marine ecosystems, but rather the concentrations of products or the parameters of factors which, working at the biotic or abiotic component level, upset their complex interaction either breaking completely or partly changing the balance between the various components.

Due to the different reactions of various marine organisms to the same concentration of a given polluting substance, and to the consequent alteration of the environmental factors, studies to bring to evidence damage to the marine ecosystems must be of a sinecological nature and the actions to be studied are of the synergic nature of the effluents as a whole, in relation to the diffusion phenomena of the polluted source.

Therefore the problem of the potential damage to the ecosystem must be regarded in an analytical way, studying the effects on the single components listed by Odum, and, in a synthetic way using statistical methods on the biotic and abiotic components as a whole, (1).

7.2.1 Potential Impairment From Eutrophication

The substances considered in this section include phosphorus, and a general reference is also made to substances that consume oxygen. Both items are relevent to eutrophication problems: a) phosphorus, for its role, sometimes limitative, as a nutrient; it is of considerable importance owing to the greater possibility of controlling its various sources; b) substances consuming oxygen, since in Mediterranean waters this element may be reduced considerably below saturation levels not so much on account of the organic load introduced, such as BOD (the organic pollution denominated "primary") as in consequence of eutrophication phenomena; in other words, on account of the considerable daily fluctuations of the dissolved oxygen caused phenomena of plant respiration and photosynthesis and by phenomena of mortality and decomposition of large masses of algae.

In fact, the problem of eutrophication does not appear to be a problem typical of industrial discharges; it is generally correlated with rain water discharges, rivers, urban discharges, and is not dissociated from natural fluctuations in the marine environment connected with the horizontal and vertical circulation of large masses of water and with seasonal, climatic and oceanographic factors.

The substances considered in this section do not include nitrogen and its compounds or the various phytostimulant substances that, with phosphorus, nitrogen and carbon, contribute to the production of the phenomena in question.

It is nevertheless considered necessary to consider the subject for a number of reasons:

- phosphorus and oxygen-consuming substances are included in Group II;
- it has been specified that the discussion of the discharge of the substances listed in Table I should be extended to natural wastewaters and urban waters, in the measure in which they may contain appreciable quantities of these substances;
- definition of the scale of organic pollution with reference to "primary" organic pollution (on the basis of colimetry) may give rise to incorrect evaluations if eutrophication phenomena are present, or could potentially be present, in the discharge zone. The extension of eutrophication phenomena deriving from a particular discharge, or from the overlapping effects of several discharges, may be, in fact, considerably greater than the extension of the zones which, from a micro-biological point of view, can be considered polluted by those discharges.

It should immediately be made clear that the subject does not lend itself to schematization or generalization. On the one hand, eutrophication phenomena induced by a particular discharge may - in certain circumstances - cause a veritable environmental catastrophy (both with regard to the aquatic environment and to tourism), and this may even be on a scale considerably larger than that of the phenomena of microbiological pollution, whilst on the other, it can also be affirmed that, in other conditions of discharge (where a greater dispersion in waters initially poorer in nutrients is possible), the same quantity of nutrients discharged may have beneficial effects, as far as fishing activities are concerned, without appreciably affecting the transparency of the water or its recreational use,(2, 3).

Before going on to consider the extension or scale of eutrophication phenomena in the sea, it is opportune to say something about the definition of the term.

The term eutrophication is in fact applied both to limited increases of primary activity and to extreme conditions in which the absence of oxygen causes the death of a large part of the aquatic organisms, and conditions of putrefaction accompanied by unpleasant odours.

These extreme conditions are generally accompanied by a marked turbidity of the waters due to the high phytoplankton biomass; the colour of the sea water ranges from brown to brick red. This last colouration is associated with the denomination "red tide", which, in general, is attributed to phenomena of intense eutrophication and, in particular, to the flowering of dinoflagellates. There are cases, however, where the reddish colouration of the water is caused by patches, of limited size (up to a few hundred square meters), of floating organisms, and where there is no manifestation of the aforesaid phenomena of anoxia and mortality.

We shall assume, for the sake of brevity, a fundamental knowledge of the mechanism of eutrophication phenomena, and merely mention, with reference to the aspects here considered, that the phenomenon in question involves both the liquid mass (increase of the phytoplankton biomass) and the vegetable biocenosis on the sea bottom. These are affected by the greater availability of nutrients, by the increased rate of sedimentation of organic substances caused by eutrophication phenomena in the liquid mass above, and by diminution of light energy.

A fairly singular characteristic of these phenomena as compared with others lies in the fact that, normally, the increase of the number of cells of phytoplankton does not occur at the point of discharge but a certain distance from it, as, with the passage of time, the nutrients are assimilated and, at the same time, in consequence of the currents, the mass of water round the discharge point is left behind.

In practice, since the circumstances in which eutrophication phenomena occur are characterized by weak currents and by a relatively "closed" coastline, it also happens that the zones most affected are situated in the vicinity of a discharge. This is constantly the case with regard to the phytobenthos. Obviously, since this type of plant does not move with the currents, the closer it is (in a particular direction) to the discharge point, the more susceptible it is to the eutrophication effects of discharges.

In the Mediterranean, eutrophication problems certainly do not concern the marine basin considered as a whole. It is well known that this sea is poor in nutrients, even though it is characterized by a fairly good level of primary productivity. The productivity with regard to nutrients is attributed to the deficit balance of exchanges through the Straits of Gibraltar, which makes the eutrophication of the Mediterranean basin a possibility which cannot reasonably be foreseen, (4, 5).(See note at end of Section 7.2.1).
This does not alter the fact that coastal zones of increasingly large extension in a direction parallel to the coast are subject, in a measure varying greatly from case to case, to this type of pollution.

In fact this type of pollution may occur (even if the conditions further out to sea are excellent in terms of water exchange and level of nutrient concentration) in coastal zones of oceans no less than in those of the Mediterranean; and this where the oceanographic conditions and the shape of the coastline do not allow a rapid dispersion of nutrients produced by urban centres or carried by percolating waters from the hinterland (which transport urban discharges, stock-farm discharges, and a certain quantity of the fertilizers used in agriculture and washed away).

It has already been said that a general and quantitative, even though approximative, definition of the scale of this phenomenon a priori, by means of some simplified expression, is not at present considered possible. In part this is due to the fact that, even though the main features of the mechanism of this phenomenon are known, there is not at present sufficient agreement as to the importance of the various factors and, in consequence, as to the most suitable systems of control.

That the main features of the mechanism are known would appear to be proved by the fact that the gravest cases of massive eutrophication to occur in recent years (with very unfavourable effects both on the aquatic environment and on tourist activities) were duly foreseen years in advance, with indication of the causes, zones and consequences. Thus, although it may not be easy to reach agreement on the theoretical plane, it can be said that in fact a certain number of factors (particularly significant with regard to the prevention of the phenomenon, and therefore to be taken into account, under the aspect of eutrophication phenomena, where the authorization, or otherwise, of discharges is concerned) have been identified.

It can, in fact, be affirmed that, where considerable volumes of domestic sewage (and of percolating waters containing large quantities of nutrients and biostimulants in general) are concerned, and when the discharge takes place in confined coastal waters having a poor exchange of waters with the open sea, in particular concomitance with rapid increases of temperature and good conditions of radiancy, eutrophication phenomena will in any case occur in some measure.

It has not so far been reported that phenomena of massive eutrophication (red tides, etc.) have occurred in cases where a fairly restrictive colimetric index has been adopted as a planning objective and as a fundamental criterion of intervention with regard to the disposal of urban effluents.

Under this aspect the definition of the scale of action with reference to the colimetric index would maintain its validity, always provided that the result was not obtained by means of the chlorination of effluents, in which case the colimetric index would lose almost all its validity with regard to the larger aspect in question. Nor is it to be excluded that, in particular regions, sanitation plans rationally based on the respect of a certain standard with regard to the colimetric index in coastal waters (and certain standards limiting the concentrations of toxic substances - or the toxicity itself - in the effluent and in the receiving waters) will serve to solve the problems of eutrophication only in a partial or, at any rate, unsatisfactory manner. For example, when the total load of nutrients in a particular zone is considerable and the receiving waters are already characterized by a certain abundance of phytoplankton, interventions based on the criteria indicated above could solve certain acute aspects of the problem (e.g. red tides along the shore), without, however, achieving the levels of water transparency that would be possible if, for example, the discharges, instead of entering the sea, were used for agricultural irrigation. In this regard, especially, a thorough study carried out by a team of specialists is a necessary step towards the definition of the area to be taken into account in the context of a sanitation plan, as also for purposes of authorization of a particular discharge.

What has been said makes it fairly clear that the problems of eutrophication are another reason why sanitation interventions should proceed, as far as possible, not so much by means of separate authorizations for each discharge, as by means of a study of adequate extension (Integrated Planning), to be conducted with regard to zones which are congruous both in administrative and in environmental terms. In the context of the results of such studies, the criteria for the authorization of single discharges could find their more appropriate place.

It may be objected that the space dedicated here to problems of eutrophication, when the sea concerned is the Mediterranean, is excessive, since this sea, compared with others, such as the North Sea, has a low nutrient level. However, it remains to be ascertained which of the two conditions of discharge calls for more attention: a certain increase of turbidity in waters already naturally turbid may be imperceptible, whereas a slight change in the value of this factor in water characterized by a high degree of transparency could make a considerable contribution towards reducing their appeal to tourists. In any case, if one is to speak of a scale of eutrophication phenomena, it would be opportune, as a preliminary, to specify the characteristic parameter of the discharge to which the scale could somehow be correlated.

Despite the difference of views existing on the subject, it can be affirmed that an important role in producing these phenomena is to be attributed to the discharge of large quantities of phosphorus, nitrogen (and perhaps, in some measure, also carbon) and, also, of other substances, such as vitamins, humic acids, metallic trace elements, which act as stimulants or, in a manner of speaking, as catalysts of the growth process. The existence of these last factors, concerning the importance of which there is considerable discussion, is demonstrated by the fact that the nutrient potential of urban discharges is not diminished in a proportion corresponding to the removal (possible by means of tertiary treatments) of nitrogen and phosphorus compounds. This is shown by algae tests with primary, oxidized and tertiary effluents. Apart from the greater or lesser importance to be attributed to these factors, there remains the problem of establishing, case by case, which of the two elements, nitrogen or phosphorus, performs the limitative function and is, therefore, the more suitable for a control of the system.

In many sea zones, it has been determined that nitrogen is the limitative element; in others, however, it would seem to be phosphorus. It is also possible that the two elements alternate in this role in the course of the year.

An efficacious method of describing the potential of a particular discharge with regard to eutrophication phenomena could be developed in close analogy to the one concerning the toxic component of discharge waters. Thus, just as the characteristics of a discharge under the toxic aspect can suitably be described in quantitative form in terms of "relative toxicity", obtained by multiplying the volume of the discharge by the toxicity unit, so would it be useful, where the forecasting of eutrophication phenomena is concerned, to introduce a concept of "relative biostimulation", obtained by multiplying the volume of a discharge by a suitable unit, which could be called a "unit of biostimulation" and assessed by means of algal bio-assay.

The concept is not new, even though it has not been applied for purposes of regulation it is considered opportune to draw attention to it in view of the importance it could assume in future years in relation to the significance of this parameter with respect to the phenomenon in question and the difficulty of replacing it with a more suitable one.

It is opportune to bear in mind that chemostate tests i.e. not in batch conditions, have proved to be most suitable for reproducing the real conditions, and that, in any case, significant results are obtained using the actual waters of the zone it is wished to investigate. For this reason the installation in proximity to the coast of suitable laboratories, which could obtain the waters to be placed in the aquariums continuously by pumping, would be particularly advantageous.

It is considered more practical, here, to draw attention to parameters which are less valid but susceptible to easier comparison with the data presently available.

In fact, in all the cases where eutrophication phenomena have been encountered, it is fairly easy to evaluate the load of nutrients in terms of the number of inhabitants per km of coast, or in terms of kg of phosphorus, or nitrogen, per km^2.

In any case, rather than providing, even in terms of order of magnitude, an indication of the scale of the phenomenon (which, as has been said, with out present knowledge is effectively impossible a priori), it is preferable at this stage to submit a series of typical cases and a number of indications and elements useful for the purposes of:

a) recognizing the existence of the problem in a particular zone and distinguishing in some way the effect of the various discharges concerned;

b) foreseeing, in relation to new discharges or to a displacement of existing discharges, whether or not the problem in question may be aggravated.

To give a quantitative idea of the scale of these phenomena with reference to concrete examples, it can be mentioned e.g. that the River Po influences the productivity and, in general, the quality of the sea waters even a distance of hundreds of km from its delta. This enrichment, though undesirable from the point of view of recreational use of the water (in which context its limpidity is its most important quality), is nevertheless substantially beneficial with regard to fishing activities. In this case it is perhaps more opportune to speak of enrichment rather than of red tides or massive eutrophication.

It is also known that in coastal zones in which particularly unfavourable hydrodynamic conditions obtain (shallow waters, confined by engineering works serving to protect the beaches against erosion), and in the presence of a pollution load to be considered exceptional (over 100 kg P/km x day), the red tides accompanied by fish mortality occur during a limited part of the year (not more than 5-10%) and extend to no further than 200-1000 meters from the shore. In the same zones the transparency of the waters, compared with that typical of zones 6 km further out to sea, is drastically reduced during a good part of the year and during nearly all the summer period.

The fact that red tides and anoxis phenomena last for some weeks or even for only a few days in the course of the year should not lead the gravity of the situation to be underestimated. These systematic episodes, though limited in time, are sufficient to damage a locality seriously, both as regards the marine environment and its reputation from the point of view of tourism, for much longer periods of time.

It can be mentioned e.g. that in the Gulf of Trieste the discharge of the wastewaters of 300,000 inhabitants in conditions particularly unfavourable as regards the shape of the coastline (though not the worst under the aspect of water exchange) creates conditions of massive eutrophication inside the port zone (Baia di Muggia) in which the discharges are made, and phenomena of eutrophication, with unfavourable effects on the transparency of the waters and on the benthos, which are detectable even at a distance of a number of km from the port zone (the Secchi disc transparency, however, remains of the order of 8-10 m, the concentration of phosphates is below 0.2 µ ga/l and the dissolved oxygen has been 90% and 120% saturation, in the waters outside the port zone).

With regard to the ascertainment in situ of existing phenomena of eutrophication, it is considered this is a particularly valid method, in view of the inconvenience of analytical evaluation and, on the other hand, the simplicity of ascertaining in an approximative manner the existence of an abnormal situation (the turbidity of the waters, measurable by means of the Secchi disc as the average value in the surface layer, strictly depends on the degree of eutrophication of the sea waters in a particular zone, provided there are no suspended solids brought by rivers).

An evaluation of the phenomenon of enrichment, which concerns marine zones as large as those affected by the action of large watercourses, cannot be included in this report. It is a problem which belongs more appropriately to Integrated Planning, in the context of which, as has already been said, discharge authorizations and interventions should be determined. But some indications can be given which serve to define the extension of those phenomena of massive eutrophication that are sometimes referred to as "red tides", which, as has been said, affect, sometimes in a striking manner, zones relatively close to the coast, and which are generally

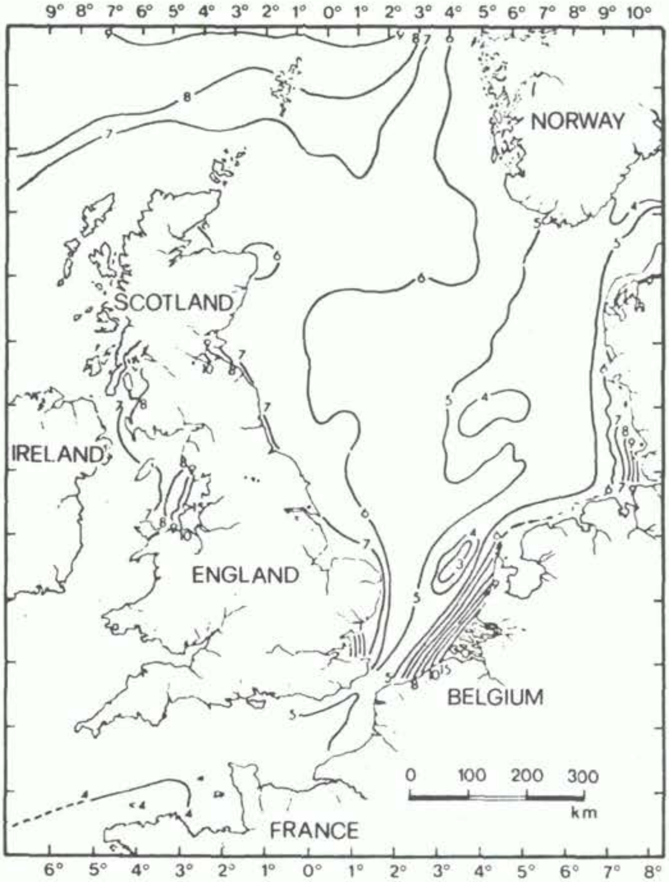


Figure 74 Winter phosphate (10^{-7} g · at PO_4-P per 1) in North Sea, (6).

attributable to the acute effects of limitrophe coastal discharges.

A first means of distinction serving to circumscribe in some manner the zone affected by these phenomena is provided by certain characteristic parameters (Secchi disc visibility, chlorophyll, biomass, cell/litre, primary productivity in grams of carbon/m^2 x day, total dissolved phosphorus, total nitrogen), with samples taken immediately off the coast in question and also from off-shore waters (a distance of 5-10 km from the shore is usually sufficient to ensure the absence of acute effects of the discharges of coastal urban settlements in any appreciable degree).

The comparison can be made between the average, minimum and maximum values. It must be borne in mind that, since massive eutrophication phenomena and their acute effects are usually the result of a concomitance of causes (increasing temperature, little water exchange compared with other periods of the year in consequence of lack of wind or small tide movements), the comparison of the average values based on only a part of the data, that is, on the data relating to the least favourable periods (average of the minimums), is particularly significant.

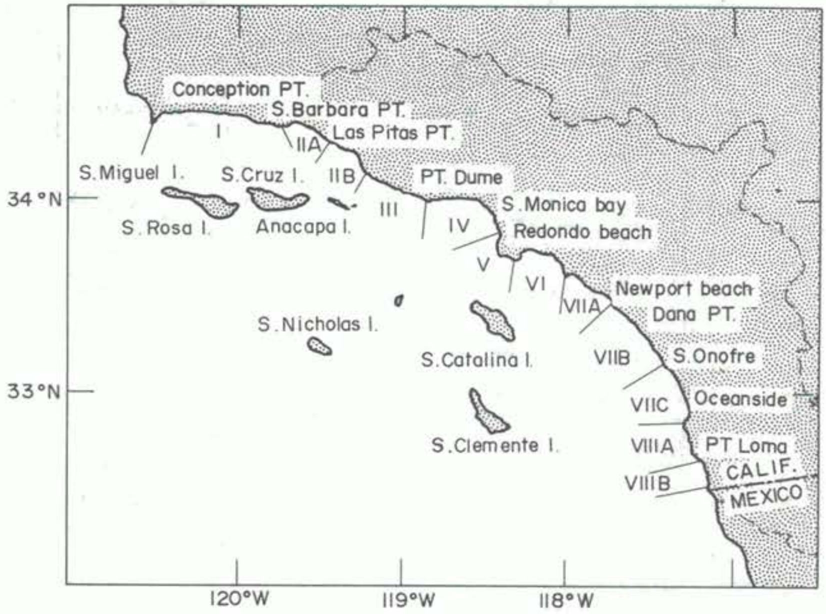


Figure 75 Water quality areas and subareas used in the Allan Hancock Foundation Survey of the Southern California Bight, (7).

The comparison of the average annual values may fail to draw attention to certain critical situations for, the differences between the immediate coastal waters and those further out being less marked during the greater part of the year, the relative average values will differ less significantly and, in any case, will not reflect the gravity of a problem which, as has been said, may manifest itself in an acute form for a very short period of the year.

In view of the differences of natural conditions that distinguish various parts of the Mediterranean e.g. the Tyrrhenian, the Aegean, the north-west Adriatic, it does not seem appropriate to seek to propose a threshold of the various parameters serving to define the advent of eutrophication problems. Whereas, for example, at the level of the delta of the River Po and along the Italian coast, a concentration of phosphate phosphorus of 0.2 - 0.3 μ ga/l is fairly frequent, such a value is to be considered exceptional and, if repeated frequently, a symptom of eutrophication phenomena, in proximity to the Dalmation coast (along which Secchi disc visibility values of over 20 m are frequent, whereas the corresponding values in the zone opposite the delta of the River Po are nearly always below 10 m).

With reference to coastal zones, it is possible to indicate a number of values which should signify unacceptable conditions of eutrophication, at least with regard to the Mediterranean:

- Secchi disc visibility:	2 - 3 m
- Concentration of dissolved oxygen:	<70%
- Chlorophyll a+B:	>10 ppm

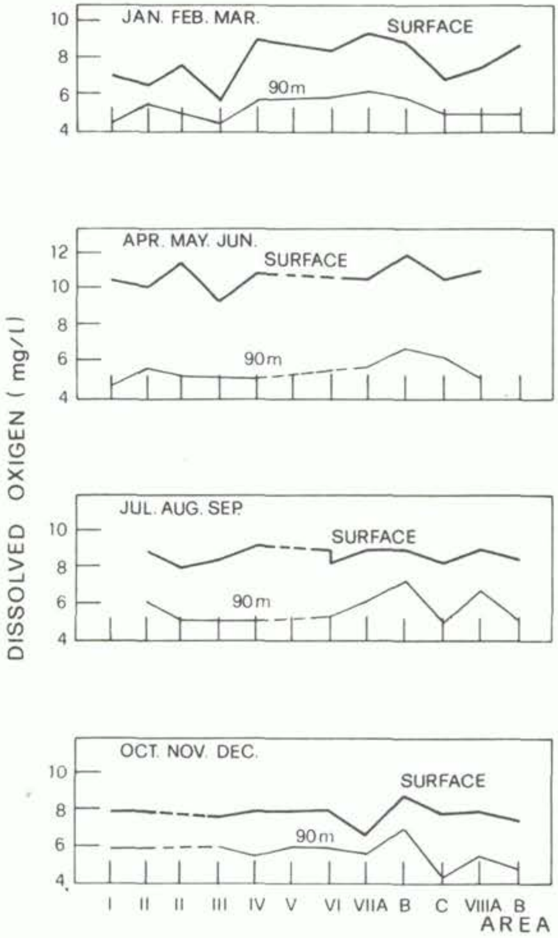


Figure 76 Distribution of mean dissolved oxygen by season in the Southern California Bight, (7).

- Cells/l: $2 \times 10^6 \div 5 \times 10^6$
- Productivity: $>300 \div 500$ gr of carbon/m^2 x year

When the conditions indicated recur in a particular zone in a significant number of cases (one could say, over 5% of the time), it is reasonable to include that in that zone the problem of eutrophication exists.

A comparison by means of suitable graphs with the conditions found in off-shore waters should permit the delimitation in this direction of the spatial extension of the phenomenon; it is to be expected that the scale of action in a direction parallel to the coast will be considerably greater, owing to the high proportion of marine and coastal currents running in this direction and, especially, to the limited capacity of dispersion of the inshore waters. A criterion for delimiting

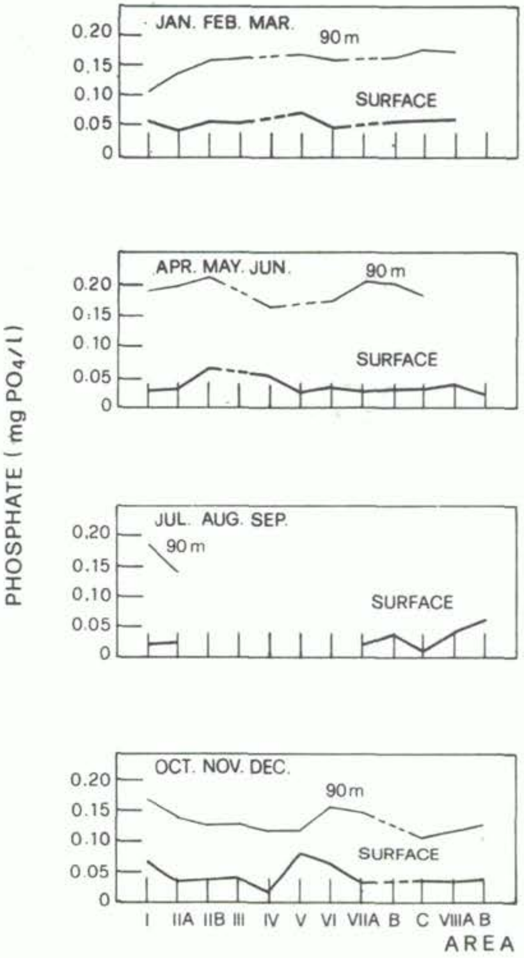


Figure 77 Distribution of mean phosphate by season in the Southern California Bight, (7).

in a direction parallel to the coast the extension of the eutrophication zone caused by a particular discharge could be the presence of waters with characteristics (in terms of transparency, number of cells, chlorophyll) similar to those found in the waters further out to sea. It can be that a succession of discharges of even minor importance creates a situation of enrichment or of eutrophication extending, practically, without interruption, for many kilometers.

In such situations it is not easy to define in a direction parallel to the coast the extension of the coastal zone directly influenced by a discharge, or by a group of discharges. This evaluation may be made by analogy with similar cases, relating, however, to isolated discharges or groups of discharges.

Aeroplane or satellite telesurveying of the quality of the water in large areas, despite considerable limitations as regards the description of complex pollution

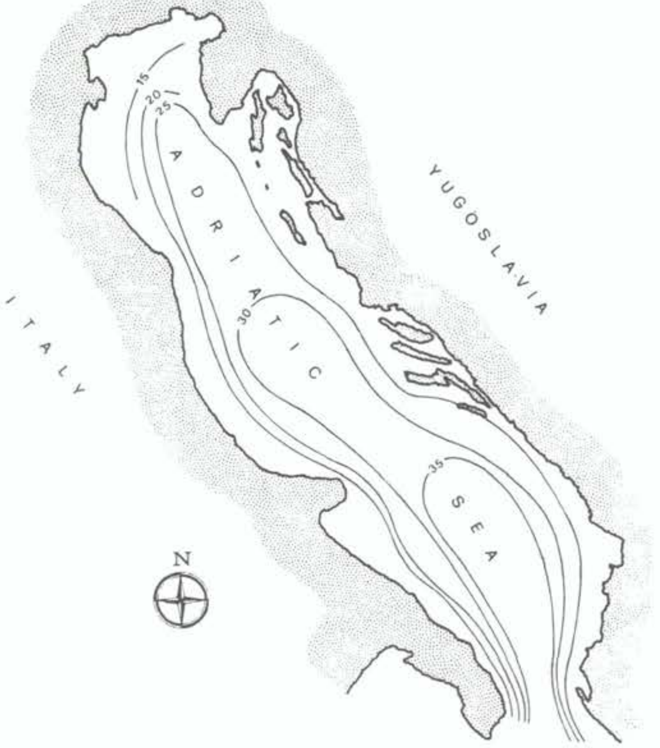


Figure 78 Secchi disc visibility (m) in Adriatic Sea (after Stirn, 1973).

phenomena in qualitative-quantitative terms, offers interesting possibilities of application for the definition of large zones of eutrophication, in relation to the possibility of distinguishing the various levels of suspended solids and also, it would appear, certain concentrations of chlorophyll. A simple criterion serving to determine the fundamental features of the role played by different discharges in producing coastal phenomena of massive eutrophication (such as those, for example, extending to a distance of between 200 m and 1 km from the shore along a large stretch of the Italian Adriatic coast) can be illustrated by the following example (Figure 81). The characteristic concentrations of nutrients, chlorophyll, number of cells of phytoplankton/l, etc., along a line running from the delta of the River Po to a certain locality of the coastal strip systematically affected by red-tide phenomena are reported in graphic form. Figure 81 also indicates the average concentrations of phosphates in the summer-autumn period.

The resultant graph reveals a distinction between the large-scale enrichment effects, caused by the river discharge (River Po), and the acute effects, which are shown to be mainly due to local discharges distributed along the stretch of coast in question.

The evaluation of the extension and degree of eutrophication phenomena in a particular zone, starting from an even summary examination of the existing situation e.g. by simple Secchi disc readings, derives its practical importance from the fact that, usually, the coastal discharge of raw sewage, as far as treatment and condition

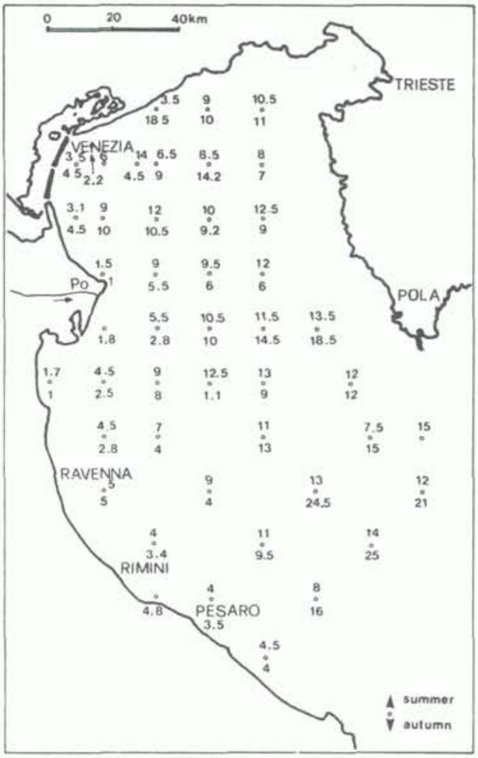


Figure 79 Transparency of waters (Secchi disc visibility-m-) in Adriatic Sea. Cruise summer/autumn, year 1965, (8).

of final discharge are concerned, constitutes a situation fairly unfavourable in comparison with the one that would probably come into being when works have been carried out with regard to sewerage, treatment, re-use (the possibility of re-use in agriculture is of particular interest where problems of eutrophication are concerned) and discharge.

It can also be affirmed that, since phenomena of eutrophication are mainly attributable to urban (and inland) discharges, generally, when the problem is confronted, these discharges are already in existence, and its therefore possible to carry out a direct evaluation of the receiving capacity of the environment in conditions of discharge generally very unfavourable in comparison with those that would exist following "hypothesiable" interventions.

It may be asked in this respect whether evaluations of the scale, or of the existence, of the problem on the basis of the existing situation may not prove to be insufficiently precautionary, in the sense that sanitation interventions (if planned without paying sufficient heed to this aspect of pollution) may give rise to phenomena of eutrophication more serious than those which existed before the intervention.

In fact - and this makes it even more difficult to treat this theme in an adequately general manner - it may happen that centralized sewerage and treatment plants - in

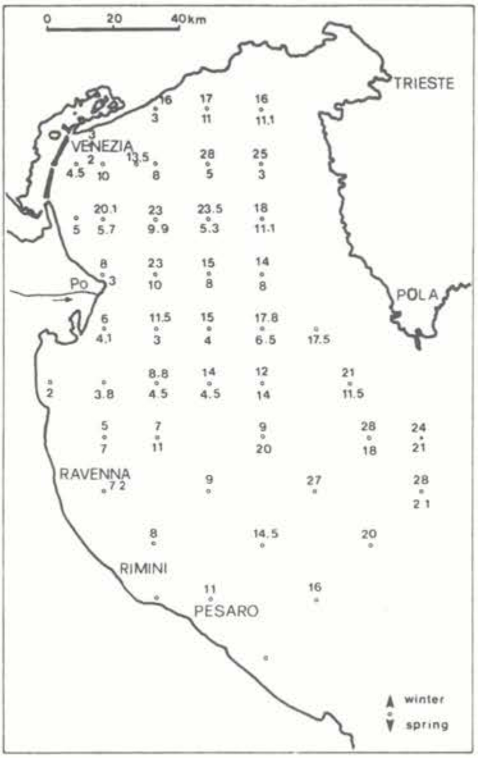


Figure 80 Transparency of waters (Secchi disc visibility-m-) in Adriatic Sea. Cruise winter/spring year 1966, (9).

other respects advantageous and desirable - discharge their effluent at a single point, instead of at numerous points, and with better possibilities of dispersion, as in the case of the isolated discharges. It may also happen that the final destination of the effluent of a treatment plant is situated, as is sometimes the case, in the interior of estuaries, lagoons or confined marine waters, where the negative effects of a concentrated discharge of large quantities of sewage are further magnified, even if it is treated according to conventional criteria (e.g. to achieve a large reduction of BOD) which do not take problems of toxicity and eutrophication sufficiently into account.

In the vast majority of cases the treatment selected is in fact the biological one; this type of treatment, despite the considerable results achieved in terms of the reduction of the organic load - which, however, is of little importance in the hypothesis of discharge into the sea - of suspended solids, fats and oils, and also, in a certain measure (from 40% to 80%), of various persistent toxic substances - removes an insubstantial part of the nutrient potential of the discharges. Even though the proportion of phosphorus removed is 20-30% and that of nitrogen of the order of 50-60%, the treated effluent contains the various compounds of phosphorus and nitrogen in an oxidized form, which is to say that they are more rapidly usable by the first link of the food chain. This rapidity of assimilation increases the problem of eutrophication, for, as the processes of utilization of the nutrients are more rapid, so, local conditions being equal, are the processes of dispersion,

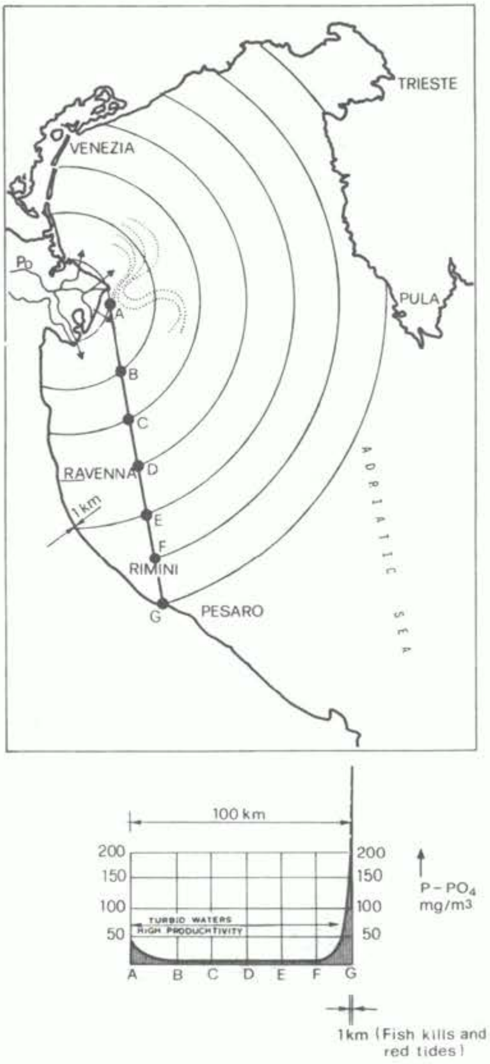


Figure 81 Spacial scale evaluation of enrichment and eutrophication phenomena (example).

serving to diminish the concentration of the nutrients and of the mass of phytoplankton produced, less developed.

There remains the problem of those phytostimulant substances which accelerate the assimilation of nutrients and which are removed only in limited measure by secondary and even by tertiary treatments.

Recently some modifications of the classic biological treatment have been developed which permit not only a considerable removal of nitrogen by biological means (by processes of nitrification and denitrification), but also a considerable removal of phosphorus; these possibilities make this type of treatment, which permits, at a moderate cost, a considerable improvement of the quality of the effluent, even more interesting. However, both the stability of these processes and the effective diminution of the stimulant potential, to be evaluated directly, as has been said, by means of algae tests, still remain to be verified in practice.

Another question concerns the correlation between causes and effects in quantitative terms. This is a rather important question with regard to the definition of the scale of action of a particular discharge and, therefore, the determination of zones or, better, of interventions, which are homogeneous.

It may in fact be thought that major phenomena of systematically recurrent eutrophication are attributable to discharges of minor importance in that these are responsible for increasing the concentration of nutrients above the level at which eutrophication phenomena become important.

This would make distinctions between the various causes very ambiguous, for it might be thought that the problem could effectively be solved by intervening with regard to factors of minor importance.

For example, with reference to Figure 81, the red-tide phenomena along the coast could be substantially attributed to the river, which, according to these hypotheses, is responsible for increasing the concentration of nutrients, over large areas, almost to the "critical" level. It is then the modest local discharges, by slightly increasing the concentration, which cause the threshold to be crossed, and thus give rise to the "red tides". That this does not correspond to the reality of the facts can be explained with reference to Figure 82, in which two hypotheses of superimposition of effects are represented; the first is completely incorrect; the second is to be considered somehow closer to the truth than the first.

In relation to two coastal discharges X_o and Δx, the intermediate sea point P is considered. The conditions of eutrophication in this zone are influenced both by the discharge X_o and by the discharge Δx: these conditions are represented by the index N(x) which refers indicatively to exposure to biostimulant substances discharged by X_o and Δx.

The greater the concentrations induced at point P and the longer the residence time, the more probable will it be, other conditions being equal, that eutrophication phenomena will arise.

According to a certain hypothesis - under discussion here- it could be supposed that there exists a certain threshold N below which eutrophication phenomena do not arise, while above it they become systematic and serious.

Supposing that between the time t_o and the time t_1 the discharge X_o, of considerably greater importance and influence at the point P than the discharge Δx, is in action, it can be hypothesized that the concentration N_o (induced at P by the discharge X_o) is a little below the threshold N. Between the time t_1 and t_2, in addition to the discharge X_o, also the discharge Δx is in action. It is supposed that at P, as a result of the discharge Δx, a modest increase of the concentration N is induced, and that it passes from N_o to $N_o + \Delta N$. In this case a proportionally modest increase ΔN could lead to a substantial change and aggravation of the situation.

By neutralizing the modest effect of the discharge Δx, it should thus be possible to solve the problem of eutrophication; at the same time the extension and intensity of the phenomenon could be associated equally with the discharge Δx and the discharge X_o. In other words, in the event that the discharge X_o could be considered a natural factor e.g. river, the discharge Δx would in effect be correlated with a

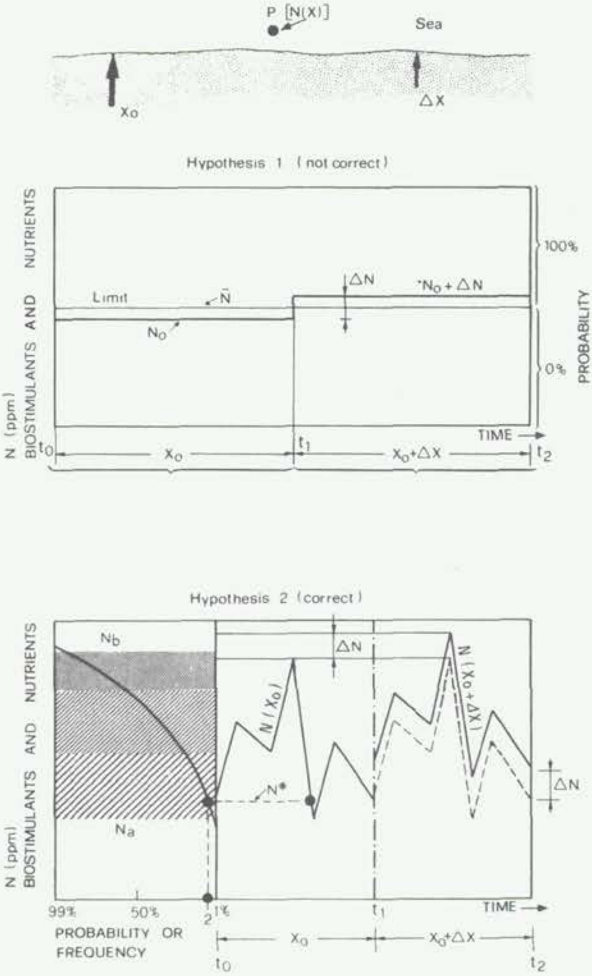


Figure 82 Schematic illustration of eutrophication effects from different sources of nutrients and biostimulants.

scale of action of magnitude comparable to that of the discharge X_o. In fact the existence of the discharge Δ_x would give rise on a large scale to conditions of eutrophication which would not be produced if it did not exist.

Such a schematization of the phenomenon of eutrophication would differ substantially from reality and would lead to incorrect conclusions both with regard to the evaluation of the scale of the phenomenon and to the determination of the causes and the planning of remedial action.

In reality (compare hypothesis 2) the action of the discharge X_o between the time t_o and the time t_1 gives rise at P to a concentration N which, in the sea, can in no way be assimilated to a constant value; on the contrary, N is subject to considerable fluctuations. Furthermore, at a certain concentration, N*, does not correspond in a unequivocal manner to a certain intensity of the phenomenon of eutrophication but rather to a certain probability that this phenomenon will occur with a certain intensity.

The occurrence of certain phenomena of eutrophication, given a certain concentration of nutrients in a particular sea zone, in fact depends also on various accessory causes of a climatic, biological and oceanographic nature, which may give rise to situations more of less favourable to the manifestation of this phenomenon.

On the left side of the graph in Figure 82, with regard to hypothesis No. 2, a curve has been drawn, for purely demonstrative purposes, which correlates a certain concentration N of biostimulant and nutrient substance with the probability of the occurrence - in a certain locality - of a phenomenon of massive eutrophication. The right side of the graph shows the indicative trend of concentrations of nutrients induced at the point P by the discharge Δ_x alone between the time t_0 and the time t_1; between the time t_1 and the time t_2, the dotted line indicates the contribution relative to the discharge X_0, and the continuous line the concentrations at the point P due to the effects of both the discharge X_0 and the discharge Δ_x. The effect of the discharge Δ_x results in an increase Δ N - certainly not constant with time - which, in general, gives rise to an increase of the concentration of nutrients and biostimulants at the point P.

A small increase of nutrients and biostimulants concentrations in the sea gives rise only to a relative small increase of the probability that a certain degree of enrichment or eutrophication will be observed in a given period of time (e.g. a year, a season), and cannot bring the quality of waters from satisfactory to unacceptable levels.

The reasoning schematically set forth above leads to the conclusion that large-scale effects cannot spring from isolated discharges of minor importance - and in themselves of relatively limited spatial action (because they cannot, by superimposing themselves on large-scale phenomena, cause a hypothetical and somewhat unreal "risk level" to be exceeded).

Problems of enrichment and eutrophication

The problem of eutrophication of coastal waters concerns to a greater or lesser degree large sections of the Mediterranean shore, just as it also affects numerous localities on oceanic coasts. However great the volume of the receiving waters and their total capacity to absorb nutrients, the limited speed of the seaward dispersion of coastal discharges gives rise, in concomitance with unfavourable hydrographic conditions, to phenomena of replenishment and eutrophication ranging from a barely noticeable diminution of the transparency of the water and slight modifications of the benthonic eco-systems to situations of great gravity in which the absence of oxygen, and the consequent phenomena of putrefaction of great masses of algae and dead fish, render the coast overlooking the affected sea zones unacceptable besides causing damage and alteration - reversible, however - to the aquatic environment affected by the phenomenon.

It can be said that the phenomenon of eutrophication is contributed to, with a particular wealth of variety, by all the typical factors of a biological, biochemical, chemical, physical and ecological nature which are considered in this report.

The main factors will be considered in relation to the practical possibility of exercising a control over them by means of suitable standards or technical intervention.

In general, the problem of marine pollution involves such complexities and calls for a knowledge of so many widely different branches of science that, as has been said, the formulation of notably different opinions is almost inevitable, above all with regard to eutrophication of sea waters. Despite the abundant literature on the subject, it is difficult, if not impossible, to find technical formulations or standards which take this phenomenon explicity into account and thus permit an efficacious and direct control.

Thus, however, imperfect the formulation of precise guidelines in this regard may be, the mere fact of drawing attention to the matter by subjecting the environmental data to certain minimum standards may be of benefit. Generally, in fact, sanitation projects in coastal marine zones have been conceived - with considerable success - essentially in relation to respect of certain standards with regard to the effluent (e.g. floating substances, suspended solids, macroscopic solids, heavy metals, pesticides) and in relation to certain colimetric standards, in the case of coastal waters used for bathing or mussel cultivation.

In fact, it has to be acknowledged that eutrophication problems have only very rarely arisen where the disposal of urban effluents has been carried out according to the guidelines which have already emerged from the Mediterranean Action Plan and have received a wide consensus, even under the aspect of realization, in the various countries. One refers to those systems of sanitation that have exploited the possibility of re-use in agriculture or disposal and dispersion at sea of pre-treated or treated effluents, making use, in this last hypothesis, of such conventional project parameters as colimetry. This fact, which could find further confirmation by means of an ad hoc survey in the various countries, lends further interest to the use of the colimetric index as a project parameter.

The adoption of these criteria, which, though not perfect, are of extremely simple conception, is in itself of notable benefit under the aspect of phenomena of replenishment and eutrophication. This does not alter the fact that in certain sea zones, even off-shore, where there is a marked increase of primary productivity compared with other parts of the Mediterranean, the disposal of large quantities of urban sewage from coastal urban agglomerations (or transported to the coast by means of sewers) can be carried out in full respect of the colimetric limit, by transferring the treatment-plant effluents to a suitable distance from the shore, without it being possible to say (even though the situation has been considerably improved) that the problem with regard to eutrophication has been solved in the most efficacious manner.

For this reason, and, in general, to permit a more efficacious control of the phenomenon, it is considered that some standards concerning the factors or consequences of the phenomena of eutrophication deserve consideration in the context of systems of regulation.

The difficulties of formulating criteria or standards in this regard are essentially of four types:

1. the consequence of eutrophication phenomena may develop in places different from those where the substances responsible are discharged. This is because nutrients take a certain time to be assimilated (during which the marine currents may have conveyed the volumes of water concerned some distance from the point of discharge). More favourable situations (rise of temperature, smaller presence of predators) may favour the development of the phenomenon (moreover, the supposition that the nutrients introduced by a discharge have first to undergo a process of dilution and then a process of reconcentration or accumulation in the dissolved phase is without physical justification);

2. the fertility of the Mediterranean waters, though conditioned as a whole by the lack of nutrients, varies over areas of tens or even hundreds of km^2 in certain zones, such as, for example, in the Italian part of the northern Adriatic, in which the greater primary productivity increases the yield of fishing activities

at the cost, but, however, leads to a certain reduction of the tourist-appeal of the coastal waters. "Natural levels", thus, cannot be formulated except in relation to the zones considered;

3. it is not clear which parameters are most suitable for purposes of control, whether parameters of a chemical, chemical-physical type, to which, although with a certain difference of views, the development of phenomenon may be attributed, or parameters of a biological nature (number of cells/litre, chlorophyll, biomass) which indicate that the process of replenishment and eutrophication has taken place, or, finally, whether control should be exercised by means of direct measurement of productivity (carbon uptake), which expresses the speed of growth of the biomass;

4. in the case of the other forms of pollution considered (toxicity phenomena, primary organic pollution, microbiological pollution) the zone in which the controls should be carried out is easily identifiable (coastal waters for hygienic aspects, waters in the proximity of discharge points where primary organic pollution or toxic substances are concerned). Not only do such zones correspond to uses it is possible and wished to protect but, at the same time, it is possible to introduce specific standards that

    a. can be respected in the zones in question;

    b. appear to be adequately precautionary with regard to the aquatic life or public hygiene;

    c. can be achieved in the medium term at a cost which is on the whole acceptable.

The situation with regard to eutrophication phenomena is different in that it is impossible to give a priori a general and reliable indication of the factors of a chemical or biochemical nature that produce them (one should bear in mind: the difficulty of identification of the limiting element, varying with sea zone and, possibly, in the same zone in different periods, and: the debate about whether limiting elements really exist and about the role of biostimulant substances, which are, according to some authors, of determinant importance and to others of negligible importance). Furthermore even if algae-growth tests serve to identify the element responsible for the phenomenon (e.g. phosphorus or nitrogen), the maintenance of concentration in proximity to the discharge points low enough to preclude undesirable replenishment phenomena is not normally economically feasible.

With reference to phosphorus, which is an element often taken into consideration, also in relation to the fact that it is possible to bring about drastic reductions in concentration at moderate cost by treating urban and agricultural effluents, it should be pointed out that the effluent of biological treatment often contains over 10,000 ppb of dissolved phosphorus as P, largely orthophosphate.

Since the process of initial dilution does not always achieve a degree of dilution higher than 1:100 - 1:200, it is impossible to reduce the phosphorus concentration (*) below 50-100 ppb except by means of tertiary treatments or particularly favourable conditions of dilution.

(*) Starting with a concentration of soluble phosphorus in the effluent of the order of 2,000 ppb and an initial dilution of at least 1:200, it is possible to reduce the soluble phosphorus concentration, downstream of the initial dilution process, to 10-15 ppb provided that the receiving waters are oligotrophic (less than 2 ppb of phosphorus). However, it appears that, even though the reduction in question can also be achieved by less costly processes (simultaneous precipitation in the aeration tanks), the formulation of a standard of this sort would involve an excessive cost of treatment and increase of disposal works. Furthermore, the final result would be conditioned in any case by the "basic" concentration of nutrients.

Now, a concentration of this order is of no danger if the sewage field is small and undergoes a rapid dispersion in oligotrophic waters which, in the course of half a day, reduce the said concentration to one-tenth, and also serve to disperse even further both the nutrients not yet utilized and the biomass that has come into being. Considerably different, at least from a technical point of view, are phosphorus concentration levels of 50-100 ppb referred to large-scale situations, which therefore concern spatial dimensions of the order of many km and drifting times of the order of several days.

It should be pointed out that in such conditions the dilution water coming to the diffuser is very often itself characterized, if not by a high concentration of nutrients, at least by a relatively high biomass (in terms of chlorophyll, cells/litre or, simply, Secchi-disc transparency). It is therefore rather unlikely that, if the effluent is discharged in marine zones characterized by a poor exchange or susceptible to eutrophication phenomena, the quality of the sea waters surrounding the discharge point will remain similar to the quality that can be obtained when dilution waters are characterized by a relatively modest concentration of nutrients and/or plankton biomass.

In considering the main parameters associated with the development of eutrophication phenomena, major attention will obviously be dedicated to those which can be influenced by man either by means of suitable purification treatments or by the transfer of the discharge point to zones in which the hydrological conditions and the environmental conditions in general are more suitable to receive and utilize the nutrients and biostimulant substances contained in the effluent.

It should be pointed out, first of all, that eutrophication phenomena concern both the plankton and the benthonic vegetation. Whereas the zones proximate to the discharge point are directly affected by the discharges as far as the phytobenthos are concerned, in certain circumstances, as has been said, this may not be so with regard to the phytoplankton.

The effects of eutrophication on the sea-floor bring about major alterations of the vegetation which have repercussions on all the other levels of life. These effects can be evaluated very efficaciously by means of direct inspections carried out by specialized biologists. Such surveys are characterized by a high benefit/cost ratio and are recommended in every case.

The transparency of the coastal waters is also affected by an abnormal growth of the phytobenthos because, in consequence of a pronounced wave movement in proximity to the shore, considerable masses of algae are placed in suspension.

The environmental parameters generally relating to eutrophication phenomena can be divided into four groups:

a. parameters which express the propensity of a certain sea zone to undergo eutrophication phenomena: the temperature and irradiation favour the rapid growth of algae. Whereas, with regard to irradiation, the coverage of the sky is the main element, apart from, obviously, the latitude and the season, temperature increases are favoured by shallow waters and a poor exchange.

   The presence of currents that transport and disperse the effluents discharged fairly rapidly, and which also bring about a good exchange of the water directly involved by the discharge, is probably the most important environmental parameter of a physical nature. Not only does a rapid dispersion of the nutrients reduce their concentration in the sea waters, with the result that, inevitably, the biomass produced per unit of volume cannot exceed a certain value, but the phytoplankton biomass is itself dispersed, or otherwise, in relation to the intensity of the currents and of the exchange movements.

b. the presence of high concentrations of nutrients (mainly composed of phosphorus, nitrogen and, according to some workers, also of carbon) constitutes a necessary condition for the formation of large quantities of algae. It would appear that, in producing this phenomenon, a role (more or less important, according to the various authors) is also played by certain vitamins, humic acids, metals, which act as catalysts of the growth process.

While large quantities of algae cannot form where concentrations of nutrient substances are very low, by reason of the requirements of cellular synthesis, it is also true that major increases of plankton do not necessarily take place even in the presence of notable quantities of nutrients; it would appear that such developments with regard to plankton require the concomitance of other hydrographic and environmental factors (e.g. predators) such as those mentioned.

It should also be mentioned that in localities where nutrients are often present in abnormal quantities, the waters are unlikely to be limpid and free from replenishment phenomena.

At the same time, low concentrations of nutrients, if they do not permit the immediate development of large quantities of algae, may nevertheless give rise to a high degree of primary productivity in the course of the year, by means of the recycling of certain nutrients, which may be repeated several times.

The observations made above are certainly not original in character and jusfity the difficulty of selecting a representative parameter that expresses potential eutrophication conditions in an adequate manner(*).

With regard to lakes, graphs have been proposed which correlate the gravity of the situation - under the aspect of eutrophication phenomena - to a contaminating load expressed, for example, in terms of grams of phosphorus per m^2 per year. An analogous parameter could be considered with regard to coastal marine zones but there would still be the problem of defining the area to which the contaminating load should be referred. In the case of inflows of rivers into the sea, this dimension can be evaluated as a function of such parameters as specific salinity or alkalinity. This permits the evaluation of the zones in which the river exerts its influence in a certain period of time, from the moment of its arrival in the sea.

In the case of discharges, the zone of influence could, as a first approximation, be taken as the area indicated by current drogues or marked masses of water over a period of a few days, from the moment of their introduction.

A parameter utilized by Sournia for comparative purposes was the phosphorus load and the nitrogen load per m^2/year, (5).

A gram of phosphate corresponds to the assimilation of 41 grams of carbon, and 1 gram of nitrate nitrogen corresponds to the assimilation of 5.7 grams of carbon, according to the relation C/N/P/ = 106/16/1.

The application of this criterion to the zone directly influenced by the outlet of the River Po would lead one to expect an annual production of 24 grams of carbon per m^2 (according to the utilization of phosphates) or of 78 grams (according to the utilization of nitrates). In fact the productivity of the zone in question is considerably higher (of the order of 100-200 or more grams of carbon/m^2 x year); this is probably due to the superimposed effects of other contributions and also to a certain recycling of nutrients.

(*) Some analytical formulations are available with regard to the phenomenon of the use of nutrients by phytoplankton.

Parameters of the type in question could in fact be considered with regard to project evaluations, but they do not appear to be very suitable, also in relation to difficulties concerning the need to evaluate at the same time the interaction of several discharges of different origin, and difficult to utilize in the context of a system of standards.

c. A method which permits the direct evaluation of the fertility of certain waters consists in measuring the "carbon uptake" with use of marked carbon 14-C. This is a classic method for the investigation of primary productivity; it can be applied on-the-spot or, perhaps with less reliability, in the laboratory.

The greater part of the works in the Mediterranean area have been carried out by means of on-the-spot procedures, and it is therefore considered that the characterization of large marine zones by means of this parameter could constitute, also by reason of the abundant availability of comparative data, the most suitable reference for a possible classification.

Other methods may be employed for the investigation of primary plankton activity (oxygen method, assimilation of marked carbon, balance of nutrient salts in situ, direct evaluation by the so-called "chlorophyll radiation method", etc.).

Discussion of the above does not fall within the purposes of this report.

d. The evaluation of the "already occurred phenomenon" that is, of the quantity of phytoplankton biomass present, can be carried out very simply, when no doubt exists as to the source of the turbidity (which can also be attributed to particles of terrigenous origin transported by the rivers or placed in suspension in proximity to the coast by wave movement). Owing to its elementary character (which may appear to be a defect), this type of measurement is of considerable importance in relation to its simplicity and low cost (so long as a large vessel is not used for the purpose).

The importance of this simple system of measurement is enhanced by the great difficulty of obtaining reliable data on nutrients at low concentrations (generally less than 0.1 micrograms/atom x litre, with the result that many of the data supplied by non specialized laboratories are of dubious interpretation) and, at the same time, by the shortage of experts capable of carrying out accurate and sufficiently reliable cell counts.

When it is necessary, especially in doubtful cases, to determine in what measure a certain degree of turbidity is attributable to the presence of phytoplankton and in what measure to the presence of clayey particles, measurement of the chlorophyll may be useful; in this respect, however, there are different opinions as to the type of chlorophyll that should be measured (a, b, caritenoids) and as to whether or not this parameter is adequately correlative to the phytoplankton biomass or to the number of cells per unit of volume.

It can be said that, where orders of magnitude, rather than small differences, are concerned, the parameter in question can certainly express particular conditions of eutrophication, in that limpid and oligotrophic waters will certainly not have a chlorophyll content of the order of several ppm or, even, of 10 ppm. The surveying of this parameter is also of interest in view of present-day possibilities of continuous and automatic measurements.

This is also the case with regard to other parameters such as nitrates, phosphates and silicates. Various cruises and surveys have been carried out using these methods.

The possibility has been proposed of making such measurements frequently (together with other measurements, such as turbidity, dissolved oxygen, salinity, temperature) using oceanographic buoys installed in coastal waters.

Before proceeding to present some data representative of extreme conditions of oligotrophic and, vice-versa, of extremely eutrophicated, waters, it should be pointed out that studies of the phenomenon should have the support of adequately efficient laboratories. The level of efficiency can be ascertained by sending samples variously diluted with distilled water and then comparing the reproducibility of the analyses, or by comparing the data supplied by different laboratories using the same methods.

As regards the concentration of nutrients, phosphorus concentrations of less than 0.05 - 0.1 micrograms/litre are frequent in Mediterranean oligotrophic waters, while concentrations frequently greater than 0.3 micrograms/litre of soluble inorganic phosphorus are found in a few, sometimes large, zones subject to a certain degree of eutrophication.

Primary productivity is less than 50 grams/m^2 x year in oligotrophic waters and exceeds 200 grams/m^2 x year in zones clearly richer than the Mediterranean average.

Secchi-disc visibility, as an average value, is between 10 and 30 m in large areas of the Thyrrhenian, Aegean and off the Yugoslav coast of the Adriatic seas. Average visibilities of between 4 and 8 meters at a distance from the shore of several km are characteristic of certain parts of the North-West Adriatic, on the Italian side, which are affected by enormous discharges of nutrients by rivers and from urban agglomerations on the coast or inland.

At a distance of 1 km from the shore, in the Gulf of Trieste (a significant locality for Mediterranean studies in that it represents the closed extremity of a branch - the Adriatic - considered more susceptible to pollution than the rest of the Mediterranean), the average Secchi-disc visibility is between 8 and 15 m, with peaks of 19 m and, sometimes, minimum values of 3-4 m (in exceptional circumstances).

As regards chlorophyll, values of a few ppm already represent waters rich in nutrients; at over 10 ppm the situation may be considered serious.

In view of the seasonal character of the phenomenon, it is generally recommended that the period of control be at least 12 months.

Note

The zone of the Mediterranean area richest in nutrients is the north-west Adriatic, which, however, has a nutrient content considerably lower than the North Sea or of the coastal waters of California, and also has a fairly good degree of transparency. The average phosphorus content in the north-west Adriatic is around 0.2 µ ga/1 and transparency in the most internal part of the Adriatic (Gulf of Trieste) has a value of about 8-12 m average visibility (Secchi disc). It oscillates between 6 and 20 m. For purposes of comparison, it can be mentioned that the North Sea water along the English coast has phosphorus concentrations over 0.5 µ ga/1 and considerably lower Secchi disc visibilities. Even in the ocean off the Californian coast, the average phosphorus concentrations are greater and the transparency of the waters slightly lower than the values cited, (6, 7). Moreover, it has been observed that the Adriatic is at the same time the zone most abundant in fish in the Mediterranean (about five times more abundant in fish per unit of surface area), and this is due to its greater production, which, in the case in point, thus has a favourable significance. If this is true of the northern part of the Adriatic (the zone which is the most "closed", most subject to river discharge transporting considerable quantities of nutrient substance and inland discharges, and which has urban agglomerations of considerable size along its coast), it is even more true of the other parts of the Mediterranean. All this serves to confirm the fact that, even though in large zones of the Mediterranean basin the average transparency of the waters is considerably reduced, and productivity considerable, conditions of massive eutrophication are destinated to remain a coastal phenomenon of Mediterranean character (where local discharge conditions, in relation to the factors mentioned above, favour this phenomenon, and where the volume of discharges - prevalently urban - exceed the local dispersion possibilities.)

Table 33 reports some characteristics of the Adriatic relevant to eutrophication phenomena (from Franco, 1973). It is interesting to compare them with Figures 74-77, reporting data relating to phosphorus concentration in other seas (North Sea and Pacific Ocean, along the Californian coast), (6, 7).

Figure 78 reports Secchi disc visibility in the Adriatic. Figures 79 and 80 is analogous to Figure 78, but instead of Stirn's data, other data were used, (8, 9).

It will be seen that the transparency of the Adriatic waters according to Figure 79, although fairly good, is notably inferior to the transparency reported by Figure 78.

TABLE 33 Northern Adriatic: average concentration of nutrient (in ga/l), and tolerances, in the surface layer (A: depth down to 5 m) and in the deeper layer (B: depth over 10 m) during the seasonal cruises 1965-66, (8, 9).

	July-Aug.1965		Oct.-Nov.1965	
Nutrients	A	B	A	B
$N - NH^{+}_{4}$	3.06 ± 0.48	1.48 ± 0.20	1.77 ± 0.32	1.02 ± 0.20
$N - NO_{2}^{-}$	0.09 ± 0.02	0.04 ± 0.01	0.11 ± 0.02	0.24 ± 0.05
$N - NO_{3}^{-}$	0.83 ± 0.24	0.22 ± 0.04	1.07 ± 0.41	0.51 ± 0.16
$P-PO^{3-}_{4}$	0.18 ± 0.03	0.09 ± 0.02	0.12 ± 0.02	0.09 ± 0.04
$Si-SiO^{4-}_{4}$	2.90 ± 0.86	3.48 ± 0.36	1.72 ± 0.81	4.20 ± 1.14

	Jan.-Feb.1966		April-May 1966	
Nutrients	A	B	A	B
$N - NH^{+}_{4}$	0.99 ± 0.17	0.53 ± 0.05	0.91 ± 0.48	0.56 ± 0.10
$N - NO^{-}_{2}$	0.23 ± 0.02	0.22 ± 0.02	0.07 ± 0.04	0.03 ± 0.01
$N - NO^{-}_{3}$	1.26 ± 0.29	0.71 ± 0.18	1.47 ± 1.25	0.19 ± 0.06
$P - PO^{3-}_{4}$	0.06 ± 0.01	0.05 ± 0.01	0.15 ± 0.03	0.09 ± 0.01
$Si-SiO^{4-}_{4}$	3.51 ± 0.57	3.16 ± 0.52	2.36 ± 1.53	2.22 ± 0.27

Light is an important factor governing the growth of the phytoplankton and of the marine plants which live attached to the sea bottom. It also influences the daily vertical migration of zooplankton and benthonic fish.

In consequence, the transparency of the waters is important not only for the obvious aesthetic reasons but also, since it is correlated to the depth of light penetration, with regard to the various biological processes.

It is therefore interesting to compare the transparency of the waters of the northern Adriatic, where the values are lower than in other parts of the Mediterranean, with the corresponding data relating to other seas.

For example, along the Californian coast the annual average Secchi disc visibility is around 10m; the values oscillate between less than 6 m and over 15 m. At a distance of about 2 km from sandy beaches, values of less than 6 m are very frequent, while at the same distance from rocky shores the most frequent transparency values are between 6 m and 12 m.

7.2.2 Potential Impairments From Toxic Substances

Another aspect of marine pollution which it is opportune to subject to preliminary evaluation and quantification as regards its radius of action and, thus the scale to be considered with regard to the location and examination of a discharge, is that of the toxic component of its polluting effects. It is in fact on account of their toxic effects that certain forms of pollution in the Mediterranean have been revealed to be particularly dangerous. These toxic effects are in the main typical of industrial discharges but they are also associated with major urban discharges when, as is common, numerous industries discharge their effluents into the city sewerage.

This report, apart from considering certain substances such as pathogenic organisms, nutrient materials, substances in general that cause oxygen consumption in the receiving environment, is also, and it could be said mainly, concerned with numerous compounds of industrial origin, also to be found in varying measure in urban discharges, which are characterized by toxic effects less dangerous as regards persistence and accumulation than the other substances not considered in this Report, and having a smaller scale of action.

But even if it is acknowledged that the scale of action of the considered substances is small, it is nonetheless opportune to establish an order of magnitude, while preparing documents relating to an authorization to discharge or to a particular phase of the planning procedure, so as not to overlook the presence of other discharges that may have concomitant effects, or certain zones in which particular uses may be compromised by the toxicity of the discharge proposed.

It will be clear that, in view of the considerable difficulties of an a prior evaluation (in a field difficult even when the problem is faced with the help of appropriate environmental studies), the indication of criteria allowing even an approximative evaluation of the magnitude of this scale could be of notable use for the purpose of this report.

It is clear that in this case the problem presented itself in terms different from those previously considered - "organic" and microbiological component of urban discharges - since this component is fairly accurately determined in the various urban and domestic discharges and is conditioned, as regards the total load discharged, only by the number of inhabitants served (and as regards the average concentrations of sewage, by water availability).

The discharges of industrial activities and of particular industrial activities and particular industrial processes may, on the other hand, differ greatly from case to case, and the synergic effects on particular ecological systems of these discharges combined together or with discharges of urban origin may differ even more.

Fortunately, the problem of somehow quantifying the toxic action of discharges has been investigated, also by means of experiments, by an important study on a practical case(*).

The fundamental parameter considered was relative toxicity, that is, the volume of the discharge multiplied by the number of toxicity units by which it is characterized.

(*) San Francisco Bay, California (USA) (10, 11).

The toxicity unit corresponds to the inverse of the lethal dose for 50% of the individuals subjected to an acute toxicity test.

Thus:

$$\text{Relative toxicity} = Q \times \frac{1}{TL_m \text{ (48 hours)}}$$

where: TL_m (48 hours) is the sewage-dilution water concentration that causes the death of 50% of the organisms tested in 48 hours.

For example, if the toxicity unit is 1, this means that, in the effluent as such, 50% of the individuals tested - obviously with sufficient oxygen and in standard conditions - die within 48 hours (or 72 hours, depending on the standard times). If the discharge volume is 1 m^3/sec, the relative toxicity will be 1 m^3/sec.

It is considered that it may be significant and useful to relate discharges defined in terms of relative toxicity (which depends on their volume and their degree of acute toxicity) to effects on the marine environment, and, in particular, on specific benthonic associations at various distances from the sources. This takes into account the probable degree of dilution of the discharges or, better, the average degree of exposure to which the various zones considered are subject.

Studies of this type have confirmed the validity of this approach and its great practical usefulness; furthermore, in this way it has been possible, with or without chronic toxicity or other long-term tests, to use the results of acute toxicity tests to evaluate long-term effect on the marine environment.

And, in fact, the relative toxicity of discharges is the parameter used to define, in terms of order of magnitude, the scale of action of discharges with regard to toxic effects.

To anticipate what will be said later, the toxicity, of discharge waters measured by means of short-term tests will constitute an important term of reference for judging the acceptability or otherwise of a particular discharge, in a particular place, and with a particular dilution.

The use of such a parameter may give rise to doubts in a technician accustomed to considering pollution in terms of concentrations of various substances or, at most, of coliform concentrations. However, it is considered that an efficacious operation of environmental sanitation calls for a knowledge and utilization of parameters of a biological nature greater than has so far been the case, and this with regard not only to toxicity but also to the possible effects of replenishment (eutrophication).

The use in practice of this parameter requires two types of measurement:

a) systematic measurements, on a large scale, of the acute toxicity of the various discharges;

b) direct measurements and evaluations of a quantitative type in the marine environment, with regard to the state of health not only of particular organisms but also of their associations. This can be done by means of appropriate use of diversity indices or biological parameters capable of representing the composition of a particular ecological system.

One of the tasks of a general programme of intervention should be that of promoting the formation of research groups to carry out routine verifications of this type in the various countries. Some countries are already well equipped in this sense even though the parameters in question have not yet been incorporated in their standards.

With regard to evaluation of the scale of the toxic effects in terms of magnitude, the wide range of approximation acceptable for the purpose (apart from being inevitable in the case of an a priori evaluation in quantitative terms of this aspect of pollution) will make it unnecessary, initially, to carry out a precise evaluation of relative toxicity. The value can be calculated by multiplying the volume of the discharge by an indicative toxicity concentration value based on a series of typical cases.

It is known, for example, that raw sewage of essentially domestic characteristics, in an average condition of freshness, where water consumption is 200-300 litres/ inhab x day, is characterized by two units of toxicity; urban sewage which has a considerable industrial component has toxicity concentrations of the order of 3-4 units. The effluent (urban) of low-load biological treatment has 1 unit of toxicity(*).

In the context of a general programme for the sanitation of the Mediterranean, a number of laboratories of regional character could be equipped to carry out accurate tests of this sort with regard to all the limitrophe zones.

An objection that may be raised with regard to the suitability of using relative toxicity to provide even an approximative quantification of the scale of action of a particular discharge could be that the problem in question has particular characteristics of complexity with regard to which a thorough and adequate knowledge can only be obtained by means of prolonged local researches, and that preliminary evaluations are therefore inappropriate.

It cannot be denied, however, that the effects on the marine environment are always observable in the vicinity of urban or industrial discharges and that they increase with the volume of the discharges and the degree in which they contain toxic substances. Nor can it be denied that according as the zone considered is closer to the discharges, more exposed to the dominant marine currents and less characterized by an exchange of water, so are the environmental effects in it greater. And it is therefore logical to admit a relationship between environmental effects and the parameters in question.

It is also known that comparative studies carried out in the Mediterranean in very different zones, such as the northern Adriatic and the Tyrrhenian have revealed a clear analogy of pollution phenomena and an evident dependence upon the parameters in question.

Furthermore, these facts, in their essentials, and also in the quantitative terms to be indicated later, should find confirmation in the experiments of scientists who, in their various countries, have dedicated themselves to experimental studies of this type.

It may also be affirmed that the use of the parameter (relative toxicity) and the good accord between forecast and observed environmental effects (in zones defined according to the distance from the discharge and the average residence time of the discharged substances) relate to experiments carried out in coastal zones of the Pacific Ocean, and therefore cannot be referred to the Mediterranean.

(*) Results of numerous toxicity tests, with regard to a wide variety of industries, are available, for example, in France, at C.E.R.B.O.M., Nice, which has examined numerous sea discharges taking this parameter into account

Such an objection is not to be considered justified for we are here concerned with proposing a methodology and not with the transfer of an experimental datum. Moreover, the Bay of San Francisco, in which the studies in question were carried out, is much smaller than the Mediterranean. The problem thus concerns, rather, the possibility of transferring to open-sea zones techniques of analysis tested in confined spaces (and it is to be considered far from impossible, provided that the differences of research and of hydrological model are duly taken into account.)

The substances considered in this Report do not include ammonia or even the biodegradable surface-active substances; the toxicity of urban sewage has been correlated with the concentration of surface-active substances and ammonia according to the following formula:

$$T_c = \frac{100}{96 \text{ h TL } 50\%} = 0{,}74 + \frac{\text{MBAS (ppm)}}{8} + \frac{NH_3 - \text{N (ppm)}}{46}$$

or, for typically domestic effluents, (12)

$$T_c = \frac{100}{96 \text{ h TL } 50\%} = \frac{\text{MBAS (ppm)}}{8} = \frac{NH_3 - \text{N (ppm)}}{46}$$

The formula may also be taken to mean that, since the content of surface-active substances and ammonia nitrogen x inhabitant is fairly constant, the concentration of the two parameters describes fairly well the concentration or strength of sewage; moreover, it is known that both ammonia (particularly in relation to temperature and at high pH) and surface-active substances (also as regards synergic effect) themselves possess a notable toxicity.

It is also understandable that purification treatments, which remove ammonia and surface-active substances in good measure, also remove, in the case of the methods of treatment adopted today at any rate, a considerable quantity of the other toxic substances which, though they are not included in the formula in question, contribute to the toxicity of sewage and, perhaps in a more determinant manner, to the so-called permanent toxicity.

A distinction between toxicity and transitory toxicity would seem to be an important purpose of this report, primarily dedicated as it is to the development of criteria and guide-lines concerning the treatment and disposal of discharges containing the substances considered in this Report. It can be said that these substances stand half-way between the other substances characterized by phenomena of persistence, accumulation and toxicity which make them particularly dangerous and the substances such as BOD, ammonia, surface-active substances, nutrients in general, the effects of which, if they exist at all, are very circumscribed when the conditions of initial dilution are adequate and the sea zone where they are discharged has suitable characteristics.

With regard to ammonia nitrogen, for example, an average starting concentration in the discharges of 20 to 30 ppm which undergoes an initial dilution of the order of 1:100 with sea water containing, usually, less than 0.05 - 0.08 ppm, leads to a concentration in proximity to the discharge point of less than 0.6 ppm (the limit in California) or less than 0.5 (the limit in the Friuli Venezia-Giulia region in Italy). This limit preceded the issue of the national regulation which established a single standard for all discharges, while maintaining, with regard to the receiving waters, only the pre-existing caterium coli standards for bathing and mollusc-cultivation).

The distinction between permanent and transitory toxicity can be established in practice by carrying out identical toxicity tests, one on a sample of sewage as soon as it is drawn and the other on a similar sample maintained in condition of aeration, and with the required degree of dilution with sea water, for some days before testing. In the case of the second sample, the acute toxicity test brings to light the characteristics which are relatively more persistent and thus more appropriately require attention under the aspect of toxicity proper.

Another matter to be settled in the desirable event of these toxicity tests being carried out according to a uniform standard concerns the type of sewage to be tested, that is, whether it is more suitable to use primary effluent or sewage as such (raw sewage).

This does not constitute a problem where the discharges of primary or secondary treatments are concerned, but it has a certain relevance to the evaluation of the effects of raw sewage. This is because it is presumable that, for a number of reasons also of a scientific nature, the minimum treatment to assign in the final analysis to all discharges of a certain significance (that is, excepting those of small urban agglomerations) is a primary treatment and, also, because, in any case, the fraction of settleable solids concerns not so much the liquid column at a distance from its source as the nature of the sediments on the sea bottom in proximity to the discharge point.

With regard to the formulation of proposals concerning the quantification of the "scale of action" by means of the concepts described above, it is considered that there are two paths which can be followed, characterized by a greater or lesser correspondence to effective local conditions but also by a greater or lesser simplicity and immediacy.

The simplest way could be that of attributing a scale of action simply on the basis of the relative toxicity:

$$X = a \cdot T = a \cdot Q \cdot L$$

The relative toxicity, as already said, can be calculated by multiplying the volume of the discharge by the concentration of toxicity either actually measured or, more simply, approximatively defined for that particular type of discharge.

It is clear that in fact the toxic effects correlatable to the presence of a certain type of discharge will depend to a considerable degree on the degree of dilution in which the discharge waters arrive at the zone considered and on the frequency with which this occurs. It would be more precise to talk of an integral concentration-time, effect, that is, of the exposure of the zone to the action of a particular discharge.

To be well on the safe side, this scale of action could be evaluated in a variety of cases, some of them particularly unfavourable, to be assumed as "typical cases".

The distance at which the toxic effects make themselves felt would, naturally, have to be evaluated by direct studies carried out either by biologists specialized in this type of research for purposes of a direct evaluation of the conditions of the phytobenthos, or by other types of research (studies of particular organisms such as Polychaeta) and, in general, by developing indices of diversity for the various zones, such as, for example, those developed by Margalef:

$$1 = \sum_{i=1}^{s} \frac{n_i}{N} \cdot \log_e \frac{W_i}{N}$$

where: - n is the number of individuals of the specie "i";

- N is the total number of individuals of all species S present in the sample examined.

For example, it was shown that in the Gulf of Trieste (Italy) toxic effects caused by discharges located in proximity to each other, with a relative toxicity not exceeding 6 m^3/s, were not detectable at distances of over 6 km (in fact, depending on the point of view, this distance could be from two to three times smaller).

Again, the effects of discharges in the coastal waters of Augusta in Sicily, characterized by heavy pollution of industrial type with a relative toxicity of the order of 20-30 m^3/s, did not make themselves felt at a distance exceeding 15-20 km measured along the coast.

In both cases the hydrodynamic conditions were very unfavourable owing to the semi-confined form of the discharge zone and the action of coastal current serving to transport the polluting substances and keep them close to the coast.

On the basis of these examples, one could assign a radius of action of 1 km x m^3/s of relative toxicity.

This value could be modified according to the direction in which the toxicity was evaluated e.g. along the coast, towards the open sea, or even inside a bay, and in relation to the position of the discharge outlet (distance from shore and depth).

It is thought that the matter could be taken into consideration and developed in the context of the various regulations. Perhaps, however, for purposes of a preliminary evaluation of the scale of action, it would be sufficient to take into account whether the discharge takes place on the shore or at a certain distance off-shore. Whereas, in the case of a surface discharge on the shore line or in an inlet the initial dilution may be considered non-existent, according to whether the discharge takes place further out to sea, greater depths and volumes of dilution water are available, with the result that the substances leave the place of discharge with a considerable degree of initial dilution.

However, if one transfers the concept of relative toxicity to the polluted area formed downstream of the diffuser, it could be affirmed that the relative toxicity of the seawater-effluent mixture would remain unaltered for, if one assumes an initial dilution ratio of 1:100, the toxicity concentration would be reduced to 1/100, but the total volume would be multiplied by 100.

This thesis has limits, however, for, by extension of this line of reasoning, an unpolluted ocean current would be characterized (in relation to the natural presence, at the level of trace elements, of a good part of the substances - heavy metals - that can play a polluting role) by a high relative toxicity.

In the absence of an accurate evaluation and solely for purposes of establishing a preliminary definition of the extension of the area to be considered with regard to the granting of a particular authorization for discharge, the radius of action could be assigned to the various discharges by reducing in a partly conventional manner the scale of action, conservatively evaluated for 54 coastal discharges, by means of the application of a coefficient. This could be established by research on off-shore discharges or evaluated by deduction and with the application of precautionary criteria, bearing in mind that the toxic effects in question become insignificant at toxicity concentrations in sea water below 0.02 - 0.01 units of toxicity; this is the case, for example, if a discharge with two units of toxicity (urban sewage, water consumption 300 litres/inhabitant x day) is diluted 1:100 to 1:200.

An interesting example is afforded by a standard introduced by the State of California some time ago and recently reconfirmed, which, establishes that the toxicity concentration of sea water must be below 0.05 immediately outside the zone of initial mixing.

These considerations with regard to the scale of action of the toxicity of discharges relate both to shore outlets, which should be the subject of further studies and interventions, and to discharges of adequately treated sewage at a suitable distance from the shore.

For purposes of the evaluations with which we are here concerned, that is, for the purpose of defining the extension of area to be taken into consideration in the context of procedures for the authorization of a particular discharge, it is proposed to assign a certain radius of action (evaluated in very precautionary terms) to all the discharges.

This proposal should not be misinterpreted, that is, it should not be thought acceptable or opportune that, in the final hypothesis, adequately treated discharges dispersed by means of a suitable underwater outfall, should give rise to toxic effects of appreciable dimensions outside the zone immediately surrounding the diffuser. On the contrary, it is considered technically and economically possible, at least in the great majority of cases, to maintain a toxicity concentration at values considered safe immediately outside the zone of initial mixing.

In the final organization of works of treatment and disposal it will be possible to accept the presence, in a certain off-shore sea zones surrounding the discharge point, of even pathogenic micro-organisms in concentrations higher than those considered admissible for purposes of mollusc-cultivation or bathing (provided that the zones used for these purposes are clearly outside the contaminated area). This does not seem to be equally reasonable with regard to the greater part of the considered substances for, while the presence of pathogenic micro-organisms does not in general harm the marine environment, though being dangerous to man in relation to the two uses mentioned, toxic effects should be circumscribed as much as possible for they are in themselves unacceptable for the marine environment.

The difficulty, furthermore, of evaluating with reasonable accuracy the development of the phenomena of transport and eddy diffusion which, after the process of initial mixing, concern the propagation of the discharge waters (and, in particular, the problem of determining in a fairly simple manner the effect of several concomitant discharges) makes it advisable, as will be explained more fully later, to take into account the quality of the sea water round the various discharge points and to ensure that even in these areas the conditions should be acceptable for the marine environment.

This simplification obviously does not alter the fact that certain sea zones (such as estuaries, reproduction zones, marine parks, coastal zones in general) are more exposed to and damaged by the toxic action of discharges than other zones further out to sea.

It is in any case a good technical principle, where pollution caused by the considered substances is concerned, both to exercise a control at source and to foresee systems of dispersion suitable for the protection of the marine environment in general and the critical zones mentioned in particular.

Clearly, the preliminary and hypothetical attribution of a certain scale of action, evaluated in a very precautionary manner, to a treated off-shore discharge does mean that appropriate and thorough verifications will not reveal the scale of action to be in fact insignificant or practically non-existent.

The reason for proposing such a criterion of evaluation lies essentially in the fact the initial dilution ratio does not depend only on the few elements which it is generally possible to know a priori (volume of discharge waters, average depth of discharge point), but also, and to a considerable degree, on the type of diffuser, the currents, and the vertical distribution of density.

Certainly, an estimate could also be attempted, using precautionary criteria and taking as the starting-point the fact that in the majority of cases, the various implications of a technical or economic character being taken into account, the degree of initial dilution obtained is somehow correlated to the depth of the discharge.

In other words, it is known that in general greater discharge depths permit greater initial dilution. However, this does not alter the fact that a long diffuser with small holes may provide a considerably greater degree of initial dilution at a depth of 20 m than a discharge of the same volume through a single orifice at twice that depth.

If one reconsiders the empirical and experimental formulas mentioned above (Pomeroy's formula and Aubert-Desirotte's formula), it will be observed that they correlate the initial dilution ratio with the inverse of the depth; the same is true of Harry's formula, according to which the initial dilution ratio may be approximatively evaluated as, (13) :

$$S = \frac{3}{2} \cdot \frac{d}{y}$$

where: - d = diameter of the jet;

- y = depth of the discharge.

This indication is adequately confirmed by practical experience in that in most cases underwater pipes with outlets at a depth of 10 m permit dilutions greater than 1:10, while at depths of the order of 50 m the minimum value of dilution obtained is over 1:50; in terms of average values the ratios are considerably greater (2-3 times and more).

With regard to the highest value that, in the context of a preliminary, and therefore necessarily precautionary, evaluation, can be taken into consideration, this is 1:50, it should be pointed out that this dilution ratio is certainly significant in the case of an urban discharge, in which a total dilution ratio of 1:100 reduces the toxicity concentration to the value of 0.02, but it is rather insignificant in the case of industrial discharges containing the considered substances in particularly high concentrations, or of chlorinated urban discharges (which may be ten times more toxic than raw sewage).

For toxicity concentrations of 10 units in the effluent, the dilution required to obtain a concentration of 0.02 units in the receiving waters is 1:500. In this case, it is clear that an initial dilution ratio, considered a priori and as a minimum value, is of limited importance. Also, the introduction of further complications and possible uncertainties in order somehow to take it into account is accordingly less justified. In any case, with regard to urban discharges (and domestic in particular) characterized by lower toxicity (especially if in terms of permanent toxicity), the scale of action of the discharges under the aspect of primary microbiological and organic pollution has already been indicated in terms of the concentration of coliforms. The dimensions of that scale are greater than the one relating to toxic effects. These last are evident where the coliform concentrations are still relatively high, that is, at distances relatively close to the discharge points.

There is thus one less reason which could justify a more detailed definition of the scale of toxicity. It should also be borne in mind that the wider the field of pollution and the more the various substances are uniformly distributed transversally to the direction of transport motion, the slower, in correspondence to the median zone of the field of pollution, are the phenomena of eddy diffusion. In consequence of this, the increase of the initial dilution ratio, obtained by means of long diffusers, which is always desirable, is neutralized in part, as far as the final benefits are concerned, by the reduced speed of the process of eddy diffusion. Thus, if the precautions recommended for the use of this evaluation procedure are borne well in mind, it would seem that a scale of action of toxic effects evaluated simply on the basis of the relative toxicity of the various discharges could be useful at least for determining the extension of the area to be taken into account.

Environmental researches carried out by specialized biologists, and also the re-elaboration of data and surveys of the biological communities (benthic in particular) surrounding discharge zones, carried out in the least favourable physiological circumstances, could serve to provide a better definition of the expression of this scale in quantitative terms.

A more precise way of defining the extension of the zone to be studied (or the spatial context sufficient to judge the effects of a given discharge and, thus, the most suitable remedies) could be by means of the "discharge parameter" introduced some years ago for the purpose of providing an adequately practical and significant instrument for efficacious regulation, planning and control with regard to toxic effect on the marine environment, (10).

The so-called "discharge parameter" (which could also be called "parameter of action of a particular discharge") was constructed by examining the essential factors contributing to the determination of the toxic effects in question in order to include them in a formula simple enough to be frequently applied and, at the same time, which adequately corresponds to the mechanism of the phenomenon being studied (emission and propagation of substances with toxic effect).

Three factors are mentioned, (10) :

- Co = quantity of polluting substances discharged or, better, in the case here considered, m^3/day or relative toxicity discharged by a particular outlet;
- F = residence time, the average time that the substances discharged remain in the zone considered;
- X = distance of the zone considered from the discharge point;
- W_p = discharge parameter = f (C, F, X).

The discharge parameter may take the following form:

$$W_p = \frac{C_o \cdot f(F)}{X}$$

where f(F) depends on the hydrodynamic characteristics of the zone considered or, in other words, on the intensity of exchange with clean waters.

It can be observed that the value of the parameter of pollution diminishes progressively in an exponential manner with the increase of distance from the polluting discharge.

In a general case in which in a certain zone - which we shall call the zone "j" - the effects of several discharges are felt (and we shall call the general discharge "i"), the expression of the discharge parameter takes the following form:

$$W_{pj} = \sum_{i=1}^{n} \frac{C_{oi} \cdot f(F)_j}{X_{ij}}$$

where X is the distance between the discharge "i" and the zone "j"(*).

This formula was applied to a real situation, that is, to the Bay of San Francisco. In this case the renewal of the waters and, therefore, the time of residence, was linked to the effects of the tide, and could be simply expressed, with a good degree of approximation, as a function of the distance d_j between the zone considered and the outlet of the bay into the open sea.

The formula thus assumed the following form:

$$W_{pj} = d_j \sum_{i=1}^{n} \frac{C_{oi}}{X_{ij}}$$

It was applied first without taking into account the term d (that is, ignoring the characteristics of the various zones as regards intensity of exchange) and then by taking this factor into account.

The result of these elaborations is given in Figures 83 and 84.

In this way each zone of the bay of San Francisco was characterized by a certain value of the discharge parameter, a function, as has already been said, of the distance of the zone from the various discharges, as well as of the significance of the discharges, expressed as relative toxicity.

Finally, as regards water exchange intensity, the zones were also characterized by their distance from the outlet of the bay into the open sea.

It was possible to ascertain that this procedure found an effective practical confirmation, that is, that it was able to represent in a synthetic and relatively simple form the action of particular toxic discharges in the marine estuary environment. In the first place the results obtained by means of this procedure was compared with those obtained using a specially adapted mathematical model. This model permitted the definition of the distribution of a substance by each of the 31 discharge outlets in the bay (in certain hydrological conditions). Finally, in a manner analogous to that of the science of constructions, the course of concentrations in the bay caused by a single discharge (1,000,000 pounds/day) was evaluated in order to determine "lines of influence" for that discharge. With regard to relative toxicity, it can be said that the distribution determined in this manner showed very similar trends to that obtained by the simple application of the discharge parameter.

It is clear that the mathematical model, apart from expressing a trend, gives results not only in conventional terms (such as the discharge parameter) but also in terms of effective units of toxicity.

(*) Geometrically a zone is represented by its central point, with respect to which the distances are adapted.

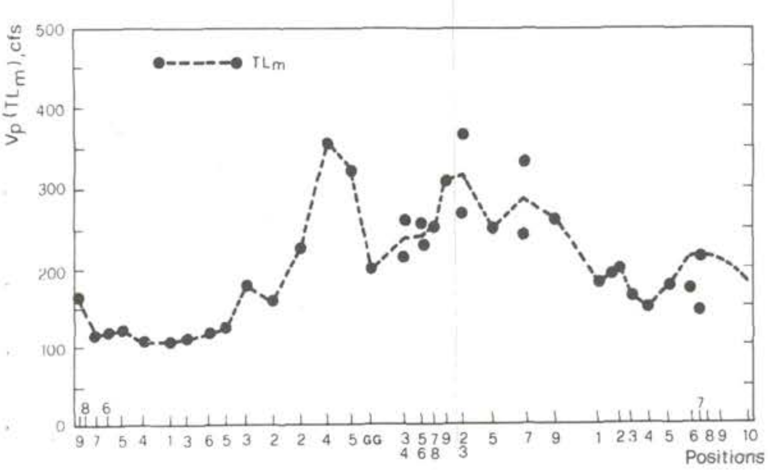


Figure 83 Distribution of relative toxicity (example), (10).

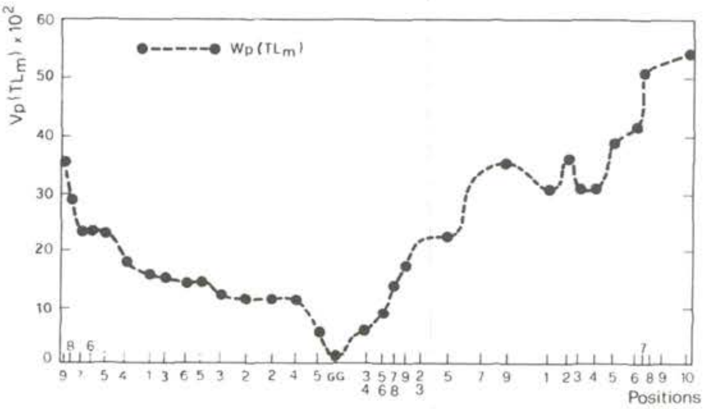


Figure 84 Distribution of relative toxicity after dispersion (example), (10).

Another very significant verification, mentioned because it constitutes a useful example for similar cases, was the following: the course of the discharge parameter was compared with the quantitative measurements of the toxic effects on the benthos. For this purpose it was necessary to take into account also the variations of the index of diversity due to natural causes. In particular, it had been ascertained that the index of diversity was a function of the granular composition of sediments and of the salinity of the water. With reference to non-polluted localities, the course of the index of diversity (as a function of the salinity and sediment characteristics) was evaluated in the various zones of the bay. Assuming that, in the absence of pollution discharges, the course of the index of diversity should have been the one calculated in this manner, the difference ascertained in reality (that is, a value of the index lower than the one hypothesized) was considered to be attributable to the effects of the discharges. This difference was compared with the discharge parameter, revealing an evident correlationship between the two (Figure 85).

To apply this concept to estuaries with more complex hydrological characteristics or to open-sea zones in general, an evaluation (at least approximate), of the residence time, (a parameter which is most difficult to determine) would seem to be necessary.

With regard to open-sea zones, it could be proposed that this parameter be expressed as a function of the distance from the shore and of the trend of the currents (in terms of frequency of their running from the discharge point to the zone in question).

As for the practical definition of the extension of the area to be taken into consideration, this could be estimated in a conventional manner. This area could comprise all the discharge outlets which induce, alone or in concomitance with others, a value of the discharge parameter above a certain minimum at the discharge point "i" considered. The consideration could be given to all the sea zones in which the discharge parameter (correlated with the said discharge point) assumed values above a certain fraction of the global value assumed by the discharge parameter in that place), (10).

$$W_{pj} = \sum_{i=1}^{n} \frac{C_{oi} \cdot f(F)_j}{X_{ij}}$$

Finally, all the discharges having a certain level of effect on the discharge zone "j" could be considered.

The adoption of a scale of action depending simply on the relative toxicity of the various discharges, on the other hand, would involve, in graphic terms, the drawing of circles round the various discharge points. In this case the area to be considered (for purposes of deciding whether or not to authorize a certain discharge) would include not only the area of the circle relating to the said discharge "i" but also that of all the circles intersecting that circle.

In this way all discharges with some interference between them or some overlapping of effect in determined zones would be included.

For an effective application, further study at the level of the individual regions is advisable. In accordance with its purposes, this report has sought to make clear the practical importance of the matter and the criteria for utilization. It is also wished to point out a curious correlation which exists between the widespread use of colimetry to represent possible health risks connected with the presence of pathogenic micro-organisms (among which in general the coliforms, that is, the organisms considered most suitable for routine and control studies, do not appear) and the solution proposed here for the general definition of the toxic effect of the various substances. It seems on the whole fairly easy and adequately satisfactory to adopt a parameter that does not refer explicitly to any of the substances, and is, moreover, of a biological and not a chemical nature: relative toxicity evaluated by means of tests of ichthyo-toxicity.

The systematic use of this parameter generally gives rise to some perplexity regarding which it is appropriate here to make some comments. In the first place it may be asked whether it is reasonable to compare the characteristics of toxicity in fish (as revealed by ichthyo-toxicity tests) to toxic effects on benthonic organisms and their associations in nature.

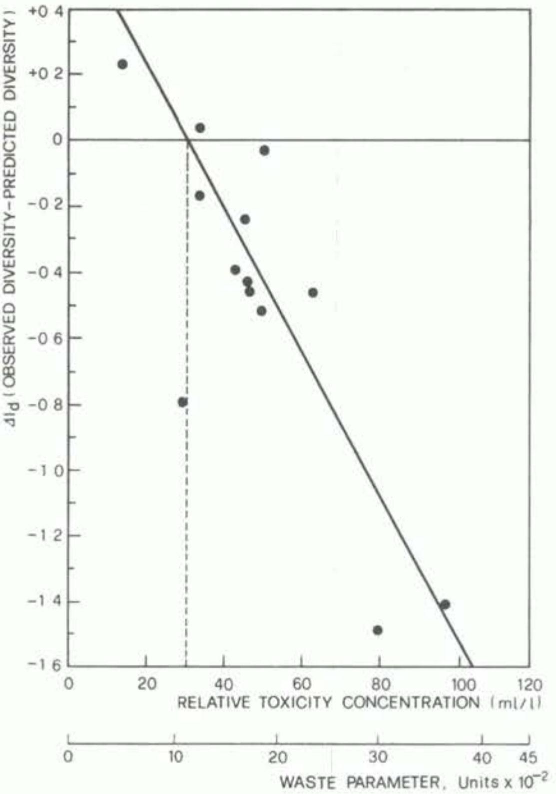


Figure 85 Species diversity depression due to toxicity (example), (10).

It should be pointed out in this regard that there exist substantial similarities between the two cases as far as metabolism is concerned. In both groups of organisms oxygen is transferred by means of fine membranes: fish and benthonic organisms such as molluscs use branchiae "or modified appendages" to effect the transfer of oxygen, whereas in other organisms the oxygen is transferred through the skin and the integuments.

Fish and various benthonic organisms have blood pigments (haemocyanin in molluscs, haemoglobin in fish and in annelida). In view of these physiological similarities, their reaction to the toxic action of certain substances, such as the heavy metals, should be fairly similar.

Clock and Pearson have ascertained that the reaction of isopoda, mollusca, annelida and fish to a certain toxic substance is notably analogous; the authors also reached the conclusion that harmful effects caused by exposure to toxic substances were manifested at concentrations considerably below 1/10 of the TLm(48 hour) value in the case of all the organisms tested. It can consequently be affirmed that negative effects on benthonic and pelagic life may occur at toxicity levels much lower than the TLm(48 hour) values, and that the behaviour of annelide, mollusca and isopoda is not substantially dissimilar from that of fish.

It is therefore reasonable to conclude that environmental effects, evaluated in terms of reduction of the index of diversity, on benthonic populations can be correlated with discharges of toxic substances evaluated by means of ichthyotoxicity tests.

It is possible to question the validity of using indices of diversity relating to benthonic animals and the toxicity of discharges as the two major criteria for determining the quality of a water environment, and to ascertain the degree of efficacity or otherwise of sanitation measures for the protection of marine life.

It should be remembered that not only benthonic animals but also benthonic plants are efficacious integrators of the quality of water. This is important not only because their final state of health reveals the result of exposure to environmental conditions varying considerably in time at a given point, but also because they express (in a manner which is certainly not always obvious and in terms independent of phenomena of natural fluctuation and evaluation) the real action of the various toxic discharges and thus by-pass, by means of direct observation of the effects, all the various problems connected with the evaluation of the synergic or antagonistic effects of the various pollution substances and the chemical, physical and biophysical transformation of the effluents discharged.

The benthonic flora and fauna are considered important in this context not only because they are endowed with little or no mobility, and therefore throw the truest light on the quality of the water in a particular zone, but also because of their importance in the marine food chain.

There is no doubt that difficulties and even resistance have been encountered with regard to the introduction of the study and quantitative effects on marine organisms into administrative practice, planning criteria and objectives, and standards. These difficulties in part derive from the fact that environmental surveys are often carried out without taking into due account the considerable applicative possibilities, and in part from the fact that, as has already been mentioned, sanitary engineers still lack an adequate knowledge of these instruments and parameters, and consequently are unable to ask the biologists the right questions.

Nor should it be forgotten that the laboratories capable of carrying out these analyses (and other environmental analyses, such as the qualitative/quantitative numeration of phytoplankton and zooplankton) in a routine manner are not numerous. It is clear that the direct study of environmental effects is necessary for a correct judgement of the validity of technical solutions. On more than one occasion operational criteria, considered satisfactory in theory, have revealed considerable shortcomings when the results have been verified directly by means of a study of the ecological system concerned.

This fact gives rise, understandably, to reticence, due to a fear of seeing the criteria of standards and technical solutions otherwise considered satisfactory called into question. It is maintained here, however, that even the recognition of mistakes that may have been made in the past can be instructive, and contribute to a more efficacious protection of the marine environment.

Although it has been ascertained that there is a good correlation between the state of health of the various ecological systems and the trend of adequate indices of diversity, these correlations cannot be expressed by general formulas, also because of the effect of natural causes, with its trends and fluctuations, they generally differ from zone to zone.

Local studies carried out by multi-specialist groups (the formation of which would be very useful) could formulate, in each individual case, the best conditions of adaptation of the method, while at the same time distinguishing fluctuations and phenomena due to natural causes from the effects of pollution.

The systematic utilization of criteria and standards of a biological character is to be considered as serving not to replace but to complement the criteria and standards relating to the single substances.

It is not considered that the proposals constitute a novelty in the Mediterranean area: the scientific aspects of the problem have been studied in several countries; in at least one country, furthermore, the various limits of physical, biochemical and microbiological character with regard to effluent have been supplemented by a limit based on the direct measurement of acute toxicity (not to exceed two units in a 72-hour test on Salmo gairdnerii). It is to be hoped that this parameter will be taken into consideration, especially if it is referred, in the case of sea discharges, to marine organisms and to tests carried out with dilution sea water.

Note:

It is perhaps opportune here to draw attention briefly to a method for evaluating in terms of units of toxicity the characteristics of an effluent in which less than 50% of the organisms die in the time e.g. 48 hours, assigned for the test.

The definition of units of toxicity corresponds to the inverse of the concentration in which 50% of the organisms tested have died after, for example, 48 hours, (12).

Example: It is supposed that 50% of the fish tested (after 48 hours) are found dead in an aquarium containing one part of the effluent to be tested and four parts of dilution water:

$$\text{48 hours } TL_m = \frac{1}{1+4} = 0.2$$

$$t{\cdot}c_{\text{48 hours}} = \frac{1}{0.2} = 5$$

If 50% of the fish die in the undiluted effluent:

$$\text{48 hours } TL_m = 1; \quad t{\cdot}c_{\text{48 hours}} = 1$$

If fewer than 50% of the organisms die in the undiluted effluent this method of defining the toxicity units is thus inapplicable.

In this case it is opportune to use the following expression:

$$T_c = \frac{\log M}{1.7}$$

where M represents the percentage of dead organisms; for example, if after 48 hours (if this is the duration of the toxicity test) 3 organisms out of ten have died:

$$M = 30\%; \quad \log M = \log 30 = 1.4$$

$$\text{thus: } T_c = \frac{1.47}{1.7} = 0.868 \quad 0.9 \text{ units}$$

This expression becomes necessary for evaluating the toxicity of secondary effluents of domestic sewage with an initially low concentration, and above all with reference to so-called permanent toxicity.

It is not considered that this approach to the problem of toxicity gives rise to insuperable difficulties in practice. It should be borne in mind that about eight years ago, in a study concerning the sanitation of the Gulf of Trieste, numerous toxicity tests were carried out, with the collaboration of CERBOM of Nice, on Asterionella, Artemia Salina and Carassius, for the purpose of determining the overall toxicity of the various discharges and to calculate the relative toxicity of each of them.

7.3 SEA-WATER USES

7.3.1 Location Of The Waste Discharge In Relation To Uses

The subject covered by this paragraph can conveniently be developed by describing the scope and criteria of two maps :

1. usage map;
2. discharge map.

These maps show the position of the discharge under consideration and its cause and effect relationship with certain zones and certain discharges.

Much has already been said about the importance of these maps (and, more precisely, of the extension of the areas they cover) with regard to the scale of action of pollution phenomena that can be correlated with the discharge under consideration.

We shall therefore not revert to this theme but instead, considering this to be the most concrete way of dealing with the subject, proceed to describe the characteristics and the form of compilation of the two maps in question.

Maps concerning various uses of coastal waters

An individualisation of the characteristic uses of the sea zone under study naturally derives from the definition of the term pollution, in that water pollution consists of an unreasonable interference with certain uses.

The drawing up of a usage map, that is to say of cartography on a scale adequate to cover the area concerned by the discharge, is not too difficult and is essential for purposes of a considered judgement as to the best way of treating and eliminating wastewaters in a given locality and therefore for judging the opportuneness of granting, or not granting, authorization for a given discharge.

In view of their characteristics of relative simplicity and considerable utility, it is in fact considered reasonable to propose that the preparation of such maps should not be postponed until the moment in which they are urgently required for decision-making. They should be prepared beforehand and cover at least that part of the coastline which is of particular importance as regards tourist activities, for the presence of parks and mollusc-cultivation, protected areas, etc.

The drawing up of a usage map should be based on the distinction of the various possible uses by which sea waters can be characterized.

Amongst these uses mention can be made, for example, of bathing, aquatic sports in which little contact is made with the water, the collection of shellfish free-growing or in specifically equipped areas, both professional and amateur fishing, sailing, safeguarding of the natural aquatic environment with particular regard to protected area, etc., to which list other items can possibly be added.

From the practical point of view, one can affirm that the main points to be taken into account are of three kinds:

- bathing: this is conditioned by certain colimetric limits and, should we so wish, by certain objectives of a chemical-physical character (for example water transparency, floating oils, or particles etc.);
- safeguarding of aquatic life: this is not so much conditioned by the microbiological quality of the sea waters but rather by their chemical-physical quality, in relation to the concentration of dissolved oxygen (usually not a limiting factor), the presence of toxic substances which can harm the life of the organisms or be transmitted to man by means of the food chain; substances or conditions (for example, temperature) which can cause long-term effects on the behaviour of the organisms and on the balance of the various ecosystems;
- protection of mollusc-cultures: this includes a variety of requirements which range from those of a hygienic nature (and which are usually determinant) to others usually inherent in the safeguarding of aquatic life and of the consumer, as shown above.

As regards the aesthetic characteristics of receiving waters and the recreational uses connected to them, the problem could be, for purposes of planning and choices, of marginal importance: in fact the maintenance of acceptable aesthetic conditions, even at discharge points, which should not be distinguishable by the naked eye in any way, from uncontaminated areas of sea, is technically and economically feasible.

The same could be said with regard to the protection of aquatic life.

In other words, under this aspect it would not be opportune to individualize those zones in which such uses or such objectives acquire importance, in that the maintenance of acceptable conditions for aquatic life and for recreational purposes should naturally be a condition of any treatment system with disposal to the sea, even at the very point of discharge.

Therefore there would be no point in defining areas for "the safeguarding of aquatic life" in that all zones can and should be considered such.

This formulation could constitute a suggestion to the various authorities, being preferable to the issuing of regulations concerning marine pollution, and it is to be considered an objective at least in the medium - or long-term period.

The advantage of such an approach, as we will illustrate below, lies also in the simplicity and in the efficacy of the relative principles, which in a certain way can be said to lie halfway between a rarely-adopted system of regulations concerning only the quality of the discharges and system of regulations based only on the particular uses of the various zones.

The establishing of requisites concerning the safeguarding of aquatic life in the waters surrounding the discharge points, that is to say, the places which potentially are more polluted, on the one hand clearly indicates the places from which control samples are taken and, on the other hand, guards against the danger of complications and controversies relating to the effect of different discharges in the same zone or on particular uses.

This does not however alter the fact that it is opportune to show the existence of certain zones of the sea in which the safeguarding of aquatic life is particularly important: marine parks, reproduction areas, zones for mollusc-culture.

While in practice, the main specific uses to be indicated are bathing and mollusc-culture (though all zones should be safeguarded from the aesthetic point of view and as regards the protection of aquatic life), it would also be opportune to show other particular use-areas, as mentioned above (marine parks, reproduction zones, marine laboratories, etc.).

Recreational uses, which in effect require certain aesthetic conditions of the sea water, could also usefully be indicated; for example, it could be important to show the position of tourist ports, in that it is preferable not to make highwater discharges there since, in concomitance with precipitations, they give rise to a certain level of pollution.

As regards mollusc-cultivations, these localities have to be indicated by differentiated symbols, depending on whether they are organized and commercially equipped mollusc-cultivations or zones in which there is free collection of sea-food.

Experience teaches us that where these latter areas of free collection are found, it is in actual practice difficult to prevent their being used; however, also in view of the precise hygienic significance of the microbiological quality of such waters, the best safeguard for the health of the population lies in endeavouring to improve the quality of the receiving waters rather than in endeavouring to prevent the collection of molluscs.

However, artificial cultivations of mussels in highly polluted areas can be easily removed, when necessary, despite the serious economic and social effect this could have on populations whose livelihood depends on these cultivations.

Stalling. The practice of mollusc stalling is becoming widespread; in this way they undergo depuration and even molluscs grown in waters characterized by a certain amount of faecal contamination are rendered edible.

One must however bear in mind that certain rules forbid the collection of mussels originally affected by micro-biological pollution over certain limits, because of certain limits to the practical possibility of depuration.

It is however necessary in any case to show on the usage map the areas in which mollusc cultivation is carried on; it is also important to show the position in which the stalling baths are placed, as also eventual sea in/outlets for exchange waters.

In fact, although recourse is made to various methods (ultra-violet rays, chlorination) in order to maintain the waters of the stalling baths acceptable from a hygienic point of view, it is desirable - where it is economically viable - to use sea water which is in itself microbiologically satisfactory in these baths.

Professional fishing with trawl nets. The localization of those areas where fishing is carried out by means of dragging nets and apparatus which scrapes the seabed should also be indicated. This should be done although this is not a use to be protected but rather a practice carried out despite the laws which forbid such exploitation of the marine bed, since it is destructive in zones too near the coast characterized by important biological functions (reproduction, etc.).

The construction of underwater discharge pipes usually concerns a relatively small coastal strip (a few kilometers) in which all fishing is forbidden; however, in actual fact, numerous breakages of underwater pipelines have been caused by this kind of fishing.

Therefore, indication of areas where fishing with trawl nets is carried out, more than serving for the protection of a use, will provide, information useful for the preparation of the executive project for the underwater discharge pipes, which may be protected by numerous blocks of concrete weighing several tons and equipped with iron hooks, in order to discourage this abusive practice and to protect the submarine outfalls.

Where the positioning of a discharge pipeline affects areas in which trawl-net fishing is allowed, obviously protective measures will not be by means of concrete blocks or similar, but the pipeline, and in particular the diffuser, will be such as to allow the passage of the fishing equipment.

The Water Pollution Research Laboratory of Stevenage (UK) has put forward some suggestions for the purpose of avoiding damage to trawl fishing nets and, at the same time, favouring the phenomena of initial dilution. This concerns concrete domes with one opening on top and several openings underneath; the sea water enters through one of the lower openings and the mixture is then ejected from the upper opening; the aspiration is caused by means of the rotating movement induced by the discharge jet, and the round form of the dome allows the fishing nets to pass over it without suffering damage in any way.

Protected marine zones. As regards the indication of marine zones of particular interest which are more delicate from the point of view of safeguarding aquatic life, they can be shown by a simple broken line along the contours of the relative area and by adding explanatory notes: (reproduction zone, marine parks, etc.). These areas could also be marked by numbers or symbols relating to a list which could give fuller information and bibliographic references.

Bathing areas. The zones used for sea bathing can be shown by means of dotted lines which can be thick or thin, depending on the numbers of bathers on a per/day x Km of coast basis.

A note could indicate the period in which most bathing is done; this period (or season) will not be characteristic of a given locality but, rather, of an entire region.

A conventional sign (i.e. an asterisk) could show those bathing areas most particularly used by the population owing to relative distance from the city, facility of approach, amenities offered by the place. A recovery plan for coastal waters could contribute to the integral reclamation of such waters under a micro-biological profile, in the sense that in most cases it is economically possible to maintain the whole coastal strip used for bathing in satisfactory condition (even judged by restrictive colimetric standards). This medium or long-term objective may, owing to limited funds, have to be achieved by stages. It therefore follows that priority should be given first to shellfish cultivation and then to highly-frequented beaches.

Synoptic maps. It is considered useful, in order to furnish a synthetic picture of the situation under its many aspects, to prepare, in addition to detailed maps (of uses, discharges, sewerage, treatments, disposals and the sampling points) also synoptic or summary card. In these principal elements mentioned above are indicated simultaneously, though obviously not in full detail.

Other uses. Besides the uses considered above, others could be mentioned and amongst these, as we have said, the position of small tourist ports has a certain importance both as a use and also a source of pollution. Other uses (such as drawing of cooling waters for power stations, drawing of waters for desalination) are too specific to be discussed in this general treatment of the subject. The use of waters for cooling seems to be compromised by a level of pollution which is such as to be unacceptable for other more restrictive uses (safeguarding of aquatic life, aesthetic aspect, etc.).

Waste discharge inventory maps

Almost all the feasibility studies include, among other documents, a map of the discharges. The position and the characteristics of the existing discharges have a primary importance both for purposes of the valuation of the most suitable technical remedies to be adopted and for preparing environmental survey campaigns and interpreting the data collected.

The pollution of a given coastal area is in fact caused by the dimensions, type and position of the various discharges; this now accepted fact is of considerable importance, albeit obvious. Because it concerns the definition of a rational policy of control of pollution. In fact, regulation criteria and technical intervention which overlook the variable importance represented by the final positioning of the discharge points planned for the various solutions are unlikely to achieve good results.

This observation does not seem to be superfluous in that it is sometimes proposed to adopt regulations which ignore this aspect despite its considerable importance.

As stated, the development of the theme of the "discharge map" does not present original characteristics; in fact, the purpose is simply to bring to mind the essential elements which, must accompany such maps, in order to give an adequate representation of the situation.

The size of the area which should be covered by a discharge map has already been dealt with in the previous paragraph. Briefly, one should bear in mind that, should the most suitable form of treatment, elimination or recycling of a given discharge be discussed, attention should be extended to cover the various uses to which the discharge in question (either at the actual time or in the final hypothesis) could be put in relation to cause/effect, as also to the various other discharges which can interact with it and affect coastal zones characterized by certain uses.

The availability of a discharge map allows fairly accurate provisions to be made by whosoever has a certain experience of pollution of coastal waters, in relation to the conformation of the coast and of the location of the various usages.

One could also reasonably sustain that a judgement on the state of pollution of the coastal waters could easily be made, rather than by means of examining occasional samples, simply by visiting the place and examining a discharge map which indicates, not only the positions but together also some of the qualitative and quantitative characteristics (listed below).

The discharge map is essentially a map (of scale varying from 1 : 1000 up to 100.000 according to the scale of pollution phenomena involved generally speaking a scale of 1 : 25.000 is sufficient) which clearly shows the coastline, the installations lying behind, the outlets into the sea of the drainage channels, the sewer discharges, the rain water overflows, the water-courses etc. The position of all these discharge points are usually shown by an arrow. The sizes of the arrows can be suitably correlated in order to indicate more clearly the importance of the discharge, whether in terms of volume or of pollution load. Thus, discharges serving a double number of inhabitants will be indicated by arrows of double size. It seems more opportune to relate the area of the arrows to the importance of the discharge, rather than their linear size; in this way a discharge of double importance with respect to another will be shown by an arrow $\sqrt{2}$ times as wide and $\sqrt{2}$ times as long as another discharge.

As regards the characterization of urban (or similar) discharges, reference can be made both to the capacity and to the population served; generally, for a similar locality, there is a reasonable correlation between inhabitants and loads, so that the choice is practically irrelevant.

On the other hand, one could relate the size of the arrows more to the load than to the number of inhabitants served. In fact, the dimensions of the sewers, pumping, elimination by means of irrigation of land lying behind, or into the sea for dispersion, the sounding-depths are more directly connected with the volume of the load. Also, the dimensioning of the wastewater line in treatment plants (as regards pre-treatment, phases of sedimentation and possible final disinfection) depends on the volume of effluent.

Should one opt for this solution (characterization of the load in terms of volume) it would nevertheless be advisable to insert, next to the arrow which shows the position and size of the discharge, a number indicating the number of inhabitants served.

It happens that, despite the good correlation which exists between load and inhabitants served, as we have said, in many cases certain discharges are extremely diluted by considerable quantities of infiltration water in the sewer system - fairly frequent in the case of coastal collectors - or by interception of drainage waters contaminated by civil discharges.

An order number next to each arrow draws the attention to a special list in which various indications are given which give a more complete description of the characteristics of the discharge. Firstly indications could be given of volumes of minimum, average, maximum, present (or expected in the near future) and dry-weather loads. Indications as to whether the sewerage is of combined or of separate type are also useful.

In the case of outlets of storm - sewers, it would be useful to give number of hours per year in which the discharges operates - such an indication can be given with references to a certain level of probability: for example it could be indicated that there is a 90% probability that all particular discharge points will function for less than 200 hours per annum. Other indications, always given in terms of frequency, can refer to the volume of the waters discharged.

Such data can be obtained by means of hydrologic analyses and, in particular, by the study of the sewers and of storm-waters overflows; these last have been the subject of specific reports and meetings.

A fairly debatable question concerns the relationship between rainfall and bathing. Rainwater is generally characterized by a high concentration of both pathogenic and non-pathogenic micro-organisms, and, in each case, by high colimetric values; these values are obviously higher in the case of mixed discharges, but they vary considerably even in the case of separate sewers (after all, it is well known that, to facilitate the connections, in many cases the separate sewers for collection of rainwater, also collect abusive discharges or drain filtered water from dispersion ditches, or from foul sewer networks of old unconnected constructions). If colimetric standards for sea-bathing are applied without taking into account the possibility of such precipitations, it is difficult for them to be respected in acceptable economic conditions.

When it rains, in fact, the volume of water arriving in the sea is such that it is not possible economically speaking, or in many cases necessary from the environmental point of view, to proceed with pretreatment, pumping and disposal at sufficient distance from the coast so as to ensure that the colimetric standards for sea bathing are respected even in these circumstances.

For this reason, and also because of the reasons which justify the emanation of a colimetric standard for bathing (and in particular the more ample significance of such a criterion, over and above a measure of hygienic protection which still has to be proved), in some countries it has been foreseen that samples for verifying the state of microbiological pollution of coastal waters reserved for bathing will not be taken immediately after rainfall; from this point of view the indication of the rainwater overflow would seem superfluous in that the contamination induced by it is not verified by controls owing to, the transitory character of the parameter.

It is, however, useful to indicate the position of these discharges, in that the sanitation of the coastal areas, at least under the aesthetic aspect, must take this aspect of the problem into account; also it is important to remember that, whilst certain discharges of rain cease to function some hours after the rain stops, in other cases these discharges remain active even for several days following the precipitation. This happens when the zone served is not a typically urban zone but partly green, possibly with hilly elements, in which the rainwater is first absorbed and then gradually released over a certain period, which can be of several days' duration, according to an extinction curve.

Therefore it becomes necessary, for aesthetic reasons and also in order to respect the standards laid down for sea-bathing, to intercept these discharges in their entirety below a certain volume and to pre-treat and possibly disinfect them before finally disposing of them to the off-shore waters (since these volumes occur periodically, the realization of specific infra-structures for their elimination by means of irrigation is usually not considered to be justified).

Apart from the discharges of those easily identifiable wastewaters, numerous others can exist which, although they represent only a small fraction of the total polluting load, manage to undermine the results of treatments and elimination works aimed at neutralizing the polluting effect of the more important discharges.

This happens, especially, with regard to the micro-biological pollution of coastal waters; this can manifest itself, albeit without progressing more than some tens or hundreds of meters, in the presence even of single dwellings.

It is therefore important, as has been said elsewhere, to indicate on maps of suitably large scale the existence of all the discharges, even those of minor importance. They can be ascertained by means of systematic controls to be carried out in inhabited coastal zones, even if these are served by sewers, especially if the sewer network is at a certain distance from these zones, or at higher levels with respect to certain installations.

These controls can be carried out by means of a certain amount of coloured tracer materials in the discharges of the various buildings, and then letting the water run, so as to avoid those stagnating effects which can be produced in the tubing, in the septic pits, and in eventual dispersion pits.

The various coastal discharges shown by the relative arrows can then be more fully described by means of some drawings which illustrate the section of the conduit, the longitudinal profiles in the terminal tract and the possible stations or sampling points for analyses.

It is also rather useful to give an indication on the map of the principal collector sewers which relate to the various discharges, delimiting the zones served; inside these zones, pre-arranged symbols, which can be checked against a list, could indicate the position of industrial or artisan activity.

It is also opportune to indicate the depth of the outlet of sewers in relation to the average sea level and the high and low tide levels in order to cater for eventual surcharging phenomena.

Discharges from industrial areas, whose, characteristics are comparable to those of urban discharges, can also be shown with an arrow proportionate in size to the size of the discharges.

It is advisable to note that an industrial discharge is generally comparable to an urban discharge as regards its composition and its treatability (generally the assimilation of industrial discharges and urban discharges is based on the COD : BOD ratio and on whether or not the discharge is suitable for purification by means of the biological treatments usually adopted for urban discharges). This extension is valid as regards the type and volume of the possible method of treatment but, on the contrary, has little or no relationship with regard to the pollution produced by discharge into seawater.

As regards enclosed waters, traditionally, the pollution caused by urban discharges results in a reduction of the dissolved oxygen and is a function, therefore, of the BOD discharged.

On the other hand, in sea water the direct effect of discharges containing degraded organic substances on the balance of dissolved oxygen is more or less non-existent whilst, still referring to urban discharges, the principal impairments of the various uses are due to micro-biological pollution, aesthetic factors and, finally, eutrophication phenomena.

A canning industry, for example, produces waste waters which are rich in BOD, suspended solids and fats, but which cause entirely negligible consequences in terms of micro-biological pollution.

Thus it is suggested that industrial discharges be indicated by arrows differently shaped from those indicating urban discharges (e.g. urban discharges by solid arrows, industrial discharges by outlined arrows) and further distinguished by a progressive number referring to a specific list, in which the types of industrial activity, number of workers, quantity produced, volume of single discharges, and possibly analytical data regarding the composition are described in detail).

As regards illustration of the collectors sewer on the map, it is useful to indicate the size of the section involved, the design capacity, the effective capacity, the gradient of the various tracts, the position and characteristics of intermediate sewage pumping stations and the relative emergency discharges.

In the event that the discharges are not on the shore but, by means of underwater pipeline, at some distance from the coast, it will be advisable to indicate the length of the pipelines, in particular, the length and orientation of the diffuser; an enlarged drawing design of this should be given separately. The diameter of the pipeline and of the diffuser should be indicated, as also the number and the diameter of the discharge outlets.

The depth of the discharge point can be referred to the terminal, central or initial part of the diffuser; the position on the map of the corresponding point should be shown, together with the relative geographical co-ordinates.

The explanatory notes and the map, should also indicate (with easily recognizable landmarks) the alignments serving for individuation of the position of the diffuser (which should in any case be marked by means of a fixed luminous buoy, also for purposes of the relative controls).

As regards the shoreworks (upstream of the various discharges), it seems useful to give some details of the treatment plant: the areas concerned should be shown, as also the areas for future extensions, the incoming and outgoing volumes of wastewaters, the capacity of the plant in e.g. kg of BOD_5/day.

Besides showing the actual discharges (including, as we have said, urban and industrial discharges and also canals) it is considered opportune to indicate, as potential causes of pollution, the discharges of earthy materials; these often produce considerable environmental damage, if protective barriers are not erected immediately. The position of commercial and tourist harbours should also be shown.

As regards commercial ports, it is a known fact that from time to time solid waste materials are discharged from ships, as is also oily bilge water, and domestic wastewaters, which can impair in varying ways the quality of the surrounding waters.

Particularly, in cases of major installations for loading and unloading hydrocarbons in a port, it is difficult to avoid, every now and then, be it accidentally or on purpose, the discharge of large quantities of hydrocarbons into the sea; these have a large range of action and considerably damage, at least from an aesthetic point of view, large stretches of the coast. A satisfactory solution to this problem lies in installing barriers of air-bubbles which prevent the floating material from leaving the port, without in any way disturbing the sea-traffic.

Commercial and tourist ports are often coupled with dockyards for ship repair and maintenance. With regard to these it should be borne in mind that the anti-vegetative paint removed from the hulls can constitute a discharge into the sea water of a significant amount of biocides.

7.4 EFFECTS ON HUMAN HEALTH OF POLLUTION OF EDIBLE MARINE ORGANISMS, BATHING WATERS AND AESTHETICS

Edible marine organisms:

Fish do not naturally carry a wide variety of pathogens and those which may contaminate the marketed product are normally derived from their environment. Thus they may be contaminated from pollution of the sea water in which they live.

Sewage bacteria and viruses like the virus of infectious hepatitis may be concentrated in shellfish such as oysters and clams. Fish may carry Vibrio parahaemoliticus, Salmonella spp., Clostridium botulinum type E and other micro-organisms.

Many outbreaks of infectious hepatitis and typhoid as well as cholera have been attributed to shellfish as vehicles. Bivalve molluscs such as oysters, clams and mussels are the usual offenders.

Chemical contamination of marine organisms by mercury and cadmium has become, increasingly, a cause of concern. High levels have been found in fish caught in polluted bays and estuaries because fish appear to be able to concentrate mercury from water several thousand-fold. They are thus the major source of food contamination by mercury.

Some marine animals are reported to be capable of concentrating cadmium more than 4500-fold from water. Shellfish have been reported to contain 0.05 mg/kg in non-polluted areas whereas this value reached 420 mg/kg in the livers of shellfish and cuttlefish.

Some other chemical contaminants are also found in relative high concentrations in fish and shellfish and may present some problems of intoxication.

Certain fish can concentrate heavy metals and will concentrate radioisotope of these metals in the same way. Thus ^{65}Zn has been accumulated by oysters at levels sufficient to present a hazard from their consumption as food.

Fish such as salmon, tuna and saury, accumulate ^{55}Fe and high levels of consumption of these fish may increase the body burden of radioactivity. Certain marine animals like molluscs have concentrated the especially dangerous ^{90}Sr and high levels have been found largely in shells or bones of the animals and also in the edible portions.

In general radioisotopes discharged into the marine environment mainly effect man through the intake of radioisotopes contained in marine foods and through exposure to radionuclides absorbed in marine sediments. An estimate of the potential impairment can be obtained from the concentration of the nuclides in the foods, their radiological characteristics and the amounts of sea foods consumed by critical groups and the general public. The estimated exposure dose can then be confronted with the recommendations of the ICRP for an estimation of the possible risk. From past experiences it can be anticipated that fishermen and persons involved in fish processing and retailing and their families will be the persons most exposed. Fishermen might also be the critical groups which will receive the largest dose from exposure to sediment.

It is highly desirable to develop appropriate criteria on which to base relevant standards for the shellfish growing areas and for the protection of contamination of the fish in general. Controlling the discharge of pollutants from the land-based sources should provide the appropriate handling in order that the established standards for the recipient sea are respected.

Bathing waters:

The hazards to human health from bathing waters arise from direct skin contact or from the swallowing of polluted water.

There is some epidemiological evidence to suggest that there may be a positive correlation between the transmission of communicable disease and the quality of bathing waters; i.e. the greater the degree of pollution of the bathing water the greater the health risk to the bathers. However additional epidemiological studies are required in order to better ascertain the relationship of cause and effect.

There seems to be universal agreement that bathing in polluted sea water increases the risk of contracting one or more of a variety of minor ailments, particularly those effecting to eye, ear, nose and throat regions.

It is important that coastal bathing waters be sufficiently free of pathogenic microbiological life so that water borne infections do not pose a significant health risk to those who use them for recreation. It is agreed that the main indicator organisms for the contamination of water by human pathogens are the faecal coliform group of bacteria.

The Working Group on Guides and Criteria on Recreational Quality of Beaches convened by WHO/EURO in October 1974 proposed that highly satisfactory bathing water in coastal areas should consistently show E.Coli counts under 100/100 ml waters. It being considered that to be acceptable from the public health viewpoint, samples of bathing waters should not give counts consistently greater than 1000/100 ml E.Coli.

The discharge of waste should not:

a) result in changing the physical and chemical characteristics of bathing water to render it toxic or irritating to the skin and membranes of the human body;

b) contain chemicals in such concentrations as to be toxic to man should small quantities be ingested;

c) contain materials which may settle as objectionable or undesirable deposits;

d) contain floating debris, oil, scum and other similar materials;

e) contain substances which may produce an objectionable or undesirable colour, odour and/or turbidity;

f) cause sewage odour at beaches (high initial dilution is required to dissipate odour-producing materials).

In the case of the discharge of radionuclides, persons swimming in seawater usually do not stay immersed long enough to accumulate a sufficiently large dose.

Aesthetics:

All coastal waters should be aesthetically pleasing. Aesthetic satisfaction can be a definite force in promoting public health and well-being. This is experienced through the senses of sight, smell, taste and touch. The assessment of what is aesthetically acceptable or objectionable is a matter of subjective opinion, and although efforts have been made to suggest quantitative standards, no authoritative standards have yet obtained general approval. Therefore, criteria concerning these aesthetic characteristics must be general and descriptive rather than specific and numerical.

The presence of gross solids represents the most important aesthetic objection to waste discharges with short outfalls. When stranded on shore and combined with floating solids they may constitute a health hazard. If the solids are wholly or even partially removed, aesthetic objections may be satisfied and the health hazard reduced. The breakdown of solids into finer particles causes greater exposure of sewage micro-organisms on to the chemical agencies of sea water and sunlight and thereby accelerates their decomposition in the sea. The presence of grease, oil, wax and fats results in the formation of a visible film on the surface of the sea in the vicinity of the discharge point. These materials, which have surface active properties, tend to smooth out ripples and small waves, thus giving a ready indication of sewage discharge. Standards relating to solids, grease and oils would be particularly relevant if an outfall were to be located off a shore which is continually susceptible to onshore winds. If solids, grease and oils come in contact with fish caught by trawling there is a risk of the catch becoming a health hazard and hence financially devalued.

7.4.1 Problems Of A Hygienic Character

The substances of Group II include pathogenic germs; the problems of a sanitary character associated with the imperfect hygienic conditions of large stretches of the Mediterranean coastline probably represent a problem of primary importance with regard to the health of the population (consumption of mussels), tourist activities and the benefits of a social and economic nature connected with a clean and healthy coastal environment.

Despite its reversible character, the problem is of major importance in that, in the Mediterranean area, it can be said to have manifested itself in proximity to all the centres of habitation that have not carried out adequate works serving for the treatment and disposal of sewage.

The problem certainly relates to a wide range of parameters considered in this paragraph, in that the presence of pathogenic germs in certain concentrations and in certain zones depends not only on the processes of physical dispersion, but also, to a considerable measure, on a complex of phenomena, collectively referred to as "disappearance" phenomena, which are in turn the result of a variety of factors, among which, attributed a greater or lesser weight by the various authors, are an anti-bacterial action of sea waters due to phytoplankton, the germicidal effect of ultra-violet rays, antagonistic conditions of life, flocculation and sedimentation phenomena, predacity, etc.

The subject could be discussed at great length, especially if one considered the particular destinies of the various pathogenic bacteria and viruses, and their correlation with indicator organisms e.g. coliforms, in the receiving waters, in mussels, in sediments.

The problem is much simpler if one bears in mind the purposes of this report and a guideline, already consolidated, that has emerged in the context of the Mediterranean Action Plan and has been adopted by many Mediterranean countries (as well as by the majority of the other countries that have taken steps to solve the problem of marine pollution). In fact, just as a satisfactory level of hygienic protection of drinking water has so far been assured by the systematic application of the colimetric index, so there is no evidence, where sufficiently restrictive colimetric requisites have been respected, that diseases have been caused by an inadequate hygienic quality of mussels (and of the sea water).

At present, therefore, though a future evolution of concepts is not to be excluded, the regulations concerning the protection of the coastal waters are based on the application of certain colimetric standards with regard to the waters and shell-fish.

Moreover, in view of the fact that the essential purpose of a sanitation programme under the hygienic-sanitary aspect is the respect of certain colimetric standards in coastal waters, it is of no particular interest to the designer (or to the bodies responsible for issuing authorizations, or to the citizens who use the waters for recreational purposes or eat the shell-fish cultivated there) if the desired result is achieved for one particular reason or for another.

Thus, rather than distinguishing between the importance of the various factors contributing to the phenomenon of extinction of bacteria (a distinction which is the subject of research and of considerable importance from a scientific point of view), what is important here is to ascertain the speed of this general process in a particular sea zone.

The fundamental datum in verifications of a hygienic nature is, therefore, a coefficient of disappearance (or coefficient of extinction also denoted T90).

The progressive diminution in time of bacteria as a result of extinction phenomena can be described by means of the following expression:

$$\text{a)}\quad Nt = No \cdot e^{-K't}$$

$$\text{b)}\quad Nt = No \cdot 10^{Kt}$$

where:

No = the quantity of bacteria discharged in a certain period of time;

Nt = the reduced quantity after the period of time t.

Adopting the expression b) one obtains $Kt = 1$, for $Nt/No = 0.1$

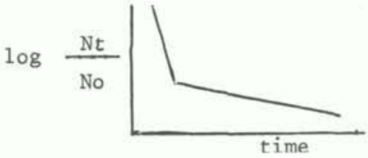
In these conditions $K = \frac{1}{t}$, and corresponds to the inverse of the time needed for the concentration of bacteria to be reduced by 90%; this time is thus represented by the sumbol T_{90}.

$$K = \frac{1}{T_{90}}$$

and $Nt = No \cdot 10^{a}$

where $a = \frac{-t}{T_{90}}$

Even the suitability of this expression for representing the phenomenon of extinction is the subject of debate in that, in a logarithmic diagram, the graphic expression of the phenomenon assumes the form, rather than of a straight line, of two straight lines which form an angle with the concavity upwards:



Moreover, with regard to the first minutes after discharge of sewage into the sea, some authors observe an almost immediate diminution of the bacterial load, while others, on the basis also of laboratory tests, point to a certain initial stasis.

The assumption of a reasonably conservative time of disappearance reduces the significance of such details and, in any case, would appear to be advisable for other reasons.

In the first place, although the speed of bacterial disappearance in the Mediterranean is greater than in other seas, as demonstrated by a comparative study made by Paoletti, (14), it should also be remembered that measurements made in different localities in the Mediterranean, and even in the same locality at different times, reveal notably different evaluations of time T_{90}.

Experiments carried out by C.E.R.B.O.M. of Nice and in Israel in the waters off Nice and off Tel-Aviv, respectively, reveal evaluations of T_{90} ranging from less than an hour to a little under two hours, (15, 16). Experiments carried out in Italy by Paoletti and Olivotti give rise to fairly concordant evaluations; in some cases, however, working, instead of with tracers, with volumes of sea water isolated by means of plastic containers or bags, Olivotti obtained values of between 3 and 4 hours.

Though it remains opportune, where possible, to carry out detailed local measurements, the variability of the data, in the absence of further information, makes it advisable to attribute to the time T_{90} a reasonably conservative value, which, with regard to the Mediterranean, could be of the order of two hours.

It is noted that the designing of pipelines in relation to a longer disappearance time would automatically lead to an increase of the lengths of the pipelines and of the efficacy of the diffusers. In consequence the dimensions of the phenomena of dispersion and of subsequent dilution would increase to the point of approaching or exceeding that value of 1:1000 which could represent a minimum dilution value permitted by regulations with regard to coastal waters (cf. Israel).

A problem of designing disposal systems on the basis of the traditional formula:

$$Ct = Co \quad So \cdot Si \cdot 10^{\frac{-t}{T_{90}}}$$

where Ct = bacterial concentration at the time t;

So = degree of initial dilution;

Si = degree of subsequent dilution;

derives from the fact that the influence of the phenomena of bacterial disappearance, (which occurs irrespective of the volume of discharge waters), being preponderant, the length of the pipeline does not distinguish between minor discharges and the discharges of major agglomeration in the measurement experiments carried out with regard to the extension of microbiological pollution caused by such discharges would lead one to expect. It is well known, in fact, that microbiological pollution caused by the discharges of few thousand inhabitants extends over surfaces far smaller than the microbiological pollution induced by urban agglomeration with hundreds of thousands of inhabitants.

This disparity in results may be due to the fact that, for purposes of the formulae in question, the bacterial load is measured along the central, and most polluted part, of the sewage field (or plume), while surveys of bacteriological quality with regard to a particular locality take into account colimetric data representative also of all the circumstances in which the locality is not affected by the sewage field, or only by the lateral, and less polluted, part of it.

This last possibility is, naturally, greater in the case of discharges of minor importance, which give rise to smaller sewage fields and are accordingly affected to a greater degree by the phenomena of dispersion.

It would seem that certain coefficients of extinction that take into account at the same time the effects of dispersion phenomena and the phenomena of extinction proper, as in Aubert-Desirotte's formula, are recommendable for practical purposes in cases where the average values or N_{80} are required. The value of these coefficients could be fixed in the various countries, possible varying from region to region in relation to certain minimum values associated with the volume discharged. Naturally, this would not prevent applicants for authorization from introducing more conservative values leading to a greater expenditure into the calculation if local surveys or more detailed researches make this advisable.

The formulation of such coefficients would, in any case, avoid the possibility of the introduction of excessively short extinction times to justify the functionality of works conditioned by limited financial resources or, as some authors have warned, of a respect of the colimetric standards being obtained, by reason of the speed of bacterial disappearance in the Mediterranean, despite excessively limited phenomena of dilution and dispersion (which appear to be important also under other aspects, among them the control of eutrophication, the disposal of the organic load and, finally, according to certain authors, the reduction of the concentrations of certain germs, in particular viruses. These germs are characterized by a smaller - 10^{-4} times - concentration in sewage, but also by an extinction time that could be 10 or 20 times greater than that of the coliforms).

There is no reason to dwell on the places or supports on which the verifications of a colimetric nature are carried out, for extensive contributions with regard to this subject have been made in the context of the Mediterranean Action Plan and are available for reference.

It can only be added that, in concomitance with the preliminary surveys with regard to the design of an underwater pipeline, it would seem reasonable to carry out certain microbiological analyses with regard to the sea waters in the vicinity of the point foreseen for the future discharge.

Here again it is considered advisable to carry out a large number of colimetric analyses, rather than extracting episodic samples for the determination of, for example, Salmonella, which may supplement, but cannot replace, the colimetric surveys.

In general, the point foreseen for a future discharge should be characterized by excellent microbiological qualities, that is, by a colimetric level at least compatible with the standards concerning waters used for mussel cultivations. In fact, in numerous samples taken from these off-shore waters, the coliform concentrations should be below 1 per 100 cc.

For economic reasons, the underwater pipelines are usually constructed not far from the location where the discharge (urban sewerage); originates, moreover, they convey the waste waters to off-shore zones sufficiently traversed by currents and characterized by an adequate dispersion, so that the influence of the coastal discharge is no longer felt in these off-shore zones.

Naturally, the points foreseen for final discharge will be further from the shore, bed slopes and current characteristics being equal, as the volume of sewage to be discharged increases.

The discovery of bacteria-contaminated waters in a zone chosen for a future discharge should put designers and the authorities on the alert because, in general, it would tend to suggest that the point chosen for the discharge was too close to the shore or, in any case, in a zone unsuitable under the hydrological aspect.

It does not seem unreasonable to suggest that it would be opportune for the discharge of a more or less treated effluent to take place by law in zones which prove not to be bacteriologically polluted by earlier discharges along the shore.

If the technique does not represent insuperable practical difficulties, use could be made of integrator organisms, such as shell-fish; a group of them could be left for a period in the zone in question and the intervalve water and the body tissue subsequently subjected to colimetric analyses. Naturally, such organisms would have to have been raised in pure waters or appropriately and reliably "cleaned in aquariums".

As to the characteristics of a physical nature relating to the control of colimetric pollution, some of them (temperature, irradiation) relate to the phenomena contributing to bacterial disappearance, which has already been considered; others relate to the phenomena of dispersion and dilution or to the conditions which cause entrapment of the jets and submersion of the sewage field. This aspect has been treated in the proceeding paragraphs and there does not seem to be any point in reverting to it.

Generally, colimetric standards with regard to coastal waters have been utilized not because of a demonstrated need for the protection of the health of bathers; nor have they been fixed at any particular numerical value, for precise scientific reasons.

It has been observed, moreover, that the control of bacterial pollution by means of an adequate dispersion and distancing of treated or pre-treated sewage provides a good solution to the various problems connected with the disposal of the organic load.

In fact, no case is known of an underwater pipeline permitting the respect of adequately restrictive colimetric standards inshore that gives rise to an excessive BOD in the receiving waters.

The evaluation of parameters of a chemical, biochemical or physical nature with regard to primary organic pollution may thus be considered, in certain respects, unnecessary, in that the reasonable application of a colimetric standard obviates such problems without further complications.

It should be mentioned, however, that respect of a colimetric limit can also be achieved by means of chlorination of the effluent (a process which should be regulated by the adoption of standards with regard to the toxicity of the effluent, measured directly on aquatic organisms - an example of this field in the Mediterranean area is provided by Italian legislation, which prescribes, also with regard to sea discharges, experiments with Salmo gairdnerii.(*).

Furthermore, the statement made above, to the effect that the respect of a colimetric standard and suitable systems of dispersion imply a satisfactory disposal of the organic load, may be considered insufficiently demonstrable or inappropriately general.

It is possible, then, to take into consideration a number of parameters of a physical, biochemical and chemical nature:

- the concentration of dissolved oxygen at various depths;
- BOD in the receiving waters;
- concentration of ammonia;
- concentration of surface - active substances;
- concentration of suspended solids or, better, Secchi-disc visibility.

Sea waters sufficiently off-shore from habitation centres to be able to be the final destination of their effluents, according to experiments carried out on the Spanish, Israeli, French, Italian and Yugoslavia coasts, have the following characteristics:

DO : 90 ÷ 120% saturation

BOD : < 1-2 ppm

ammonia : < 30-60 ppb

surface active substances: not detectable by normal routine methods (< 10-20 ppb)

phosphates : < 5 ppb (as P)

In view of the fact that a minimum initial dilution ratio of the order of 1:100 to 1:200 can be achieved in nearly every situation, standards intended to provide for an adequate disposal of the organic load could prescribe the following (referred, for example, to 90-95% of the samples in order to allow for possible errors of analysis):

BOD_5: < 5 ppm

DO : > 90% ppm

ammonia nitrogen : < 0.5 ppm

surface active substances : < 0.1 - 0.2 ppm

phosphates : < 0.1 - 0.2 ppm (as P)

Assuming average water consumption of 250 l/inhab/day, a contribution per inhabitant of the order of:

(*) Naturally this standard may be criticized on the grounds that marine organisms are more suitable for this type of test; however, the existence of this limit is a point of considerable merit in comparison with regulations which do not contemplate any such limit.

BOD : 60 g/d
surface - active substances : 2.5 g/d
phosphates : 2 g/d (soluble inorganic phosphorus)
ammonia nitrogen : 8 g/d

and dilution ratios varying between 1:100 and 1:500, it is verifiable that the values mentioned above, which in themselves represent acceptable conditions of organic load discharged into sea water, can be respected in a variety of cases, even with discharge of a primary effluent (from which, for aesthetic reasons, the floating particles have been removed and also the settleable solids to protect the benthonic biocenosis).

Naturally each coastal centre can be left free to decide whether it is advantageous to achieve these results by attributing more or less weight to treatment processes on land, re-use of sewage, system of final disposal and dispersion at sea.

Although the numerical definition of the limits set forth above is to a great extent arbitrary and obviously can be modified considerably in the various countries, it is considered to be a useful example of how some parameters of a physical, chemical and biochemical character, with regard to the so-called primary organic pollution, can be the subject of controls in the vicinity of the off-shore discharge points, thereby ensuring, under this aspect, a satisfactory measure of environmental protection well within the range of engineering feasibility.

Some sea zones, above all in relation to phenomena of greater fertilization, may be characterized by a level of dissolved oxygen that, in the deeper layer, is below the 90% mentioned above. It may happen that the rising movement of the discharge water jets will draw water from the deeper layers up into the surface layers. In this case the oxygen level in the surface layer affected by the discharge will be lower than that of the surrounding zones, not so much because the organic matter discharged gives rise to an absorption of oxygen, but because waters initially with a low oxygen level have been drawn up to the surface. This aspect should be taken into account.

It may occur in various cases that the characteristics of the off-shore waters not only do not conform to the values indicated above, but differ considerably from them. The existence of such limits would even in this serve a useful purpose, for it would justify the calling in of a team of experts to carry out thorough examination in order to ascertain whether the locality chosen was suitable for the discharge.

With regard to the influence of suspended solids in discharge waters on the transparency of the waters surrounding the discharge point, experiments carried out in naturally very turbid waters (North Sea) reveal that the effect of sewage diluted 1:80 to 1:100 on transparency is invisible to the naked eye. In view of the great transparency generally typical of the Mediterranean waters, it would be advisable to increase this ratio: under this aspect a 1:100 - 1:200 dilution ratio for a primary effluent could be suitable. In the case of the effluent of a biological treatment, this ratio could be reduced considerably (1:5 - 1:10); the same applies for the effluent of a chemical precipitation treatment which reduces the suspended solid content in a measure analogous to a biological treatment.

In quantitative terms, considering that a primary sewage has a suspended-solid content of the order of 150 - 250 ppm (in relation to water consumption), a dilution of 1:100 would bring about an increase of concentration, compared with the level naturally characteristic of sea water, of the order of 15-25 ppm. It is therefore understandable that for stronger sewage a dilution ratio of the order of 1:200

would be desirable to limit the increase of the concentration of suspended solids to the order of 10 ppm.

The effluent of a biological treatment or of a chemical-precipitation treatment has a suspended-solid content of from 20 to 80 ppm; thus, in this respect, a modest dilution ratio (from 1:5 to 1:10) could be sufficient.

There are in fact other reasons for diluting to a considerably greater extent the effluent of a biological treatment which has not been disinfected or subjected to a suitable tertiary treatment, so in this case the limits concerning the suspended - solid concentration would not be important.

All considered, it is reasonable to require that the natural suspended-solid content of sea waters should not be increased by more than 5 - 10 ppm in the vicinity of the discharge point (applying the lower level in the case of more limpid waters).

It could also be required that the transparency of the waters measured by means of the Secchi disc (naturally, by the same observer, at the same time, in the same sky conditions and in the same position in relation to the shadow of the boat) did not reveal appreciable differences between zones upstream and, in the direction of the current, downstream of the discharge.

The use of turbidimeters for the measurement of turbidity in sea waters should be confined to special instruments, with a long optical path, for the normal turbidimeters used for turbidity measurements in rivers and raw or treated sewage are not sufficiently sensitive for oceanographic use. (The degree of turbidity of sea waters not directly affected by discharges is normally less than 0.3 - 0.4 FTU).

7.5 EFFECTS ON MARINE ECOSYSTEMS AND LIVING RESOURCES

The protection of any living marine resource can certainly be accomplished by the protection of the integrity and balance of the greater or smaller ecosystem of which it is a part. Therefore living resources depend upon the maintenance of primary and secondary production, as wastes which damage the plankton or bethos may undetectably affect these resources. Both larvae of fish and shellfish are generally more sensitive to pollution damage than later in life and may also live in different areas. Fish and shrimp nursery areas, in particular, are often in shallow estuarine or coastal areas where pollution has a major effect. Although fish are frequently able to swim away from polluted areas, their very young stages are planktonic and drift only with tides and currents. Fish spawning and nursery areas are more or less fixed in position, and if affected by pollution, the stock may be severely damaged.

Crustacea have a limited capacity for moving out of polluted areas, but molluscs and other exploited invertebrates and especially edible seaweeds are static and may require conditions for their cultivation which, if altered by pollution, cannot be easily provided on alternative sites.

Generally for the protection of living resources from waste discharges the following should be avoided:

a) concentrations likely to be directly toxic at any stage of the life cycle;

b) long term exposure to lower levels of pollution likely to cause behavioural effects or physiological damage;

c) bio-accumulation eventually leading to direct toxicity or loss of quality as seafood;

d) tainting;

e) reduction of growth either directly or by impoverishment of food supply, e.g. by excessive turbidity;

f) eutrophication;

g) alteration of environment e.g. by deposition of sediments or ecosystem imbalance;

h) accumulation of surface films.

These requirements can be related directly to the characteristics of the waste and the control measures taken and to the choice of site and means of disposal. Treatment should be made to reduce or eliminate particularly undesirable substances from the waste, e.g. those with a capacity to taint fish or shellfish, whereas disposal is concerned mainly with removing the discharge point from the vicinity of important resources, effective utilization of the dispersal characteristics of the available sites or achieving a high initial dilution by special outfall diffusers. The removal of nutrient substances from the waste may require special attention in areas where hydrographical characteristics lead to the risk of eutrophication, in others they may give a valuable boost to production.

No effects on ecosystems due to the discharge of radionuclides are anticipated since the more stringent requirement for the protection of human population will limit the discharge to levels which on the basis of our present knowledge should not have adverse effects on the marine environment.

7.6 EFFECTS ON OTHER LEGITIMATE USES OF THE SEA

Some of the more important uses of the sea are: shipping, fishing, undersea mining, power station operation, industrial activities dependent on sea water, desalination etc. Certain of these, such as power station operation, desalination and also most forms of mariculture, require particular standards of pollution control which must be kept firmly in mind when making a choice of treatment and disposal methods.

Settleable matter in the waste may interfere in the long run with shipping routes through the formation of sludge banks, and also through the blockage of cooling systems and fouling propellers. Certain pollutants may interfere with the cooling-system in power plants which take their cooling water from polluted areas in the sea.

Ocean mining and extraction of chemicals from sea water may be affected by impurities of physical obstructions introduced by marine outfalls.

Certain scientific purposes, e.g. nature reserve, wild life conservation (especially of sea mammals and seabirds) and marine parks, may be critically dependent upon freedom from pollution damage, and their presence may influence waste disposal policy outside their immediate vicinity.

It must also be noted that cultured organisms are essentially captive and cannot escape a toxic water mass. Development of criteria for aquaculture should include the consideration of: environmental stability, prevention of deleterious chemicals, physical and biological conditions and prevention of those environmental conditions favourable for the development of diseases.

Outdoor recreation increases continually and sea shore recreation ranks as one of the most important, both economically and socially. Floating matter and grease constituents of wastes interfere with these activities and should be removed before discharge.

The production of drinking and irrigation water from sea water does not pose any risk because the processes used to prepare freshwater from seawater will practically eliminate any radionuclides present. The only limitation the discharge of radionuclides may impose are restrictions in the use of beaches and coastal waters in the direct vicinity of the discharge outfall.

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APPENDIX I - APPROXIMATE EVALUATION OF THE POSSIBLE EXTENT OF MICROBIOLOGICAL POLLUTION PROPAGATION

For References see list at end of Chapter 5

The Pomeroy Formula. The Pomeroy formula, (118), is applied and the precautionary objective established is 10 faecal coliforms/100 ml. The recommended method of analysis is MPN; it is characterized by a probable fairly high difference to the actual value. There is a 5% probability that the data supplied by analyses is three times as great - or as low - as the actual value.

For example, by analysing 10 equal samples containing 90 faecal coliforms/100 ml, at least 30-40% of the reports are expected to be higher than 100 faecal coliforms/100 ml.

One has:

$$N_{80} = \frac{k\ Q^2}{y\ x^2}$$

where:

$Q_{(m^3/g)}$ = sewage flow;

k = coefficient - in the units here adopted - $k=0{,}01$ to $0{,}02$

N_{80} = according to the standard 100 faecal coliforms/100 ml, it is $N_{80} = 1$ coli/ml; due to the above reasons we assume $N_{80} = 0{,}1$ coli/ml;

$y_{(m)}$ = sea depth at discharge point;

$x_{(m)}$ = distance from the discharge point.

In the hypothesis, fairly precautionary for the Mediterranean area, that the slope of the sea bed is 10%, one has:

$$y = \frac{x}{100}$$

and therefore:

$$x^2 = \frac{k\ Q^2}{\frac{x}{100} \cdot N_{80}}$$

$$x^3 = \frac{0{,}015 \cdot 0{,}0625 \cdot n^2 \cdot 100}{0.1}$$

$$x = \sqrt[3]{0.937 \cdot n^2} \simeq 1 \cdot n^{2/3}$$

where:

n = number of inhabitants served.

Example

n = 50,000 inhabitants

1) off-shore discharge though a submarine outfall - pretreated or primary effluent

$$x_1 = n^{2/3} = 50{,}000^{2/3} = 1{,}262 \text{ m} \quad 1{,}300 \text{ m}$$

2) off-shore discharge - secondary effluent

$$x_2 = x_1 \frac{2}{3} = 1{,}262 \ \frac{2}{3} = 841 \text{ m} \quad 900 \text{ m}$$

3) discharge on shore - raw sewage (or pretreated or primary effluent)

$$x_3 = 2x_1 = 2 \cdot 1{,}262 \text{ m} = 2{,}524 \text{ m} \quad 2{,}500 \text{ m}$$

4) discharge on shore - secondary effluent

$$x_4 = 0.85 \cdot 2 \cdot x_1 = 2{,}524 \cdot 0{,}85 = 2{,}145 \text{ m} \quad 2{,}000 \text{ m}$$

The application of the Pomeroy formula to the Mediterranean area should be made with caution: as a matter of fact, tests have shown that the coliform disappearance rate is higher than in Californian waters, where the relative coefficient k was calibrated (1-2 hrs in the Mediterranean against 4 hrs in Californian coastal waters, (106).

A problem arises when trying to determine the depth "y", if the formula is applied to a discharge on the shore; this difficulty has been overcome by assuming that the range of action of shore discharges is twice as great as that of off-shore discharges. The result obtained from the Pomeroy formula obviously depends on the slope of the sea bed and, to a lesser extent, on the water supply - if the number of inhabitants served is introduced as a variable instead of the sewage flow. As to the first item, tables or graphs may be used, which correlate scale and depth; in this case, a sea bed slope of 10% has been assumed as a precaution. With regard to water supply, an average contribution into the sewer of 250 l/inh x day has been considered. Obviously, if opportune, such coefficients can be adjusted in the different regions, in relation to local conditions.

For discharges on the shore, if sewage is subjected to secondary treatment, the scale may be decreased, as already stated, by 15-30%; such a decrease makes sense during the periods in which the purification plant is fully efficient. In emergency conditions, which are not infrequent, such a decrease does not occur; it follows that, with regard to all discharges on the shore the same scale of action, as defined in Table 36 and in the graph of Figure 88 depending on the inhabitants served, should be assumed as a precaution.

TABLE 34 Off-shore discharge. Pretreated or primary effluent. According to the Pomeroy Formula, (118). Sea bed slope, J = 10% (See Figure 86)

Inhabitants served n.	Range of action x_1 (m)
10.000 *	461 500
50.000	1262 ~ 1300
100.000	2137 ~ 2200
500.000	5700 ~ 5800
1.000.000	9908 ~ 10000

*The Pomeroy formula does not lend itself to application in the case of small urban centres.

TABLE 35 Off-shore discharge. Secondary effluent. According to the Pomeroy Formula*, (118). Sea bed slope, J = 10% (See Figure 87)

Inhabitants served n.	Range of action x_2 (m)
10.000 *	300
50.000	840 ~ 800
100.000	1423 ~ 1500
500.000	3496 ~ 3800
1.000.000	6598 ~ 6600

*The Pomeroy formula does not lend itself to application in the case of small urban centres.

TABLE 36 Discharge on shore. Raw sewage or pretreated or primary effluent. According to the Pomeroy Formula*, (118). (See Figure 88)

Inhabitants served n.	Range of action x_3 (m)
10.000 *	922 ~ 900
50.000	2524 ~ 2500
100.000	4274 ~ 4300
500.000	11400 ~ 11500 **
1.000.000	19816 ~ 20000 **

* The Pomeroy formula does not lend itself to application in the case of small urban centres.

** Values perhaps exaggeratedly precautionary.

TABLE 37 Discharge on shore. Secondary effluent. According to the Pomeroy Formula*, (118). (See Figure 89)

Inhabitants served	Range of Action
n.	x (m)
10.000 *	700
50.000	2.000
100.000	3.500
500.000	9.000 **
1.000.000	17.000 **

* The Pomeroy formula does not lend itself to application in the case of small urban centres.

** Values perhaps excessively precautionary.

TABLE 38 Off-shore discharge. Pretreated or primary effluent. According to the Pomeroy Formula*, (118). Sea bed slope, J = 30% (*) (See graph of Figure 90)

Inhabitants served	Range of Action
n.	$0.6 \cdot n^{2/3}$
10.000 (**)	276 ~ 300
50.000	757 ~ 800
100.000	1282 ~ 1300
500.000	3020 ~ 3400
1.000.000	6000

(*) In the hypotheses that the slope of the sea bed equals 30%, one obtains:

$$x^3 = \frac{0.015 \cdot 0.0625 \cdot n^2 \cdot 100}{0.3}$$

$$x = \sqrt[3]{0.312 \cdot n^2} = 0.558 \cdot n^{2/3} \simeq 0.6\, n^{2/3}$$

(**) The Pomeroy formula does not lend itself to application in the case of small urban centres.

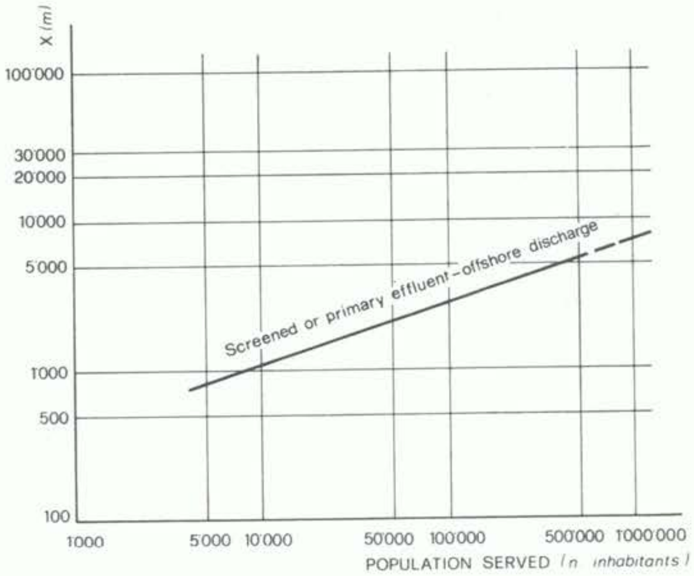

Figure 86 Discharge in open marine waters by submarine pipeline. Screened or primary effluent. Evaluation after Pomeroy formula. Gross and prudential evaluation of microbiological pollution's spatial scale. Bottom slope, J = 10% (See Table 34)

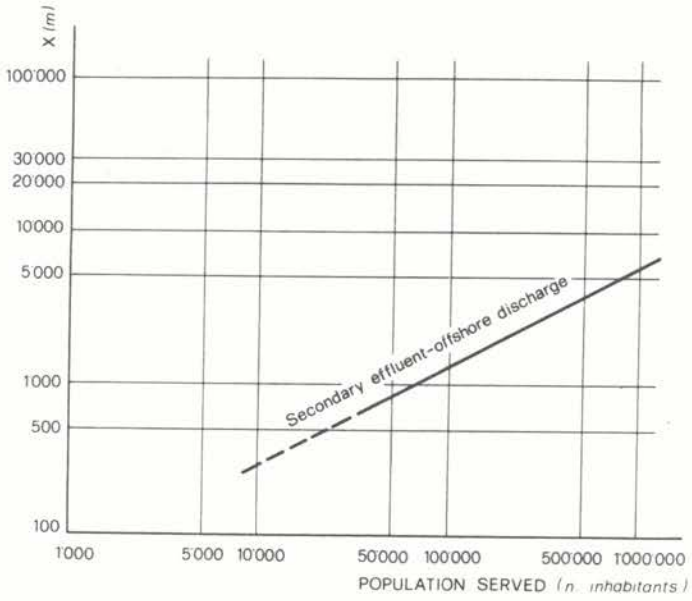

Figure 87 Discharge in open marine waters by submarine pipeline. Secondary effluent. Evaluation after Pomeroy formula. Gross and prudential evaluation of microbiological pollution's spatial scale. Bottom slope, J = 10% (see Table 35)

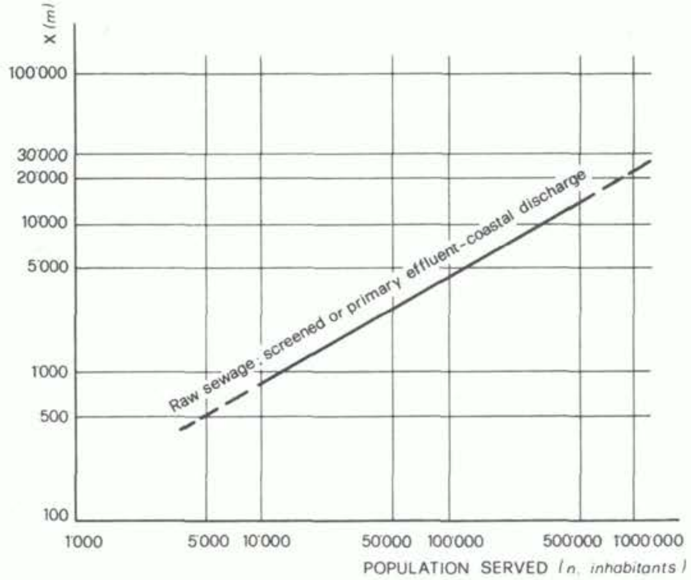

Figure 88 Surface discharge at the coast. Raw sewage; screened or primary effluent. Evaluation after Pomeroy formula. Gross and prudential evaluation of microbiological pollution's spatial scale (see Table 36)

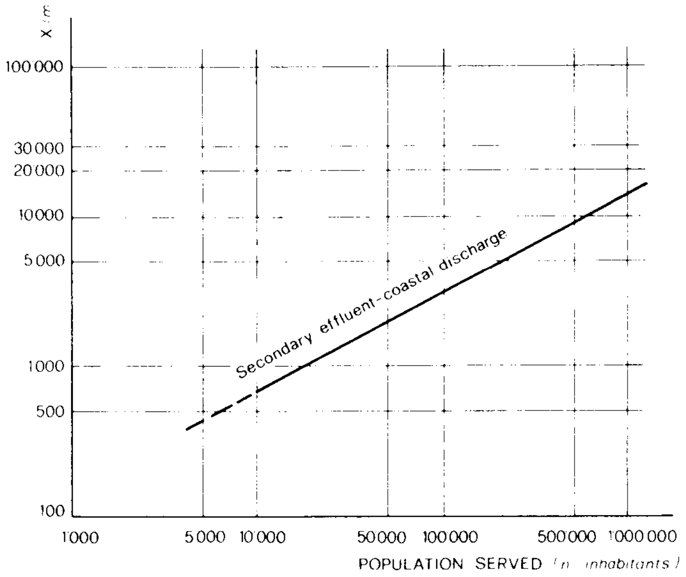

Figure 89 Surface discharge at the coast. Secondary effluent. Evaluation after Pomeroy formula. Gross and prudential evaluation of microbiological pollution's spatial scale (see Table 37)

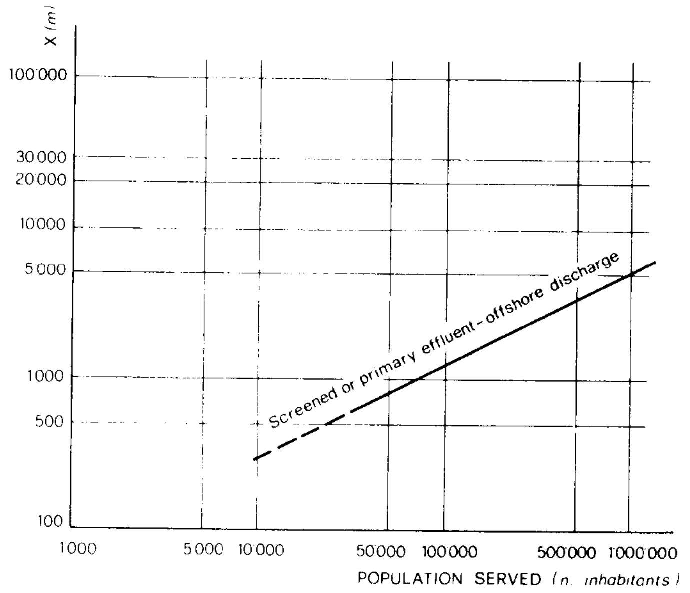

Figure 90 Discharge in open marine waters by submarine pipeline. Screened or primary effluent. Evaluation after Pomeroy formula. Gross and prudential evaluation of microbiological pollution's spatial scale. Bottom slope, J = 30% (see Table 38)

In the case of off-shore discharging of secondary effluents, such a decrease is more marked; by attributing a reduction of two orders of magnitude to initial dilution, the further reduction required for primary of pretreated effluent is about 10^4; in the case of a secondary effluent, it drops to 10^2 to 10^3 (in respect of a 99% to 90% efficiency of colimetric load reduction). In these hypotheses the scale of action would be reduced by 25-50%; on the basis of average values, such a decrease will be assumed to be 33% (1/3).

The Aubert-Desirotte Formula, (13). This gives results which are in some ways analogous to those obtained from the Pomeroy formula. Important variables of the formula are the discharge volume, the outlet depth and, even more so, the sea current velocity. The current speed enables distances from the point of discharge to be attributed to given drift times (and thus the relative scale of the phenomenon may be evaluated). With regard to this parameter, i.e. the sea current velocity and direction, it is possible in such approximate evaluations, - to consider acceptable for the Mediterranean a very precautionary hypothesis, i.e. a sea current velocity of 25 cm/sec, independently of the direction chosen. With regard to the determination of depth "y" the Tables given below have been elaborated (after trials) on the hypothesis of a sea-bed slope of 10‰.

Hence, according to the Aubert Desirotte formula:

$$C_t = C_o \cdot \frac{1}{y} \cdot 10^{-Kt}$$

where:

- C_t is the coliform concentration (in our case faecal coliforms) at time t. Decrease, in respect of the initial concentration in the crude sewage, is due both to dilution and to bacterial disappearance phenomena; the Aubert-Desirotte formula, based on experimentation, simultaneously considers the two phenomena.

  It is not stated whether some coefficients refer to total or to faecal coliforms; as is known, the rate of disappearance of some coliforms, not faecal coliforms, is higher than that of faecal coliforms.

  In the order of approximation of these evaluations, such a distinction is probably unjustified.

  Yet, by making C_t = 10 faecal coliforms/100 ml, the goal, no error is made to the detriment of safety, since, if sea waters contain less than 10 total coliforms/100 ml, they will all the more surely contain fewer than 10 faecal coliforms/100 ml.

- C_o is the initial concentration of the microorganisms considered.

  In our case we have assumed:

  $C_o = 10^8$ faecal coliforms/100 ml.

- y is the depth of the discharge point, expressed in m.

  Such a term approximately takes into account the initial dilution ratio that may be achieved.

  This evaluation is very precautionary if discharge is by means of a diffuser; in this case, the expression $1/_y$ - rather than representing average values of the dilution ratio obtained - indicates the lowest value obtainable in particularly unfavourable current and stratification conditions.

- K is the coefficient that takes into account the rate of the bacterial disappearance phenomena and the speed of eddy diffusion. Such a coefficient is a function of the volume discharged, as shown in Figure 91.
- t is the drift time, i.e. the time elapsing from the very moment when the effluent leaves the discharge outlet to the moment when an observer moving with the current draws a hypothetical sample.

The original Aubert-Desirotte formula was as follows:

$$\log 10\, C_t = (\log_{10} C_o + a) \cdot \frac{\gamma \cdot \beta}{1,1} \cdot t$$

where:

C_t, C_o, t keep the meaning indicated above

$a = - \log y$

$\gamma =$ a coefficient depending on the volume discharged

$\beta =$ a coefficient of the bactericidal action of sea water, which in the Mediterranean sea is equal to 1.

The authors of the formula supply some analytical expressions to determine the coefficient γ as a function of the flow-rate.

Therefore, the expression shown here is a simple re-elaboration, in which the term

$$\frac{\gamma \cdot \beta}{1,1}$$

is directly expressed by coefficient K of Figure 91.

Almost all actual cases fall within the field of depth values of less than 50-60 m, the installation of pipelines and in particular of diffusers at greater depths being extremely expensive (in fact, immersion costs increase exponentially with depth when depths exceed 50 m).

Comparing the relative results obtained from the Aubert-Desirotte formula and from the Pomeroy formula a remarkable difference may be observed, although the order of magnitude is comparable. Even greater differences would be obtained if other hypotheses had been assumed in the application of the two formulas. The aim here, however, is to obtain a somehow reliable order of magnitude with regard to the spatial dimensions of mibrobiological pollution caused by a off-shore or on-shore discharges of a certain volume. Tables 43 to 46 and the graph of Figures 96 to 99 were prepared by superimposing the data supplied by the two above formulas. In other words, wherever higher values were obtained by applying one formula rather than the other, the most precautionary value was assumed as valid.

Therefore, the graphs of Figures 96 to 99 thus obtained are very precautionary and can in no way be used to evaluate precisely the extent of microbiological pollution and, even less so, to compare different discharge hypotheses. In particular, discharges on shore have been "penalized" by the "zero dilution" hypothesis, put forth for the sake of simplicity, but approximated only in extreme conditions. This having been said, it should be clear to the expert that the evaluations made, albeit with a tendency towards over-estimation, serve to determine the order of magnitude of the scale of the phenomenon. This could be the most reasonable justification of the practical validity of both tables and graphs.

Before passing to another aspect of marine pollution and trying to define its scale of action, it seems opportune to say something about the validity of the parameter adopted to define the action range of organic pollution.

Epidemiological surveys outside the Mediterranean area have shown that the relationship between water pollution and disease contracted whilst bathing is negligible, (87, 88, 89); consequently the only reasonable element for judging whether coastal waters are fit for bathing is based on aesthetic grounds.

It has been objected that such surveys were carried out where the incidence of contagious diseases transmittable by water is much lower than in a number of Mediterranean areas and consequently that the conclusions reached are not of general validity. However, this relationship has not been shown even in the Mediterranean area, masked as it perhaps is by other causes (injestion of contaminated vegetables, of infected molluscs, etc). It remains a fact that, on a rational basis, coliform concentration cannot be related to sanitary hazards for bathers. It has also been observed that the wide variability of colimetric data makes it very hard, if not impossible, to classify one sea area in terms of given colimetric limits.

In this respect, while admitting the particularly variable characteristics of the colimetric limit it may be objected that where there are no outlets of microbiologically polluted rivers which are at a given distance from sewer outlets which are above restricting levels. This is despite the inaccuracy of the analytical methods e.g. MPN, the colimetric values are in 90-95% of the cases considerably below restrictive levels, i.e. below 10 coli/100 ml. Notwithstanding this, in proximity to discharges, especially in the presence of coastal currents of direction variable from one sampling to the other, the colimetric values in any one point may vary by several orders of magnitude. In this sense, therefore, it seems possible to use the colimetric index also in order to define the range of action or the scale of a certain type of pollution.

Furthermore, the fact that no evident relationship exists between bathing hygiene and coliform concentration is probably not of essential importance where these evaluations are concerned. In fact, even in those countries where a colimetric standard for bathing has not been adopted, due to absence of relationship between cause and effect, this parameter has been adopted as a reference for the design of sea discharges, instead of other parameters - such as the degree of cleanness of a beach - which in practice are more subjective and uncertain. Finally, the problem of mollusc-culture should not be ignored.

It has been reasonably assumed that colimetry is to some extent an "aesthetic" parameter. To conclude, the above evaluations and considerations can probably be reconciled with the results obtained from epidemiological investigations, which bear witness to the significance of this index as regards hygiene, (102).

TABLE 39 Off-shore discharge. Pretreated or primary effluent. According to the Aubert-Desirotte formula. Sea bed slope, J = 10‰ (see Figure 92)

Inhabitants served n.	Range of action x (m)
5.000	800
10.000	1.050
50.000	1.900
100.000	2.770
500.000	5.900
1.000.000	7.680

TABLE 40 Off-shore discharge. Secondary effluent. According to the Aubert-Desirotte formula. Sea bed slope, J = 10‰ (see Figure 93)

Inhabitants served n.	Range of action x (m)
5.000	580
10.000	700
50.000	1.254
100.000	1.800
500.000	3.900
1.000.000	5.000

TABLE 41 Shore discharge. Raw sewage or pretreated or primary effluent (see Figure 94)

Inhabitants served n.	Range of Action x (m)
5.000	1.600
10.000	2.000
50.000	3.800
100.000	5.400
500.000	12.000
1.000.000	15.000

TABLE 42 Shore discharge. Secondary effluent (see Figure 95)

Inhabitants served n.	Range of action x (m)
5.000	1.300
10.000	1.700
50.000	3.200
100.000	4.500
500.000	10.000
1.000.000	13.000

TABLE 43 Off-shore discharge. Pretreated or primary effluent. Sea bed slope, J = 10‰. Recapitulation according to Pomeroy and Aubert-Desirotte Formulas (see Figure 96)

Inhabitants served n.	Range of action x (m)
5.000	800
10.000	1.050
50.000	1.900
100.000	2.770
500.000	5.900
1.000.000	10.000

TABLE 44 Off-shore discharge. Secondary effluent. Sea bed slope j = 10‰. Recapitulation according to the Pomeroy and Aubert-Desirotte Formulas (see Figure 97)

Inhabitants served n.	Range of action x (m)
5.000	500
10.000	700
50.000	1.200
100.000	1.800
500.000	3.900
1.000.000	6.600

TABLE 45 Shore discharge. Raw sewage or pretreated or primary effluent. Recapitulation according to Pomeroy and Aubert-Desirotte Formulas (see Figure 98) (*)

Inhabitants served n.	Range of action x (m)
5.000	1.600
10.000	2.000
50.000	3.800
100.000	5.400
500.000	12.000 (*)
1.000.000	20.000 (*)

(*) Values perhaps excessively precautionary.

TABLE 46 Shore discharge. Secondary effluent. Recapitulation according to Pomeroy and Aubert-Desirotte Formulas (see Figure 99) (*)

Inhabitants served n.	Range of action x (m)
5.000	1.300
10.000	1.400
50.000	3.200
100.000	4.500
500.000	10.000 (*)
1.000.000	17.000 (*)

(*) Values perhaps excessively precautionary

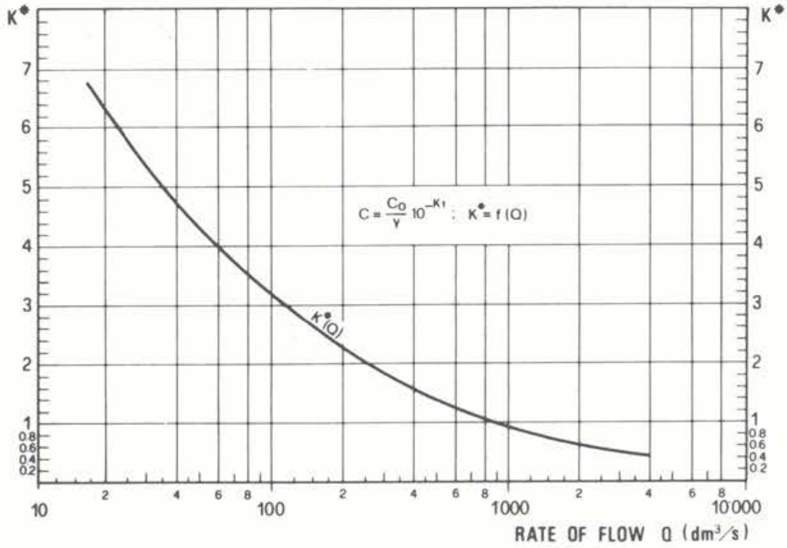

Figure 91 Coefficient K, appearing in Aubert-Desirotte formula, (100).

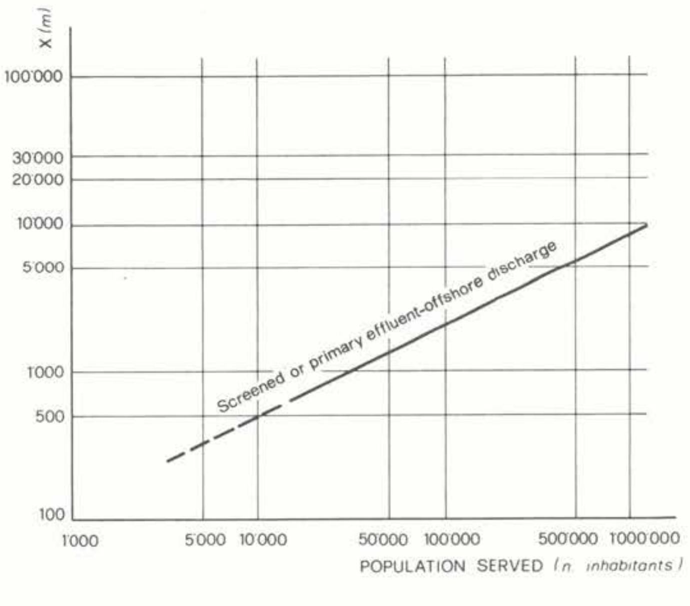

Figure 92 Discharge in open marine waters by submarine pipeline. Screened or primary effluent. Evaluation after Aubert-Desirotte formula. Spatial scale of bacterial pollution. Bottom slope, J = 10‰ (see Table 39).

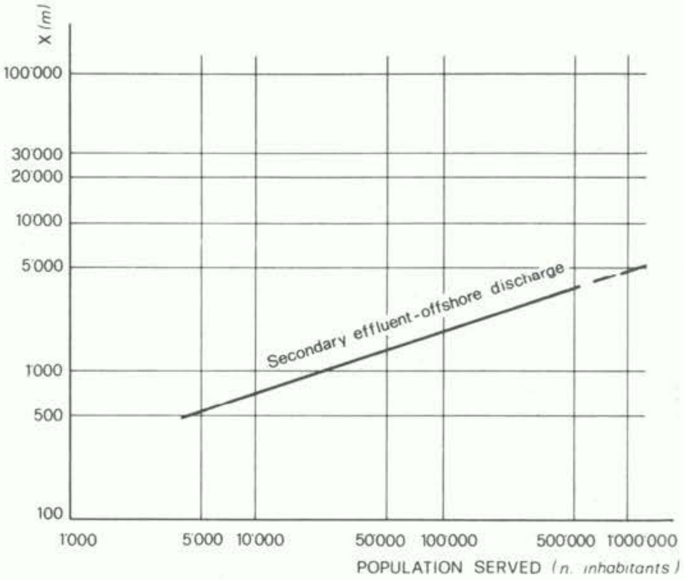

Figure 93 Discharge in open marine waters by submarine pipeline. Secondary effluent. Evaluation after Aubert-Desirotte formula. Spatial scale of bacterial pollution. Bottom slope, J = 10%o (see Table 40).

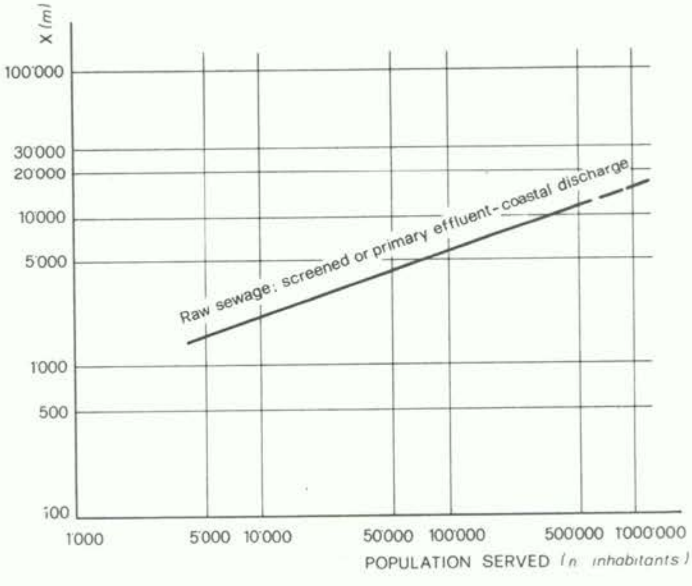

Figure 94 Surface discharge along the coast. Raw sewage; screened or primary effluent. Spatial scale of bacterial pollution (see Table 41).

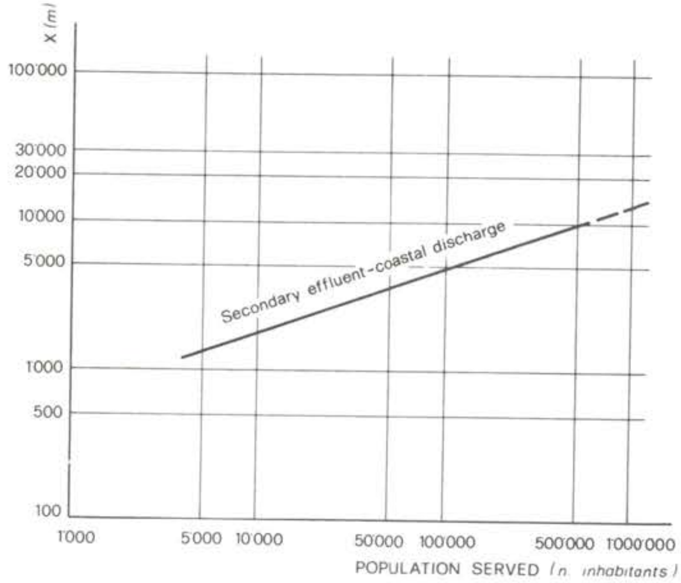

Figure 95 Surface discharge along the coast. Secondary effluent. Spatial scale of bacterial pollution (see Table 42).

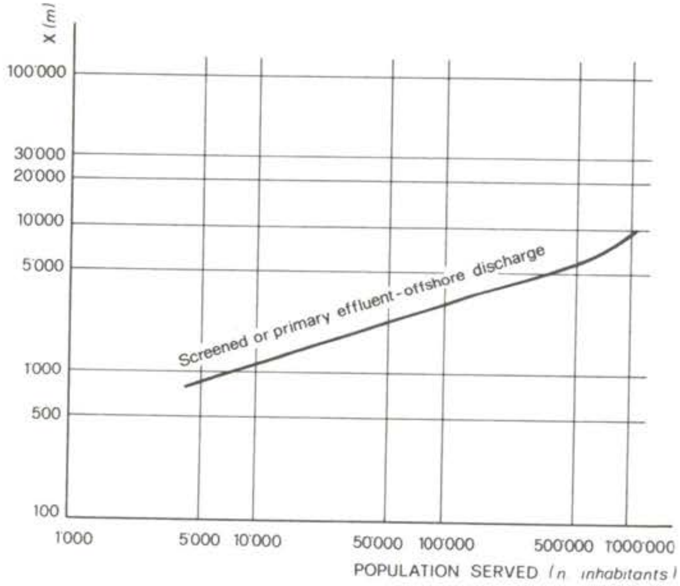

Figure 96 Discharge in open marine waters by submarine pipeline. Screened or primary effluent. Conclusive prudential evaluation of scale of action after Pomeroy and Aubert-Desirotte formulas (see Table 43)

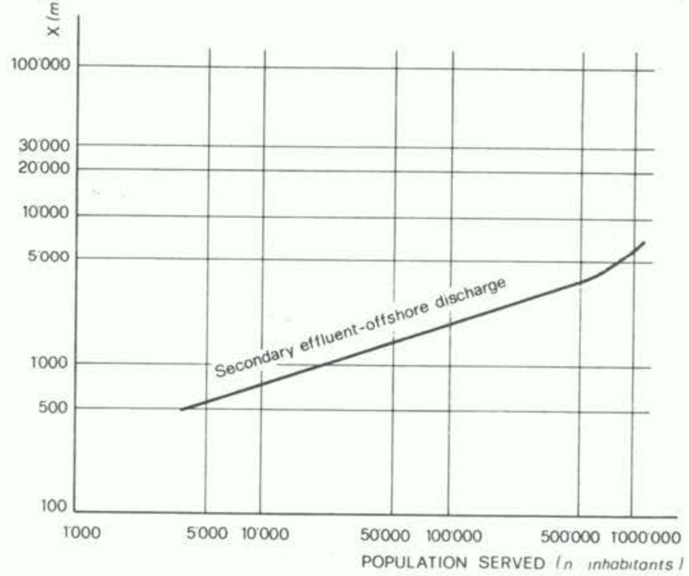

Figure 97 Discharge in open marine waters by submarine pipeline. Secondary effluent. Conclusive prudential evaluation of scale of action after Pomeroy and Aubert-Desirotte formulas (see Table 44).

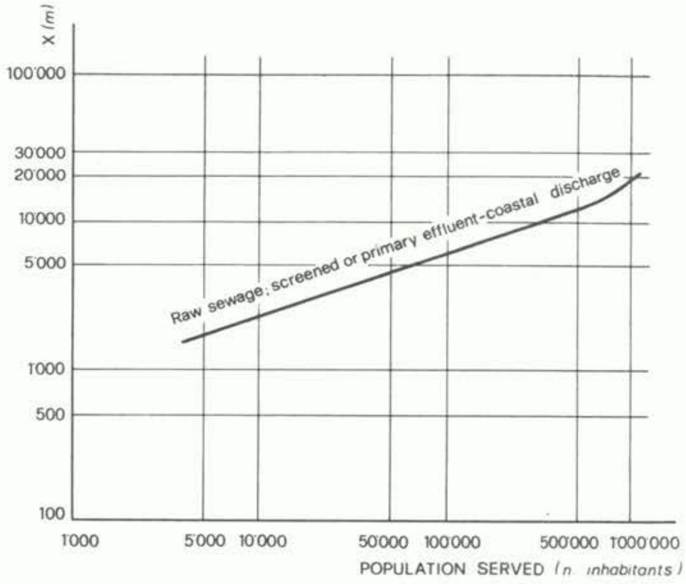

Figure 98 Surface discharge at the coast. Raw sewage; screened or primary effluent. Conclusive prudential evaluation of scale of action after Pomeroy and Aubert-Desirotte formulas (see Table 45).

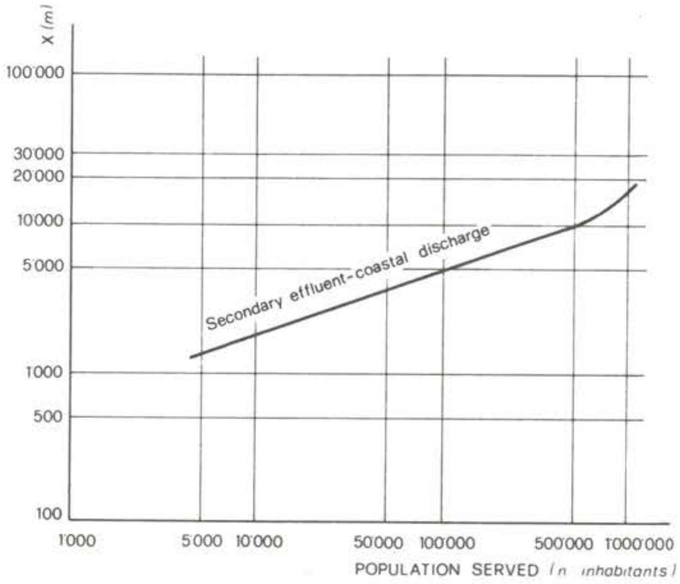

Figure 99 Surface discharge at the coast. Secondary effluent. Conclusive prudential evaluation of scale of action after Pomeroy and Aubert-Desirotte formulas (see Table 46).

APPENDIX II - MEASUREMENTS OF MARINE CURRENTS

(a) Measurement of flow, or the Euler method

Measurement by means of rotors. Measurement of water speed are made by measuring the speed of rotation of a propeller submerged at a certain depth. The principle is analogous to that of the hydrometric propeller traditionally used to measure the speed of river waters and discharges. In the case of measurements at sea, a fixed supporting platform is lacking and it is therefore necessary to devise ways of eliminating excessive oscillations or movements of the measuring device. The rotor is not always a propeller; sometimes it is a wheel with cups, or it may be constituted by a series of compartments (the Savonius rotor).

The first propeller-type current-gauges had large metal blades, and the number of revolutions was measured mechanically by means of a system of gears.

The device was lowered to a certain depth and the counting of revolutions began when a weight was sent down to it; after a suitable period from a few minutes to some tens of minutes a second weight stopped the counting device and, furthermore, caused a metallic ball to fall into a container provided with a series of grooves which would receive and hold it. This container could move in relation to the body of the device and rotated round its central axis like a compass, so as to maintain in normal conditions a certain orientation in relation to North. From the position of the ball it was thus possible to deduce the direction of the marine current at the depth considered.

Modern devices have a propeller of plastic material, of specific gravity approximately equal to that of sea water, so as to reduce to a considerable extent the friction on the axis of rotation; the number of revolutions is counted by electrical or electronic means and, likewise. The evaluation of the orientation of the device in relation to North was carried out with the help of a compass incorporated in the device. The current-meter is generally anchored to the sea bottom and supported by a submerged body so as to avoid the effects of wave movements; an electrical cable connects the instruments to a boat anchored nearby and transmits instant by instant the indications concerning the speed and direction of the marine current at that particular depth.

There are also recording devices which can be left, even at considerable depths, for a certain period of time; these are frequently used for large-scale oceanographic surveys. At regular intervals the speed and direction of the current are recorded on magnetic tape or in other ways. Some models make use of a camera which, at regular intervals of time, photographs the instrument's dial-plate, on which the speed, direction of current and the time are indicated.

These recording instruments can be released automatically from their anchorages by means of acoustic or electromagnetic signals, to be recovered on rising to the surface. The loss of instruments is not infrequent.

The sensitivity of these instruments is such that they can measure current speeds of over 5 cm/sec (in some cases the sensitivity reaches 2-3 cm/sec).

Thus, nearly the whole range of speeds of interest for purposes of forecasting dilution and transport phenomena is covered; not covered, however, is the range of speeds below 3-4 cm/sec, which is of considerable importance because critical conditions of initial dilution occur in concomitance with low current speeds, protracted for a number of hours, above all in the presence of high density gradients.

Though rotors are the system generally used for current-speed measurement in a particular point there also exist a variety of instruments of operating on different principles which are of interest on account of their simplicity of construction, lower cost, or for other reasons.

One type of these is based on the hydrodynamic force exerted by the current on a submerged body which may have the form of a plate, a sphere or a cylinder attached to the end of a shaft in the manner of a pendulum. The more intense the current at the depth in question, the greater the angle assumed by the pendulum, which is sometimes held back by a spring. The inclination is registered either mechanically or by means of transducers, which permit a direct reading of the speed from the boat.

Pilot Tube. Another instrument is the Pilot tube; the range of measurement is rather limited in that, using this system, speeds of a few cm/sec are not detectable.

It is known that sea water is an electrical conductor and that the earth has a magnetic field. A movement of masses of water in relation to the earth's magnetic field thus produces a difference of potential.

Geo-magnetic current-meters. This is the basic principle of the geo-magnetic current-meters, which measure, in effect, the difference of potential between two electrodes. The principal interest of this technique of measurement lies in the fact that it makes it possible to survey large-scale movements of water masses; however, since the technique is based on the vertical component of the earth's magnetic field, it cannot be used in the vicinity of the magnetic equator (this, obviously, is not a problem where the Mediterranean is concerned). The measurements are influenced by magnetic storms and also be variations of the magnetic field, which can easily give rise to errors of the order of 5 cm/sec.

The electro-magnetic current-meters function on a principle analogous to the one described above, with the difference that the electro-magnetic field is produced by the apparatus itself. These instruments are commonly used today to measure delivery in closed conduits and, in particular, in treatment plants. A typical disadvantage of these instruments consists of the impossibility of using the classic compass for indication of current direction in depth measurements. Instruments of this type are also used to measure ship speeds

Ultrasonic speed meters. These instruments consist of a generator of ultrasonic waves, a receiver, and an apparatus which measures the speed of transmission of these waves; if the speed of the ultrasonic wave in the water is v and the component of the speed of the water in the direction of transmission of the ultrasonic wave is V, the time t needed to cover the distance D in the direction of the speed v is given by:

$$t = \frac{D}{v+V}$$

The speed of the ultrasonic wave in the water varies according to the density of the water; the problems created by this variability can be overcome by measuring not so much the time taken by the wave to complete a certain journey as the difference between the times taken to complete equal journeys in opposite directions.

Thus:

$$t_1 = t_2 = \frac{D}{v+V} - \frac{D}{v+V}$$

$$V = \frac{D}{2} \left(\frac{1}{t_1} - \frac{1}{t_2} \right)$$

where:

- t_1 = the time needed to complete the journey in the direction of the marine current;
- t_2 = the time taken to complete the journey in the opposite direction.

Hot-wire anemometers. The use of hot-wire anemometers for oceanographic purposes still has considerable disadvantages owing to the speed with which the sensor gets dirty.

These anemometers are essentially of two types:

- constant electric current - constant temperature

Both systems require rather complex apparatus to ensure the constancy of the parameters mentioned. As has been pointed out, neither of the systems is yet suitable for continuous and prolonged measurements.

A very simple device which has been used in the past, consists of transparent spheres filled with a gelatinous substance or wax solidifying at the temperature of sea water. Inside the sphere a magnetized disc is placed. When a certain number of these spheres are attached by wires to a supporting cable (anchored to the bottom and supported on the surface by a float) the discs take up a position, in relation to the transparent container, which depends both on the direction of the current and on its intensity.

The spheres are so constructed that they have a small positive weight; thus in the absence of current, they hang downwards, while, in the presence of very strong currents, they assume a horizontal position.

The measurement of surface currents is of particular importance in concomitance with surveys of the qualitative characteristics of coastal marine waters in zones polluted by surface discharges or discharges that come to involve the surface layers; it is generally recommended that, in the course of these surveys, measurements should be made not only of some fairly simple meteorological data (air and water temperature, wind speed, cloud coverage, state of sea) but also of the speed of the marine current. Generally, this last parameter is not measured, owing to the not inconsiderable difficulties which, as has been said, are involved. The simple technique described here may prove useful for this purpose (Figure 100).

A few minutes before the measurement of the current, a dead weight of about 1-2 kg is lowered to the bottom; attached to it is a surface float; to the surface float a drifter is attached by means of a thread of known length (generally from 4 to 10 m); the drifter may consist simply of a wooden pole provided with metal vanes to

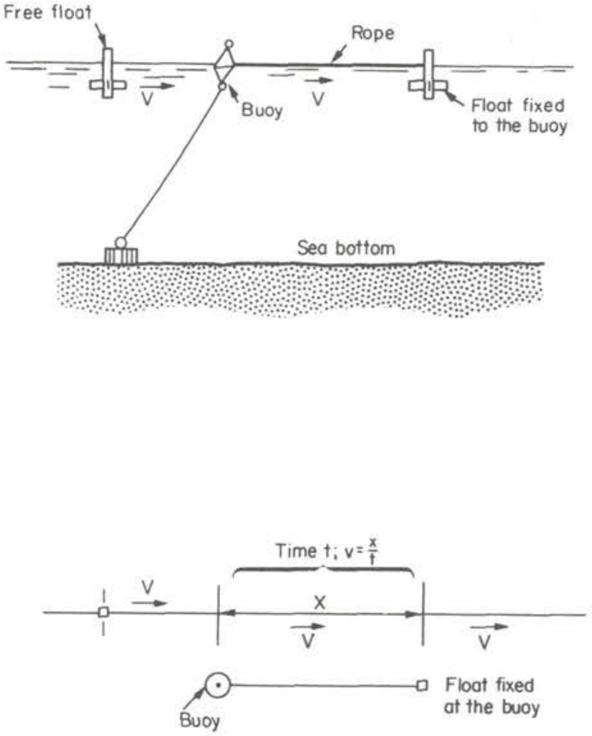

Figure 100 A simple way of estimating surface current velocity.

increase its hydrodynamic resistence. After a few minutes the float and the drifter are aligned in the direction of the marine current and at a distance from each other equal to the length of the thread that joins them. By placing in the water upstream of the main float a drifter which is identical or similar to the other, it is possible to measure, by means of a stop-watch, the time taken for the free drifter to cover the distance between the float and the fixed drifter.

(b) Measurement of paths, or the Lagrange method

These measurements are essentially carried out by means of three systems:

- current drogues or parachute drogues: their paths are followed and noted;
- surface drift cards and bed drifters, introduced into the sea simultaneously in a certain number and at a certain point.

  The drift cards and bed drifters are then located by means of systematic inspections of the coast;
- measurements by means of radioactive or fluorescent tracers.

Current drogues. Enough has already been said about the structure of the current drogues. It can be added that these drogues may consist of metallic vanes, often foldable so as to facilitate transport. They may also consist of a metal framework across which lengths of cloth are stretched to serve as vanes. The blades may be 3 or 4 in number; other current drogues have a closed form (square section).

If they are equipped with blinking lights, the position of the current crosses can be detected even at night. With the use of the radar screens (Figure 101), lagrangian surveys can be carried out continuously by day and by night, even in unfavourable meteorological-marine conditions.

When radar is not used, the position of the drogues can be established in various ways. The simplest system involves the use of a surveying compass which in this case is particularly useful since the coastal zone concerned usually does not extend more than a few km. from the shore. Moreover, in the Mediterranean the conditions of transparency of the atmosphere are generally very good.

In any case, it is necessary, at the beginning of measurement, to place a buoy at the launching point of the drogues; in this way the speed of the current and the movements of the drogues can be recorded with much greater accuracy and reliability.

When the waters are not deep, it is possible in practice to make use of several fixed buoys, which constitute elements of reference supplementary to the land points. Those buoys can be left in place if there is no danger of loss or damage; otherwise they are installed at the beginning of each survey and then removed. The position of the launching point can be identified by means of a surveying compass and, if it is possible, in relation to a number of easily definable alignments.

Fairly precise measurements can be made up to a distance of 4 or 5 km in conditions of good visibility (or even at greater distances when high observation points on the land are available) by means of the classic topographical instruments; in this case it is necessary that the sea team be in radio contact with the surveying stations on land.

Very precise measurements, especially with regard to alignments, can be made by means of a laser; the use of this technique is justified above all in relation to certain operations concerning the laying of underwater pipelines (see bottom pull). There exist instruments, which in fact are fairly expensive (Decca, Loran), that detect the position of the vessel moment by moment and automatically mark it on a map.

These types of equipment find their justification in surveys carried out at an appreciable distance from the shore, especially when, in concomitance with measurements with tracers, continuous surveys are carried out along alternate paths that cover the surface of the patch or plume marked by tracers in movement.

For investigation of the paths of deep currents, it is preferred to use, instead of drifters consisting of poles, parachute drogues made of canvas or dacron, which offer a great resistence to the current. The use and recovery of such devices is generally more complicated than in the case of the other types considered above.

Drift cards. Placing a certain number of surface floaters in the sea in a particular position can provide interesting information concerning the trends of surface currents, provided it is possible to identify the locality and, if possible, also the time, of their arrival at the shore.

These floating bodies are provided with identification labels which indicate the batch (defined by the launching point and the time) to which the recovered card belongs. They also carry indications as to the organization or institute to whom the floating bodies should be transmitted by persons happening to find them. In certain cases, in order to encourage finders to consign the drift cards, a small reward is offered on their delivery. The reliability of the information relating to a particular launching of drift cards depends on the proportion of drift cards recovered.

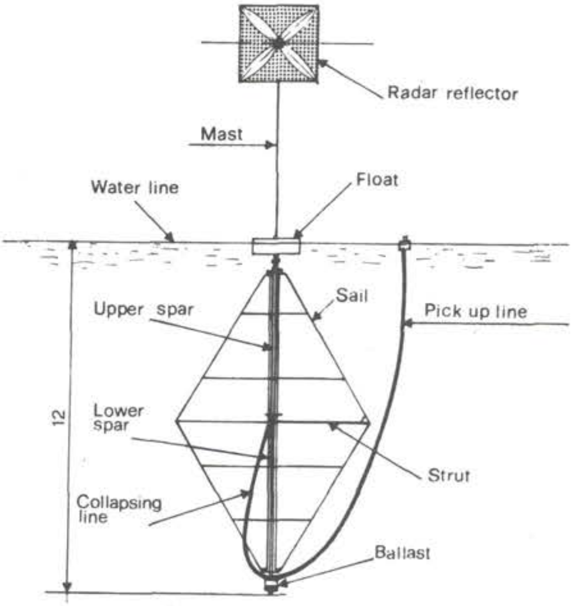

Figure 101 Current drogue with radar reflector, (147).

The use of this technique has been criticized on the grounds that the drift cards are considerably affected by the action of the wind and of the movement of the top surface layer of water; it is to be noted, however that the movement of these layers is of particular interest in the hypothesis of the surfacing of discharges, in that it represents particularly unfavourable situations, to be taken into account for precautionary reasons, with regard to the forecasting of coastal pollution. It is in fact to be expected that the minimum times of return to shore associated with off-shore discharges of contaminants are correlative with the action of strong shoreward winds on the surface layers. Finally, on the surface of the sea, films of floating substances may form which have not been removed, as they should have been, in the treatment on land.

Figure 102 shows a form that could be used for registration of data (time and place) relating to the finding of drift cards or sea bed drifters on the shore.

Naturally, this type of survey is facilitated by the presence of easily transitable sandy shores; rocky coasts constitute an almost insuperable problem because both the drift cards and the bed drifters end up hidden among the rocks.

An interesting prerogative of drift cards is that they are more suitable for indicating the movement of a mass of water than single drifters. It is in fact known that a number of drifters launched at the same point will tend, in any case (in consequence of the turbulence present in a greater or lesser degree in the marine environment) to drift apart as, with the passage of time, they move away from the launching point. The simultaneous launching of a considerable number of drift cards (of the order of a few hundreds) makes it possible to ascertain in a more appropriate manner the movements of masses of surface waters or, rather, the positions in which these masses touch the shore. It is not in fact possible to define the precise path followed by the drift cards during their journeys. The greater the turbulence in

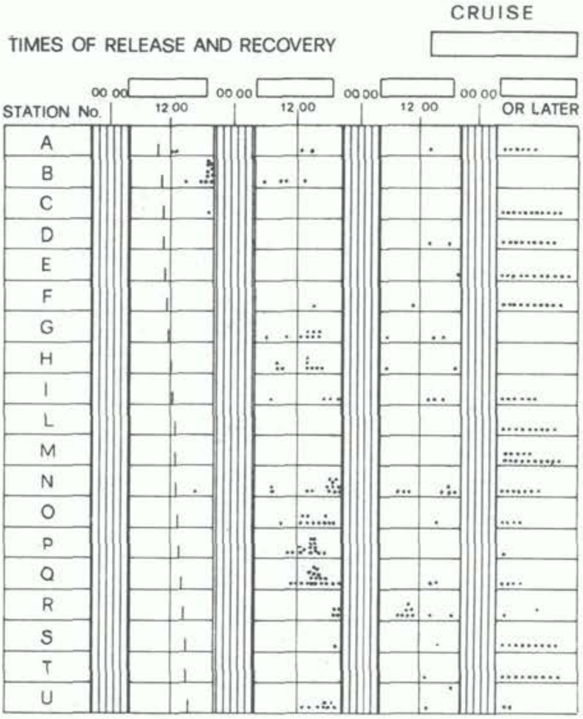

Figure 102 Drift card release and recovery form.

the marine environment, the greater will be the dispersion of the points of arrival on the shore.

Figure 103 presents some simple graphic elaborations which permit the deduction of coefficients of turbulent diffusion as a function of the degree of dispersion of the various cards found.

Sea bed drifters and drift cards are available on the market and this considerably facilitates their widespread use.

Figure 104 shows examples of sea bed drifters and drift cards.

Use of tracers. The Lagrangian technique of measurement includes the use of radioactive or fluorescent tracers to mark particular masses of sea water in a continuous or discontinuous manner.

The most frequently used method consists in the formation of patches which are followed, as they move off and disperse, by a vessel equipped for the continuous recording of the concentration of the tracers (and, thus, the dimensions of the patch). In this way information is obtained concerning the movement (transport) of the masses of water and the degree of eddy diffusion to which a (future) discharge will probably be subject. The dimensions of the process of eddy diffusion can be evaluated directly or indirectly.

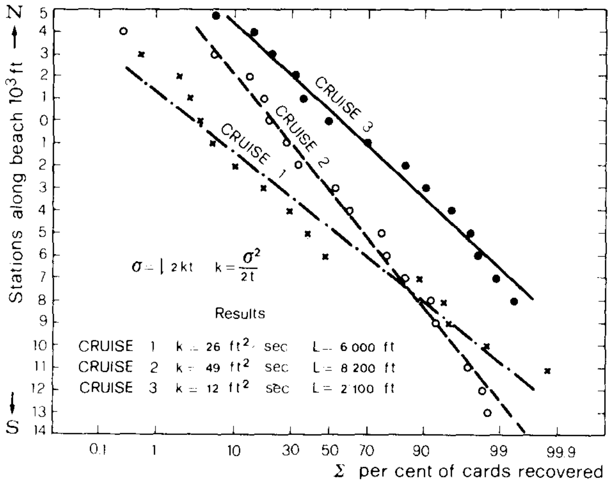

Figure 103 Eddy diffusion analysis by use of drift cards.

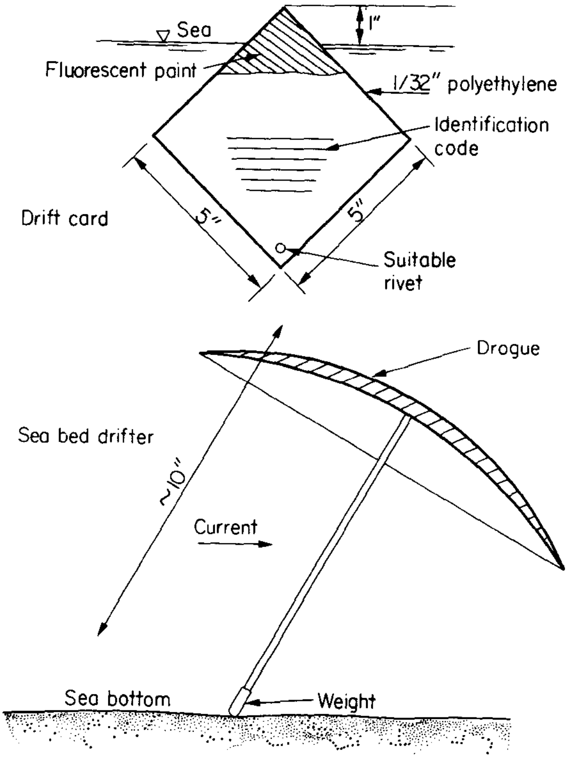

Figure 104 Drift card and sea bed drifters.

The so-called direct method consists of the "construction" by integration of the effect of a continuous discharge by superimposing a number of times, in an appropriately staggered manner, the diagram of the concentrations caused by a continuous discharge and observed inside the patches. A continuous discharge can, in fact be considered as if it were the result of an uninterrupted series of discontinuous discharges. This topic will be treated at greater length later.

The so-called indirect method consists in comparing the development in time of a number of parameters characteristic of the patch (dimensions, concentration at centre, etc.) with theoretical models that describe the development in time of these parameters as a function of determined coefficients of eddy diffusion. The comparison serves to identify the value of the coefficients that enables the theoretical model to conform most closely to the exerpimental data.

Continuous immission. An interesting use of coloured or fluorescent tracers is their "continuous" introduction to simulate, generally with a far smaller volume, a future discharge; the examination of the plume and, in particular, of the speed with which it spreads. This method also enables certain coefficients of eddy diffusion to be determined. Aerial photography provides an immediate vision of the trend of the current that traverses the point of introduction of the tracer during the period of the test.

A technique which is fairly expensive but of efficacious visual effect consists of dropping from an aeroplane or helicopter a number of buoys equipped with cable and anchor and a simple device for the release of coloured tracers (bags containing rapidly soluble solid powders of the type used to facilitate the location of shipwrecked persons). These devices are dropped in pre-established zones and the introduction of the tracers takes place almost simultaneously at all points; subsequent aerial photographs reveal the trend of the currents throughout the zone. It should be pointed out that normally (and also for economic reasons) it is not possible to use this method of observation at distances greater than 1 km from the introduction point of the tracer.

Tracer tests and current-gauge surveys. In preparing a programme of preliminary surveys, it should be borne in mind that, in view of the great variability of inshore currents, reliable findings necessitate that surveys are repeated many times and extending over a period of a number of seasons. In consequence, accurate but episodic tracer surveys carried out only on a small number of occasions and, therefore, in only some of the many current conditions, will not provide an adequate knowledge of the situation; it is necessary in addition, to obtain, possibly by simpler methods, reliable information concerning the circulation in the zone and, in particular, concerning the frequency and speed of the marine currents running towards the shore in a variety of cases sufficiently representative of the situation in statistical terms.

APPENDIX III - SEA WATER DENSITY EVALUATION

(a) Determination of density

The density is determined and deduced by means of the temperature and salinity measurements.

The more general formula, which takes the pressure into account, is given in the footnote(*) but as has been said, it has no practical relevance to the problem in question; even oceanographers rarely make use of it owing to its complexity; they resort instead to hydrographic tables which give the density as a function of temperature, salinity and pressure.

For reasons of practicality the density is expressed in terms of reduced density:

$$\sigma t = (\rho_t - 1) \cdot 1000$$

The symbol ρ_o refers to the density at 0°.

σ_o reduced density at 0° can be expressed as a function of the content of chlorine or, directly, as a function of the salinity:

$$\sigma_o = -0{,}069 + 1{,}4708\ Cl - 0{,}001570\ Cl^2 + 0{,}0000398\ Cl^3$$

$$\sigma_o = -0{,}093 + 0{,}8149\ S - 0{,}000482\ S^2 + 0{,}0000068\ S^3$$

The relationship between chlorine content and salinity is in fact the following:

$$S = 0{,}030 + 1{,}8050\ Cl$$

The existence of these relationships is made possible by the fact that in sea water the various dissolved substances are more or less diluted, but their ratios are substantially constant.

(*) Ekman's formula (The pressure p is measured in decibars; the temperature T in °C)

$$\frac{1}{1 + 10^{-3}\ \sigma_{S.T.p}} = \frac{1}{1 + 10^{-3}\ \sigma_{S.T.0}} - \frac{p}{1 + 10^{-3}\ \sigma_{S.T.0}}\ 10^{-9} \Big\{ \frac{4886}{1 + 0{,}0000183p} - \left[227 + 28{,}33\ T - 0{,}551\ T^2 + 0{,}004\ T^3\right] + p\ 10^{-4} \left[105{,}5 + 9{,}50\ T - 0{,}158\ T^2\right] - 1{,}5\ p^2\ T \cdot 10^{-8} - \frac{\sigma_o - 28}{10} \left[147{,}3 - 2{,}72\ T + 0{,}04\ T^2 - p\ 10^{-4}\ (32{,}4 - 0{,}87\ T + 0{,}002\ T^2)\right] + \left(\frac{\sigma_o - 28}{10}\right)^2 \left[4{,}5 + 0.1\ T - p\ 10^{-4}\ (1.8 - 0{,}006\ T)\right] \Big\}$$

The definition of salinity was provided by an international mission (Forch, Knudsen and Sorenson, 1902): salinity corresponds to the total quantity of solid substances in grams contained in 1 kg of sea water when all the carbonate has been converted into oxygen, the bromine and iodine replaced by chlorine, and all organic matter completely oxidized.

The reduced density (σ_t) of sea water at a certain temperature can be obtained in relation to the reduced density at the temperature of 0° (σ_o) by means of the following formula:

$$\sigma_t = \sigma_o - D$$

where:

$$D = - \Sigma_T - 0{,}1324 + (\sigma_o + 0{,}1324) \left[A_T - B_T\ (\sigma_o - 0{,}1324)\right]$$

and

A_T, B_T, Σ_T are expressed by:

$$A_T = 10^{-3}T\ (4{,}7867 - 0{,}098185\ T + 0{,}0010843\ T^2)$$

$$B_T = 10^{-6}T\ (18{,}030 - 0{,}8164\ T + 0{,}01667\ T^2)$$

$$\Sigma_T = -\left[\frac{(T - 3^{\circ}{,}98)^2}{503{,}570} \cdot \frac{T + 283^{\circ}}{T+67^{\circ}26}\right]$$

The application of this formula is somewhat laborious and it is therefore convenient to carry it out by means of simple computer calculation programmes.

An approximate evaluation of the density as a function of the salinity and the temperature can be made with the help of the graphs shown in Figure 105.

Certain instruments allow the salinity of the water to be ascertained by means of the direct measurement of its conductivity and of the temperature.

The formula correlating conductivity and temperature is the following:

$$C = \left(2{,}1923 + 0{,}12842 \frac{T^{1{,}032}}{1 + T^{0{,}032}} \cdot e^{0{,}029\ T}\right) \cdot \frac{S}{1 + S^{0{,}1243}} \cdot e^{-0{,}000978 . S} \cdot e^{-0{,}0000165\ (S-35)(T-20)}$$

where: C = conductivity (mmho/cm)

T = temperature (°C)

S = salinity in parts per thousand 9ppt)

The calculation can be avoided by making use of Table 47 or the graph shown in Figure 106.

For the sake of completeness, we also give, in Figure 107, the graphic relationship between sound velocity, temperature and salinity. The speed of sound is in fact correlated to the density of the water and this is important in cases of accurate bathymetric measurements; such measurements must be accurate (with precisions less than ± 1%) in certain cases where a contract requires the verification of the depth

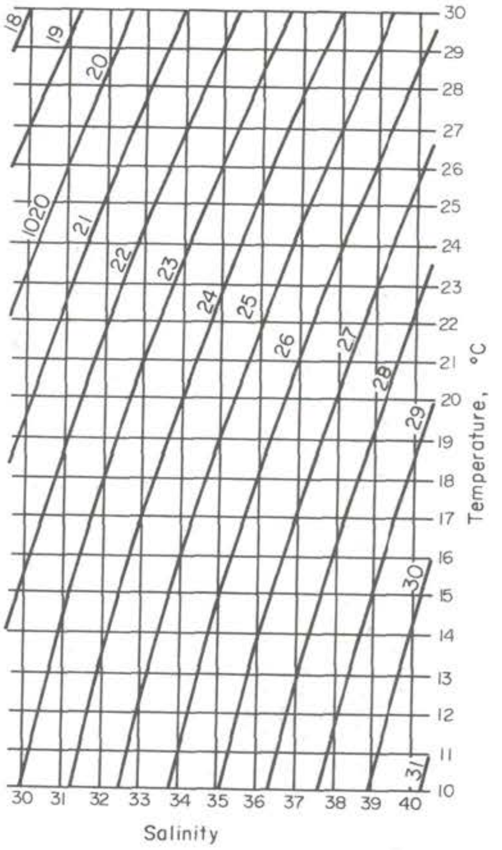

Figure 105 Evaluation of density (Kg/m^3) of sea water as function of salinity and temperature.

of a trench excavation for an underwater pipeline.

(b) Precision required in determination of density

In general, the precision required of calculations of density does not exceed 0.1 kg/m^3. This precision can be achieved when the temperature measurements are made with an accuracy of 1/10 - 2/10 of a degree and the salinity measurements with an accuracy of 0.1%o. With regard to conductivity measurements, the error may not exceed 0.1 mmho/cm.

As has been said, these degrees of precision are much smaller than those commonly required in the case of oceanographic surveys; they can be achieved by means of apparatus of relatively modest cost (a few thousands of dollars) requiring relatively simple maintenance.

Laboratory analyses of salinity and temperature measurements by means of reversion thermometer permit considerably greater precision and are recommended when the measurements are few in number or serve to verify the reliability of a series of

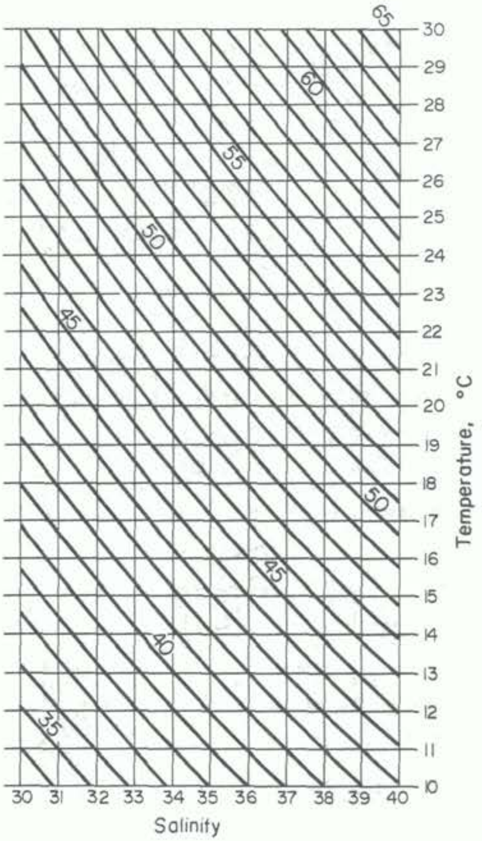

Figure 106 Evaluation of conductivity (mmho/cm) as function of salinity and temperature.

data obtained by means of a sensor.

However, there are available on the market numerous pieces of apparatus (for the measurement of salinity in estuaries or in effluents) which, although originally conceived for other uses and characterized by a notably poor accuracy, are sometimes taken into consideration for purposes of oceanographic surveys. Such apparatus should not, therefore, be used for the purposes considered here. Moreover, some salinity-meters used in other seas do not cover values of salinity above 38.5% and of temperature above 20°C, values which are common in the Mediterranean.

(c) Measurement of salinity

Salinity can be measured in the laboratory or on site.

Laboratory measurements of salinity. This can be done by means of the determination of the chlorides by means of the Volhard method or, better, by the Mohr method. On the basis of the chloride content, the salinity can be calculated by means of the formulae:

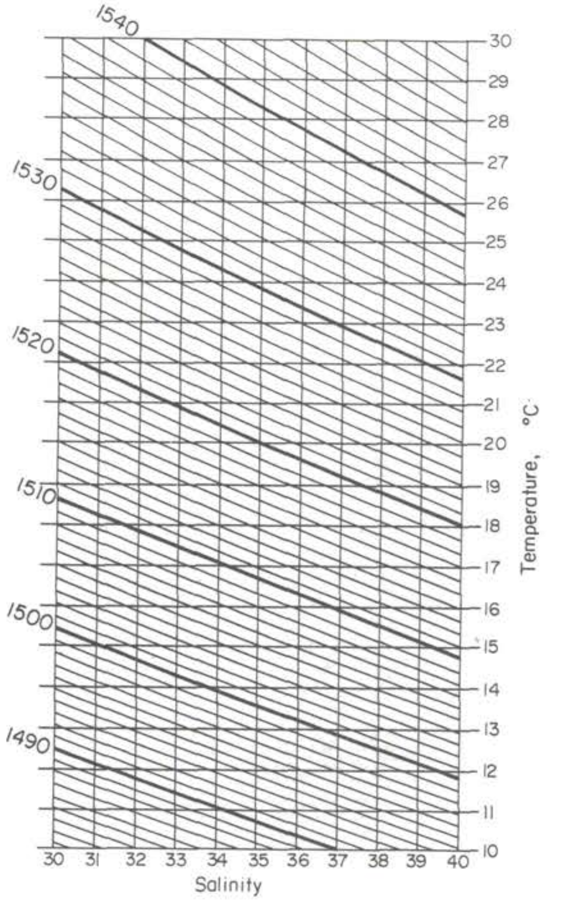

Figure 107 Evaluation of the sound velocity (m/s) as function of salinity and temperature.

$$S = 0.030 + 1.8050 \; Cl$$

Use can be made of equipment which measures the conductivity of the water and which are similar to those used for on site measurements.

Measurement of salinity on site is done by means of measurement of the temperature and of the conductivity; from the conductivity and the temperature, as already explained, the salinity is calculated. The instrument simply provides the measurement of conductivity, from which, by means of appropriate graphs, or tables, or by applying the formula mentioned above, it is possible to arrive at the salinity value. There are other instruments available which permit, in a more or less immediate manner, the direct measurement of salinity.

The instruments for measurement on site vary considerably in precision and may permit the measurement only of the conductivity and temperature or of other values as well; in fact some are equipped with probes or sensors suitable for the simultaneous measurement of other qualitative characteristics of the marine waters (the

TABLE 47 CONDUCTIVITY (mmho/cm) VS TEMPERATURE (°C) AND SALINITY (ppt)

TEMP	SALINITY										
	30.0	31.0	32.0	33.0	34.0	35.0	36.0	37.0	38.0	39.0	40.0
0.0	25.24	26.00	26.76	27.51	28.26	29.01	29.76	30.50	31.24	31.98	32.72
1.0	25.98	26.77	27.55	28.32	29.09	29.87	30.63	31.40	32.16	32.92	33.68
2.0	26.75	27.55	28.35	29.15	29.95	30.74	31.53	32.32	33.10	33.88	34.66
3.0	27.52	28.35	29.18	30.00	30.81	31.63	32.44	33.25	34.06	34.86	35.66
4.0	28.31	29.16	30.01	30.85	31.69	32.53	33.36	34.19	35.02	35.85	36.67
5.0	29.10	29.97	30.84	31.71	32.57	33.43	34.29	35.15	36.00	36.84	37.69
6.0	29.90	30.80	31.69	32.58	33.47	34.35	35.23	36.11	36.98	37.85	38.72
7.0	30.70	31.62	32.54	33.46	34.37	35.27	36.17	37.07	37.97	38.86	39.75
8.0	31.52	32.46	33.40	34.34	35.27	36.20	37.13	38.05	38.97	39.88	40.80
9.0	32.33	33.30	34.27	35.23	36.19	37.14	38.09	39.03	39.98	40.91	41.85
10.0	33.16	34.15	35.14	36.13	37.11	38.08	39.06	40.02	40.99	41.95	42.91
11.0	33.99	35.01	36.02	37.03	38.03	39.03	40.03	41.02	42.01	43.00	43.98
12.0	34.83	35.87	36.90	37.94	38.97	39.99	41.01	42.03	43.04	44.05	45.05
13.0	35.67	36.73	37.80	38.85	39.91	40.95	42.00	43.04	44.07	45.11	46.13
14.0	36.52	37.61	38.69	39.78	40.85	41.93	42.99	44.06	45.12	46.17	47.22
15.0	37.37	38.49	39.60	40.70	41.81	42.90	43.99	45.08	46.17	47.25	48.32
16.0	38.23	39.37	40.51	41.64	42.76	43.89	45.00	46.11	47.22	48.33	49.42
17.0	39.10	40.26	41.42	42.54	43.73	44.88	46.02	47.15	48.29	49.41	50.53
18.0	39.97	41.16	42.35	43.53	44.70	45.87	47.04	48.20	49.36	50.51	51.65
19.0	40.84	42.06	43.27	44.48	45.68	46.88	48.07	49.25	50.43	51.61	52.78
20.0	41.73	42.97	44.21	45.44	46.66	47.89	49.10	50.31	51.52	52.72	53.91
21.0	42.62	43.89	45.15	46.40	47.66	48.90	50.14	51.38	52.61	53.83	55.05
22.0	43.51	44.81	46.09	47.38	48.65	49.92	51.19	52.45	53.70	54.95	56.20
23.0	44.41	45.73	47.05	48.35	49.66	50.95	52.24	53.53	54.81	56.08	57.35
24.0	45.32	46.66	48.00	49.34	50.67	51.99	53.30	54.61	55.92	57.22	58.51
25.0	46.23	47.60	48.97	50.33	51.68	53.03	54.37	55.71	57.04	58.36	59.68
26.0	47.15	48.55	49.94	51.33	52.70	54.08	55.44	56.81	58.16	59.51	60.85
27.0	48.07	49.50	50.92	52.33	53.73	55.13	56.52	57.91	59.29	60.66	62.03
28.0	49.00	50.45	51.90	53.34	54.77	56.19	57.61	59.02	60.43	61.83	63.22
29.0	49.93	51.41	52.89	54.35	55.81	57.26	58.71	60.14	61.57	63.00	64.42
30.0	50.88	52.38	53.88	55.37	56.86	58.33	59.81	61.27	62.73	64.18	65.62
31.0	51.82	53.36	54.88	56.40	57.91	59.42	60.91	62.40	63.88	65.36	66.83
32.0	52.77	54.34	55.89	57.43	58.97	60.50	62.03	63.54	65.05	66.55	68.05
33.0	53.73	55.32	56.90	58.47	60.04	61.60	63.15	64.69	66.22	67.75	69.27
34.0	54.70	56.31	57.92	59.52	61.11	62.70	64.27	65.84	67.40	68.96	70.50
35.0	55.67	57.31	58.95	60.57	62.19	63.80	65.41	67.00	68.59	70.17	71.74
36.0	56.64	58.31	59.98	61.63	63.28	64.92	66.55	68.17	69.78	71.39	72.99
37.0	57.62	59.32	61.01	62.70	64.37	66.04	67.69	69.34	70.98	72.61	74.24
38.0	58.61	60.34	62.06	63.77	65.47	67.16	68.85	70.52	72.19	73.85	75.50
39.0	59.61	61.36	63.11	64.85	66.57	68.29	70.01	71.71	73.40	75.09	76.77

depth, the dissolved oxygen content, turbidity, etc.). The cost of instruments for on site measurement varies from a few thousand dollars to a few tens of thousands of dollars for the more accurate models; these last are equipped also with apparatus for the recording on tape (or the direct printing) of the data. As has been said, the parameter that is measured directly is the conductivity.

This measurement is carried out by means of two main systems: measurement of electrolytic conductivity and induction salinity-meters.

Measurement of electrolytic conductivity. This is carried out by means of a cell with annular electrodes. These electrodes have to be cleaned frequently; in general, this type of equipment is more difficult to maintain and is more open to error than the induction salinity-meters.

Induction salinometers. This technique consists fundamentally of a conductivity cell without electrodes, which is sealed off by epoxy resins so as to eliminate problems of maintenance. The measurement is based on the direct proportionality existing between the magnitude of an electric induction current and the electrical conductivity of the medium in which it is induced. Instruments of this type are recommendable for their strength and because the sensor requires practically no maintenance. Generally, these devices include an automatic calculation circuit which provides direct indication of the salinity.

Other aspects. It is recommended that a number of samples (volume 100-300 cc) for laboratory analysis should be taken at the beginning and the end of on site measurements, in order to verify the constancy of the calibration and the reliability of the measurements. It is also recommended that the accuracy of the temperature measurements be verified by means of a reversion thermometer for oceanographic use, which, when the appropriate corrections have been made with regard to room temperature at the moment of calibration, permit a precision of the order of one-hundredth of a degree.

There is one further thing which should be said here, though it relates to the whole body of preliminary surveys carried out to ascertain an environmental situation and to plan the most suitable remedies. Perhaps, following the example of the large-scale oceanographic surveys in the open sea, carried out with the use of large vessels (actual oceanographic ships), it might be considered useful to base the surveys considered here on the use of vessels of this type. Such a choice, however, should not be made without reservation. The use of large vessels, characterized by a considerable draught, which impose limitations on their movements in proximity to sandy coasts or in shallow waters, is generally not preferable to the use of smaller vessels (generally 6 to 12 m) characterized by high speed of movement, reduced draught, which can be handled by a small number of people, who could even be those responsible for taking samples and making measurements. The reasons for this preference are fairly obvious and take into account, above all, the coastal environment in which the surveys are to be carried out, the importance of curtailing expenditure (and dedicating any surpluses that may be possible to the training of laboratory personnel), and the need to convey rapidly the various samples to the existing land laboratories equipped for accurate analysis.

APPENDIX IV - ELEMENTS FOR A DISCHARGE AUTHORIZATION

(a) First approach (effluents which can be defined as of essentially domestic type)

The first proposal is based on a distinction being made between essentially domestic municipal waste waters and other waste waters which cannot be defined as such.

It has been said on several occasions that a distinction between essentially domestic waste and effluents which show a marked industrial origin together with increasing toxicity is an important point in the choice of the regulations and technical solutions which must suit the needs of effective environmental protection. This statement has also been made in several documents of the Mediterranean Action Plan and of the international scientific group of experts (GESANP). Therefore it may be useful to point out some criteria of distinction in order to define and distinguish types of waste waters in the above mentioned terms (domestic or not).

The benefits of such a distinction come from the fact that for the first type of waste waters more simple procedures of authorization may be used. A restricted set of parameters may also be considered satisfactory for adequate control in such cases. These benefits appear to be relevant if we think of the number of such discharges and of the overwhelming importance of the simplicity of regulations and controls. These distinctions may also induce some municipalities to control some pollutants at source in order to "re-classify" their effluent in the first category.

Traditionally, a distinction has been made based on to COD to BOD ratio. It is often assumed that for the waste water treatable by conventional biological means this ratio should be less than 2 - 2,5. It is however known that biological treatment is able to withstand much higher concentrations of pollutants than the ones which could generally be accepted for discharge in the sea. At the same time this treatment shows only a limited efficiency (from 40 to 80% depending on the different toxicants).

The COD/BOD ratio may then be considered a useful parameter but, generally speaking, not sufficient in itself to allow a satisfactory distribution between types of discharge. However, if a more refined way of evaluation cannot be considered for practical reasons the use of COD/BOD ratio, together with a direct analysis of the number and type of industries discharging their wastes in the sewage may be a first and useful approach.

A better distinction could be made by means of a toxicity bio assay on marine organisms such as artemia salina, asterionella and mugilus.

These tests may be done on fresh samples or after the samples have been mixed to the desired ratio with sea water and kept aerated for a given time, so as to highlight the persistant and more serious toxic elements (see proceding paragraph). In order to compare different toxicities and make the above distinction the unit toxicity contribution (relative toxicity emmision rate divided by number of inhabitants) should be considered; otherwise different per capita water consumption will distort the comparison.

With consistent discharges from industries whose effluents are characterized mostly by a high organic load the number of inhabitants may be estimated by dividing the total daily BOD by the usual contribution (from 50 to 70 grams/inhabitant per day).

Another way to show such distinctions is to make a comparison between the unit contributions of toxicants of Group II which are typical of a given discharge with the unit contributions which may be defined as typical of municipal waste waters of essentially domestic origin. For this purpose useful information can be found in technical literature and also in preceding reports by the Mediterranean Action Plan.

It is therefore suggested that, for the purpose of any further investigation in this field, essentially domestic municipal wastewaters such as the following should be considered:

1) those which when diluted 1:50 - 1:100 do not produce chronic or behavioural effects on sensitive marine organisms;
2) those which do not induce, around the point of actual discharge, a significant build-up of toxicants in marine organisms, with particular reference to those organisms which show the lowest level of biological regulation.

It may be accepted that unit contribution may not exceed fixed values by certain amounts (e.g. 10-20%); this could be applied to single toxicants and, with a different percentage, to their cumulative presence.

Guidelines for the authorization of effluent discharges of essentially domestic origin according to the local receiving water capacity

A) Requirements concerning the quality of effluents

A.1) Fine screening, or straining, and some degree of floatables removal should be mandatory in any case. Better than standards, the performances of the equipment should be more practically specified (e.g. bar or mesh openings, residence time and surface loading, air addition). A specified fraction of storm-waters should also undergo such pre-treatment, but to a lesser degree (e.g. coarse screening).

A.2) Standards regarding settleable solids should be mandatory (e.g. from 0,1 to 0,5 cm^3/l) in any of the following circumstances:

- When straight forward sedimentation is feasible without exceptional costs (e.g. when it is not necessary to construct the plant underground or to build many miles of main sewer);
- when the depth of discharge is less than a given value (e.g. from 10-20 m);
- when the served population is in excess of a given value (e.g. from 10,000 - 50,000 inhabitants) taking into account at the same time local economic conditions and the urgency with which other sanitary works are needed.

A more restrictive standard may be introduced by various governments in place of the above mentioned standard on settleable solids. For example, a removal of 80% of suspended solids or a maximum effluent concentration of 80 - 100 ppm may be required, whichever is more restrictive.

The same circumstances may be taken into account in order to make a decision about cases in which this kind of standard should be considered mandatory.

A turbidity limit may also be considered together with, or in place of, the limit on suspended solids. The removal efficiency of microparticles, which appear to be more and more relevant regarding the adsorption and final destiny of many toxicants, may then be better taken into account.

A.3) Acute toxicity should be less than X units for a given marine organism. Total residual chlorine should be less than Y ppm (e.g. for primary sewage and water consumption of 300 l /day per inhabitant $X < 2,5$ toxicity units when diluted 1:10 - 1:50 is harmless if $Y < 0.02$ ppm).

A.4) Further treatment, according to the particular case, should be considered in in order to comply with the standards for receiving waters which are dealt with in the following paragraphs.

Of course these standards for receiving waters should be attained by that combination of treatment and disposal works which is least expensive and/or, taken overall, is more reliable and better adapted to protect the environment.

B) Microbiological objectives and standards for bathing waters and shellfish growing areas

Fortunately a set of micro-biological standards, pertaining to the protection of these uses, is available today, on which wide agreement has been reached thanks to the action of the International Institutions.

It is therefore suggested that reference be made, for record purposes, to the specific CAA guidelines and to reports already prepared at previous sessions of the Mediterranean Action Plan.

A list of standards adopted by different countries is put forward in the appendix (of course standards to protect shellfish themselves are applied both to the waters and to the actual shellfish).

Some guidelines of physical-chemical character have been put forward with regard to bathing waters and shellfish growing areas in some countries (e.g. France) involving, for instance, turbidity, dissolved oxygen, transparency and oils.

It is thought that such standards can be achieved in most cases near the point of discharge of the effluent (see below). This procedure gives a margin of safety for the coastal zones where bathing and shellfish growing are practised, as far as these particular parameters are concerned.

C) Requirements concerning the quality of the receiving marine waters in proximity to the point of discharge

In proximity to the point of discharge certain standards are necessary to insure a satisfactory degree of treatment and disposal with reference to the organic load and aesthetic aspects. The following parameters could be taken into consideration: BOD, OD, $N\text{-}NH_4^+$, MBAS, suspended solids, turbidity, transparency, nutrients.

As an example ordinary primary sewage with initial dilution of $1/80 \div 1/100$ might produce the following concentrations outside the mixing zone:

BOD $< 4 \div 6$ ppm

OD $>$ 85%-100% saturation (depending on "Natural values")

MBAS $<$ 0,2 ppm

$N\text{-}NH_4^+ < 0{,}4 \div 0{,}6$ ppm

Suspended solids $< 5 \div 10$ above natural level

Toxicity concentration $<$ 0,05 toxicity units

As regards BOD, it has been widely stated that this parameter has very small meaning for discharge in open marine waters. However as opinions differ it may be better to take it into consideration too.

The level of dissolved oxygen in open Mediterranean waters and at depths of less than 60 meters, which are relevant to the practical discharge of effluents, is very seldom below 85% of saturation. However in certain high growth areas, bottom waters in some periods of the year do show a lower concentration of dissolved oxygen. A decrease in the surface water concentration may be induced by the effect of rising bottom water and should be distinguished from oxygen depletion induced by the organic load of the discharge.

Conditions around the mixing zone may be predicted with relation to the parameters considered here and by means of the described methods.

Monitoring of all parameters, except toxicity concentration, may be carried out by means of sampling.

Toxicity in receiving waters outside the mixing zone should be evaluated according to the measured toxicity characteristics of the effluent and the measured "minimum" degree of initial dilution in situ.

For larger discharges direct evaluation of possible long-term effects, mainly on benthic fauna and flora, are also suggested by means of quantitative environmental assessment.

For smaller discharges (which may be classified as such according to the rate of discharge, population served, location with respect to other discharges, relative toxicity, etc.) the simplest routine control may be the measurement of the quality of the effluent (which is more practical) and of the degree of "minimum" initial dilution.

(b) Second approach (effluents which cannot be defined as of essentially domestic type)

No distinction a priori is assumed between different types of wastewaters. The same guidelines apply to all wastewaters.

A') <u>Requirements concerning the quality of effluents:</u>

A'.1) = the same as A.1)

A'.2) = the same as A.2)

A'.3) = the same as A.3)

A'.4) = the unit mass emission rates for each discharge should be - if necessary - reduced so as to meet two requirements:

1st. Taking into account the initial dilution, water quality standards set up for the various constituents outside the mixing zone must be complied with and

2nd. Every authority may in any case require reduction to a certain degree of the emission of some pollutants.

The evaluation of pollution limits depends on scientific and economic factors and also on the competent authorities involved.

In any case it is suggested that unit mass emission rates, rather than concentrations, should be controlled as this principle helps towards the conservation of water resources.

When only concentrations are limited by the regulations, standards may be complied with by artificially increasing the consumption of process waters.

B') Microbiological objective and standards for bathing waters and shellfish growing areas

The guidelines put forward in B) are also relevant as far as microbiological aspects of pollution are concerned. For all other substances of Group II, satisfactory water quality and environmental protection should be achieved just outside the mixing zone of the effluent (see following).

C') Requirements concerning the quality of receiving marine waters in proximity to the point of discharge

When the "minimum" ratio of initial dilution occurs, "safe" concentrations of substances of Group II must be achieved near the point of discharge, outside the mixing zone.

These "safe" concentrations can be formulated at different levels:

- less "safe", but mandatory and readily complied with in a short time;
- quite satisfactory, but attainable only in the long run.

For the evaluation of "safe" concentrations, one of the following criteria may be followed (whichever is the more restrictive):

- results of behavioural and chronic toxicity tests, when they are available.

An average value may be chosen, when differences exist between results;

- concentrations deduced from short-term acute toxicity tests dividing LC_{50} by an application factor which should have an order of two magnitudes;

- concentration of the substance at which level the most sensitive organism cannot fully regulate the concentration in its body.

It may be that "safe" concentrations so determined happen to be inferior to the background natural concentration in sea water.

This is unrealistic, as it would then be necessary to dilute the sea water with effluent in order to comply with the limits.

The respect of particular "safe" concentrations for a given substance, "C_e", can be incorporated in the design as a function of following factors:

- C_o = concentration of the substance in the effluent;
- S = initial dilution ratio;
- C = concentration of the substance just outside the mixing zone;
- C_s = natural background level in the sea water (which must be known for the area, e.g. from samples taken off the coast).

$$\frac{C_o + (S-1) \cdot C_s}{S} \qquad C_e$$

Viceversa, for the purpose of control, the "minimum" dilution rate "S" must be measured, in order to verify whether $C_o < C_o*$

$$C_o < C_o* \quad = \quad C_s + S\ (C_e - C_s)$$

where: C_o* = max concentration of the substance acceptable in the effluent, in order to be

$$C < C_e$$

If "S", "C_e" and "C_s" are known, it is possible to calculate the maximum concentration (of the given substance) in the effluent to be discharged, C_o*, in order to be $C < C_e$. The discharge will be finally authorized if, for every substance, $C_o < C_o*$.

ANNEX : AUTHORS AND CONTRIBUTORS

A number of experts from various disciplines have been involved at different stages and in various forms in the preparation of this document. Special attention was given to using, as much as possible, scientists from the Mediterranean region. However, this has not been applied at the expense of the quality of the undertaken task.

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WASTE DISCHARGE INTO THE MARINE ENVIRONMENT

Principles and Guidelines for the Mediterranean Action Plan

On its establishment by the United Nations General Assembly, the United Nations Environment Programme (UNEP) selected the Mediterranean Region as one of its "concentration areas" providing assistance to the coastal states in their endeavours to secure measures for the adequate protection of the marine and coastal environment.

Following collaboration between a number of United Nations Specialized Agencies including WHO, UNEP and the coastal states, an Action Plan was adopted the legal instruments of which were

— a Convention for the Protection of the Mediterranean Sea against Pollution
— a Protocol for the Prevention of Pollution of the Mediterranean Sea by Dumping from Ships and Aircraft and
— a Protocol concerning Co-operation in Combating Pollution of the Mediterranean Sea by Oil and other Harmful Substances in Cases of Emergency

A further Protocol, covering the protection of the Mediterranean against pollution from land-based sources, was subsequently added.

The present volume was prepared to assist responsible national authorities in the implementation of this protocol, by providing principles and guidelines for the issuance of permits by national authorities for the discharge of certain types of waste and other matter into the marine environment. It is intended to meet environmental quality criteria for receiving water.

It was prepared by the Institute of Sanitary Engineering of the Polytechnic of Milan (Italy), but the contents of the various chapters were developed by a multi-disciplinary team of experts from the Mediterranean States, together with UNEP and WHO staff.

There is an integrated approach combining engineering and scientific aspects with the content divided into theoretical and technical and practical papers. Up to date treatment methods for municipal and industrial liquid wastes are covered and the changing relationship between pollution and standards depending on the expected use of the receiving water is a subject not usually covered in a work of this sort.

It is intended that the material presented will be useful both in relation to the Mediterranean Action Plan and for other programmes relating to marine pollution control and will form the basis for the development of a model code of practice for the management of waste from coastal sources. Government policy makers, environmental researchers, civil, sanitary and environmental engineers, and water technologists will consequently all find the book of great use.

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