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MONITORING FOR COMPLIANCE CONTROL

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I. INTRODUCTION

The uncontrolled liquid waste discharge into the Mediterranean Sea during the previous decades has caused a severe damage in the marine environment, so that all Mediterranean countries have decided to combat this situation by ratifying and implementing the Barcelona Convention and its related protocols. The Mediterranean Action Plan (MAP), which is the result or this common decision is the necessary scheme for the problem identification and implementation of related management techniques.

During the first decade of MAP the problem of improper pollution control programmes have been recognized as one of the main reasons for the deterioration of the marine environment: liquid waste discharge without adequate treatment, no elaboration of environmental impact assessment studies (EIA), miscalculation of the environmental capacity of the Mediterranean Sea, bad operation of the existing wastewater treatment plants, etc.

Being already in the third decade of MAP the necessity for an efficient control of the main pollution sources around the Mediterranean Sea is now obvious: the ratification of the Protocol for the land-based sources and the Genoa Declaration are the first paces towards this directions.

Being actively involed in this common effort, UNEP/Athens Unit has elaborated this document that is can be a very useful tool for proper compliance monitoring control of effluents and ambient marine system included hot spot areas.

The philosophy of this document is to provide useful instructions and guidance for the collection and evaluation of information needed for the compliance monitoring of effluents and ambient marine system.

The technical aspects themselves should be found in the included list of literature and supplementary technical documents (i.e. handbooks and manuals).

The importance of the evaluation of the environmental capacity of a water body, the elaboration of regional planning and assessment, the development of quality criteria and quality objectives and the proper handling of monitoring data are pointed out, being aware that these aspects are frequently ignored or underestimated.

Since this document is a first step for the elaboration of pollution control programmes, some further actions with more technical details should be initiated in the near future in connection with the efficient implementation, of the Protocol of the land-based sources (LBS).

Some indicative ideas are listed below:

- Management techniques for industrial and urban pollution sources (river loads).
- Development of quality criteria in effluents and in the ambient marine environment and their implementation.
- Measures for the control of diffuse sources of pollution.
- A continuous up to date evaluation of point sources of pollution.
- Development of an Attainability analyses document.
- Development of a document for the compliance monitoring of sediments.
- Establishment of a body for the enforcement of protocols.
- Identification of sensitive and hot spot areas in the Mediterranean.
- Development and elaboration of inspection procedures.

Some of these actions are already elaborated and implemented by some countries, but the well defined operational methods suitable to the special conditions of the Mediterranean environment are missing.

II. POLLUTION CONTROL[*]

A scientific assessment of pollution - related problems of the Mediterranean region is only the first step towards action to prevent, abate and control pollution and its effects. Therefore, the substantive focus of MED POL-Phase II gradually shifted from assessment of the problems related to pollution to the development of proposals for concrete pollution control measures. Taking into account the data and information obtained in the previous phases of MED POL and relying on a permanent system for keeping the present assessment up to date through activities envisaged, MED POL - Phase III further emphasizes the development of action plans, programmes and measures for the control of pollution and compliance with those adopted by the Contracting Parties, as its central activities.

1. DEVELOPMENT AND IMPLEMENTATION OF POLLUTION CONTROL MEASURES[1]

1.1 Basis for action

Pollution from land-based sources was recognized in the very early stages of MAP as the major problem for the Mediterranean region. The adoption of the LBS Protocol (1980), its entry into force (1983), and its amendment (1996), provided the legal basis for the development of action plans, programmes and measures for the control of pollution from land-based sources and activities in accordance with the Protocol.

Although the control of pollution from land-based sources remains a major objective of MAP-Phase II, the control of pollutants from other sources and activtities not neglected, as exemplified by the adoption of protocols associated with the Barcelona Convention which deal with pollution from dumping and emergency situations, as well as with offshore exploration and exploitation[2] .

2. COMPLIANCE CONTROL

2.1 Basis for action

Compliance with the provisions of MAP-Phase II, the Barcelona Convention and its Protocols (in particular the LBS and Dumpling Protocols), and specifically with the decisions

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[*] UNEP, 1996

[1] In the context of this document, pollution control measures are broadly interpreted as a combination of technical (technological), economic, legal and administrative policies, measures and practices contributing to the:

- prevention and mitigation of pollutants' impact on human health and on the quality of the marine and coastal environment, including their living and non-living resources, and amenities;
- general decrease of pollution load reaching the Mediterranean Sea;
- rehabilitation of marine and coastal environment damaged by the present impact of pollution; and
- achievement of sustainable development

[2] Protocol concerning Cooperation in Combating Pollution of the Mediterranean Sea by Oil and Other Harmful Substances (adopted in 1976, entered into force in 1978); Protocol for the Prevention of Pollution of the Mediterranean Sea by Dumping from Ships and Aircraft (adopted in 1976, entered into force in 1978, amended in 1995); Protocol for the Protection of the Mediterranean Sea against Pollution resulting from Exploration and Exploitation of the Continental Shelf, the Seabed and its Subsoil (adopted in 1994).

and recommendations adopted by the meetings of the Parties to the Convention[1], is the key to successful environmental protection of the Mediterranean Sea. The most relevant decisions and recommendations pertinent to the abatement, prevention and control of pollution are:

(a) the relevant targets of the Genoa Declaration, adopted by the Contracting Parties in 1985[2], to the achieved as a matter of priority during the second decade of the Mediterranean Action Plan;

(b) the specific action plans, programmes and measures adopted by the Contracting Parties in the context of the implementation of the LBS Protocol[3] and

(c) the relevant decisions of the Contracting Parties and especially paragraph 6 of the Barcelona Resolution adopted by the Conference of Plenipotentiaries (Barcelona, 9-10 June 1995).

2.2 Objectives

The specific objectives of this programme element shall be:

(a) to monitor, on a continuous basis, the implementation and to assess the effectiveness of the implementation of action plans, programmes and measures for the control of pollution adopted or recommended by the Contracting Parties;

(b) to identify problems experienced by the Contracting Parties in the implementation of the action plans, programmes and measures, and formulated proposals that may assist in overcoming those problems[4], and

(c) to keep the Contracting Parties regularly informed about the status of the implementation of the adopted action plans, programmes and measures[5].

2.3 Activities

The stated objectives shall be achieved through:

(a) analysis and evaluation at a national, subregional or regional level of data and information generated action plans, programmes and measures for the control of pollution[6]

(b) compliance monitoring programmes[7] carried out by National MED POL Collaborating Institutions.

(c) analysis and evaluation of data and information received through the National Coordinators for MED POL from national compliance monitoring programmes.

(d) target-oriented research in support of national compliance monitoring programmes, and

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[1] Article 13.3 of the Barcelona Convention (1995) and Article 10 of the LBS Protocol (1996).

[2] Genoa Declaration. UNEP (OCA)/IG.56/5.

[3] The common measures adopted so far are included in MAP Technical Reports Series No. 95

[4] Paragraph 17.25 (b) of Agenda 21.

[5] Paragraph 17.35 (b) of Agenda 21

[6] Article 26 of the Barcelona Convention (1995); Articles 4,5 and 6 of the Dumping protocol (1995); and Article 13 of the LBS Protocol (1996).

[7] Article 12 of the Barcelona Convention (1995), and Article 8 of the LBS Protocol (1996).

(e) preparation of consolidated reports for the Contracting Parties on the status of the implementation of the action plans, programmes and measues, including recommendations on the ways and means to improve the efficiency of their implementation.

3. MONITORING OF THE LEVELS AND EFFECTS OF CONTAMINANTS IN THE CONTEXT OF MED POL PHASE III

1. Two basic types of monitoring are identified withing the framework of the MED POL - Phase III Programme: compliance and trend monitoring. Surveys will also be carried out in order to complement the monitoring data and facilitate decision-making for management purposes.

2. Compliance monitoring is defined as the collection of data through surveillance programmes to verify that the regulatory conditions for a given activity are being met e.g. concentration of mercury in effluents. In the case of identifying an instance of non-compliance, appropriate enforcement can be established which can be escalated until compliance is achieved.

3. Trend monitoring is defined as the repeated measurement of concentrations or effects over a period of time to detect possible changes with time. This type of monitoring will provide information that can be used for the assessment of the state of the environment and the effectiveness of pollution control measures taken. If the effectiveness of measures is deemed inadequate, additional activities may be initiated such as the formulation of new measures or the revision of existing ones, etc.

4. Depending on the matrices and parameters included in the programme, monitoring will be carried out for the following purposes:

(a) compliance monitoring
(b) trend monitoring

3.1 Compliance monitoring

- **Compliance monitoring of health-related conditions** (eg. sanitary quality of bathing areas and waters used for aquaculture, quality of seafood). This type of monitoring has a national significance, but data may also be used for regional assessments. A comprehensive approach on microbiological and health related monitoring of recreational and shell-fish, growing areas is given to an extensive detail in documents, WHO/UNEP (1994) and (1996).

- **Compliance monitoring of effluents** to determine whether the adopted common measures concerning concentrations of contaminants in effluents (e.g. mercury, cadmium) are complied with; and

- **Compliance monitoring in «hot spot» areas** to determine whether the environmental quality objectives or limit values set are complied with (e.g. DDT in water).

3.2 Trend monitoring

- **Coastal zone trend monitoring,** through a regional network of selected fixed coastal stations. of parameters that contribute to the assessment of trends and the overall quality status of the Mediterranean Sea. This type of monitoring will be carried out on a regional basis;

- **Trend monitoring in «hot spot» areas** (intensively polluted areas) and high risk areas that are likely to become heavily polluted, are subject to harmful seasonal phenomena such as algal blooms, or where control measures have been taken. This type of monitoring will be designed as necessary at the subregional level, and will be carried out on a national basis, and the data will be utilized for taking management decisions at a local level, including the assessment of the effectiveness of the control measures taken;

- **Trend monitoring of loads** (e.g. from land-based sources of pollution in general or from identified sources, pollutants transported by atmosphere, pollutants carried by rivers) and assessment of loads originating from non-point sources. Data from this type of monitoring will be utilized locally but also for regional assessments; and

- **Trend monitoring of biological effects** at different organizational levels, including molecular, cellular, physiological, behavioural, community and ecosystem levels, can also be used as an early warning system. This type of monitoring can be included in national monitoring programmes as well as in the regional trend programmes.

- This documents deals with compliance monitoring of effluents as well as with compliance monitoring in «hot spot» areas.

- In case of compliance monitoring, the selection of the parameter(s) to be monitored is determined by the pollution control measure whose compliance is being monitored.

3.3 Programme design[1]

For both compliance and trend monitoring, it is essential that the question being posed is both testable and specific, i.e. withing a statistical context. The question must relate to a specific environmental compartment, i.e. water, suspended material, sediment or biota. The sequence then is:

- to identify meaningful levels of change and the confidence limits of that change that are to be detected (e.g with what precision can a 20 per cent loss in number of species of a benthic sediment-living community be detected?);

- to obtain knowledge of special and temporal variability of the element being sampled from a desk study or pilot study;

- application of power analyses is essential in order to rationalize the programme[2]

- selection of elements of the programme taking into account logistic constraints[3] ,

- define data quality objectives and decide a priori on the statistical methods to be applied in analysing the data; and

- to select sampling sites and sampling frequency based on the foregoing information.

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[1] See Guidelines for monitoring chemical contaminants in the sea using marine organisms. UNEP Reference Methods for Marine Pollution Studies No. 6

[2] See Peterman, R.M. and M'Gonigle, M., Statistical Power Analysis and the Precautionary Principle, Marine Pollution Bulletin, Vol. 24, No.5, pp.231.234, 1992.

[3] See also new experimental designs (Underwood, Aust. J. Mar. Sci. 1993)

3.4 Data Quality Assurance Programme

Following the design of a scientifically-based national monitoring programme, a Data Quality Assurance (DQA) programme is required to ensure data reliability. The required quality assurance must address all aspects of the programme, including:

- trained staff;
- appropriate facilities, sampling and measurement equipment and other consumables;
- regular calibration, maintenance, and servicing of the equipment;
- sampling that conforms to sampling design
- sample handling procedures, including, for example, transportation, preservation, storage, tissue dissection, bone grinder, homogenization, sub-sampling (sub-sampling includes all steps up to the measurements);
- regular checks of accuracy and precision of routine measurements, by analyses of appropriate reference materials (when available) and the documentation of the results on control charts;
- external quality assessment (e.g. participation in intercomparison exercises);
- standard operating procedures (written protocols with precise descriptions of all elements of the measurements and quality control procedures);
- record of all calculations such as data translation and transcriptions prior to final documentation (record books and/or computers);
- data evaluation procedures (e.g. converting data into a report).

The results obtained by sampling, measurement and observation must be of adequate quality not only analytical (accuracy and precision) but also meet the requirements of the objectives[1] and be comparable on a Mediterranean-wide basis. Failure to include DQA information with the submission of monitoring data will mean that the data may not be included in the MED POL database and therefore will not be considered in the overall evaluation. The results must be reported to the Secretariat according to agreed formats and schedules. The results must be reported to the Secretariat according to agreed formats and schedules, in order to satisfy the reporting requirements. The Secretariat will assist countries in the interpretation of data.

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[1] The experience with quality assurance programmes, largely based on the practices of MED POL, is described in Contaminant Monitoring Programmes using Marine Organisms: Quality Assurance and Good Laboratory Practice (Reference Methods of Marine Pollution Studies No. 57, UNEP 1990).

III. WATER USES (PRESENT AND PLANNED) AND THE ASSESSMENT OF THEIR IMPORTANCE

1. MAINTENANCE OF THE ECOSYSTEM

Many of the principal human uses of marine waters depend upon successful maintenance and enhancement of the existing ecosystems or, in a few circumstances, upon creating and continuing new and artificial ecosystems for specific purposes.

The ecosystem includes all of the biological and non-biological (geological, physical, and chemical) components of the environment and their high complex interactions. Studies of ecosystems must include all that is within the body of water as well as imports to and exports from it. Research in such situations has shown that the biotic elements include producers of organic meterial, several levels of consumers, and decomposers. In the least complex situation, these act at rates controlled by the abiotic factors to transfer energy and recycle materials.

In each environment the existing characteristics of the system have been produced by dynamic interaction among the components, forces, and processes present. Some of these are small or transitory, but others are massive and enduring. If any of these forces of processes is changed, a new balance is produced in the system. Relative stability, therefore, results from the balancing forces, not the absence.

The estuaries, lagoons and coastal wetlands are in many ways the most complicated and variable of aquatic ecosystems, Materials carried from the land vary in quantity and quality, sometimes, with strong seasonal patterns of high biological significance. Tidal oscillations cause vigorous reversals of flow. Inherent hydrographic patterns can lead to accumulation of materials. Dense urban populations on the shores produce large amounts of waste, and engineering projects have changed the boundaries and flows of water courses. The biologically rich estuaries, lagoons and coastal wetlands are the most variable and the most endangered parts of the marine environment.

2. USES OF THE MARINE SYSTEM TO BE PROTECTED

Coastal marine waters serve a wide variety of exceptionally important human uses. Many of these uses produce high local benefits such as the yield of shellfish and recreational activities. Others involve regional benefits on the global unity of the marine system, since local events influence, and are influenced by, water quality at distant points.

Many of the human uses of marine waters are directly dependent upon the nature and quality of the biological, chemical, and physical systems present. Efforts to protect and enhance these uses will be limited principally by our ability to understand and protect the environmental conditions which are essential for the biota.

Principal uses of estuaries and coastal waters[*]

- Commercial shipping
- Shoreline development:
  (a) for residences;
  (b) for industry;
  (c) for recreation
- Recreation and aesthetics:

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[*] U.S.D.C. NOAA. ERL, 1979

  (a) boating;
  (b) swimming, surfing;
  (c) hunting;
  (d) fishing;
  (e) aesthetic enjoyment
- Mining:
  (a) aggregates;
  (b) oil and gas
- Electricity generation (and cooling water usage).
- Water extraction (desalinization).
- Military purposes
- Research and education
- Climate control
- Biological harvest:
  (a) food;
  (b) industrial materials
- Preservation:
  (a) species;
  (b) ecosystems;
  (c) productivity;
  (d) other features
- Waste disposal:
  (a) human wastes;
  (b) industrial wastes

2.1 Human health

Criteria for coastal waters in regard to human health should ideally be sets of quantitative exposure-response relationships between environmental exposure factors and effects on the pollution groups exposed. When dealing with human subjects, it is often difficult to establish even a basic cause-effect relationship, and even more difficult to obtain a graded response.

Acute effects of exposure to high levels of chemical or pathogens are more easily linked to human response than are effects of chronic exposure to the low levels so often typical of the environment. At the lower end of the response spectrum, sub-clinical changes in behaviour or enzyme activity have been detected down to the «no-effect level». The observed no-effect level is, of course, related to the choise of the indicator(s) of response and the sensitivity of the methods available or adopted for its measurement.

Sea waters are becoming increasingly contaminated chemically and microbiologically and may be a health hazard for man. One of the scientific approaches to demonstrating the relationship between water quality and disease is the epidemiological survey.

Monitoring of water quality is one of the means of assessing the potential risk. However, the recovery of pathogens from bathing waters does not necessarily indicate that the incidence of desease will be significantly increased.

In practice, the routine monitoring for pathogens presents various difficulties. Recovery of pathogens from bathing water is not normally done for routine surveillance as the bacteriological quality.

2.2 Amenity and aesthetics-recreation

Aesthetic qualities of water address the general principles laid down in common law. They embody the beauty and quality of water and their concepts may vary within the minds of individual encountering the waterway. A rationale for these qualities cannot be developed with quantifying definitions; however, decisions concerning such quality factors can portray the best in the public interest.

Aesthetic qualities provide the general rules to protect water against environmental insults; they provide minimal requirements for freedom from pollution; they are essential to the enjoyment of the nations' waterways.

The enjoyment of amenities is heavily dependent, not merely on the availability of an activity, but on the aesthetic satisfaction which it affords. Aesthetic satisfaction can be a very positive force in promoting public health and well-being. It is experienced through the senses of sight, smell, taste and touch.

In seeking criteria to protect aesthetic quality one requires, ideally, a knowledge of the relationships between quality and other environmental factors, its detectability by the senses, and the degree of associated adverse or favourable reaction. In attempting to derive such informaion it is obviously necessary to ensure that the population, whose reaction is to be assessed, is reasonably representative of those whose interests the criteria adopted are intended to protect. In many coastal areas, this may involve obtaining a proper balance of reactions of residents and non-residents whose requirements and sensitivity may differ.

Determination of the association between aesthetic reactions and water quality presents considerable difficulties, because it is rarely possible to expose people in a controlled manner to a range of conditions in coastal waters themselves, though some guidance can be obtained from assessment of experience at different sites.

Among measures that might be applicable in different situations are: verbal or written expressions of opinion in graded categories as determined by interview or questionnaire, trends in the ratio of numbers of visitors to a site and the accommodation available; trends in the price of property; or expressed willingness to pay for measures designed to reduce adverse effects.

The visible effects, whose thresholds of detection are required, principally include appearance of floating or suspended debris, turbidity, foams, slicks and colour. Development of criteria for odour presents the difficulty of establishing a relevant test.

2.3 Aquaculture and fisheries [*]

Major marine and coastal fisheries are based upon the capture of wild crops produced in estuaries, coastal waters and oceans. The quality and quantity of the available supply of useful species are controlled by the nature and efficiency of the several ecosystems upon which each species depends for its life cycle. Serious pollution at any point in the lower river, the estuary, or the inshore ocean might, therefore, break the necessary patterns and reduce the fishery.

Estuaries have exceptional usefulness in support of fisheries. Estuaries are used as obligatory spawning grounds, nursery areas, havens for parasites and predators, and as rich sources of food because of high productivity. The estuaries as recipients of wastes both from rivers entering them and cities and industries along their shores, are obviously more

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[*] UNEP, 1987

immediately susceptible to pollution damage than any other part of the marine system. Although the vulnerability of such inshore bodies of water to physical and chemical damage is exceptional, the open waters along the coast are also subject to damage from the use of these waters from waste disposal.

Pollutants can be detrimental to fisheries by reducing desired species through direct mortality from toxicity, smothering, intolerable heat, or other killing changes. Reduction may also occur when a pollutant has a sublethal stressing effect that significantly interferes with feeding, movement, reproduction, or some other essential function.

Fisheries provide useful indications of the biological health and productivity of marine waters. Continuous high yield of a harvestable crop of indigenous fish or shellfish free of toxicity or pathogens is an indication that water quality is satisfactory, that the environmental conditions are favourable for the total biological community, and that no contaminant is present in sufficient quantity to destroy major components of the ecosystem. Fisheries production statistics can thus serve as a sensitive indicator of environmental quality.

The general requirements for water quality in relation to successful fisheries include:

- Favourable, not merely tolerable, environmental conditions at every location which is required in the life history of each species.

- Freedom from tainting substances or conditions where useful species exist, including elements and compounds which can be accumulated by organisms to unacceptable levels.

- Absence of toxic conditions or substances wherever useful species occur at any time in their life history.

- Absence of sublethal deleterious conditions which reduce survival and reproductive success.

- Water sufficient to maintain the health of the biological systems which support useful species.

The open waters of the Mediterranean are relatively low in nutrients. Nevertheless, many of the lagoonal or estuarine areas receive nutrients from land- based sources. Hence those sites suitably protected for aquaculture purpose are often also those of higher nutrients concentrations. For the same reasons, however, they may also be more subject to various types of pollutants.

The general recommendations for the quality of water for use in culture include:

- continuously adequate control of those materials and conditions which are required for good health and efficient production;
- absence of deleterious chemical and physical conditions;
- environmental stability;
- prevention of introduction of diseases.

Factors other than water pollution may influence the microbiological and hygienic quality of fishery products. Catching, handling, processing, storage, marketing and the way the product is prepared may affect the transmission of disease by such products and occasionally falsely indicate inferior water quality. These factors should not ifluence the role of criteria for quality of the water where fish and shellfish are grown.

The influence of the physical, chemical and biological quality of fish and shellfish growing waters may extend beyond the effects on marine organisms themselves. Effects on consumers include: viral and bacterial infections and intoxications; parasitic disease, intoxications due to accumulated chemical poisons or biotoxins such as paralytic shellfish toxin; allergic reactions; responses of undetermined etiology; and offensive flavour causing nausea or more acute illness due to tainting of the product.

2.4 Tourism

Tourism constitutes a major economic activity in a number of countries and its further expansion will continue and is desirable both for the economy and for the social well-being of the community. Also tourism can further the creation of employment and regional development.

Environmental resources are a major element of tourism and a good environmnet is an essential quality of tourist areas. Unrestrained growth of tourism would reduce the quality of tourist areas and possibly their income-earning capacity.

In order to conserve natural cultural and man-made resources which are the basic qualitative elements of tourism, it is essential that the competent authorities should develop environmental guidelines for tourism development plans, in particular with respect to the quality of air and water, soil conservation, the protection of natural and cultural heritage and the quality of human settlements.

The competent authorities should ensure that decisions on touristic development plans are based on the fullest available information concerning their environmental implications. Environmental Impact Assessment should be used for major tourist development to evaluate the potential damage to the environment in the light of forecast tourism growth and peak demand.

The common problems of the majority of the Mediterranean countries as regards tourism harmonized with the environment are:

- overbuilding in some coastal areas and poor architectural and/or technical quality of construction in others;
- insufficiency of necessary infrastructure;
- social conflicts due to tourism;
- inappropriate land-use, and land speculation;
- conflicts between tourism and traditional activities;
- frequently inadequate tourism development plans and their inconsistent implementation;
- negative effects of seasonality of tourism on the environment;
- adverse impact of increased traffic due to tourism;

In terms of waste residuals, the most widespread problem in resort communities is water pollution through the discharge of inadequately treated effluents. Water bodies which are among the most attractive resources for tourist development are also frequently used for the cheap and convenient disposal of sewage.

2.5 Industrial water uses

Water is used in the industry for many purposes, such as cooling, cleaning of equipment, production, washing, etc. The final disposal of industrial effluents is another important use which should be mentioned.

Sea water is mostly used as receiving body for industrial effluents. The criteria for establishing ambient and effluent quality standards are mentioned elsewhere. Its usage in industrial units is rather limited, being only applied for cooling and washing of floors, etc. In those cases no special environmental quality standards are required which will be higher than those applied for bathing and fishing purposes. Special precaution is given only to the protection of cooling towers, etc, from the salinity of sea water, whereas the washing of floors causes no special problems.

In desalination facilities for the production of drinking water, which can be classified as «industrial» activity, the sea water quality must be as high as possible. The ambient standards for bathing are normally accepted as suitable for drinking water production from the sea.

2.6 Commercial water uses

Ports, ship reception facilities and transport are the main fields of commercial activities related to sea water use, whereas marinas are normally belonging to the touristic sector.

Sea water is mainly used for washing and cleaning of ship equipment and for the discharge of ship effluents. The water use has seldom been taken into consideration in development plans, thus causing the present bad conditions of almost all ports and reception facilities in the Mediterranean. Only recently regulations for port reception facilities have started to be applied in an effort to limit sea pollution caused by ships.

Criteria for implementation of ambient and effluent quality standards for the sea traffic have still to be analyzed and estimated.

IV. QUALITY CRITERIA

1. ENVIRONMENTAL CAPACITY*

The use of the seas as waste recipient for human discards has been accepted throughout history. Only recently has such use been questioned because of possible loss of or restricted use of marine resources. The recognition that such marine pollutants as artificial radionuclides can jeopardize human health through the consumption of seafoods or through exposure on beaches, and catastrophes such as the Minamata Bay mercury poisoning have resulted in restrictions upon the release of certain substances to the marine environment. However, some of these restrictions have appeared arbitrary to the scientific community inasmuch as they were not based upon present day concepts. There must be an awareness that the marine environment must be treated as a resource for society and that the ability of waters and sediments to accept waste must be assessed continually to keep the resources renewable.

There is an awareness that much of the information now being gathered on wastes is irrelevant to the appropriate management of wastes. With research or with a review of existing information, we need to learn more about the following:

- The toxicity of pollutants to marine organisms, especially those of the benthos.
- The fate of discharged materials in the coastal environment.
- National and regional amounts and kinds of wastes being generated.
- The chemical, physical, and biological data needed for mathematical models to assess the assimilative capacity of a system.

This information must be used to establish criteria for the acceptability of waste materials in coastal waters and to formulate testing protocols for characterizing materials for potential disposal into coastal waters.

Various terms are used to describe the extent to which the environment is able to accommodate waste without unacceptable effects. One such term is Environmental Capacity. Environmental Capacity is a property of the environment and can be defined as its ability to accommodate a particular activity or rate of activity without unacceptable impact.

It must be stressed that Environmental Capacity will vary with the characteristics of each site and with the type and number of discharges or activities or affected resources and uses. Use of the capacity of an environment to assimilate a waste or activity must recognize the defined capacity as an upper limit.

In Table IV.1 and Figure IV.1 are given the different processes involved in the assimilation capacity of the marine environment.

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* U.S.EPA, 1972

Table IV.1

Processes involved in assimilation or accumulation of anthropogenic substances by the marine environment (U.S.D.C.NOAA.ERL, 1979)

Process	Effect
Passive substances (not affected by biological and chemical processes	
Dilution	- Reduction in concentration of substance by mixing with seawater
Dispersion	- Spread of substance horizontally and vertically from point of introduction.
Transport	
- Horizontal	- Movement of substance along a horizontal plane from point of origin
- vertical	- Movement of substance along a vertical plane from point of orgin.
Active substances (affected by biological, physical and chemical processes)	
Flocculation and sorption by electrostatic processes	- Aggregation of fine particles (including those in colloidal suspension) into flocs and adsorption of dissolved and particulate matter (organic and inorganic) on the flocs. A process that is characteristic of estuaries, where silt-laden freshwater mixes with seawater causing sedimentation at the delta.
Precipitation and coprecipitation	- Reaction of some introduced substances with constituents in seawater to form a precipitate; e.g iron salts produce flocculent ferric hydroxide. Other substances may coprecipitate.
Sedimentation and scavenging	- Flocs of silt and flocculent precipitates settle to the bottom by gravitation and may scavenge dissolved and suspended matter and adhere to detritus and dead organisms in the water column as they settle. Meterials become fixed in bottom sediments.
Consumption and respiration by bacteria	- Decomposition of matter with uptake of oxygen and release of carbon dioxide.

Uptake and bioaccumulation by marine plants and animals	- Removal of substances from seawater and incorporation into marine plant and animal tissues.
Biomagnification through the marine food chain	- Accumulation of substances from marine organisms by predation at different trophic levels.
Detoxification by metabolic processes	- Conversion of toxic substances to harmless constituents by biochemical action in marine organisms.
Transport by marine organisms	- Vertical transport by zooplan-kton in diurnal migration, and horizontal transport by fish and invertebrates in feeding and spawning migrations.

Determining assimilative capacity, which is a form of environmental modelling, requires a combination of data and should distinguish between the probability that an ecological unit will recover from perturbation (resilience) and the probability that it will succumb to perturbation (degradation). Furthermore, in the case of systems that have already become unacceptably degraded, assessment of assimilative capacity should guide decision - making environmental managers in choosing methods of restoration.

Water quality modelling is a means of quantification of environmental impacts. Among the instruments for quantification, mathematical modeling plays an important role. Depending on the knowledge of the processes involved and under certain assumptions concerning the behaviour of the system, the impact of actions can be expressed numerically.

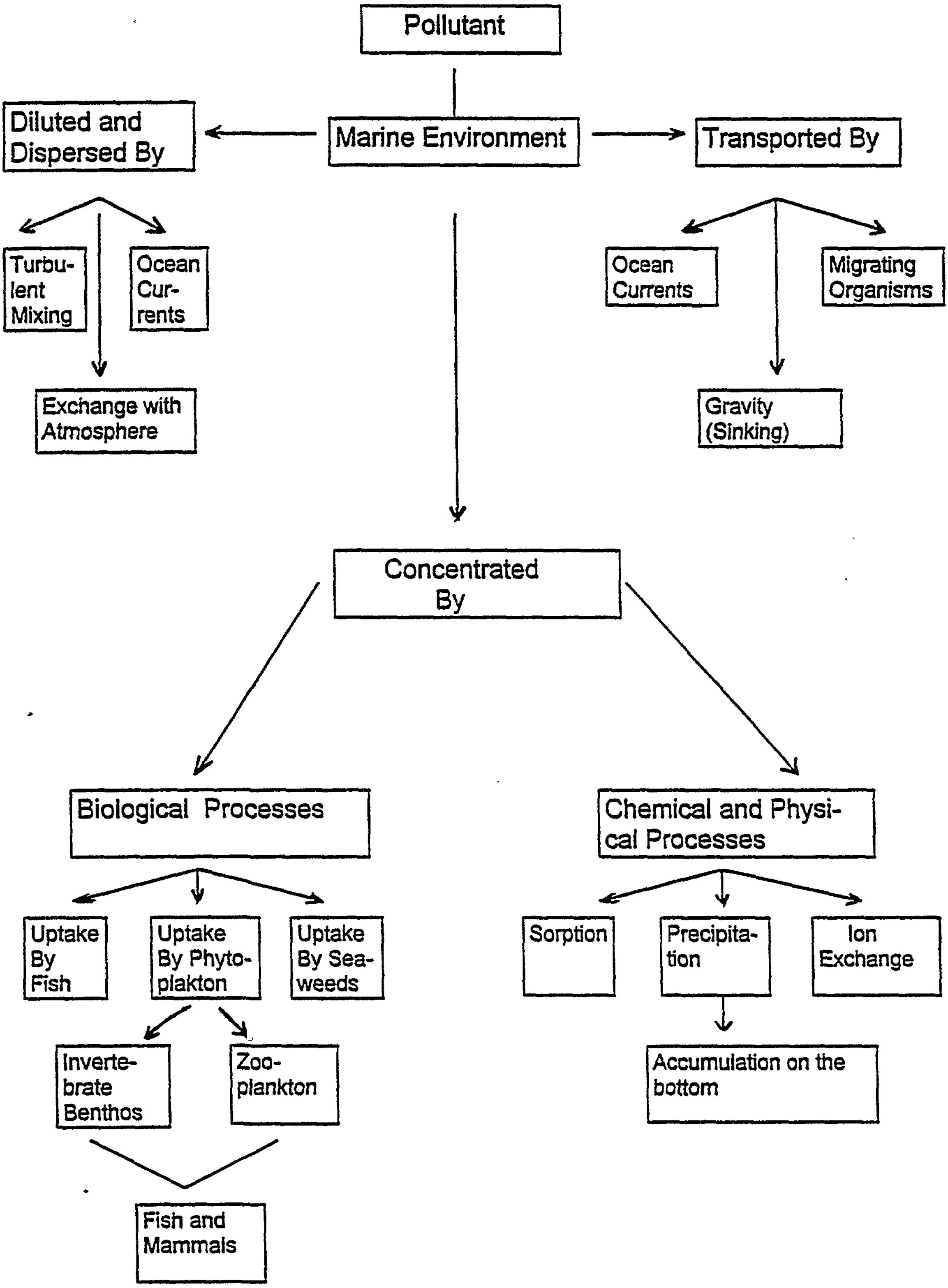

Figure IV.1. Processes that determine the fate and distribution of a pollutant added to the marine environment (U.S.DC.NOAA.ERL, 1979)

2. WATER QUALITY CRITERIA - STANDARDS

Water quality criteria specify concentrations of water constituents which, if not exceeded, are expected to result in an aquatic ecosystem suitable for the higher uses of water. Such criteria are derived from scientific facts obtained from experimental or in situ observations that depict organism responses to a defined stimulus or material under identifiable or regulated environmental conditions for a specified time period.

Water quality criteria are not intended to offer the same degree of safety or survival and propagation at all times to all organisms within a given ecosystem. They are intended not only to protect essential and significant life in water, as well as the direct users of water, but also to protect life that is dependent on life in water for its existence, or what may consume intentionally or unintentionally any edible portion of such life.

The world «criterion» should not be used interchangeably with, or as a synonym for, the word «standard». The word «criterion» represents a constituent concentration or level associated with a degree of environmnetal effect upon which scientific judgement may be based. As it is currently associated with the water environment it has come to mean a designated concentration of a constituent that, when not exceeded, will protect an organism, an organism community, or a prescribed water use of quality with an adequate degree of safety. A criterion, in some cases, may be narrative statement instead of a constituent concentration.

On the other hand, a «standard» connotes a legal entity for a particular reach of wateway or for an effluent. A water quality standard may use a water quality criterion as a basis for regulation or enforcement, but the standard may differ from a criterion because of prevailing local natural conditions, such as naturally occuring organic acids, or because of the importance of a particular waterway, economic consideration, or the degree of safety to a particular ecosystem that may be desired.

Quality criteria have been designed to provide long-term protection. Thus, they provide a basis for effluent standards, but it is not intended that criteria become effluent standards.

2.1 Suggested procedure for establishing criteria

1. Critically review the relevant literature

2. Determine physical, chemical and biological characteristics, including variability in space and time, which influence the desired use or property of the environment. This can be partially achieved by preliminary field observations and laboratory experiments. Such data, together with judicious use of mathematical modelling techniques, will limit the number of variables to be considered.

3. Establish the relative importance of each characteristic usually to within an order of magnitude. This again can be achieved in both the field and laboratory and will further limit the number of variables to be considered.

4. Determine the amount of stress being applied to the water mass to be protected. This should be expressed in appropriate units (e.g. concentration, *mass, volume, energy, number of organisms). This will help define the* magnitude of the problem.

5. Determine the chemical and physical fate and distribution of the stress in the system taking into account time factors. This will require chemical, physical and/or biological analyses of various compartments in the system as well as hydrological data.

6. Determine the portions of the population or use in the area to be protected (or chosen for study) that are subjects to each of several different degrees of risk. This information will be of several different degrees of risk. This information will be needed when deriving standards from criteria, and requires estimation of the rates of input to defined portions of the system.

7. Determine the exposure/response relationship which holds for the local system in question. This is a fundamental and nearly universally applicable procedure and will involve determination of the most vulnerable point in the system (e.g. top predator, man, fish, life stage, required food organism, enzyme, physiological process).

8. Experimental exposures in the laboratory and/or field should be made whenever possible to establish a family of exposure response curves reflecting the effects of expected variations in conditions and pollutant input on observed response.

9. Estimate the effects of several degrees of target response on trophic levels immediately above and below target. This will provide a first estimate of the probability of remote effects in the ecosystem and requires consideration of patterns of biomagnification.

3. CONTROL OF DISCHARGES BASED ON ENVIRONMENTAL QUALITY OBJECTIVES

Various methods have been employed to control the discharge of polluting materials in a water body. The oldest is probably that involving the imposition of identical limits to all discharges. This method is often called «uniform emission standards». It 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 legitimate and required uses.

The «Environmental Quality Objectives» system is based on the philoshophy of controlling discharges so that the quality of the receiving water body at any specified place is suitable for its established legitimate uses. The procedure for the control of discharges based on environmental quality objectives is illustrated in Figure IV.2.

The upper left part of the diagram concerns the derivation of the environmental quality levels taking into consideration the area of the water body and the local uses. The quality objectives 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 objectives attached to each use. This is indicated in the upper right part of the diagram.

The next stage is to decide what conditions and restrictions must be applied to the discharge in order to attain the required quality levels. There are two variables to be considered: the discharge point and the pollution load of the effluent. In general, the longer the pipeline in the sea the greater the acceptable polluting load of the effluent. 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 faecal coliforms in the effluent must be such that the dilution, dispersion and death-rate of the indicator will reduce the faecal coliform concentration at the boundary of the bathing area to within the limit.

The controlling authority will carry on a programme of sampling and analysis of the effluent to ensure that discharge is within the prescribed limits, and of seawater to confirm that the environmental quality within the defined zone meets the use objectives (Compliance monitoring procedure) (Figure IV.3 supplements Figure IV.2; they illustrate the machinery of control).

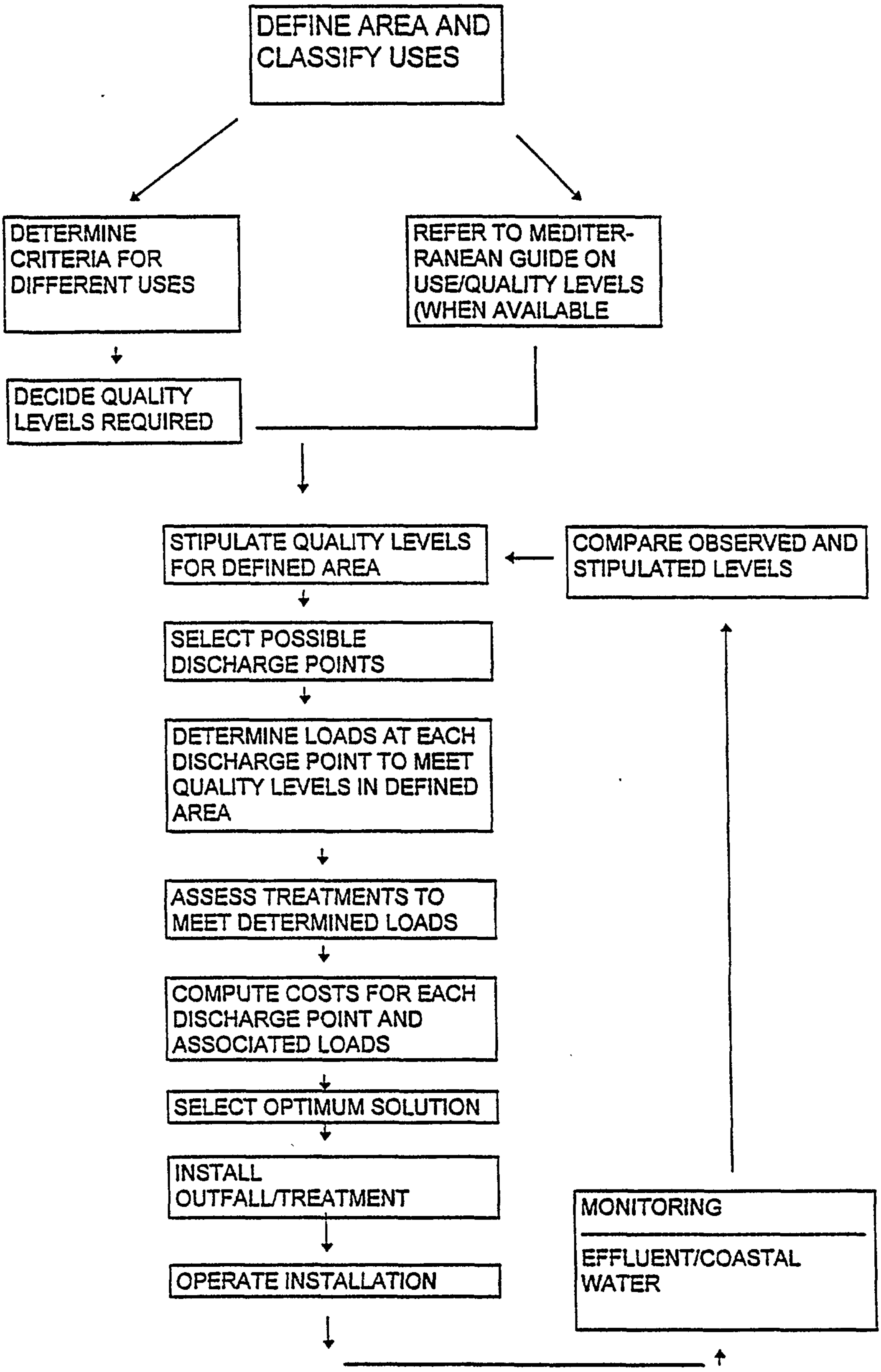

Figure IV.2. Diagram illustrating procedure for control of discharges by environmental quality objectives based on water use (WHO/UNEP, 1979 and UNEP/WHO,1996)

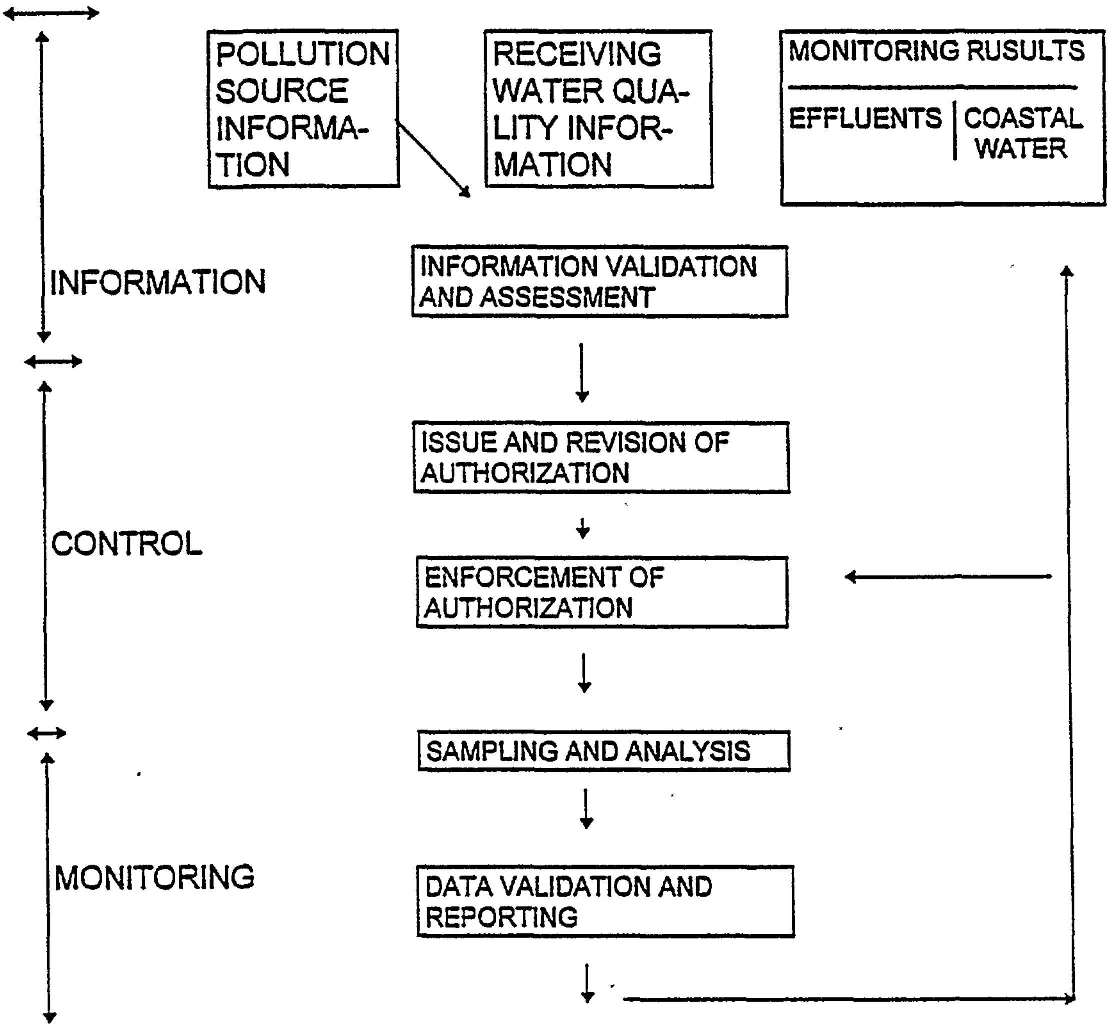

Figure IV.3. Diagram illustrating the executive functions of coastal pollution control (WHO/UNEP, 1979 and UNEP/WHO, 1996)

V. POLLUTION SOURCES[*]

Land-based pollution sources can be classified into two main types: point sources and diffuse (non-point) sources.

1. POINT SOURCES (30)

Point sources are those from which pollutants are continuously or discontinuously discharged into a receiving water body from a single point. Examples of this type of source are:

a) **Domestic sewage**

b) **Industrial wastes**

c) **Urban runoff**
Outfalls and combined outfalls: All above may either discharge into the immediate coastal area from points above or below sea level, or enter the marine environment away from the coastline via a submarine pipeline.

d) **Rivers:** polluted rivers discharging in coastal areas may be important carriers of pollutants originating from points located, inland, far away from the sea.

e) **Coastal lagoons:** These may be also important sources of pollution, particularly if they act as final recipients of wastes.

f) **Solid waste - sludge disposal and dumping sites:** Solid wastes and sludge disposed of directly into the sea, whether from specific points on land or from barges or ships can be considered as a point source of pollution.

g) **Major accidents and leakages:** Discharges of pollutants into the sea as a result of incidental or continuous leakage, or arising out of terrestrial accidents, such as an explosion in a coastal refinery, are also included in the category of point sources.

2. DIFFUSE (NON-POINT) SOURCES

Sources from which pollutants do not flow into the receiving water from a single point but are spread along the coast, are considered diffuse sources. They can be classified as:

a) **Run-off, rainfall:** stormwater which flows in an uncontrolled way into the sea, or leachate reaching the sea from dumping sites in the vicinity of the coastline are the main examples of diffused sources.

b) **Small outfalls:** untreated sanitary outfalls that are present in large numbers along the coast behave as diffused sources.

c) **Airborne pollution:** There is evidence that considerable quantities of lead and possibly other trace metals, DDT, PCBs, low molecular weight petroleum hydrocarbons and other organic substances are transported to the open ocean by the atmosphere, either as particles or in the gas phase (Duce, et al. 1976; SCEP, 1979; FAO, 1971). The source thus contributing to airborne pollution are also diffused sources.

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[*] WHO/UNEP, 1994

d) **Offshore activities**

A. POINT SOURCES

1. Domestic sewage

As domestic sewage are characterized all wastewaters coming out from urban sources (houses, tourist units, schools, athletic centres, etc) without any contribution of industrial discharges. Their composition can be easily predicted, since it remains almost the same for all above mentioned sources with only slight difference in different parts of the world.

Therefore, an urban wastewater quality consists of the following components:

Suspended solids: Settleable matter being removed in sedimentation tanks.

Dissolved solids: Non-settleable matter present in solution and/or suspension.

Biochemical oxygen demand (BOD): Measure of organic matter present in waste water.

Chemical oxygen demand (COD): Measure of strength of wastewaters under prescribed chemical conditions.

Nutrients: Mainly nitrogen and phosphorus

Oil and grease: In form of floating matter

Coliform organisms: Contained in human faeces.

2. Industrial wastes

In cases of an industrial wastewater discharge into the communal sewer system or directly into the sea, the estimation of the related quantities and loads is essential for an efficient wastewater management.

Table 1 in Annex 1 gives the main characteristics of industrial wastes and the related parameters of concern. Emission factors can be used for the calculation of industrial discharges, allowing a rough estimation of pollution loads omitting excessive sampling and measuring procedures. Therefore, a realistic first estimation of the magnitude of the problem deriving from industrial discharge can be made allowing the further elaboration of a detailed programme for waste management.

3. Rivers

Rivers are the major routes, from the land to the sea, of the natural products of weathering and many man-made materials. Compared to the total amounts of dissolved and suspended materials carried by rivers, the amount carried through the atmosphere is relatively small, and the contribution through the direct water runoff from the coastal zone and from ground water is unknown but is believed to be small.

Dissolved materials and solids held in suspension enter rivers in the course of weathering and erosion of rocks and soils, and as a result of human activity. The tendency of man to settle on river banks, assuring himself a steady water supply, defensive advantages and transportation routes, has inevitably led to input of man-made materials and wastes into the river water.

The characteristics of the individual river basins, such as their climate, vegetation, geomorphology, and the mineralogical compositions of their soils and rocks, constitute the background conditions that determine the chemical composition and quantities of materials carried by rivers. The human factor superimposed on the natural, pristine conditions largely arises from the technology and culture of the inhabitants of a river basin, the population density and the political and economic awareness of the processes in the river system.

Identification and quantitative analysis of the major chemical species, trace metals, nutrient elements, and organic compounds are far from being universally satisfactory.

To estimate the pollutant input to the ocean and to make the appropriate corrections for the understanding of natural processes, it is necessary to study long-term trends in major rivers and to undertake intensive studies on selected, highly polluted basins which could link water uses with the water quality considerations.

In the broadest context, river-quality assessment is a problem-oriented approach for developing information that is appropriate and adequate for sound resource management. In a more specific sense, river-quality assessment is the science and art of identifying the significant resource problems, defining them with adequate relevant data, and developing methods for evaluating the inpacts of planning alternatives on each specific problem. Assessment, therefore, extends far beyond basic data on the physical, chemical, and biological quality of water to measurement of pollution sources and the prevailing hydrologic conditions that cause the observed effect.

In keeping with this philosophy, in Figure V.1 are given the basic steps of the assessment and planning components.

To calculate the transport of material from the rivers, through estuaries and into the oceans, it is necessary to have detailed measurements of the water flow as well as the concentrations of substances within the estuary. It is possible to calculate the total river-borne material entering the estuary from the river, but because of modifications due to processes in the estuary this is not necessarily the same as that entering the ocean. The ocean can form a partial trap for many substances and this is most clearly true for sediment.

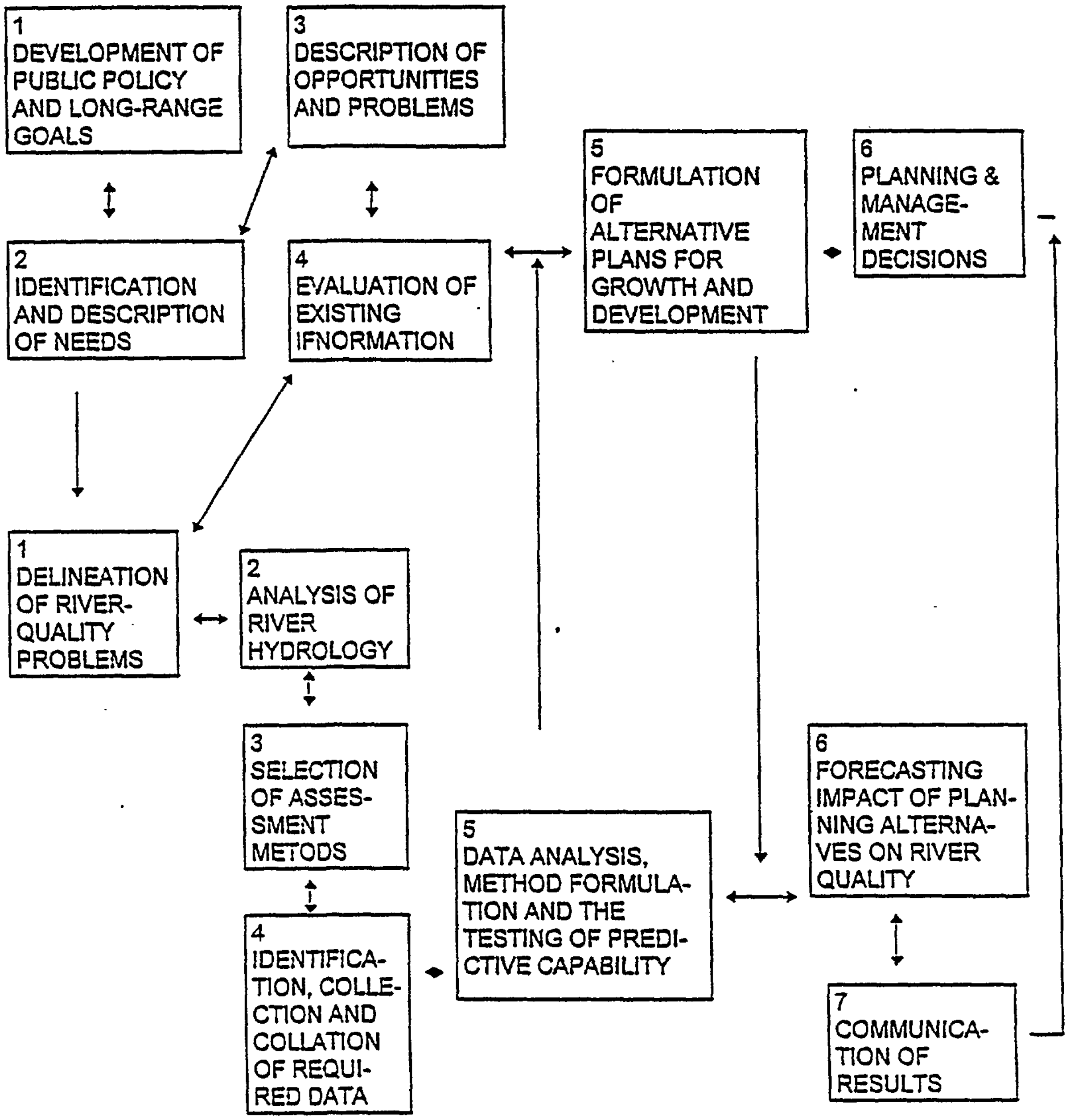

Figure V.1. **The interrelation of river-quality assessment to river-basin planning (Groot and Schilperoort, 1984).**

In general, a monitoring network for compliance purposes should be based upon two main aspects:

- the water system to be monitored;
- the monitoring objectives

The water system determines, together with the objectives, the dimensionality of the monitoring network. Moreover, the monitoring objectives strongly determine the scale of changes to be detected in the quality variable and hence dictate the kind of information to be extracted from the measured data.

4. Solid waste - sludge disposal and dumping sites [*]

Although it is not a recommended practice, solid wastes and sludge can, in some countries, be dumped into a receiving water either legally (with an authorization) or illegally, directly from the coast or from barges used for such purpose.

In the case of authorized dumping, the amount of waste should be determined either by weighing the load in a specially allocated scale or, if this is not available, by estimating the amount by volume. All municipalities or other institutions dumping their solid wastes and sludge in this way should be obliged to provide information in an appropriate format regarding the amount and composition of the material dumped. Random sampling is normally performed on the basis of taking one sample for every 500 tons of municipal solid wastes and one sample for every 10 tons of industrial solid wastes, taking into consideration the waste's origin and classification. Samples should be collected from different parts of the solid waste load carefully trying to be as representative as possible. In cases when it is proven that the declaration of a certain industry is not correct, all loads coming from that particular industry should be examined.

The sampling of solid wastes and sludges from unauthorized dumping into receiving water is very difficult, if not impossible. The only possible way for controlling unauthorized dumping and estimating the possible amount, is source control. To achieve this, all sources of hazardous wastes should be obliged to fill in a declaration form giving information about the amount, properties and place of disposal of hazardous wastes.

The correctness of the information given in the declaration should be investigated by random inspection.

5. Major accidents and leakages

Major accidents undoubtedly contribute to the pollution of the sea. If detailed information about the characteristics of the material flowing into the sea as a result of an accident is available, estimation of the volume of the material in question reaching the sea is enough for determining the amount of pollutant. If the analysis of the leaking material is not available, samples should be collected from the accident site and affected areas.

B. DIFFUSE (NON-POINT) SOURCES

1. Runoff - rainfall [*]

When precipitation, either in the form of rain or snow, falls on the urban area, some of the moisture is taken up by various forms of vegetation, some is stored temporarily in

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[*] WHO/UNEP, 1994

[*] OECD, 1985

surface depressions and other retention areas for eventual evaporation back to the atmosphere or infiltrated and the remainder runs off from the watershed catchment.

Runoff from rainfall and snowmelt is considered to be comprised of two components:

(a) the horizontal component which is discharged through the man-made and natural drainage system components, including both underground pipes and overland flow paths;
(b) the vertical component which infiltrates into the soil.

Although the pollutant characteristics of urban runoff may vary widely, generally it may be stated that:

(a) BOD strength is of the same order of magnitude as treated domestic sewage;
(b) concentrations of suspended solids often exceed by many times the levels found in treated sewage;
(c) bacterial parameters may exceed the levels found in treated sewage;
(d) many organic and inorganic pollutants found in industrial and municipal sewage are often found in urban runoff.

Runoff from a watershed is affected by various factors including:

(a) the slope of the ground surface along which the water is flowing;
(b) the relative permeability/impermeability of the soil surface;
(c) the amount of natural surface storage available to retain volumes of surface runoff.

<u>Parthways:</u> The parhways are those components of the system which transport not only the urban runoff, but also the pollutants associated with the urban runoff, both during the build-up stage prior to the rainfall event and also during the runoff event. These are:

(a) The atmosphere
(b) Pipe sewer systems
(c) Overland flow paths
(d) Sub-surface aquifers.

<u>Sources of pollutants:</u> The sources of pollutants, both accumulating on the ground surface and washed off an urban area in the stormwater, are contributed from a number of various sources including:

(a) Every - day urban activities
(b) Atmospheric fallout
(c) Corrosion
(d) Industrial/commercial activities
(waste landfill, raw material stock pile, contaminated land)
(e) Vegetation
(f) Soil erosion
(g) Construction activities
(h) Abrasion of solid surfaces

<u>Magnitude and signification of urban pollutant build-up and runoff:</u> It is difficult to quantity the magnitude of pollutant discharge associated with urban runoff, as there are many factors affecting this loading which depend on such things as the mangitude and density of the urban development, the nature of the development in terms of residential/industrial proportions, the type of sewer system servicing the area, climatological region, etc.

Problems relating to urban runoff: The problems relating to urban runoff can be broadly classified under two categories:

A. Those problems relating to quantity

   (a) increase peak flows in receiving streams
   (b) deplete groundwater aquifer recharge
   (c) decrease base flows in receiving streams.

B. Those problems relating to quality
   The impacts of storm runoff water quality problems can be generally classified into the following categories:

   (a) Public health protection
   (b) Stream entrophication
   (c) Aquatic life
   (d) Ecological changes

Stormwater runoff pollution control measures: Stormwater runoff pollution control measures are classified as:

A. Preventive control measures at source: are those which can be implemented in the planning and development of an urban area and in the operation and the management of the various activities within the urban area. Typical examples of preventive measures will include:

   1. The use of un-leaded fuels
   2. Stack emission control
   3. Local legislation and ordinances
   4. Stock pile protection and control
   5. Management of chemicals
   6. Management of roadway and highway de-icing practices
   7. Corosion control.

B. Corrective control measures: are those techniques which are applied to the management of the drainage system, in order to remove pollutants from the drainage pathways, either from the ground surface, from the pipe system or from the flow prior to being discharged into the receiving water bodies.

   1. Site controls

      (a) Storage:
         - rooftop storage;
         - parking lot storage;
         - dry ponding

      (b) Forced infiltration:
         - porous pavements;
         - seepage pits and trenches;
         - recharge basins

      (c) Site grading

      (d) Street sweeping

2. Drainage system controls

   (a) Sewer system maintenance
   (b) Storage

3. End-of-pipe treatment facilities

   (a) Storage
   (b) Screening
   (c) Swirl concentrator
   (d) Dissolved air floatation
   (e) High gradient magnetic separation
   (f) High rate filtration
   (g) Marsh treatment

4. In-river controls

   Policy for urban drainage should relate to an overall pollution control strategy and include both quality and quantity objective. A comprehensive policy should include the following criteria:

   - Municipalities should develop master drainage plants for all watersheds within their boundaries. The purpose of this policy is to foster master drainage planning in developing municipalities.

   - Municipalities with sewage collection and treatment systems should formulate a pollution control strategy that considers both wet and dry weather pollution sources.

   - Pollution control from urban drainage is a long-term commitment. Operation and maintenance of control structures and treatment facilities are part of this commitment.

2. Agricultural wastes[*]

2.1 Fertilizers and animal wastes

The growing world demand for food in the post-war period has led to greatly increased crop and animal production. This has generally occured on a constant or diminishing area of agricultural land. Increased intensity of production has resulted in most cases in a high turnover rate of plant and animal nutrients (nitrogen and phosphorus in particular) in the soil, which has tended to increase losses to water.

The pollution of water by nitrogen and phosphorus from agricultural land is of particular concern for a number of reasons. First, these has been a general rising trend in pollution from this source in most countries in the last twenty years, which shows no sign of levelling off. Second, ground water is seriously affected: this water (usually of very high quality) is a main source of drinking water. Moreover, the pollution of aquifers is in practice often irreversible, at least in the short/medium term. Finally, such pollution is very difficult to control owing to its diffuse origin.

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[*] OECD, 1982 and 1983

Most nitrogen in the soil is in organic form. The small proportion of inorganic nitrogen is largely in the form of nitrate. The main nitrogen inputs to the soil-plant system besides aerial deposition and biological fixation are chemical fertilizers and animal wastes. Nitrogen is cycled within the soil-plant system by the following processes: plant uptake, immobilization by microorganisms, decay of organic material, mineralization and nitrification. Nitrogen is lost from the soil-plant system in the harvested crop by leaching and erosion to ground and surface water and by denitrification and volatilization to the atmosphere.

Nitrogen losses from the soil-plant system by leaching are generally quite significant (up to an equivalent of 50% of the fertilizer applied).

When nitrate and phosphorus are transported from the soil by surface run off, the travel time is short. Rivers therefore respond quickly to variations in losses of these nutrients from the soil, and tend to have a peak concentration in the winter. Transport to groundwater applies mainly to nitrate, since phosphorus is generally eroded rather than leached.

Animal production has become more intensive in terms of number of animals per hectare at two scales: the individual farm and the animal-producing region. This is due to changes in methods of animal rearing, and to increasing specialization at farm and regional level.

There is often an imbalance between animal numbers and the available land for disposal of their waste on the same animal farm, or in the immediate vicinity. Thus manure utilization frequently is oriented towards disposal of waste rather than rational fertilization. This is more a local than a regional problem, as available land for fertilization could, with appropriate organization, generally be found within a reasonalbe distance. Excess fertilization is likely to produce considerable nitrate leaching to groundwaters and phosphate/nitrate runoff to surface waters according to geographic and climatic conditions. This is a particular danger on slopes and saturated or frozen soil, and it concerns all the contaminatns found in the waste.

Other possible effects of animal waste on water include oxygen depletion and the introduction of pathogens.

In the last twenty years there have been considerable efforts made, largely successful, to reduce pollution from point sources. However, increasing pollution from diffuse sources, in particular from fertilizers and animal wastes, has counteracted these improvements in many areas.

Eutrophication is the term used for the excessive increase in concentration of nutrients in surface water, followed by the uncontrolled growth of algae and aquatic plants. Eutrophication is ususally phosphorus-limited rather that nitrogen-limited. It has serious implications for the ecological and recreational value of aquatic resources.

2.2 Pesticides

«Pesticide» is taken to include not only the general plant protection products but also a number of other biocides and products to protect food storage, i.e. acaricides, fungicides, insecticides, etc.

Pesticides are by design biologically active materials. Mostly they exercise their effects by disrupting the normal biochemical balance of the target organisms. In practice the effects of a pesticide are not limited to the target organisms and may affect, directly or indirectly, a much broader spectrum of species.

Although the use of chemical agents in agriculture to prevent crop damage by pests and diseases is by no means a modern phenomenon, it was the technological stimulus of the Second World War which resulted in the development of the modern agrochemical industry and thus provided the basis for the extensive use of pesticides in to-day's agricultural industry.

Whilst these development must provide some grounds for optimism, it remains extremely difficult to give a realistic appraisal of the practical extent to which they afford protection to the environment. The diverse and continually changing nature of pesticide formulations, changes in methods of cultivation and pesticide application techniques made the generation of scientifically valid comparative and quantitative data almost impossible to achieve in the field.

Pesticide contamination and pathways

A. Surface Water
- Direct contamination:
    - Use : e.g. herbicide application
      : mosquito control
    - Misuse : e.g. rinsing of spraying equipment and containers
      : effluents from pesticide factories or other industries using pesticides
- Indirect contamination by runoff:
    - Pesticides in solution in rainwater
    - Pesticides absorbed on soil particles
    - Leaching by contaminated groundwater

- Indirect contamination by spraying

B. Groundwater

- Leaching into the ground after application in agriculture
- Leaching from waste disposals containing pesticide residues

It should be realized that the importance of a pathway and process contributing to the persistence of the pesticides and their residues, depend on the local situation and may vary from place to place.

In general it is felt that monitoring systems for the presence of pesticides and pesticide residues in water should only be initiated if clear indication are found that pesticides and their residues are finding their way into water in such manner of quantity as to suggest a possible, developing public health or serious environmental risk.

3. Off-shore activities

Off-shore activities could include:

(a) oil and gas production platforms;
(b) drilling rings and drill ships;
(c) off-shore storage facilities, including tankers when used for that purpose.

Pollutants from the above activities are:

1. Production water (water already mixed with the oil which emerged from the well). It may have been naturally in the reservoir before operations began, or was pumped into the reservoir to increase pressure there.
2. Machinery space.
3. Processing drainage and platform drainage.
4. Oily waste and sludges from separation processes.
5. Oil and condensates from well testing
6. Other wastes:
    - (a) oil-based fluids;
    - (b) water-based drilling fluids;
    - (c) garbage;
    - (d) sewage.

7. Use of chemicals, sacrificial anodes and other materials.

VI. COMPLIANCE MONITORING PROGRAMME

1. SCOPE OF ACTIVITY

The aims of a programme of monitoring land-based sources of marine pollution for compliance purposes should be:

a) Completion of baseline studies necessary to survey the types and amounts of pollutants discharged or dumped into the coastal marine environment in any given area;

b) Compilation, and regular updating, of an inventory of land-based sources of marine pollution, including data of the probable fate of the pollutants;

c) Effluent quality control where criteria or standards already exist, and assessment of control measures being implemented;

d) Compilation of data on the basis of which decisions on the promulgation and implementation of control measures can be taken where such measures do not already exist.

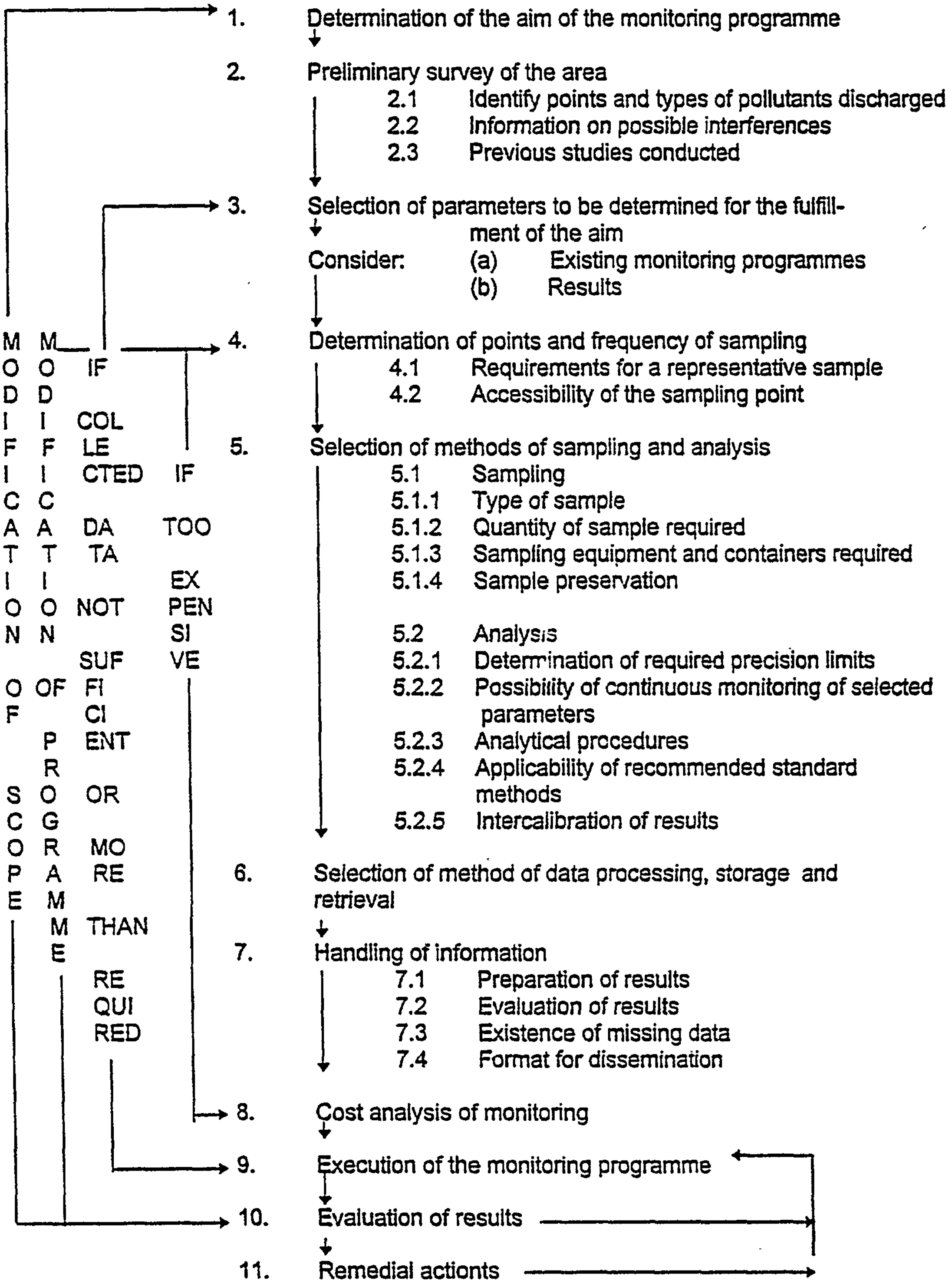
e) Formulation of a database to be used for the environmental impact assessment of any future coastal development

Proper planning of a compliance monitoring programme enables the collection of all the necessary information at the lowest possible cost and, at the same time, results in the programme becoming easily readjustable in the light of experience acquired, to enable improvements consonant with both local requirements and development in technology.

A well planned compliance monitoring programme should specify clearly:

(a) The purpose of the monitoring programme;
(b) The parameters to be determined;
(c) The methodology to be followed;
(d) The methodology of quality control and assurance.

During the planning of an effective compliance monitoring programme, the outline given in Figure VI.1 (modified from Mancy Allen, 1978) could be followed. The main flow-chart is provided at the left side of this figure, while the right side contains information regarding the considerations to be made for a proper decision. As can be seen in the outline, several factors are affecting decisions related to the planning of a programme, among which financial restrictions may be the most important. A realistic decision related to monitoring should be always financially feasible, and the compliance monitoring programme prepared accordingly.



1. Determination of the aim of the monitoring programme
2. Preliminary survey of the area
    - 2.1 Identify points and types of pollutants discharged
    - 2.2 Information on possible interferences
    - 2.3 Previous studies conducted
3. Selection of parameters to be determined for the fulfillment of the aim
    - Consider: (a) Existing monitoring programmes
    - (b) Results
4. Determination of points and frequency of sampling
    - 4.1 Requirements for a representative sample
    - 4.2 Accessibility of the sampling point
5. Selection of methods of sampling and analysis
    - 5.1 Sampling
    - 5.1.1 Type of sample
    - 5.1.2 Quantity of sample required
    - 5.1.3 Sampling equipment and containers required
    - 5.1.4 Sample preservation
    - 5.2 Analysis
    - 5.2.1 Determination of required precision limits
    - 5.2.2 Possibility of continuous monitoring of selected parameters
    - 5.2.3 Analytical procedures
    - 5.2.4 Applicability of recommended standard methods
    - 5.2.5 Intercalibration of results
6. Selection of method of data processing, storage and retrieval
7. Handling of information
    - 7.1 Preparation of results
    - 7.2 Evaluation of results
    - 7.3 Existence of missing data
    - 7.4 Format for dissemination
8. Cost analysis of monitoring
9. Execution of the monitoring programme
10. Evaluation of results
11. Remedial actionts

Figure VI.1. Suggested flow diagram of an effective compliance monitoring programme (Mancy, 1978 and WHO/UNEP, 1994).

The determination of parameters to be measured is very important in planning a compliance monitoring programme. Generally speaking, these parameters will depend on the types of sources present and the pollutants discharged. The determination can be based on data from existing minitoring programmes as well as on the water uses needed to be protected. For example priority parameters had been agreed on by Mediterranean States for pollution source monitoring in the region within the framework of the Long-term Programme of Pollution Monitoring and Research in the Mediterranean Sea (MED POL Phase II). These parameters were essentially designed for a coordinated regional programme, and the final choice in any particular area would depend mainly on local circumstances. However, consideration should be given to both required and obtainable precision because these factors may affect the significance, performance, and cost of the monitoring programme.

Once the compliance monitoring programme is planned, it should be kept in mind that this programme is not, by its very nature, permanent as to detail. On the contrary, it should be readjusted continuously, or periodically, in the light of experience gained during its implementation.

It should be stressed that the parameters only apply to that part of national monitoring programme which is being performed as a contribution to the overall regional programme. Local requirements will require adjustments depending on the situation prevailing in each particular area monitored.

In the case of municipal effluents, the minimum parameters should be determined on the basis of a comprehensive evaluation of the general situation. In this case, when results obtained through a baseline survey indicate that certain parameters are not encountered at all, they may be omitted. A similar evaluation should be performed for mixed effluents of municipal and industrial wastes, taking into account (beyond the others) the number and types of industries discharging into the common system. From the public health viewpoint, pathogens or an appropriate indicator microorganism (faecal coliform or equivalent) may be included in the list of components to be determined. Parasites should be monitored, particularly in municipal effluents from heavily-populated areas with a well-documented history of endemic parasitic diseases.

2. MONITORING AREA

The carrying out of a problem assessment is an essential prerequisite for any compliance monitoring programme, and for the preparations thereof. Prior to establishing the programme, the impact of pollution (both actual and potential) on the various uses of the coastal waters in question should be determined through the acquisition of relevant data (area assessment). The area assessment should include both landward and seaward descriptions of the area, and the data obtained should be noted either on a fact sheet, or on a descriptive map, or on both, depending on circumstances.

2.1 Area assessment

From the landward side, the following should be noted, wherever appropriate with regard to the aims and objectives of the programme:

- **Land use:** categories of land use within the general area, including use of immediate coastal areas, e.g. industrial, residential, forestry, agricultural, recreational or mixed;

- **Run-off:** identification of rivers and streams, including location, flow and individual monthly discharge into the sea, as well as areas where erosion is known to occur;

- **Wastewater discharges and outfalls:** outfall sites, beach and offshore, including type, e.g. industrial, domestic or mixed, and total daily flow. Industrial discharges should be specified;
- **Waste treatment:** location of treatment plants, capacity in m^3 per day, and degree of treatment;
- **Dumping sites:** identification of dumping sites in the vicinity of the beach, indicating whether for solid waste, sewage disposal or both, and giving volume of deposit per year;
- **Coastline:** sand, rock, gravel, cliffs. Also, whether shallow or deep water.

From the seaward side, the following should be noted, again wherever appropriate with regard to the aims and objectives of the programme:

- **Shellfish areas:** Site and type of shellfish should be indicated on a map, and information about catch (tonnage per year) should be given;
- **Fishing grounds:** Site, type of fish and, if possible, information about catch, tonnage, etc should be indicated;
- **Protected areas:** Information about fish in marine parks and other similar protected areas:
- **Dumping sites:** Determination of locations, material and amount dumped;
- **Marine biota:** General information about marine fauna and flora, wildlife and nature reserves should be provided.

The following meteorological and oceanographic observations will also have to be made, wherever relevant:

- **Winds:** drawing up of seasonal wind roses;
- **Precipitaion and air temperatures:** annual precipitation in tabular form. The same table to include average monthly air temperatures;
- **Currents and tides:** description and seasonal fluctuation of currents, tidal cycles where applicable;
- **Salinity and temperature:** from existing studies the data should be sufficient to provide information on water column stratification and its seasonal variations;
- **Depth contours:** from nautical charts;
- **Buoys and other navigational aids:** these, as well as any important obstacles such as wrecks or rocks, should be indicated.

Since a monitoring programme is a prerequisite step for compliance monitoring, it is understood that all above data should be available prior to compliance monitoring, unless specific conditions require additional data and therefore modification of the monitoring programme.

2.2 Maps

The use of adequate maps and nautical charts is an essential prerequisite for such a programme. The first step to be taken is the drawing up of a detailed map of the areas selected for monitoring. Such maps should incorporate as much as possible of the information collected during the area assessment, in particular:

(a) Sewage outlets and any waste or other discharge points;
(b) Inshore and offshore solid waste dumping sites;
(c) local currents in the coastal waters relative to point sources and beach locations;

If insufficient quantitative information exists, discharge measurements (flow gauging) or current measurements will have to be made prior to, or in conjunction with, the sampling and analytical programme in the area. The importance of coastal currents, their speed, direction and rebound on the coast have to be particularly noted because of the important role they play in the transport of pollutants, especially those found on floating matter which is submissive to the movement of the currents.

The most recent geodetic and nautical maps of the coastal area to be studied should be obtained. The neutical charts will normally be of prime interest. The situation and use of each map will normally define the appropriate scale. A map of practical size could be the European A3 format (approximately 42 x 60 centimetres). Many copying machines allow for direct reduction from A3 to A4, resulting in economic reproduction and presentation of results.

Each map should be clearly identified by location, coordinates, scale and orientation. This must be assured before any copying or reproduction is made. Such identification should include:

(a) **Location:** use the name of a typical town or conspicuous landmark. Always indicate the country;

(b) **Coordinates:** give the approximate latitude and longitude of the location;

(c) **Scale:** this should be graphed, e.g. in divisions of 100 metres or in kilometres, not numerical, as the latter may change with enlargement or reduction;

(d) **Orientantion:** indicate N for north, or give lines for latitude and longitude of the main location;

(e) **Date:** give date of preparation of map, if available

3. GENERAL DESIGN

Prior to the actual implementation of the compliance monitoring programme, it is essential to decide on:

(a) the matrices to be monitored;
(b) the parameters to be monitored in each matrix;

(c) the number and location of sampling points;
(d) the frequency of sampling

The extent of the programme will depend entirely on already-existing resources and on extra resources which can be made available to meet the required demand. These resources will consist in:

(a) trained manpower for sampling and analysis;
(b) laboratory facilities (apparatus, equipment and materials);
(c) transport facilities

It should be borne in mind that in practically all cases, the essential minimum is dictated by the provisions of international conventions or other similar legal instruments. In most countries, national legislation provides for coverage over and above this minimum, to conform with local requirements.

4. PREPARATION OF PRELIMINARY REPORT

A brief and concise report stating clearly the aims of the compliance monitoring programme, and including information collected during the preliminary survey, summary of previous studies and related maps, should be prepared. This report should form the basis for finalization of the compliance monitoring programme.

5. SAMPLING

Sampling techniques should be determined with great care as, even with the most sensitive analytical techniques, it is not possible to obtain more accurate and dependable results than the collected sample can provide.

It is not possible to provide specific sampling instructions which would be suitable and applicable under all conditions. Because of this, only general principles are outlined in the following sections.

The most important principle in sampling is to enable the performance of analysis on samples which are «representative» of the water being samples. In other words, the sample and its source should have the same composition. Furthermore, the sample should be able to provide a true presentation of the variations in the characteristics of the source with time. Sampling should be performed in a systematic way in order to minimize discrepancies.

Selection of the sampling point location as well as the frequency of sampling for the determination and monitoring of land-based marine pollution sources depends mainly on the sensitivity required as well as the resources allocated for the compliance programme. There is a basic difference between the selection of sampling methodology for application by all Mediterranean countries on a common joint basis, and the selection of a methodology in order to comply with national or even local requirements.

5.1 Matrices and locations

In programmes aimed at the determination of land-based pollution and compliance therefore, details will have to be determined in the light of the situation existing in each particular locality. These will necessary differ according to land-use and related activities, as well as water use, in the area in question.

In a regional compliance monitoring programme aiming at the determination of land-based marine pollution originating from all Mediterranean countries, mandatory monitoring would be restricted to major sources of pollution while at the same time allowing for additional components to enable the satisfaction of national and local requirements (compliance to local legislation).

In keeping with these general principles, the matrices to be monitored and the location of sampling points should be as explained below.

5.1.1 Point sources[*]

When samples are to be collected from a point source, the homogeneity of the system should first be checked and, if possible, sampling points should be located at points where homogeneous distribution of the parameters to be measured is observed. This is not always possible, especially if undissolved materials with densities different from that of the water are involved or when chemical and/or biiological reactions vary in extent in different parts of the system.

When the system is of a heterogeneous nature, the number and location of samples to be collected should be adjusted accordingly to enable results to be representative. Variations in the homogeneous character of a system with time should be checked because seasonal variations etc. are possible. Sampling locations near the boundaries of water systems, such as the banks of rivers or the walls of pipes and channels, should be avoided unless these locations are of special interest. The following principles should be adhered to in relation to the different types of point sources:

- **Outfalls**

The collection of samples from an outfall (domestic sewage or industrial effluent) is described in details in document: WHO/UNEP, 1994. Guidelines for monitoring land-based sources of marine pollution EUR/ICP/CHH 041(1). Regional Office for Europe, Copenhagen.

In Annex 2 is given as an example information based on directives of the European Union on:

a. Urban Wastewater about: collecting systems, discharges to receiving waters, reference methods, parameters to be measured, limit values etc, necessary for compliance control.

b. Industrial Effluents about: limit values, industrial sectors, frequency of sampling, quality objectives, etc. for Cadmium in effluents. It is a guide which could be used for compliance control.

Also in the same Annex (2), is given general guidance concerning the basic inspection procedures.

- **Rivers and streams:**

Monitoring stations on rivers should be established, provided that they satisfy one of the conditions given below:

(i) Their average flow is above 100 m^3/sec;

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[*] WHO/UNEP, 1994

(ii) Their watershed is larger than 100 km^2
(iii) They are expected to be heavily polluted

The location of the monitoring station on a river should be chosen outside the limits affected by tides and waves, at a point downstream from the last effluent discharge at a distance sufficient to obtain an homogeneous distribution. If there is any possibility of non-homogeneous distribution of quality at the chosen location, experimental tests of the nature and magnitude of any heterogeneity should be made. If the results indicate that the river is of homogeneous character, one position for sampling will be enough otherwise, either the location of the sampling point should be changed for one of an homogeneous character, or samples should be taken from several additional locations in addition to the original one selected, so that the overall characteristics can be represented. For main rivers, even if homogeneous, it is advisable for more than one sample to be taken from different depths on the same cross section, forming a sampling point grid if necessary. In such a case, the effect of variation of flow rate at the different points should be taken into consideration when preparing composite samples or estimating the overall input of any specific pollutant to the receiving water. When a limited number of samples need to be taken for determination of existent pollutants, if equipment is available, it is recommended to take an «integrated» sample from top to bottonm in midstream, or from side to side at mid-depth, in such a way that the sample is integrated according to flow. If only a grab or catch sample can be collected, this is best taken in mide-stream at mide-depth (APHA, 1990). On the other hand, velocity measurements, which are essential in order to determine the flow and, consequently, the total amount of pollutant discharged into the receiving water, sampling should be performed at a point located at 0.6 of the total depth measured from the bottom or, to increase accuracy, at points located 0.2 and 0.8 of the total depth (Linsley, 1964) and taking the average of these (Figure VI.2). Special attention is necessary when dealing with rivers which have a flooding tendency or a seasonally- varying stratification.

Bridges located over the river are an easily accessible and convenient sampling point. However, before a decision is taken regarding their use, it should be verified that samples collected from there are valid and representative. Sampling from areas where stagnation may occur and from areas located near the inside bank of a curve in the stream which may not be representative of the main channel should be avoided.

- **Solid waste and sludge disposal:**

Although it is not recommended practice, solid wastes and sludge can, in some countries, be dumped into a receiving water either legally (with an authorization) or illegaly, directly from the coast or from barges used for such purpose.

In the case of authorized dumping, the amount of waste should be determined either by weighing the load in a specially allocated scale or, if this is not available, by estimating the amount by volume. All municipalities or other institutions dumping their solid wastes and sludge in this way should be obliged to provide information in an appropriate format regarding the amount and composition of the material dumped. Random sampling is normally performed on the basis of taking one sample for every 500 tons of municipal solid wastes and one sample for every 10 tons of industrial solid wastes, taking into consideration the waste's origin and classification. Samples should be collected from different parts of the solid waste load carefully trying to be as representative as possible. In cases when it is proven that the declaration of a certain industry is not correct, all loads coming from that particular industry should be examined.

The sampling of solid wastes and sludges from unauthorized dumping into receiving water is very difficult, if not impossible. The only possible way for controlling unauthorized dumping and estimating the possible amount, is source control. To achieve this, all sources of hazardous wastes should be obliged to fill in a declaration form giving information about the amount, properties and place of disposal of hazardous wastes. The correctness of the information given in the declaration should be investigated by random inspection.

- **Major accidents:**

Major accidents undoubtedly contribute to the pollution of the sea. If detailed information about the characteristics of the material flowing into the sea as a result of an accident is available, estimation of the volume of the material in question reaching the sea is enough for determining the amount of pollutant. If the analysis of the leaking material is not available, samples should be collected from the accident site and affected areas.

5.1.2 Diffuse sources

Sampling from diffuse sources is a very complicated process for which a generally acceptable procedure is not available. In such cases, the following approaches are suggested:

(i) Collection of a representative sample and estimation of the overall effect;

(ii) Determination of the concentrations of selected pollutants in various parts of the receiving marine environment in combination with salinity or other tracers, extrapolating to zero salinity and flow estimations;

(iii) Utilization of information obtained from similar situations in which accurate load calculations are available;

(iv) In the case of urban waste, calculation of the population equivalent on the basis of previous experience.

As can be seen from the four possible methods outlined above, only the first two require an actual sampling, while the other two are based purely on estimates. The collection of a representative sample in order to make an overall estimate can be easily achieved if the diffuse source is in the form of small outfalls. In this case, one of them should be chosen arbitarily, and the results obtained extended to all the others. In the case of a «runoff», it is recommended that a channel at least 50 m. long perpendicular to the direction of the runoff be constructed, and samples collected from the outlet of this channel. It is considered that a 50 m-length collection channel would be sufficient in most cases.

Selection of the location of sampling points in the receiving marine environment in order to apply approach (ii) above, depends entirely on local conditions. However, the following general principles can still be applied:

(a) A grid of sampling points should be formed covering all the immediately affected marine environment;

(b) The depth from which the sample is to be collected should be decided according to local conditions. However, it is recommended that, at points where the depth exceeds 10 m, at least three samples (one below the surface, one at mid depth, and one at 1m above the bottom) should be collected.

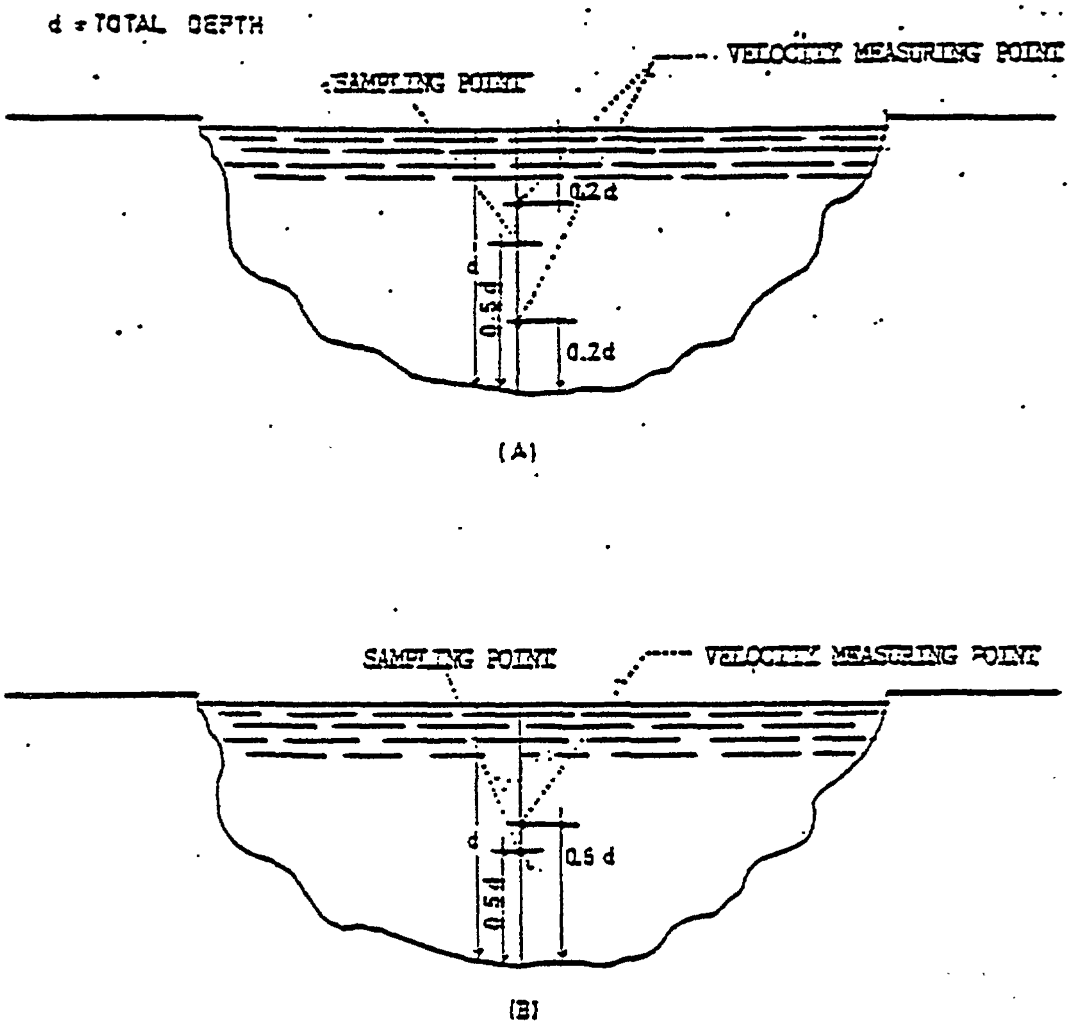

Figure VI.2. Velocity measuring location in a river (WHO/UNEP,1994)

5.2 Sampling frequency

The frequency of sampling should be selected in such a way as to adequately represent true quality and variation but, at the same time, should not exceed the minimum essential requirements, in order to avoid unnecessary effort and cost.

The best solution to the question of frequency is the use of continuously and automatically measuring instruments. This, however, is not always possible due to the unavailability of adequate instrumentation and the high cost involved.

The decision on the frequency of sampling can be taken only after available data are examined and an evaluation of the variation of characteristics is conducted.

When systematical data are not available, the following sampling programme should be followed, at least for major sources:

(a) Hourly sampling during one 24-hour period in each quarter (season) to assess daily cyclic effects

(b) Daily sampling during 7 consecutive days in each season, to determine any weekly cyclic effects;

(c) Weekly samples to delineate seasonal effects and to determine how less frequent sampling would have affected the results;

After a one-year trial period on the basis of the above programme, an evaluation should be performed to enable a decision on the suitable sampling frequency providing the required confidence limit of the means.

If the parameters to be determined show systematic trends or cyclic variations, in addition to the number of samples, the time of sampling should be considered. Both should be chosen in such a way as to reflect the actual situation. Whatever the results of the above-mentioned analysis, the frequency of sampling should not be less than once per month. For practical reasons, whenever applicable, the sampling frequency may be adjusted to fit other monitoring programmes, such as the compliance monitoring of the quality of coastal recreational and shellfish-growing areas.

5.3 Reference methods*

Four decades ago, adequate analytical techniques were not widely available for chemists to quantify contaminants causing pollution and to assess their impact. With the increased concern for measuring potential pollutants in the marine environment, techniques were rapidly adapted from other areas of pure and applied chemistry and a large number of methodologies and data sets began to appear in the scientific literature.

Since the early days of marine pollution studies, the field has developed very rapidly. We are now aware of a vast number of contaminants in the marine environment and some (such as PCB's) are complex commercial formulations in which some components are highly toxic and others are not. More sophisticated techniques are now being developed and tested to quantify the biological effects of pollution at the sub-lethal level.

For the more inexperienced scientists, keeping abreast of the scientific literature on methodology is a daunting challenge and it would be difficult to test the many hundreds of methodological modifications (not always improvements) published each year. Most conventional textbooks cannot be re-edited with sufficient rapidity to keep up with the pace of these developments. Clearly a more dynamic and flexible approach to this issue is required. The UNEP Reference Methods for Marine Pollution Studies series was established in 1983 as an attempt to address this issue and to provide a mechanism for testing, optimizing and updating methodologies and communicating them to marine scientists throughout the world.

The very best method is not always that which is chosen even by the more experienced scientists. Sometimes, very accurate and sensitive procedures may require highly sophisticated instruments which are beyond the financial or technological capabilities of many environmental laboratories. In many cases the best available alternative techniques must be sought which utilize widely available and easily serviceable equipment but which give data of sufficient accuracy for meaningful monitoring of contaminants. A good method for measuring the contaminant is often not sufficient to conduct a meaningful pollution assessment. Guidelines for a satisfactory sampling strategy must be devised and samples must be taken in such a way as to avoid contamination. Background chemical, physical and meteorological information may be required and the contaminant measurements themselves should be supported by well established quality assurance procedures. Finally, well-tested

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* UNEP/IAEA/IOC, 1990

techniques should be available for evaluating the toxicity of the contaminant to selected organisms both at sub-lethal and acute (lethal) levels.

Having a good method alone does not necessarily ensure good data quality. In order for any method to generate comparable data it should be used with good quality assurance practices including employment of reference materials. Reference materials are large homogeneous batches of environmental samples for which a number of analytical parameters have been accurately determined and certified. The analyst periodically measures Reference Materials alongside his samples of unknown concentration and checks that the results he is obtaining for these materials are the right ones.

By providing a flexible mechanism for technical support, adjusted to real environmental problems, the UN agencies are endeavouring to keep marine environmental scientists well-armed to face these challenges, not alone, but as part of a global team whith a common aim.

There are now over 70 Reference Methods published or shortly to be issued for testing. The methods are now being used by investigators in the UNEP and IOC sponsored marine research and monitoring programmes in order to ensure the global comparability and the necessary quality control of data. They are also extensively employed for training cources. In addition, some of the reference methods have been adopted by Governments as standards in discharging their obligations under regional agreements negotiated under UNEP's auspices. In parallel to the development of Reference Methods, regional and global intercalibration exercises are being conducted by IAEA (in collaboration with IOC and UNEP). These are showing a general improvement in data quality but demonstrate the urgent need for a more concerted effort in the field of data quality assurance (QA) in its broadest sense (including training, instrument calibration and maintenance, the preparation of working reference materials, joint monitoring exercises, quality control and data review).

The reference Methods programme provides a wide-ranging series of methods and guidelines for marine pollution studies. Each method is self-contained and is written to follow, as closely as possible, the format and terminology recommended by ISO (the International Organization for Standards). They are designed to be applicable throughout the world and to produce data of sufficient accuracy, reliability and precision to allow meaningful interpretation for the purposes of regional marine pollution studies, as well as inter-regional comparisons (and so to contribute to UNEP's Global Environmental Monitoring System, GEMS).

Reference Methods which have been thoroughly tested and found to satisfy the legal requirements of the countries participating in the Regional Seas Programme are submitted to the governments (at intergovernmental meetings) for formal adoption as mandatory methods in the context of specific Regional Seas Action Plans and Conventions.

The Reference Method Catalogue (Annex 3) gives a full listing of methods now available and those which are currently being prepared or tested. Many of the methods are inter-related to form a structrured series of texts on monitoring strategy, sampling technique, analysis, quality assurance and data interpretation. Each text is self-contained and can be updated without altering the rest of the series. The reader should make sure he has the latest edition of each method he or she requires.

Also in Table 1 of the same Annex (3) a recommendation is given for sampling and preservation of samples according to measurement.

VII. COMPLIANCE MONITORING IN THE MARINE ENVIRONMENT

1. SUBSTANCES REGULATED UNDER THE BARCELONA CONVENTION

1.1 Regulated substances

A system used in all marine conventions is to regulate the use and/or discharges of certain substances and material that is known, or at least suspected, to be harmful to the marine environemnt. The usual procedure has been to define a set of criteria on which to base the selection of a number of substances that should be regulated. Typical criteria were: toxicity, peristence and bioaccumulation. Substances showing high toxicity together with high persistence or ability to bioaccumulate were «banned» which means that they should be eliminated from discharges. A list of such substances was normally referred to as the «Black List» although the term is not used anymore. Other substances of environmental concern are identified although they are considered as being less harmful. The convention text normally allows these substances to be discharged although their discharges should be minimised. In a similar way as previously mentioned, a list of such substances was usually referred to as the «Grey List».

The regulations in the text of the Barcelona Convention (as it came into force in 1978) are rather general. As an example Article 8 states: «The Contracting Parties shall take all appropriate measures to prevent, abate and combat pollution of the Mediterranean Sea Area caused by discharges from rivers, coastal establishments or outfalls, or emanating from any other land-based sources within their territories». However, together with the Convention there is a set of Protocols. The «Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources» (LBS protocol), that came into force in 1983, has text which is somewhat more specific (Articles 5 and 6) and four detailed annexes (two of which appear in below) where substances are listed.

Annex I

A

The following substances, families and groups of substances are listed, not in order of priority, for the purposes of article 5 of this Protocol. They have been selected mainly on the basis of their:

Toxicity;
Persistence;
Bioaccumulation

1. Organohalogen compounds and substances which may form such compounds in the marine environment.

2. Organophosphorus compounds and substances which may form such compounds in the marine environment.[1]
3. Organotin compounds and substances which may form such compounds in the marine environment.[1]

4. Mercury and mercury compounds.

5. Cadmium and cadmium compounds.

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[1] With the exception of those which are biologically harmless or which are rapidly converted into biologically harmless substances.

6. Used lubricating oils.

7. Persistent synthetic materials which may float, sink or remain in suspension and which may interfere with any legitimate use of the sea.

8. Substances having proven carcinogenic, teratogenic or mutagenic properties in or through the marine environment.

9. Radioactive substances, including their wastes, when their discharges do not comply with the principles of radiation protection as defined by the competent international organizations, taking into account the protection of the marine environment.

B

The present annex does not apply to discharges which contain substances listed in section A that are below the limits defined jointly by the Parties.

Annex II

A

The following substances, families and groups of substances, or sources of pollution, listed not in order of priority for the purpose of article 6 of this Protocol, have been selected mainly on the basis of criteria used for annex I, while taking into account the fact that they are generally less noxious or are more readily rendered harmless by natural process and therefore generally affect more limited coastal areas.

1. The following elements and their compounds:

   1. zinc
   2. copper
   3. nickel
   4. chromium
   5. lead
   6. selenium
   7. arsenic
   8. antimony
   9. molybdenum
   10. titanium
   11. tin
   12. barium
   13. beryllium
   14. boron
   15. uranium
   16. vanadium
   17. cobalt
   18. thallium
   19. tellurium
   20. silver

2. Biocides and their derivatives not covered in annex I.

3. Crude oils and hydrocarbons of any origin.

4. Cyanides and fluorides.
5. Non-biodegradable detergents and other surface-active substances.
6. Inorganic compounds of phosphorus and elemental phosphorus.

7. Pathogenic micro-organisms.

8. Thermal discharges.

9. Substances which have a deleterious effect on the taste and/or smell of products for human consumption derived from the aquatic environment, and compounds liable to give rise to such substances in the marine environment.

10. Substances which have, directly or indirecly , an adverse effect on the oxygen content of the marine environment, especially those which may cause eutrophication.

11. Acid or alkaline compounds of such composition and in such quantity that they may impair the quality of sea-water.

12. Substances which, though of a non-toxic nature, may become harmful to the marine environment or may interfere with any legitimate use of the sea owing to the quantities in which they are discharged.

B

The control and strict limitation of the discharge of substances referred to in section A above must be implemented in accordance with annex III.

There are long lists of contaminants monitored by the PARCOM, the North Sea Task Force and the HELCOM. In view of the principles laid down by the revised conventions the lists could possibly be made even longer, since there is an obvious need for managers and the general public to be able to see that programmes for the reduction of harmful substances in discharges are really effective. However, inclusion of a substance in the monitoring programme must be defendable by the aims for the programme!

In this context it must be underlined that rather few of the existing substances have been tested and studied in relation to the criteria laid down in the conventions. A large number of new substances, mainly organic ones, are synthesized every year and very little is known about their hazardous properties.

However, as compiance monitoring of contaminants is very resource demanding there is a clearer need for a good procedure for the identification and selection of the substances that are most likely to cause harm to the environment and, therefore, should be given priority in monitoring programmes.

The International Council for the Exploration of the Sea (ICES), in its role as scientific advisor to HELCOM, responded to a request to recommend a procedure on how to identify «new» contaminants presenting particular hazards to the environment. The term «new» contaminant could be understood in several ways in this context. It can refer to contaminants not currently controlled under the various conventions, newly synthesized substances, substances showing increases in production or changes of use, existing substances which have undergone revised hazard assessments, or substances that recently came to our attention (e.g. intentional or unintentional by-products of industrial processes).

For the process of identifying new contaminants it is necessary to define goals for environmental protection. Furthermore, it is necessary to have knowledge on key scientific elements including: sources; transport; transformation; fate of contaminants as well as effects of conaminants on Man, living resources and amenities.

1.2. Measures adopted by contracting parties

From the viewpoint of human health, the protocol on pollution from land-based sources is the most important. In view of the considerable economic and legal implications of this protocol, the text itself is similar to the Convention in that it provides the framework for prevention and control measures, implementation being achieved progressively. To date, the following measures have been adopted by contracting parties on a joint basis in terms of the protocol, and are presented here as an example on the measures which would be taken before compliance monitoring would begin.

1. Interim environmental quality criteria for bathing waters (September 1985);
2. Interim environmental quality for mercury (September 1985);
3. Measures to prevent mercury pollution (September 1987);
4. Environmental quality criteria for shellfish waters (September 1987);
5. Measures for control of pollution by used lubricating oils (October 1989);
6. Measures for control of pollution by cadmium and cadmium compounds (October 1989);
7. Measures for control of pollution by organotin compounds (October 1989);
8. Measures for control of pollution by organohalogen compounds (October 1989);
9. Measures for the control of pollution by organo-phosphorus compounds (October 1991);
10. Measures for the control of pollution by persistent synthetic materials in the Mediterranean Sea (October 1991);
11. Measures for the control of radioactive pollution (October 1991);
12. Measures for the control of pollution by pathogenic microorganisms (October 1991);
13. Measures for the control of pollutuion by carcinogenic, teratogenic and mutagenic substances (October 1993).

All these measures represent minimum ones agreed to by all Mediterranean countries. At national level, several countries already possess stricter ones. In a number of instances, no quantitative control in the form of standards is included, mainly because either the current state of the art, or other considerations, precluded the adoption of definitive standards at the particular time. All measures are subject to upadating.

In October 1985 in Genoa, Mediterranean States adopted interim quality criteria for bathing waters (Table VII.1), while in 1987, microbiological quality criteria and standards for Mediterranean shellfish waters and shellfish were also adopted (Table VII.2).

Its beyond the scope of this document the presentation of the legal basis for marine pollution prevention and control in the Mediterranean. Part of this legal basis appears in the document:
WHO/UNEP (1995) Health risks from marine pollution in the Mediterranean. Part II Review of hazards and health risks EUR/ICP/EHZ 9501/MT01(2), WHO Regional Office for Europe, Copenhagen.

2. MEDIA IN WHICH CONTAMINANTS SHOULD BE MONITORED

The ICES, in its role as scientific advisor to PARCOM and partner with PARCOM in the North Sea Task Force (NSTF), responded to a request to recommend to PARCOM and NSTF a scheme to describe in which media the different contaminants or hazardous substances preferably should be monitored. The scheme should preferably also assign priorities between different media for sampling in order to make the monitoring more cost effective. The advice given appears below.

It is important to stress that the information contained in the tables should not be used alone but always be combined with the explanatory text!.

The martices considered included sea water, sediments, and biota, as are included in the current JMP. The martices were selected as those most appropriate for the provision of the greatest information in relation to each monitoring purpose. They were selected on scientific grounds, and did not take any account of relative costs or convenience of the alternative choices.

In some cases, no matrix has been recommended, either because the monitoring of a particular contaminant was not appropriate to the monitoring purpose, or because advice could not be given for technical reasons.

The reliability of the information from a monitoring programme, and its consequent value, is dependent upon the attention paid to quality assurance at all stages of the measurement programme (sample collection, storage, preparation, preconcentration, analysis, standardisation and interpretation). Participating laboratories should be required to adopt appropriate procedures in this area.

Table VII.1

Interim quality criteria for bathing waters adopted by Mediterranean states in 1985

Parameter	Concentration per 100 ml not to be exceeded		Minimum number of samples	Analytical method	Interpretation method
	50%	90%			
	of the samples				
Faecal coliforms	100	1000	10	WHO/UNEP Reference Method No.3, «Determination of Faecal coliforms in seawater by the Membrane Filtration Culture Method», or WHO/UNEP Reference Method No.22, «Determination of Faecal coliforms in seawater by the Multiple Test Tube Method»	Graphical or analytical adjustment to a lognormal probability distribution

Table VII.2

Mcriobiological quality criteria and standards for Mediterranean shellfish waters and shellfish adopted by States in 1987

FAECAL COLIFORMS IN SHELLFISH-GROWING WATERS			
Concentration of faecal coliforms per 100 ml not to be exceeded 80% 100% of the samples	Minimum sampling frequency	Analytical method	Interpretation method
10 100	In winter montlhy in summer fortnightly	Membrane filtration m-FC broth of agar incubated at 44.5 ± 0.2° C for 24h	Graphical or analytical adjustment of a lognormal probability distribution
FAECAL COLIFORMS IN SHELLFISH FLESH			
Concentration of faecal coliforms per gram of flesh	Minimum sampling frequency	Analytical method	Interpretation method
2: sale permitted between 2 and 10: temporary prohibition of sale 10 and above: sale prohibited	In winter monthly; In summer fortnightly	Multiple tube fermentation and counting according to MPN. MacConkey broth incubated at 36 ± 0.5°C for 24h and then at 44.5 ± 0.2° C for 24h	By individual results histograms of graphical adjustment of a lognormal probability distribution

2.1 Compliance monitoring of health - related conditions

Table VII.3 provides advice on the contaminants and matrices that should be included in a regional or wider scale survey to assess the possible hazards to human health presented by the presence of selected contaminants in marine foodstuffs. In several cases, primary and secondary choices of matrix are given.

Areas of contamination could exist which could give rise to localised increases of concentration in foodstuffs. Such situations were unlikely to be detected or adequately described by large-scale surveys, and were better approached through specially designed and targeted monitoring exercises by national or local authorities. In such circumstances, the relevant authorities should assess the most important exposure pathway by which the contaminant reached the public through marine foodstuffs. The monitoring programme should be directed at that pathway, and not be constrained by the advice given in Table VII.3 in relation to broader scale surveys.

Compliance monitoring of health-related conditions (eg. sanitary quality of bathing areas and waters used for aquaculture, quality of seafood) has a national significance, but data may also be used for regional assessments. A comprehensive approach on microbiological and health related monitoring of recreational and shell-fish, growing areas is given to an extensive detail in documents:

a. WHO/UNEP (1994) Guidelines for health-related monitoring of coastal recreational and shellfish areas. Parts I to V. Document EUR/ICP/CEH 041(3). WHO Regional Office for Europe, Copenhagen.

b. WHO/UNEP (1996) Micribiological monitoring of recreational and shellfish growing areas. Document EUR/ICP/EHAZ 9501/MT02. WHO Regional Office for Europe, Copenhagen.

2.2 Compliance monitoring of seawater (Table VII.4)

The use of water analysis to reflect current levels of marine contamination is attractive in that it concerns the important aqueous phase, the environment in which both biota and sediment exist. The requirements for precision and accuracy of analysis at low concentrations limit the number of determinants that could be considered in off-shore waters to mercury, cadmium copper, zinc and lead, all at secondary matrix level. Even in these cases, it would be assential for each laboratory to establish in-house quality control procedures, and for rigorous assessments to be made to establish comparability between laboratories, with particular attention to lead.

Table VII.3

In relation to the assessment of possible hazards to human health (Chassard-Bouchaud, 1993)

Matrix	Contaminant																					
	CBs	γ-HCH	Hg^5	Cd	Cu^3	Zn^3	As^4	Cr^3	Ni^3	Pb	MeHg	TBT^3	Chlordane^3	Planar CB	PCDD/ PCDF	DDT^3	Dieldrin	PAH	PCC	Triazines^3	PPDE^4	PBB^4
Shellfish	P	P	P	P						P	P	P		P	P		P	P	P			P
Fish muscle			P								P											
Fish liver	S^2	S^2		S^2										S^2	S^2		S^2		S^2			S^2

P: primary matrix
S: secondary matrix

Notes and Qualifications:

1. If fish liver is not a consumed fisheries product, no analysis is needed
2. If fish liver is not a consumed fisheries product and there remain human health concerns, transfer attention to fish muscle.
3. These contaminants are not normally of cocnern in respect to the consuption of fisheries products
4. Arsenic is present in seafood in measurable concentrations, but its chemical form makes it of little concern with respect to human halth
5. Hg should be understood to include methyl-mercury compounds. In countries where public health regulations refer to methyl-mercury rather than total mercury, samples may be analysed for methylmercury.
6. Too little is known about the toxicity to assess potential hazard

Table VII.4

In relation to the assessment of the existing level of marine pollution (i.e., contamination) (Chassard-Bouchaud, 1993)

Matrix	Contaminant																					
	CBs	γ-HCH	Hg	Cd	Cu	Zn	As	Cr	Ni	Pb	TBT	MeHg	Chlor-dane	Planar CB	PCDD/ PCDF	DDT	Diel-drin	PAH	PCC	Tria-zines	PPDE	PBB
Nearshorewater		P	P^1	P^1	P^1	P^1		P^1	P^1	P^1	S^1									P		
Offshore water		S	S^1	S^1	S^1	S^1				S^1												
Surficial sediments^2	P		P	P	P	P	P^5	P	P	P	P	P	P	P	P	P	P	P	P		P	P
Shellfish	S^3	S^3	S^1	S^1		S^1				S^1	P	P	S^3	S^3	S^3	S^3	S^3	S^3	S^3		S^3	S^3
Fish muscle			$T^{1.4}$				$S^{1.4}$					S^4										
Fish liver	S^4			$T^{1.4}$						$T^{1.4}$		S^4	S^4	S^4	S^4	S^4	S^4	S^4	S^4		S^4	S^4

P: primary matrix
S: secondary matrix
T: tertiary matrix

Notes and Qualifications:

1. Potential addition/alternative to sediment measurements in areas where sediment conditions are not wholly favourable
2. Should be accompanied by total organic carbon measurements, size fractionation (<63 μm), and description of the sediment type. Sampling should be carried out following current ICES guidelines.
3. Could be carried out on an opportunistic basis, as may provide additional information on distribution.
4. Sedentary species only (e.g., flatfish).
5. The signal-to-noise ratio for discriminating between anthropogenic and natural influences is extremely low.

In near-shore waters, concentrations may be somewhat more variable and subject to anthropogenic influences, and chromium and nickel analyses might also be considered. The same quality assurance precautions would be needed. In near-shore waters, it is necessary to take account of any correlation between contaminant concentrations and salinity, and of the influence of the concentration and composition of suspended matter on the dissolved contaminants.

Sea water is not a matrix of choice for CBs, as the octano: water partition coefficients indicate that the compounds would be predominantly associated with sediment or biota.

The concentrations of arsenic naturally present in sea water make the discrimination of anthropogenic influences from natural processes difficult and, therefore, sea water is not indicated as an appropriate matrix.

Some sea areas (usually small and isolated) existed in which the inputs of contaminants are sufficiently large to cause marked elevations of contaminant concentrations in sea water, or in which changes in concentrations could be expected. In such areas it might be appropriate for national authorities to give more prominence to water analysis in monitoring programmes.

The monitoring of seawater at a more regular frequency than once every five years could be justified:

(1) in areas with enhanced levels of contaminants: and
(2) in areas where changes could be expected as a result, for example, of known reduction in inputs.

A distrinction must be made between near-shore waters, in which marked salinity gradients may be found and which are more likely to be influenced by riverine or land-based inputs of contaminants, and off-shore waters where gradients are normally substantially less marked, and which are more remote from the above-mentioned inputs of contaminants.

In document IMCO/FAO/UNESCO/WMO/IAEA/UN/UNEP (1980), Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP), Marine Pollution Implications of Coastal Area Development. Rep. Stud. GESAMP, (11): 114 p., is given a synoptic table of a preliminary programme of oceanographic observations which could be used for a compliance monitoring programme in seawater.

2.3 Compliance monitoring of sediments*

2.3.1 Introduction

While methods for the chemical and biological characterisation of water-borne contaminants are applied in regulatory and monitoring programmes in many countries, methods for the assessment of sediments are less widely or uniformly established.

Sediments may act as a sink for, and source of, toxic chemicals through sorption of contaminants to particulate matter. The effects of surface water contamination become integrated over time and space, and a hazard to aquatic communities (both pelagic and benthic) is created which is not directly predictable from observations of contaminant concentrations in the water column. Sediments can serve as historical records of change due to both man-made pollution and natural environmental causes. For example, lake

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* OECD, 1992

sediments reflect surface water quality more consistently than do flowing rivers even though there may be seasonal changes in the lake environment, e.g. metal cycling in hypolimnetic waters.

Effects on benthic organisms are of concern because in many ecosystems the sediment community plays an important role in the recycling of detrital material to the pelagic community. In addition, benthic organisms are a critical component of a variety of aquatic food webs. Thus there is a need for sediment quality objectives that may be used as a scientific basis for the development of standards to protect ecosystems from the effects of sediment contamination, and to manage contaminated sediment in the long term. Therefore the main objectives are:

(i) to consider the methods available for use in developing environmental quality objectives (or criteria) for sediments, and to reach consensus on the methods most appropriate for this purpose;

(ii) to recommend the most appropriate test methods to assess:

(a) the toxicity of sediments;
(b) the toxicity of a particular chemical or group of chemicals to sediment-dwelling organisms

2.3.2 Useful methods

A number of potentially useful methods exist which namely are:

- equilibrium partinioning;
- interstitial water quality;
- spiked sediment toxicity;
- reference concentrations;
- apparent effects threshold;
- screening level concentrations;
- sediment quality triad;
- tissue residue

The main methods for use in the development of sediment quality objectives are:

(i) Equilibrium partitioning:

The equilibrium partitioning method is limited to chemicals for which a partitioning model is available describing the partition as a function of the properties of the chemical and the characteristics of the sediment. An appropriate guideline must be developed to measure K_{ow} for non-ionic organic chemicals (log K_{ow}>5).

(ii) Interstitial water quality:

This method is similar to the equilibrium partitioning method except that, instead of interstitial water concentrations being predicted, they are measured. The interstitial water quality method could be used for chemicals for which no adequate partitioning model is available.

(iii) Spiked sediment toxicity:

This method is an empirical determination of dose-response data for individual chemicals and chemical mixtures. The test data are used to predict concentrations of concern under field conditions. The method is only applicable to chemicals for which analytical techniques for determining interstitial water concentration are available.

In order to consider test methods for assessing toxicity of sediment, and for determining chemicals' toxicity to sediment-dwelling organisms, a series of questions must be answered such as:

(i) Which sediment phase is most appropriate for testing?

(ii) What test methods are available and what are their limitations?

(iii) How might toxicity identification evaluation (TIE) methods be used in assessments of contaminated sediments?

(iv) How might toxicity tests be field validated? How necessary is this?

(v) Which laboratory test variables need addressing?
  - organisms;
  - organism culture system;
  - toxic endpoint;
  - statistical method;
  - test sediment type;
  - effects of particle size;
  - others.

(vi) Do field or in situ methods need addressing? If so, what are the significant test variables?

Toxicity tests can be useful tools for assessing the degree and extent of impact of contaminant sediments on aquatic ecosystems. They are also useful for deriving sediment quality objectives via spiking of test chemicals into clean sediments. Careful consideration must be given, however, to the study objectives when selecting appropriate sediments, test organisms and response endpoints. The test species selected must be appropriate for the study objective and shown to be sensitive to relevant chemicals or classes of chemicals. Study objectives must also be carefully considered when designing sampling strategies and techniques for handling sediments. Ultimately, in order to provide a solid regulatory basis for the use of sediment toxicity tests the approaches used must be subjected to rigorous field validations and testing as well as laboratory development in order to determine optimal testing procedures.

Ideally, regulatory decision should be based upon sediment assessments such as the sediment quality triad where all the following data would be available: benthic community structure, toxicity test results and chemical analyses. This is seen as a strategic aim rather than an immediate possibility.

Toxicity identification evaluation (TIE) procedures which utilise toxicity-based fraction approaches are the only methods currently available to link toxicity to specific contaminants in a causal manner for field-collected sediments. These procedures present a logical and useful extension of integrated assessment approaches, such as the sediment quality triad.

Each method is evaluated with respect to the following characteristics:

(i) Chemical specificity: Can the method be used to derive a concentration for a specific chemical?

(ii) Causality: Are the observed effects caused by the specific chemical?

(iii) Chronic effects: Does the method consider chronic toxicity endpoints?

(iv) Bioaccumulation: Does the method consider food chain accumulation and ingestion of contaminated sediment for (i) benthos, (ii) fish?

(v) State of development: Is the method ready for use (tested, validated, used)?

(vi) Bioavailabiltiy: How generally applicable is the method across sediment types? Are sediment quality objectives a function of the bioavailable phase?

(vii) Applicability: Is the method applicable to bedded sediments or suspensions?

(viii) Recommendation: On the basis of the foregoing evaluations, can the method be recommended for use in deriving sediment quality objectives?

Scores are shown in Table VII.5

The most important characteristics were felt to be chemical specificity, causality, chronic effects, state of development and bioavailability. Causality and bioavailability were considered particularly important. If a method failed to meet one or more of these criteria, it was eliminated. None of the methods was judged acceptable, in the present state of development of sediment quality objectives, for chemical substances that bioaccumulate.

Table VII.5

Evaluation of the present state of development of eight method for deriving sediment quality objectives

Elements/characteristics Method	Chemical Specificity	Causality	Chronic Effects	Bioaccu-mulation benthos/ fish	State of Develop-ment	Bioavalla-bility	Applicabi-lity (a)	Can be reccomen-ded
Equilibrium Partitioning	++	++	+	+/--	++b)	++b)	BS*	yes
Interstitial Water Quality	++	++	+	-/--	-	+	B	yes
Spiked Sediment Toxicity	++	++	+c)	+/--	+d)	+e)	BS*	yes
Reference Concentrations	++	--	--	+/	++	--	BS	no
Apparent Effects Threshold	++	--	-/+f)	-/--	++	+e)	B	no
Screening Level Concen-trations	++	--	+	-/--	-	+	B	no
Sediment Quality Triad	--	--	+	-/--	+	-	B	no
Tissue Residue	*	*	*	*/--	--	*	B*S*	no

Table key:

++ High - Low
+ Medium -- Very low
a) To bedded sediments (B), suspended sediments (S)
b) Well developed for organic chemicals and is being developed for metals and other chemicals
c) For freshwater organisms only
d) Methods and guidelines need to be developed
e) If concentrations are properly normalised to reflect biological availability, e.g. by organic carbon or acid volatile sulphides.
f) Chronic effects on benthic organisms in field situations can be considered
* There is potential for development

2.3.3 Objectives of sediment toxicity tests

At all times it is important to be clear about the objectives of contaminated sediment studies, as the objectives are vital to selection and/or development of appropriate test systems.

There are a number of reasons for developing and utilising sediment toxicity tests:

(i) to aid in setting quality standards for individual compounds;

(ii) to assess the impact of discharges of sediments associated with receiving waters, such as sediment disposal associated with dredging activities;

(iii) to assess the persistence of toxicity in sediments following the alteration, amelioration or cessation of toxic discharges;

(iv) to predict the impact on sediment-dwelling organisms exposed to new substances that may be released to the environment;

(v) to estimate the degree to which toxicity is responsible for low benthic species diversity in impacted systems.

2.3.4 Sediment characterisation

A wide range of marameters may be relevant in characteristing the sediment associated with solid phase tests; they depend on the purpose of the investigation. The following key parameters are frequently necessary for interpretation of the toxicity test results:

- **Particle size distribution:**

Particle size may influence the partitioning of chemicals, particularly ionisable organics, between sediment and water. In solid phase tests, the tolerance range of the chosen organism to particle size must also be considered (Dewitt et al., 1989).

- **Dissolved oxygen:**

A critical factor to monitor in overlying water, particularly in sediments with high biological or chemical oxygen demand.

- **Organic carbon content:**

The dominant normalizing factor for bioavailability of nonpolar organic chemicals

- **Total ammonium concentration:**

Frequently a source of toxicity in sediments from eutrophic water systems, resulting from the natural degradation of organic matter, and should be measured in overlying water or in some instances pore water.

- **Acid volatile sulphides (AVS):**

A dominant factor controlling the bioavailability of some cationic heavy metals.

- **pH:**

  A key factor influencing the bioavailability/toxicity of some contaminants (e.g. ammonia), pH is also an important determinant in evaluating the tolerance range of some organisms. It should be measured in overlying water and the solid phase sample, if possible.

The following may also be relevant on a site-specific basis:

- Biochemical Oxygen Demand;
- Chemical Oxygen Demand;
- Nitrate/nitrite;
- Chloride;
- Sulphate;
- Redox (Eh) potential;
- Dissolved Organic Carbon (pore water);
- Conductivity;
- Salinity;
- Hydrogen sulphide;
- Suspected or spiked chemical contaminants

2.3.5 Sampling and storage of test sediment

Sediments for toxicity tests should be fresh, and handled in a way that minimises alterations that may affect the toxicity to organisms exposed in the laboratory. When sediments are sampled for toxicity tests, parallel samples are often subjected to chemical, physical and/or biological investigations. Therefore the combined objectives of the particular investigation determine the sampling design, including the equipment used, sampling points, depth of sediment and time for sampling.

Sediments for biological investigations (evaluation of benthic community structure) are usually processed (screened) and preserved on-site, while samples for chemical and physical characterisation are handled and stored according to procedures more or less specific to the particular test. For purposes of sediment toxicity evaluations it is important to obtain sediments with as little disruption as possible, to allow for realistic laboratory evaluation of *in situ* conditions.

In order to make it possible to verify test results from a toxicity test, the following points should be considered carefully:

(i) The point of sampling is described in enough detail (map, coordinates, water depth).

(ii) The time (year, month, day, hour) of sampling and person (organisation) responsible for sampling are reported.

(ii) The equipment (sampling device) and the approximate amount and depth of sediment taken should be recorded. If toxicity test results will be compared with other measurements, then samples must be collected in the same way.

(iv) Sediments for toxicity testing must be kept cool (4°C) during transport and storage. This is to minimise alterations that may occur.

(v) Toxicity tests should be initiated as soon as possible after sampling. The time between sampling and test initiation should be as soon as possible, but preferably in less than two weeks. This is applicable when sediments have been stored at 4°C. Freezing is not recommended for sediments to be used in toxicity tests.

2.3.6 Assessing contaminated sediments

The ability to define contaminants responsible for toxicity in contaminated sediments provides a unique opportunity for insights concerning remedial and regulatory activities, including:

(i) identification of discharges responsible for sediment contamination resulting toxicity;
(ii) identification of unsuspected contaminants responsible for toxicity in sediments;
(iii) identification of point versus non-point source impacts resulting in toxic sediments;
(iv) evaluation of disposal options for dredged materials.

One of the most attractive features of the TIE for evaluating contaminated sediments is that it enables a toxicilogically and chemically focused approach to identifying cause and effect relationships. Overall, it is felt that TIE procedures represent a logical and useful extension to integrated assessment approaches such as the sediment quality triad.

2.3.7 Water Quality Criteria Approach

The water quality criteria approach compares the concentrations of individual contaminants present in sediment interstitial water with water quality criteria (WQC). Existing WQC have been developed from a broad range of toxicological studies using a wide range of aquatic organisms. These criteria have been used in the regulatory context to specify contaminant levels that if not exceeded will protect 95% of aquatic life from adverse effects.

A major assumption of the approach is that water column organisms used to develop WQC have the same sensitivities as infaunal benthic organisms. Also, it is assumed that the major route of contaminant exposure is from the interstitial water and exposure from ingestion of contaminants on sediments is not significant.

The principal advantage of this approach is that it relies on existing toxicological databases used to develope WQC. The approach requires only the additional measurement of the contaminant concentration in the interstitial water.

The approach has several disadvantages: (a) WQC are available only for a limited number of contaminants; (b) the toxicological data used to develop WQC were from sediment-free bioassays so there is no consideration of the effect that soluble or particulate organic matter, present in interstitial water, may have on contaminant bioavailabiltiy; (c) the potential to increase contaminant body burden through ingestion or direct contact with sediment contaminants is not taken into account; and (d) suitable methods are still being developed for the isolation and measurement of contaminant concentrations in interstitial water.

2.4 Compliance monitoring of biota

For monitoring chemical contaminants in the sea, marine organisms are commonly used. It is well known that they can concentrate toxicants by uptaking them from water and sediment as dissolved or particulate matter, which enter their organism via gills, digestive tract or tegument epithelia. Toxicants are then stored in various tissues and organs, among which a target is generally determined which will be used then as main indicator. Elimination and excretion happen via several routes.

It is difficult to find the right species for monitoring purposes. Environmental indicators are suitable for the observation of long-term development in an ecosystem, as well as for planning and controlling effects of anthropogenic activities.

2.4.1 Definitions

Figure VII.1 shows a proposal for the classification of bioindication (Hertz, 1991).

Bioindication means the time-dependent, sensitive response of measurable quantities of biological objects and systems to anthropogenic influences on the environment. In general, a distinction can be made between:

- bioindication as a qualitative method for the detection of the presence of pollutants, and
- biomonitoring as a more quantitative method for the determination of the effects of the pollutants present.

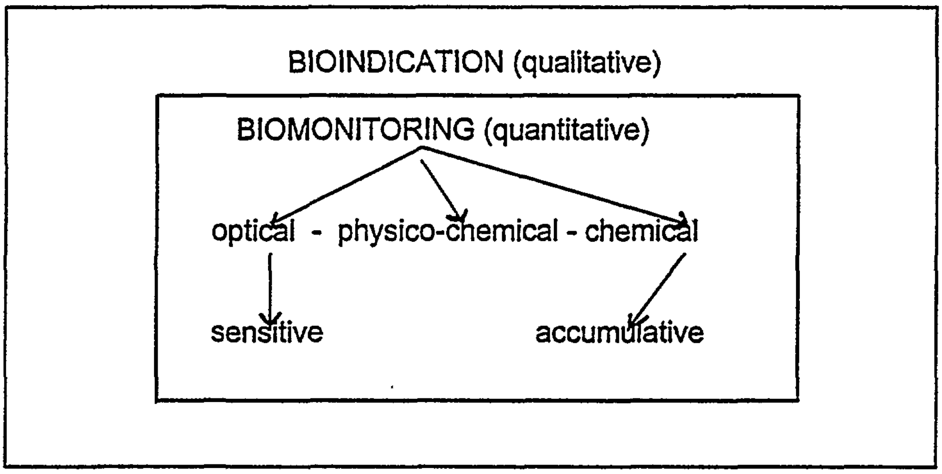

Figure VII.1 Classification of bioindication (from Hertz, 1991)

«Biomonitors are organisms which can be used for the recognition and quantitative determination of anthropogenically induced environmental factors». For the detection and recognition of water pollution, biological organisms which respond sensitively and specifically to a given pollutant can be used. In addition, organisms that readily amass the polluting components without changing their chemical nature may be used as accumulators. This classification into sensitive and accumulative biomonitors is now a well-accepted terminology.

2.4.2 Sensitive biomonitors

They are used in aquatic ecosystems as integrator of the pollution stresses caused by contaminants in order to provide early warning systems. They can be divided into two categories:

- ecological surveys
- toxicity testing

Ecological surveys

They may use indicator species or assessments based on the composition of biological communities and numerical diversity. By making comparisons between affected and control areas, ecological surveys can indicate the health of a water body exposed to pollutant loadings.

Toxicity testing

It is used to obtain badic information about the general toxicity of effluents which are expected to be introduced into an ecosystem. A great number of toxicity tests have been performed to answer various questions.

The most commonly used are summarized as follows:
Acute toxicity induces death or strong physiological problems after a short term exposure following contaminant absorption through:

- skin
- gill
- digestive tract

Long term toxicity concerns toxic effects induced by a low level contamination of pollutants which, when repeated, have cumulative effects.

The first one consists of determining mortality after a fixed time of exposure (24 h to 3 months) in correlation with increasing doses of toxicant:

Lethal dose 50 (LD50) induces 50% mortality within the investigated population.

The second one consists of determining consecutive mortality by using a constant dose of toxicant in correlation with increasing duration:

Lethal time 50 (LT50) is the theoretical duration after which 50% of the investigated oranisms exposed to a given dose will die.

The investigations can be used for the prediction of environmental effects of a waste, for the comparison of toxicants on animals or for the regulations of effluent discharge.

2.4.3 Selection of contaminants

Among the many possible chemical species which could be considered, the bioaccumulation of heavy metals has been studied most extensively. They are important polluting elements in many biological systems. They correspond to trace metals which are the following: arsenic, cadmium, chromium, copper, lead, mercury, nickel, tin and zinc.

Many other chemical substances are measured for monitoring purposes: DDT and other chlorinated pesticides, polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons.

The selection of substances to be monitored should be based on the following considerations:

- the *aims of the monitoring programme*; (see Table VII.6)
- the findings of the pilot study (which contaminant present at a significant level will justify further study?);
- the ability of the analyst to measure these substances with the required accuracy and precision.

2.4.4 Selection of organisms

The choise of the test organisms must be guided by several criteria:

- the abundance of the species;
- their geographical range: organisms must be ubiquitous so that the comparisons could be made between areas, countries, continents and possibly hemispheres;
- whether or not they constitute an important link in the food chain;
- the organisms accumulates the contaminant without being affected by the levels encountered;
- the organism is sessile and thus representative of the area of collection;
- the organism is sufficiently long-lived, to allow sampling of more than one year class if desired;
- the organism is of a reasonable size, to give adequate tissue for analysis;
- the organism is easy to sample all the year long;
- the organism is easy to handle in experimental work, robust to survive in the laboratory, allowing investigations on uptake, storage and elimination of contaminants;
- the organisms must offer the possibility of working in situ on the population level and with native communities;
- the organism exhibits high concentration factors;
- the organism is tolerant of brackish waters, to allow comparisons to be made between estuarine and offshore sites.

2.4.5 List of suggested organisms to be used for monitoring chemical contaminants

MED-POL species

For the purposes of the long-term programme for pollution monitoring in the Mediterranean, the following species, which are nearly all edible and which represent different ecotypes have been recommended:

Table VII.6

Chemical substances usually measured in marine organisms for compliance monitoring purpose (UNEP/FAO/IAEA, 1993)

Trace metals
Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg) Nickel (Ni), Tin (Sn) and Zinc (Zn).

DDT and its metabolites
o,p' - DDD, p,p'-DDD, o,p'-DDE, o,p'-DT and p,p' - DDT.

Chlorinated pesticides other than DDT
Aldrin, Alpha-Chlordane, Trans-Nonachlor, Dieldrin, Heptachlor, Heptaclor epoxide, Hexachlorobenzene, Lindane (gamma-BHC) and Mirex.

Polychlorinated biphenyls (PCBs)
Measurements are usually restricted to either a small number of individual compounds (known as congeners) or to the total concentration of PCBs.

Polyaromatic hydrocarbons
These can include:

2-ring compounds Naphthalene, 1-Methylnaphthalene, 2-Methylnaphthalene,
2,6-Dimethylnaphthalene and Acenaphthene.

3-ring compounds Fluorene, Phenanthrene, 1-Methylphenanthrene and Anthracene.

4-ring compounds Fluoranthrene, Pyrene and Benz(a) anthracene

5-ring compounds Chrysene, Benzo(a)pyrene, Benzo(e)pyrene and
Dibenz(a,h)anthracene

For the purposes of the Long-term programme for pollution monitoring and research in the Mediterranean sea (MED POL - Phase II) the following chemical contaminants were identified for analysis in marine organisms.

category I (mandatory)	category II (optional)
total mercury	total arsenic
organic mercury	radionuclides
cadmium	polynuclear aromatic hydrocarbons
halogenated hydrocarbons	

a) Bivalves

Mytilus galloprovincialis, or
Mytilus edulis, or
Perna perna, or
Donax trunculus

M. edulis, P. perna or D.trunculus can only be monitored as alternative species if Mytilus galloprovincialis does not occur in the area.

b) Demersal fish

Mullus barbatus, or
Mullus surmuletus, or
Upeneus molluccensis

M.surmuletus or U.molluccensis can only be monitored as alternative species if Mullus barbatus does not occur in the area.

c) Pelagic carnivore fish

Thunnus thynnus, or
Thunnus alalunga, or
Xiphias gladius

d) Pelagic plankton feeding fish

Sardina pilchardus

Other clupeids should only be monitored as alternative species if S.pilchardus does not occur in the area.

e) Crustaceans

Parapenaeus longirostris, or
Nephrops norvegicus, or
Penaeus kerathurus

N. norvegicus or P.kerathurus can only be monitored as alternative species if P.longirostris does not occur in the area.

The choise of organisms depends on the objective of the programme and the following examples may be proposed:

- filter feeding molluscs (Mytilus edulis) reflect contaminants in the water.
- herbivorous molluscs (Littorina littorea, Patella vulgata) are indicative of contaminants in plants and sea weeds.
- deposit feeders (Scrobicularia plana, Macoma balthica, Nereis diversicolor) reflect contaminants of the water but are also influenced by the ones of sediments.

The aims of programmes involving the collection and analysis of marine organisms, the sampling strategy, the storage and pre-treatment of samples, the analytical quality assurance and the documentation and reporting of data, are presented in a comprehensive manner in document UNEP/IOC/IAEA/FAO: Contaminant monitoring programmes using marine organisms: Quality Assurance and Good Laboratory Practice. Reference Methods for Marine Pollution Studies No.57, UNEP 1990.

VIII. COMPLIANCE MONITORING IN «HOT SPOT» AREAS[*]

1. DEFINITIONS

Hot spots areas are:

(a) **Point sources** on the coast which potentially **affect** human health, ecosystems, biodiversity, sustainability or economy in a significant manner. They are the **main points where high levels of pollution loads** originating from domestic or industrial sources are being discharged;

(b) Defined **coastal areas** where the **coastal marine environment is subject to pollution** from one or more point or diffused sources on the coast which potentially **affect** human health in a significant manner, ecosystems, biodiversity, sustainability or economy.

2. HOT SPOTS INDICATORS (PRIMARY)

- BOD, COD
- nutrients (phosphorus, nitrogen)
- total suspended solids
- oil (petroleum hydrocarbons)
- heavy metals
- persistent organic pollutants
- radioactive substances (whenever applicable)
- litter
- microorganisms (faecal coliforms, E.coli)
- organisms (e.g macroalgae for the soluble phase, mussels for the particulate phase and a detritus feeder for the sediment phase).

3. EVALUATION OF PRIORITY HOT SPOTS

A ranking system must be developed to show the severity of each of the effects on the identified hot spots.

It will be required to prepare a table on the priority hot spots by evaluating them using the following criteria:

- public health
- drinking water quality
- recreation
- other beneficial uses
- aquatic life (including biodiversity)
- economy and welfare (including marine resources of economic value).

4. TRANSBOUNDARY EFFECTS

- The transboundary effects of the hot spots should be mentioned in a separate column. These possible transboundary effects would involve the following:

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[*] WHO/UNEP, 1997

- Fisheries (F)
- Biodiversity (B)
- Reduction of regional value on tourism (L)
- Public Health (P)
- Habitats (H)

5. NATURE OF INVESTMENT AND ECONOMIC COSTS

The identification of the hot spots is necessarily linked to the identification of the causes and the problems that led to this critical situation. Therefore it is essential that a determination of the nature of investment, based on the causes identified and the intervention to be followed are required and a preliminary estimated financial requirement be proposed, taking into consideration the costs involved for similar projects in the particular country.

6. EXAMPLE

In Table VIII.1 are given the criteria which have to be evaluated having in mind that a weighing procedure with a ranking system have to be developed.

In Annex 4 are given questionnaires, necessary for the evaluation of municipal, industrial, and river discharges. Through the completion of the questionnaires with the necessary data, compliance control procedures could be followed, such as attainability analyses for the consideration of the suitability of the water bodies.

Table VIII.1

Hot spots Identification

Country	Name	Type	Public Health	Drinking Water Quality	Aquatic Life	Recreation	Other Beneficial Uses	Welfare and Economy*	WEIGHTED TOTAL	Relative Importance Index	Nature of Investment	Transboundary Aspect(s)	Preliminary Estimated Financial Requirements

IX. ANALYTICAL QUALITY CONTROL[*]

1. GENERAL

The role of the analytical laboratory is to provide qualitative and quantitative data to be used in decision making. To be valuable, the data must accurately describe the characteristics or the concentration of constituents in the sample submitted to the laboratory. In many cases, an approximate answer or incorrect result is worse than no answer at all, because it will lead to faulty interpretations.

Decisions made using water and wastewater data are far-reaching. Water quality standards are set to establish satisfactory conditions for a given water use. The laboratory data define whether that condition is being met, and whether the water can be used for its intended purpose. If the laboratory results indicate a violation of the standard, action is required on the part of pollution control authorities. With the present emphasis on legal action and social pressures to abate pollution, the analyst should be aware of his responsibility to provide laboratory results that are a reliable description of the sample. Furthermore, the analyst must be aware that his professional competence, the procedures he has used, and the reported values may be used and challenged in court. To satisfactorily meet this challenge, the laboratory data must be backed up by an adequate program to document the proper control and application of all of the factors which affect the final result.

In wastewater analyses, the laboratory data define the treatment plant influent, the status of the steps in the treatment process, and the final load imposed upon the water resources. Decisions on process changes, plant modification, or even the construction of a new facility may be based upon the results of laboratory analyses. The financial implications alone are significant reasons for extreme care in analysis.

2. QUALITY CONTROL PROGRAMME

Because of the importance of laboratory analyses and the resulting actions which they produce, a program to insure the reliability of the data is essential. It is recognized that all analysts practice quality control to varying degrees, depending somewhat upon their training, professional pride, and awareness of the importance of the work they are doing. However, under the pressure of daily workload, analytical quality control may be easily neglected. Therefore, an established, routine control program applied to every analytical test is important in assuring the reliability of the final results.

The quality control program in the laboratory has two primary functions. First, the program should monitor the reliability (truth) of the results reported. It should continually provide an answer to «How good (true) are the results submitted?» This phase may be termed «measurement of quality». The second function is the control of quality in order to meet the program requirements for reliability. For example, the processing of spiked samples is the measurement of quality, while the use of analytical grade reagents is a control measure.

This chapter considers the factors which go into creating an analytical result, and provides recommendations for the control of these factors in order to insure that the best possible answer is obtained. A program based upon these recommendations will give the analyst and his supervisor confidence in the reliability and the representative nature of the sample characteristics being reported.

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[*] U.S.EPA, 1973 and UNEP/IOC/IAEA/FAO, 1990

3. ANALYTICAL METHODS

In general, the widespread use of an analytical method indicates that it is a reliable means of analysis, and this fact tends to support the validity of the test result reported. Conversely, the use of a little-known technique forces the data user to place faith in the judgement of the analyst. When the analyst uses a «private» method, or one not commonly accepted in the field, he must stand alone in defining both his choice of the method and the result obtained.

The need for standardization of methods within a single laboratory is readily apparent. Uniform methods between cooperating laboratories are also important in order to remove the methodology as a variable in comparison or joint use of data between laboratories. Uniformity of methods is particularly important when laboratories are providing data to a common data bank, or when several laboratories are cooperating in joint field surveys. A lack of standardization of methods raises doubts as to the validity of the results reported. If the same constituent is measured by different analytical procedures within a single laboratory, or in several laboratories, the question is raised as to which procedure is superior, and why the superior method is not used throughout.

In field operations, the problem of transport of samples to the laboratory, or the need to examine a large number of samples to arrive at gross values will sometimes require the use of rapid field methods yielding approximate answers. Such methods should be used with caution, and with a clear understanding that the results obtained do not compare in reliability with those obtained using standard laboratory methods. The fact that «quick and dirty» methods have been used should be noted, and the results should not be reported along with more reliable laboratory- derived analytical information. The data user is entitled to know that approximate values have been obtained for screening purposes only, and that the results do not represent the customary precision and accuracy obtained in the laboratory.

4. CONTROL OF ANALYTICAL PERFORMANCE

4.1 Introduction

This chapter is limited to a discussion of the control of analytical performance in the laboratory. It is assumed that a valid sample has been properly taken, preserved, and delivered to the laboratory for analyses; that the laboratory analyses were done according to currently-recognized methods; and that the recording and reporting of subsequent laboratory results were done in a systematic, uniform, and permanent fashion. It must be recognized (and practiced!), however, that quality control begins with the sample collection and does not end until the resulting data are reported. The laboratory control of analytical performance is but one vital link in obtaining valid data. A continuous rapport and conscientious use of quality control between field sampling, laboratory analyses, and management decisions are necessary to insure this validity.

4.2 Precision and Accuracy

Precision refers to the reproducibility among replicate observations. In an Analytical Quality Control Program, it is determined, not on reference standards, but by the use of actual water samples which cover a range of concentrations and a variety of interfering materials usually encountered by the analyst. Obviously, such data should not be collected until the analyst is thoroughly familiar with the method, and has obtained a reproducible standard curve. For colorimetric analyses, the initial standard curve should include a blank and a series of at least eight standards encompassing the full concentration range to be used for routine sample analyses. Subsequently, at least two standards (a high and a low) should be analyzed to verify the original standard curve. For other measurements, such as pH, conductivity, turbidity, etc., instruments should be standardized according to *manufacturer's instructions and sound, scientific practices.*

There are a number of different methods available for the determination of precision. One method that has been successfully employed by experienced Auto Analyzer users, and can be adapted to many other analytical instrumentation and chemical procedures, is described as follows:

a. Four separate concentration levels should be studied, including a low concentration near the sensitivity level of the method, two intermediate concentrations, and a concentration near the upper limit of application of the method.

b. Seven replicate determinations should be made at each of the concentrations tested.

c. To allow for changes in instrument conditions, the precision study should cover at least two hours of normal laboratory operation.

d. In order to permit the maximum interferences in sequential operation, it is suggested that the samples be run in the following order: high, low, intermediate, intermediate. This series is then repeated seven times to obtain the desired replication.

e. The precision statement should include a range of standard deviations over the tested range of concentration. Thus, four standard deviations will be obtained over a range of four concentrations, but the statement should contain only the extremes of standard deviations and concentrations studied.

An example of data generated from such an approach is shown in Table IX.1

Table IX.1

Precision data on water samples for phosphorus autoanalyzer method

Conc., (mg P/l)

Sample	Area 1	Area 2	Area 3	Area 4
1	0.05	0.10	0.48	0.62
2	0.06	0.10	0.48	0.62
3	0.06	0.10	0.49	0.62
4	0.06	0.11	0.48	0.63
5	0.06	0.11	0.48	0.62
6	0.06	0.11	0.48	0.62
7	0.06	-	-	0.62
Avg.	0.059	0.105	0.482	0.621
s	0.004	0.005	0.004	0.004

The resulting precision statement would read as follows:

«In a single laboratory, using surface water samples at concentrations of 0.06 and 0.62 mg P/l, the standard deviation was ± 0.004 (Analytical Quality Control Laboratory)»

Thus, the statement contains the number of laboratories involved, the type of samples, the concentrations used, the resulting standard deviation(s) and the reference source.

Accuracy refers to a degree of difference between observed and known, or actual, values. Again, accuracy should be determined on actual water samples routinely analyzed, and preferably, on the same series as those used in the precision determinations. The method employed by experienced AutoAnalyzer users consists of the following key steps:

a. Known amounts of the particular consituent should be added to actual samples at concentrations where the precision of the method is satisfactory. It is suggested that amounts be added to the low-concentration sample, sufficient to double that concentration, and that an amount be added to one of the intermediate concentrations, sufficient to bring the final concentration in the sample to approximately 75% of the upper limit of application of the method.

b. Seven replicate determinations at each concentration should be made.

c. Accuracy should be reported as the percent recovery at the final concentration of the spiked sample. Percent recovery at each concentration should be the mean of the seven replicate results.

Data were obtained with this approach by using two of the water samples previously used in the precision study reported in Table IX.1 (Area 1 and Area 3). They are reported in Table IX.2.

Table IX.2

Accuracy data on water samples for phosphorus autoanalyzer method

	Conc., (mg P/l)	
Sample	Area 1 (Added 0.06 mg/l P)	Area 3 (Added 0.3 mg/l P)
1	0.105	0.74
2	0.105	0.75
3	0.105	0.75
4	0.110	0.73
5	0.110	0.74
6	0.110	0.75
7	0.105	0.75
Avg.	0.107	0.74
% Recovery	$\left[\frac{0.107}{0.059+0.06}\right] \times 100 = 90$	$\left[\frac{0.74}{0.48+030}\right] \times 100 = 95$

Again, in order to contain the key elements, the accuracy statement would read as follows:

«In a single laboratory, using surface water samples at concentrations of 0.11 and 0.74 mg P/l, recoveries were 90% and 95%, respectively (Analytical Quality Control Laboratory)».

Once collected and documented, these precision and accuracy data may be used in a number of ways. Two important examples are: (1) They present clearcut evidence that the analyst in question is indeed capable of analyzing the water samples for that particular parameter. That is, he has the standard method under control, and is capable of generating valid data; and (2) the data can be used in the evaluation of daily performance in reference to replicate samples, spiked standards and samples, and in the preparation of quality control charts.

As observed, the above methods can be adapted to other chemical procedures and analytical instruments. They have been used on manual titration methods for such parameters as alkalinity, chloride, and hardness; on general inorganic instruments such as pH, conductivity, selective ion, and turbidity meters; and on the Beckman Carbonaceous Analyzer. Other instruments, such as atomic absorption and flame emission spectrophotometers, could also be evaluated by these methods; however, radiological instrumentation and gas chromatography systems require special techniques.

4.3 Evaluation of Daily Performance

Once valid precision and accuracy data are available on the method and the analyst, systematic daily checks are necessary to insure that valid data are being generated. As previously noted, at least two standards (a high and a low) should be analyzed routinely along with a blank to determine that comparable operating conditions exist. If the data do not substantiate such control, the anlyst must systematically trouble-shoot his system until the problem is corrected.

In order to document that reproducible results are being obtained (i.e., precision of the method), it is necessary to run replicate samples. Although frequency of such replicate analyses is, by nature, dependent on such factors as the original precision of the method, the reliability of the instrumentation involved, and the experience of the analyst, good laboratory technique is to run duplicate analyses at least ten percent of the time. The resulting data should agree favorably with the known precision of the method. If they do not, the system is not under control, and results are subject to question.

Concurrently, quality control should include assurance that the daily system is actually measuring what is in the sample (i.e., accuracy of the method). Although it is far preferable to have obtained values check with known or actual values, it should be recognized that inaccuracy does not destroy the value of data if the degree and precision of the error is known and taken into account. In order to account for background contamination and/or sample interferences, and as a matter of practice, spiked samples should be used in addition to standards. As in the case of duplicate sample analyses, good laboratory technique dictates that spiked samples be run at least ten percent of the time.

Thus, daily control of analytical performance in the laboratory requires approximately 15-20 percent of the analyst's time. Considering the elapsed time and combined efforts of skilled personnel that are represented in a final laboratory result, this is a comparatively small price to pay for, not a «number», but a valid concentration value.

<u>A most convenient way of recording the obtained precision and accuracy data is through the preperation of quality control charts.</u> Plotting of said data systematically answers the question as to whether the laboratory analyses are under control, and is useful in observing developing trends of positive or negative bias.

4.4 Quality Control Charts

Quality control charts were originally developed for the control of production processes where large numbers of items were being manufactured and inspected on an essentially continuous basis. As shown in Figure IX.1 a control chart consists of a graphical chart with the vertical scale plotted in units of the test result and the horizontal scale in units of time or sequence of results. The upper and lower control shown on the chart are used as criteria for action, or for judging the significance of variations between duplicate samples. The central line represents the average or the standard value of the statistical measure being plotted.

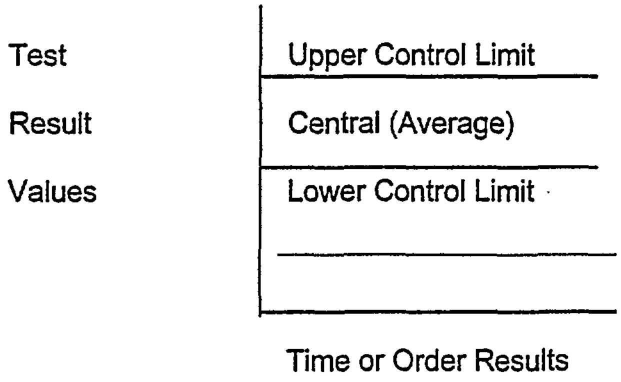

Figure IX.1 Essentials of control chart

As observed in the previous section on the evaluation of daily performance, daily precision and accuracy data can be plotted by means of these quality control charts to determine if valid, questionable, or invalid data are being generated from day to day. There are several techniques available for actually constructing quality control charts and plotting subsequent data. Two currently is use are the Shewhart technique and the CuSum technique. In both techniques, precision control charts are constructed from duplicate sample analysis, whereas, accuracy control charts are constructed from spiked samples or standards data generated in monitoring recovery efficiencies. At least 15 to 20 sets of duplicate and 15 to 20 sets of spiked sample data from an in-control process are necessary for the initial construction. A system is initially said to be in control when the standard deviation and recovery efficiency data for a given parameter are comparable to those obtained by other experienced laboratories. It is also necessary that the initial and subsequent sets of data be obtained under normal laboratory operation conditions, that the same analyst or group of analysts run the analysis, and that the same analytical method is used.

4.4.1 Cumulative - Summation (CuSum) Quality Control Charts

There are various systems currently available for plotting data in the form of cumulative sum charts. One system that has been in continuous use is that of Anon. (1969). It has proved most useful in monitoring the validity of data generated by a contracting laboratory and is currently being used routinery to daily record intra-laboratory performance in technical operations.

4.4.2 Shewhart Quality Control Charts

Dr. Walter A. Shewhart of Bell Telephone developed the basic theory of control charts in the 1920's. His book on statistical quality control grew out of this original work. Since then, industrial acceptance of these control (Shewhart, 1931) chart concepts and other statistical techniques have refined and quantitated the quest for quality in manufacturing. Although originally developed for control of production processes when large number of articles were being manufactured and inspected on an essentially continuous basis, these same concepts have been readily adapted to laboratory operations where the analyst produces comparatively fewer results on an intermittent basis.

As in the CuSum approach, precision control charts are prepared from data resulting from duplicate sample analyses and accuracy control charts from duplicate spiked standards or samples. Once the control charts are constructed, however, data are plotted as individual values rather than cumulative sums.

Certain constants (factors) are also involved in the preparation of Shewhart Charts. Depending upon how the data are grouped, what the size of each grouping is, and what control limit formulation is being calculated.

4.4.3 Precision Control Charts

These charts are developed by collecting data for many samples, a minimum of 15 to 20, run in duplicate under assumed controlled conditions.

4.4.4 Accuracy Control Charts

As in the above system, these charts developed by collecting data for many samples, a minimum of 15 to 20, but on spiked samples (preferably) or standards under assumed controlled conditions. Again, these data should be generated over an extended period of laboratory time, and be representative of normal operating conditions

5. DATA HANDLING AND REPORTING

5.1 Introduction

To obtain meaningful data on water quality, the laboratory must first collect a representative sample and deliver it unchanged for analysis. The analyst must then complete the proper analysis in the prescribed fashion. Having accomplished these steps, one other important step must be completed before the data are of use. This step includes the permanent recording of the analytical data in meaningful, exact terms, and reporting it in proper form to some storage facility for future interpretation and use.

The brief sections (see Annex 5) discuss the data value itself (the Analytical Value), recording and reporting the value in the proper way, means of quality control of data, and storage and retrieval.

X. ATTAINABILITY ANALYSES[*]

Consideration of the suitability of a water body for attaining a given use is an integral part of the water quality standards review and revision process. This is intended to assist States in answering three central questions:

(1) What are the aquatic protection uses currently being achieved in the water body?
(2) What are the potential uses that can be attained based on the physical, chemical and biological characteristics of the water body? and,
(3) What are the causes of any impairment of the uses?

The data and information collected from the water body survey provide a basis for evaluating whether the water body is suitable for a particular use. It is not envisioned that each water body would necessarily have a unique set of uses. Rather the characteristics necessary to support a use could be identified so that water bodies having those characteristics might be grouped together as likely to support particular uses.

Since the complexity of an aquatic ecosystem does not lend itself to simple evaluations, there is no single formula or model that will provide all the answers. Thus, the professional judgment of the evaluator is key to the interpretation of data which is gathered.

The most common desktop evaluations of use attainability are stastistical analyses of water quality monitoring data to determine the frequency of violation of criteria for the designated aquatic use. Statistical evaluations of contraventions of water qaulity criteria should consider the confidence intervals for the number of violations that are attributable to random variations (rather than actual water quality deteriorations).

For example, consider a monitoring station with 12 dissolved oxygen observations per year with a standard of 5 mg/l DO. If statistical analyses of the D.O observations indicate that the upper and lower confidence limits for the frequency of random violations of the 5 mg/l DO standard cover a range of 1 to 4 violations per year, a regulatory agency should be cautious in deciding whether actural use impairment has occured unless more that 4 violations are observed annually.

<u>The development of a manual on Attainability analyses should be a priority in a compliance monitoring programme.</u>

Tools that would be applicable to a use of attainability analyses and particularly for chemical evaluations is by use of indices. Many water quality indices have been developed.

The Denius water quality index is presented here as an example to show its applicability.

This index includes 11 variables and it has a scale which decreases with increased pollution, ranging from 0 to 100. The index is computed as the weighted sum of its sub indices. The 11 variables included in the index are: dissolved oxygen, biochemical oxygen demand, Eschericia coli, alkalinity, hardness, specific conductivity, chlorides, pH, temperature, coliform, and color. This index is unique in that the calculated water quality index could be matched to specific water uses. Dinius proposed different descriptor language for different index ranges depending on the specific water use under consideration as illustrated in Figure X.1. The index values can be derived from the following formula:

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[*] U.S.EPA, 1993

$$Q = \frac{5(DO) + 214(BOD)^{-0.642} + 400(5E.Coli)^{-0.30} + 300\ (Coli)^{-0.30} + 535\ (SC)^{-0.3565} +}{5 \quad + \quad 2 \quad + \quad 4 \quad + \quad 3 \quad + \quad 1}$$

$$\frac{+\ 62.9\ (Cl)^{-0.207} \quad + 10^{\ 1.974 - 0.00132(HA)} + 54\ (ALK)^{-0.178} + 10^{0.235\ pH + 0.440}}{+ \quad 5 \qquad\qquad 1 \qquad\qquad 0.5 \qquad\qquad 1} \quad \overline{+}$$

$$\frac{+\ 8\ (Ta\text{-}Ts) + 224 + 128\ (C)^{-0.288}}{2 \quad + \quad 1}$$

Note: If the pH is between 6.7 and 7.3, 100 should be substituted for the pH expression. If pH is greater than 7.3, the pH expression should be 10.

DO = dissolved oxygen in percent saturation
BOD = biochemical oxygen demand in mg/l
E.Coli = Eschericia coli as E.coli per ml
Coli = coliform per ml
SC = specific conductivity expressed in microohms per cm at 25°C
Cl = chlorides in mg/l
HA = hardness as ppm $CaCO_3$
ALK = alkalinity as ppm $CaCO_3$
pH = pH untis
Ta = actual temperature
Ts = standard temperature (average monthly temperature)
C = Color units

Once the quality unit is determined based on the above calculation, a comparison to Figure X.1 should reveal the quality of the water for a specific use.

Another useful index is the contamination index which helps to the assessment of the contribution of anthropogenic sources of metal contamination over time, in sediments. The Wedepohl ratio compares the amount of metal in the sediment sample with the concentration in an average shale (or sandstone). If, for example, scientists have measured silicon and aluminum, then have correlated metals with Si/Al ratios, a contamination factor (Cf) may be computed as follows:

Cf = (Co-Cp)/Cp
where: Co = surface sediment concentration
Cp = predicted concentration, derived from the statistical relation between the Si/Al ratio and the log metal content of old, pre-pollution sediments.

<table>
<thead>
<tr><th>PERCENT</th><th>PUBLIC WATER SUPPLY</th><th>RECREATION</th><th>FISH-SHELLFISH AND WILD LIFE</th><th>INDUSTRIAL AND AGRICULTURAL</th><th>NAVIGATION</th><th>TREATED WASTE TRANSPORTATION</th></tr>
</thead>
<tbody>
<tr><td>100
90</td><td>PURIFICATION NOT NECESSARY</td><td rowspan="3">ACCEPTABLE FOR WATER SPORTS</td><td rowspan="3">ACCEPT- FOR ALL FISH</td><td>PURIFICATION NOT NECESSARY</td><td rowspan="7">ACCEPTABLE</td><td rowspan="9">ACCEPTABLE</td></tr>
<tr><td></td><td>MINOR PURIFICATION REQUIRED</td><td rowspan="2">MINOR PURIFICATION NECESSARY FOR INDUSTRY REQUIRING QUALITY WATER</td></tr>
<tr><td>80
70</td><td rowspan="3">NECESSARY TREATMENT RECEIVING MORE EXTENSIVE</td></tr>
<tr><td></td><td rowspan="2">BECOMING POLLUTED
-
STILL ACCEPTABLE BACTERIA COUNT</td><td>MARGINAL FOR TROUT</td><td rowspan="2">NO TREATMENT NECESSARY FOR NORMAL INDUSTRY</td></tr>
<tr><td>60
50</td><td>DOUBTFUL FOR SENSITIVE FISH</td></tr>
<tr><td></td><td>DOUBTFUL</td><td>DOUBTFUL FOR WATER CONDUCT</td><td>HARDY FISH ONLY</td><td rowspan="2">EXTENSIVE TREATMENT FOR MOST INDUSTRY</td></tr>
<tr><td>40</td><td rowspan="4">NOT ACCEPTABLE</td><td>ONLY BOATING NO WATER CONTACT</td><td>COARSE FISH ONLY</td></tr>
<tr><td>30</td><td>OBVIOUS POLLUTION APPEARING</td><td rowspan="3">NOT ACCEPTABLE</td><td>ROUGH INDUSTRY USE ONLY</td><td>OBVIOUS POLLUTION APPEARING</td></tr>
<tr><td>20</td><td rowspan="2">OBVIOUS POLLUTION
-
NOT ACCEPTABLE</td><td rowspan="2">NOT ACCEPTABLE</td><td rowspan="2">OBVIOUS POLLUTION
-
NOT ACCEPTABLE</td></tr>
<tr><td>10</td><td>NOT ACCEPTABLE</td></tr>
</tbody>
</table>

Figure X.1 General raiting scale for the quality unit

Thus, $Cf < 0$ when the observed metal concentration is less than the predicted value; $Cf = 0$ when observed and predicted are the same; $Cf > 0$ when the observed is greater than the predicted value.

The Contamination Index (C_I) is found by summing contamination factors for metals in a given sediment.

Then,

$$C_I = \sum_{n=1}^{n} Cf = \sum_{n=1}^{n} (Co-Cp)/Cp$$

The toxicity Index (T_I) is related to the Contamination Index and is expressed by the following equation:

$$T_I = \sum_{i=1}^{i} (M_1/M_i) \,.\, Cf_i$$

where: M_i = the «acute» anytime criterion for any of the metals,
but : M_1 is always the criterion value for the most toxic of the metals.

The «acute» anytime criterion is defined as the concentration of a material that may not be exceeded in a given environment at any time. When evaluating Toxicity Indices, sampling stations should be characterized by their minimum salinities. This is because the toxicity of metals is often greater in freshwater than in saltwater.

A more detailed discussion of the development of the Contamination Index may be found in the U.S EPA publication, Chesapeake Bay: A Profile of Environmental Change (1983a) and A Framework for Action (1983c).

XI. ENFORCEMENT[*]

It is important to emphasize that enforcement is but one component of environmental quality management (EQM). As such, it must be consistent with the other components of EQM. For example, if legislation, development of standards, and permit conditions are not clear and unambiguous to both the discharging activity and to the regulatory agency, enforcement will be difficult, if not impossible.

One characterization of the components of EQM is:

- Perception of an environmental quality problem;
- Data collection, analysis, development of strategies to «solve» the problem;
- Legislation and rulemaking;
- Development and promulgation of standards;
- Issuance of permits;
- Application of environmental instruments to induce initial compliance;
- Enforcement of permit conditions against noncomplying activities.

From each component of the EQM cycle there should be feed-back to previous components of the cycle. It is also important to emphasize that all levels of government are involved in, and carry out activities with respect to, environmental management.

One of the important questions with respect to EQM, and with respect to the enforcement component EQM, is the allocation of management tasks among the levels of government. In addition, an integral problem of environmental quality management is the allocation of resources among the components of the EQM cycle and within the enforcement component.

Multiple actors are involved in each component of environmental quality management, including enforcement. An illustrative listing of actors and their roles is indicated in the following:

Public agencies: as regulatory bodies at all levels of governments of general jurisdiction and special agencies, such as the water authorities in the U.K., the Genossenschaften in Germany, air quality management districts in the U.S., and river basin agency in France. Their role consists of:

- rule making
- standard setting/developing guidelines
- issuing permits, making inspections
- monitoring discharges, checking accuracy of data collected by discharges (i.e. self-monitoring data)
- imposing sanctions for non-compliance
- developing cooperative agreements with public and private dischargers
- assisting in environmental audits
- publicizing performances, good and bad, of discharging activities maintaining and providing access to information on discharging activities
- developing and operating a complaint response system
- promoting cleaner process technologies.

Public agenices as discharging activities: Same role as for private entities/ activities.

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[*] OECD, 1985

Courts:

- determining whether or not discharging activity has been in compliance
- determining whether or not standards are «fair», or «reasonable»;
- determining whether or not the regulatory agency has performed its designated functions;
- *imposing judicial sanctions.*

Private activities, e.g., industrial activities, agricultural operations, mining operations, forest products operations, institutional operations. They are or should be involved in:

- rule making;
- setting of standards/developing guidelines;
- self-monitoring of quality of input raw materials;
  self-monitoring of discharges;
- developing cooperative agreements with regulatory bodies
  performing environmental audits.

Trade association

- presenting testimony in rule making, standard setting proceedings, performing research on pollution control and process modification technology;
- participating in the development of guidelines for environmental audits.

Insurance companies

- requiring environmental audits as condition of providing insurance coverage;
- establishing various standards of operations by activities before providing insurance coverage.

Public interest groups: e.g. environmental groups

- rule making;
- permitting;
- monitoring of performance of private activities and of public agencies;
- participating in joint groups with private activities and public bodies in developing standards and monitoring procedures;
- having access to courts against private and public polluting activities as well as against public regulatory agencies.

Enforcement can be improved by developing nine courses of action:

- At the level of regulations;
- At the level of permits;
- Improving monitoring;
- Developing cooperative agreements;
- Developing environmental auditing;
- Strenghtening controls and sanctions;
- Devising incentive measures;
- Enhancing information and publicity;
- Increasing agency capacity.

Because not all contexts of enforcement involve the same elements, these suggestions do not necessarily apply to all contexts or countries. Besides Governments should set their enforcement priorities.

The Mediterannean countries exhibit a wide spectrum of stages of political, social and economic development and the most appropriate form of control organization 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 governments.

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.

Information supply covers the assesmbly 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 which is normally responsible for enforcement. The analyses will also be supplied back to the information collecion 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 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.

XII. ORGANIZATION

1. INTRODUCTION

The organizational requirements for an effective pollution management programme cover a wide range of activities which have to be undertaken in order to achieve practical results in combating water pollution with the least expediture of money and time. The main such factors are:

- establishment of a coastal water control organization
- management of wastewater facilities (collection,treatment and disposal)
- monitoring of coastal waters and effluents
- research

2. ESTABLISHMENT OF A COASTAL WATER CONTROL ORGANIZATION

The task of coastal water control organization will be focussed on:

- collection of information
- decision and approval of pollution control policy
- implementation of policy
- control of achieved results

Normally all these items are under the responsibility of one organizational body but there are cases of splitting of these activities over one or two different administrative structures. The advantage of combining all these aspects under the same organization is the better synchronization of the different technical departments and the unique thinking pattern, which avoids the controversies between several responsible agencies.

2.1 Collection of information

For the development of the appropriate policy and strategy for water pollution control, the knowledge of the existing situation is very important, in order to enable the decision-makers to base this policy on precise and realistic data without imaginary predictions.

This information would cover the condition of the coastal and the inland waters (i.e. rivers) in the water catchment area, the estimation of the hydraulic and pollution loads of all pollution sources (land based and off-shore) and the content of development plans for the region, in order to predict the future impacts on the environment.

This procedure should be executed in the shortest possible time period in order to avoid discrepancies between the start and the end of the data collecting operation. Simple, quick and precise methods for data collection and interpretation are therefore very important. In this context the introduction and implementation of computerized systems is strongly recommended.

The collected data should be renewed at regular time intervals, in order to keep the information always updated to the changes occuring as time passes by. The importance of computer systems also for this procedure should again be pointed out.

2.2 Decision and approval of pollution control policy

After the completion of data collection, the main outlines of the pollution control strategy should be planned and analyzed. In this case the scientists, managers, technicians etc. responsible for the technical aspects of environmental measurements, should elaborate a strategy based on simple and reliable control methods taking into account all possible data and the related environmental impacts. A well designed and argumented technical plan with the least possible financial expenditures has many chances to be approved by the decision-makers. In this context it should be emphasized that highly sophisticated control methods with increased failure risks and financial costs should be avoided.

Due to the complexity of the environmental problems and the many technical, financial, social and political aspects involved in many pollution control strategy, the related decision-makers should consider all possible implications deriving from the proposed policy. Cooperation of regional authorities with governmental and international agencies is therefore essential for examining the correctness of the policy to be applied.

2.3 Implementation of policy

After the approval of the policy, the water control organization is responsible for its implementation. For a successful execution of this task the high eductional level and experience of the employed manpower is a basic assumption. In parallel, the cooperation and the discipline of a convinced public opinion, industry, communities etc with the responsible implementing body is the second condition which should be fulfilled in order to achieve permanent results. In this case, a simple and effective policy causing quick and visible improvements of the marine environment is the best persuading argument.

The implementation of the policy consists of the following general steps:

- legal cover (regulations, laws, etc)
- technical measures (i.e. installation of treatment plants, changes in industrial production, etc.)
- advertisement campaigns for the public

These actions should be executed simultaneously in order to obtain the aforementioned cooperation and acceptance of the policy by the interested bodies.

2.4 Control of achieved results

Once a policy is correctly applied the expected results will be achieved after a while. Nevertheless, a continuous control of the policy implementing conditions is necessary, since practice has shown that even the best strategy for combating pollution will be demolished when the control of the related conditions has not been continuously applied.

The relevant controlling department of the organization will be responsible for the regular inspection of industrial processes, wastewater installations, agricultural acitivties, etc. locating failures, lack of maintenance, operating problems, etc. The high professional background of the controlling personnel is essential for this procedure in order to keep the authority of the organization on the highest possible level. The second task of a controlling mechanism, is the monitoring of water quality and effluents.

3. MANAGEMENT OF WASTEWATER FACILITIES (COLLECTION, TREATMENT AND DISPOSAL)

3.1 Introduction

The administrative organization of wastewater installations is an essential part for the successful implementation of pollution control plan besides the efficient engineering solution. The experience has shown that even very sophisticated-designed facilities have failed to work successfully due to bad administrative organization and support.

No one type of administrative organization can be recommended as being suitable in all cases, since the economic, political and geographical conditions vary from one country to another. Some main factors which have to be considered in establishing the organizational scheme suitable for a particular case are the following:

- Existing organization of water supply
- Size of the area
- Development plans in the area
- Regional organizational scheme in the country

3.1.1 Existing organization of water supply

Since water supply programmes are normally in operation before the installation of wastewater facilities, the existing organizational body of water supply is often expanded, in order to cope with the programme of wastewater management. This expansion should always be based on the existing possibilities (manpower, financial capacity, operational autonomy) of the water supply body (company or agency), which will allow the prediction of an efficient management of the wastewater system (collection-treatment-disposal).

In some cases the establishment of a wastewater agency independent from the water supply system, which will be responsible for the design, construction and operation of the wastewater facilities is advisable, when the organizational capabilities of the existing water supply body are rather limited.

3.1.2 Size of the area

The size of the area to be served by a system wastewater collection, treatment and disposal has a significant importance for the establishment of the relevant organizational scheme: large communities producing large ammounts of urban and industrial wastes need a different organizational structure from small towns or villages where the existing technical services of the municipality can mostly cope with the related problems. An independent agency is normally established in large communities being responsible for all wastewater facilities.

3.1.3 Development plans in the area

Development plans cause the concentration of industrial, agricultural, touristic and ekistic activities according to the decided land uses. Therefore, the administrative organization for the management of the related wastewater facilities should be adapted to the complexity of the encountered problems and the variety and size of the installed units. Independent bodies with several departments for industrial, municipal and agricultural pollution control are often established in large areas with fast development rates for all abovementioned activities. This organizational scheme should follow the present state of development, in order to cope with the existing problems, without being too expanded in advance in the expectation of any development which eventually will never be achieved.

3.1.4 Regional organizational scheme in the country

The aforementioned considerations should always take into consideration the existing political and administrative structure in the region and in the country in general. Several organizational patterns exist all over the world, where central control of regional matters exists besides fully autonomous regions. Therefore, the establishment of the relevant wastewater management bodies should be adapted to the given political and administrative frame suitable for each country.

International experience in organizational aspects should then always be studied and analyzed by the local authorities in cooperation with experts, in order to take advantage from it without ignoring the existing circumstances in the region.

The most efficient way for managing a wastewater system is to create an independent organizational body which will be responsible for the operation and maintenance of the wastewater treatment plant.

The supervisor of this body will be the technical department of the municipality, which will control administratively the actions, expenditures, etc. of the above mentioned body, without interventing in the every-day operational and administrative matters. Therefore, the needed autonomy is secured, so that decisions about operational failure, personnel requirements, equipment maintenance, etc. which require a certain flexibility will not be delayed by bureaucracy.

This organizational way is mostly applied in treatment plants of large towns, where the size and complexity of most of the treatment units cannot be managed directly by the municipality authorities.

For small plants, where the scale of problems is rather limited, the technical department of the municipality can cope with the operation of the plant. Of course, operational personnel is here also needed, but an independent body does not have to be created.

For the collection and disposal system, the water supply company is mostly also responsible for the installation and maintentance of the pipes and for the connection of the house sewers to the central system.

In small towns, the municipal services also deal with the collection and disposal of wastewater besides the treatment plant.

4. MONITORING OF COASTAL WATER AND EFFLUENTS

The monitoring of the quality of coastal water and effluents is usually a part of the controlling programme of a water pollution control authority and very often it belongs administratively to it.

Effluent sampling and analysis form the part of monitoring programmes, which refer to this aspect. In this case the controlling authorities carry out sampling and analysis of effluents in order to check the acceptance of the prescribed limits and of the sea water for adjustments of the water uses to the found conditions. Neverthless, it is mentioned separately since water quality monitoring, besides pollution control, is also used for other purposes.

Apart from the valuable help to the controlling bodies, a water quality monitoring programme is essential for continuous estimation of sea water conditions before any pollution effect would stimulate the authorities for action. This knowledge is an important part of the informaion needed for the decision and implementation of pollution control strategies and the estimation of the related impacts on the marine environment caused by any development plans.

The related organizational agencies responsible for monitoring programmes should be equipped with chemical, biological and microbiological laboratories for sampling analysis. In some cases, already working laboratories in universities, institutions, etc. can serve as support to the agency, in order to avoid new installations and quipment. Although it is not the optimal solution, it works sometimes when the sampling frequency is not too high. The sampling procedures should be simple and reliable following a well defined pattern for the assessment of the quality of the studied sea area. The frequency of sampling varies depending on local conditions, but it will be increased during the summer months when bathing takes place.

5. RESEARCH

Research programmes supporting coastal pollution control management are always oriented towards applied technical methods, avoiding theoretical considerations which are mostly left to universities and other scientific institutions. The organizational scheme for establishing related research programmes varies according to the administrative structure of each country.

An autonomous scientific-technical body is the optimal solution from the organizational point of view, acting as scientific advisor to the water pollution control organization. In some cases, the technical needs of the authorities are covered by contracts with research bodies (universities, institutes, etc) which carry out the scientific work on behalf of them. This is the cheapest solution widely used for financial savings.

An applied research programme has to cover the following items:

- pilot-plant studies on water pollution control techniques;
- development of full-scale projects for wastewater treatment methods;
- elaboration of new cost-effective sampling and analysis techniques;
- cost-benefit analysis of applied technical pollution control measures.

The operational pattern for a quick execution of such a programme should be adapted to the following procedure:

1. Task definition and priorities set by the water pollution control organization;
2. Time-table for programme completion;
3. Approval of completed intermediate work phases by the supervising authorities;

REFERENCES

1. Anon. (1969), «Laboratory Quality Control Manual», Federal Water Pollution Control Administration, Robert S. Kerr Water Research Center.

2. APHA (1990), Standard methods for the examination of water and wastewater, 17th edition. American Public Health Association, Washington D.C.

3. Chassard - Bouchaud, C. (1993), Criteria for the selection of organisms for monitoring purposes. In: UNEP/FAO/IAEA: Designing of monitoring programmes and management of data concerning chemical contaminants in marine organisms. MAP Technical Report Series No 77. UNEP, Athens, 1993.

4. DeWitt, T.H., R.C. Swartz and J.O. Lamberson (1989), Measuring the toxicity of estuarine sediment. Environ. Toxicol. Chem. 8: 1035 - 1048.

5. Duce, R.A. (1976), Transport Paths. In Goldberg E.D (ed) Strategies for Marine Pollution Monitoring. John Wiley and Sons, Inc., New York.

6. FAO (1971), Report of Seminar on Methods of Detection Measurements and Monitoring of pollutants in the Marine Environment. FAO Fisheries Report No. 99, Supplements, FAO, Rome.

7. Groot, S. and Schilperoort, T. (1984), Optimization of water quality monitoring networks. Wat. Sci. Tech. Vol. 16, York, pp. 275-287.

8. Hertz, J. (1991), Bioindicators for monitoring heavy metals in the environment. In: Metals and their compounds in the environment, edited by E. Merian, V.C.H. Weinheim, New York, pp 221-231.

9. Linsley, R.K. (1964), Water Resources Engineering. McGraw-Hill Book Company Inc., New York.

10. Mancy, K.H and Allen, H.E. (1978), Design of Measurement Systems and Environmental sampling, Sample Preservation and in-situ Measurements, Course 1. Modern Environmental Analysis Methods. Middle East Technical University, Ankara.

11. Middlebrooks, G.E. (1979), Industrial pollution control, Agro-Industries. J. Wiley and Sons.

12. OECD (1982), Diffuse sources of agricultural pollution - Pesticides - Problems posed by their residues in the water environment. ENV/WAT/82.1, Paris.

13. OECD (1992), Draft report of the OECD workshop on effects assessment of chemicals in sediment. HASED 91.182. Copenhagen.

14. OECD (1983), Diffuse sources of water pollution: Agriculture activities, fertilizer and animal waste. Water Management Policy Group. ENV/WAT/82.2.

15. (1985), Improving the enforcement of environmental policies. ENV/ECO/ 85.9, Paris.

16. (1986), Control of water pollution from urban run-off. OECD, Environment Monographs No. 3, Paris.

17. OECD (1996), Seminar on environmental data quality. Group on the State of the Environment. ENV/EPO4 SE/RD (96)1. Paris

18. SCEP (1970), Man's impact on the Global Environment, MIT Press, Cambridge, Massachussetts.

19. Schilperoort, T. and Groot, S. (1983), Design and optimization of water quality monitoring networks. Delft Hydraulics Laboratory, Publication No. 286, The Netherlands.

20. Shewhart, W.A. (1931), Economic Control of Quality of Manufactured Product.

21. UNEP (1987), Definition of ecological criteria for a rational development and protection of aquaculture in Mediterranean coastal zones. UNEP/WG. 170/7.

22. UNEP (1996), MED POL-Phase III. Programme for the assessment and control of pollution in the Mediterranean Region (1996-2005). Document UNEP (OCA)/MED IG. 8/7.

23. UNEP/FAO/IAEA (1993), Designing of monitoring programmes and manage-ment of data concerning chemical contaminants in marine organisms MAP Technical Reports Series No 77. UNEP, Athens.

24. UNEP/IOC/IAEA/FAO (1990), Contaminant monitoring programmes using marine organisms: Quality Assurance and Good Laboratory Practice. Reference Methods for Marine Pollution Studies No 57. UNEP.

25. UNEP/IAEA/IOC (1990), Reference methods and Materials: A programme of support for regional and grobal marine pollution assessments.

26. U.S. Department of Commerce, NOAA.ERL. (1979), Assimilative capacity of U.S. coastal waters for pollutants. Proc. of workshop, Crystal Mountain, Washington, 284 p.

27. U.S. EPA (1973), Handbook for analytical quality control in water and wastewater laboratories Cincinnati, Ohio.

28. (1972), Quality Criteria for Water. Washington D.C.

29. (1974), Methods for chemical analysis of water and wastes. Environ- mental Monitoring and Support Laboratory. E.R.C Cincinati, Ohio.

30. (1983), Technical Support Manual: Waterbody Surveys and Assessments for Conducting Use Attainability Analyses. Washington D.C

31. (1984), Multi - Media Compliance Inspection Manual, for enforcement programs in air, water, solid waste, toxic substances, et al, Government Institutes, Inc.

32. WHO/UNEP (1979), Principles and guidelines for the discharge of wastes into the marine environment. Regional Office for Europe, Copenhagen.

33. WHO/UNEP (1994), Guidelines for health - related monitoring of coastal recreational and shellfish areas. Parts I to V. Document EUR/ICP/CEH 041(3). WHO Regional Office for Europe, Copenhagen.

34. WHO/UNEP (1994), Guidelines for monitoring land-based sources of marine pollution. Document EUR/ICP/CEH 04 (1). WHO Regional Office for Europe, Copenhagen.

35. WHO/UNEP (1995), Health risks from marine pollution in the Mediterranean. Part II. Review of hazards and health risks EUR/ICP/EHZ 9501/MT 01 (2), WHO Regional Office for Europe, Copenhagen.

36. UNEP/WHO (1996), Guidelines for authorizations for the discharge of liquid wastes into the Mediterranean Sea. MAP Technical Reports Series No.107 UNEP, Athens.

37. WHO/UNEP (1996), Microbiological monitoring of recreational and shellfish growing areas. Document EUR/ICP/EHAZ 950/MT02. WHO Regional Office for Europe, Copenhagen.

38. WHO/UNEP (1997), Identification of Pollution, Hot Spots and Sensitive Areas. Under Preparation. Athens.

ANNEX 1

Table 1

Summary of waste water effluents (Middlebrooks, 1979)

Activity Product	Origin of Wastes	Waste Characteristics	Parameters of concern**
Canned and preserved seafood	Eviscarating, cooking, pickling, preserving, packaging	Protein,fats,dissolved and suspended organics odor	BOD, TSS, COD, O and G
Canned and preserved fruits and vegetable	Trimming, culling, juicing and blanching	High in suspended solids, colloidal and dissolved organic metter	BOD
Diary products	Dilution of whole milk, separated milk, buttermilk, and whey	High in dissolved organic matter, mainly protein, fat, and lactose	BOD, TSS, TDS, COD, pH Colour P
Brewed and distilled beverages	Steeping and processing of grain; residue from distillation of alcohol; condensate from scillage evaporation	High in dissolved organic solids, containing nitrogen and fermented starches or their products	BOD
Meat and poultry products	Stockyards; slaughtering of animals; rendering of bones and fats; residues in condensates; grease and wash water; picking of chickens	High in dissolved and suspended organic matter, blood, other proteins, and fats	BOD, TDS, COD, Colour, O and G
Animals feedlots	Excreta from animals	High in organic suspended solids	BOD,TSS,NH_3 TDS, COD,
Sugar beet	Transfer, screening, and juicing waters; drainings from lime sludge; condensates after evaporator; juice and extracted sugar	High in dissolved and suspended organic matter, containing sugar and protein	BOD, TSS, TDS
Pharmaceutical products	Mycelium, spent filtrate, and wash waters	High in suspended and dissolved organic matter, including vitamins	BOD, TSS, TDS
Yeast	Residue from yeast	High in solids (mainly organic)	BOD, TSS
Pickles	Lime water, brine, alum and turmeric, syrup, seeds and pieces of cucumber	Variable pH, high suspended solids, colour and organic matter	BOD, TSS
Coffee	Pulping and fermenting of coffee beans	High organics	BOD,TSS
Grain mills	Milling, oil production,	Organics, solids	BOD, TSS,

	starch production, syrup production	(mainly starch)	TDS, COD,pH, P,O and G
Soft drinks	Bottle washing; floor and equipment cleaning; syrup storage tank drains	High pH, suspended solids, and organics	BOD, TSS, COD, pH, O and G
Bakeries	Washing and greasing of pans; floor washing	High organics, grease, floor washings, sugars, flour, detergents	
Water production	Filter backwash; lime-soda sludge; brine; alum sludge	Minerals and suspended solids	BOD, TSS, COD, colour, F, Fe, Al
Textiles	Cooking of fibers; desizing of fabric	Highly alkaline, coloured high temperature, high suspended solids	BOD, TSS, TDS,COD,pH, colour, O and G, Cr, Zn, toxic organics
Leather goods	Unhairing, soaking de-liming and bathing of hides	High total solids, hardness, salt, sulfides, chromiun, pH, and precipitated lime	BOD, TSS, COD, pH, O and G, Cr, sulfide
Laundry trades	Washing of fabrics	High turbidity, alkalinity, and organic solids	BOD,TSS,TDS pH,Cr,Cu,Pb, Zn,Cd,Fe,Ni, Hg, O and G
Pulp and paper	Cooking, refining, washing of fibers, screening of paper pulp	High organics, high or low pH; high suspended colloidal, and dissolved solids; inorganic filters, colour	BOD, TSS, pH, colour
Photographic products	Spent solutions of developer and fixer	Alkaline, containing various organic and inorganic reducing agents	Metals, CN
Steel	Coking of coal, washing of blast-furnace gases, and pickling of steel	Low pH; acids, cyanogen, phenol, ore, coke, limestone, alkali, oils, mill scale and fine SS	BOD, CN, O and G, NH3, Pb, Zn, sulfide, Mn
Nonferrous metals	Refining, smelting, grinding, washing	Metals, acids, alkalis, slag, lime sludge	TDS,TSS,pH, O and G, F,Cu Pb, Zn,Cd,As, Se
Metalplated products	Stripping of oxides, cleaning and plating of metals	Acid, metals, toxic, low volume, mainly mineral matter	TSS, pH, CN, P,F,Cr,Cu,Pb, Zn,Cd,Fe,Ni
Oil extraction and refining	Drilling muds, salt, oil, and some natural gas; acid sludges and miscellaneous oils from refining	High dissolved salts from field; high organics, odor, sulfur compounds from refinery	BOD, O and G NH3, Cd, Cr, Zn, sulfide, phenol
fuel oil use	Spills from fuel-tank filling waste; auto crank-case oils	High in emulsified and dissolved oils	O and G

Rubber	Washing of latex, coagulated rubber, exyded impurities from crude rubber	High organic, odor, high suspended solids, variable pH, high chlorides	BOD,TSS, TDS, COD, O and G, Pb, Zn
Glass	Polishing and cleaning of glass	Red Colour, alkaline nonsettleable suspended solids	BOD, TSS, TDS, COD,pH colour, O and G, phenols
Naval stores	Washing of stumpes, drop solution, solvent recovery, and oil-recovery water	Acid, organics	Toxic organics
Glue manufacture	Lime wash, acid washes, extraction of nonspecific proteins	Organics, periodic strong mineral acids	BOD, COD, pH, Cr, phenols
Wood preservation	Steam condensates, preservations	High in organics, solids, phenols, toxic organics	BOD,COD, phenols, metals
Candle manufacture	Wax spills, steatic acid condensates	Organic (fatty) acids	BOD, TDS, COD
Plywood manufacture	Glue washings	High pH, potential toxicity	BOD, TSS, P, phenols
Asbestos	Mixing, forming, finishing, curing	Dissolved solids	BOD, TDS, COD, pH
Paint and ink	Mixing, grinding, thinning, filling	Dissolved organics, metals, oils	BOD,TSS,TDS COD,pH, colour, O and G, Cr, Cu, Pb, Zn, Cd, Fe, Hg
Fertilizers	Phospate processing ammonia production, blending	Clays, slimes, acid wastes	TSS, pH, P, NH_3, F,K
Explosives	Washing TNT and guncotton for purification, washing and pickling of cartridges	TNT,coloured, acid, odorous, and contains organic acids and alcohol from powder and cotton, metals, acid, oils and soaps	COD, NH_3
Pesticides	Washing and purification products, such as 2,4-D	High organic matter, benzenering structure, toxics, acid, low biodegradabiltiy	Toxic organics
Phosphate and phosphorus	Washing, screening, floating rock,condenser bleedoff from phosphate reduction plant	Clays, slimes and tall oils, low pH, high suspended solids, phosphorus silica and flouride	TSS, TDS,pH, P, F, Zn, Fe, As
Mining and Milling	Overburdern, mill tailing, leach residue	Inert rock with low concentration of metal sulfides or oxides	TSS, sulfide, metals
Formaldehyde	Residues from manufacturing synthetic and from dyeing synthetic fibres		BOD, toxicity

Plastics and resins	Unit operations from polymer preparation and use; spills and equipment wash-downs	Acids, caustic, nitrogenous compounds, organic matter such as phenols, formaldehyde, etc.	BOD, TSS, TDS,COD, pH, O and G, NH_3, F, Cr, phenols
Steam power	Cooling water, boiler blowdown, coal drainage	Hot, high volume, high inorganic and dissolved solids	TSS, pH, O and G, P,Cr, Cu, Zn, Fe, phenols
Coal processing	Cleaning and classification of coal, leaching of sulfur strata with water	High suspended solids, mainly coal; low pH, high H_2SO_4 and $FeSO_4$	TSS, COD, pH, sulfate
Acids	Dilute wash waters; many varied dilute acids	Low pH, low organic content	
Soap and detergents	Washing and purifying soaps and detergents	High in organic and saponified soaps	BOD, TSS, TDS, COD, pH O and G
Cornstarch	Evaporator condesate or bottoms when not reused or recovered, syrup from final washes, waste from «bottling up» process	High dissolved organic matter; mainly starch and related material	BOD, TDS
Nuclear power and radioactive materials	Processing ores; laundering of contaminated clothes; research lab wastes; processing of fuel; power-plant colling waters	Radioactive elements, can be very acid and «not»	Radiioactivity

** <u>Clossary:</u>

BOD (biochemical oxygen demand);
COD (chemical oxygen demand);
TDS (total dissolved solids);
O and G (oil and grease);
Cn (cyanide);
TSS (total suspended solids);

All others are standard chemical nomenclature.

ANNEX 2

URBAN WASTEWATER

The information given below were based on Directive 91/271/EEC of May 21st 1991, concerning municipal waste water treatment, and it is presented here as an example.

1. COLLECTING SYSTEMS[x]

Collecting systems shall take into account waste water treatment requirements.

The design, construction and maintenance of collecting systems shall be undertaken according to the best technical knowledge not entailing excessive costs, notably regarding:

- Volume and characteristics of urban waste water
- Prevention of leaks.
- Limitation of pollution of receiving waters due to storm water overflows.

2. DISCHARGE FROM URBAN WASTE WATER TREATMENT PLANTS TO RECEIVING WATERS

1. Waste water treatment plants shall be designed or modified so that representative samples of the incoming waste water and of treated effluent can be obtained before discharge to receiving waters.

2. Discharges from urban waste water treatment plants subjected to treatment according to points 1 and 2 (presented below) shall meet the requirements shown in Table 1.

3. Discharges from urban waste water treatment plants to those sensitive areas which are subject to eutrophication, shall meet in addition the requirements shown in Table 2.

4. More stringent requirements than those shown in Tables 1 and/or 2 shall be applied where required to ensure that the receiving waters satisfy any other relevant directives.

5. The points of discharge of urban waste water shall be chosen, as far as possible, so as to minimise the effects on receiving waters.

3. INDUSTRIAL WASTE WATER

Industrial waste water entering collecting systems and urban waste water treatment plants shall be subject to such pre-treatment as is required in order to:

- protect the health of staff working in collecting systems and treatment plants,

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[x] Given that it is not possible in practice to construct collecting systems and treatment plants in a way such that all waste water can be treated during situations such as unusual heavy rain, Member States shall decide on measures to limit the pollution from storm water overflows. Such mesures could be based on dilution rates, capacity in relation to dry weather flow or in relation to a certain acceptable number of overflows per year.

- ensure that collecting systems, waste water treatment plants and associated equipment are not damaged.
- ensure that the operation of the waste water treatment plant and the treatment of sludge are not impeded.
- ensure that discharges from the treatment plants do not adversely affect the environment, or prevent receiving water from complying with other relevant provisions.
- ensure that sludge can be disposed of safely in an environmentally acceptable manner.

4. REFERENCE METHODS FOR MONITORING AND EVALUATION OF RESULTS

1. Ensure that a monitoring method is applied which corresponds at least with the level of requirements described below.

Alternative methods to those mentioned in paragraphs 2-4 below can be used provided that it can be demonstrated that equivalent results are obtained.

2. Flow proportional or time based 24 hours samples shall be collected at the same well defined point in the outlet and if necessary in the inlet of the treatment plant to monitor compliance with the requirements for discharged waste water laid down.

Good international laboratory practices aiming at minimising the degradation of samples between collection and analysis shall be applied.

3. The minimum annual number of samples shall be fixed according to the size of the treatment plant and be collected at regular intervals during the year:

2.000 - 9.999 p.e*:	12 samples during the first year 4 samples in subsequent years, if it can be shown that the water during the first year complies with the provisions of the directive; if one sample of the 4 fails, 12 samples must be taken in the year that follows.
10.000-49.999 p.e:	12 samples
50.000 p.e. or over:	24 samples

4. The treated waste water shall be assumed to conform to the relevant parameters if, for each relevant parameter considered individually, samples of the water show that it complies with the relevant parametric value in the following way:

(a) For the parameters which are specified for primary treatment* a maximum permitted number of samples which are allowed to exceed the numerical limits is specified in table 3.

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* 1 p.e (population equivalent) means: the organic degradable load having a 5 day Biochemical Oxygen Demand (BOD_5) of 60 gr of oxygen per day.

* Primary treatment = treatment of urban waste water by a physical and/or chemical process involving settlement of suspended solids, or other processes in which the 5 day BOD of the incoming waste

(b) For the parameters which are specified in table 1 a maximum permitted number of samples which are allowed to exceed the numerical limits are specified in table 3. For the failing samples and under normal operating conditions the water must not deviate from the parametric values in concentration in question by more that 100%. For the parametric values in concentration relating to total suspended solids deviation up to 150% may be accepted.

(c) For those parameters specified in table 2 the annual mean of the samples for each parameter shall conform to the relevant parametric values.

5. Extreme values for the water quality in question shall not be taken into consideration when they are the result of unusual situations such as those due to heavy rain.

POINT 1

1. States shall ensure that urban waste water entering collecting systems shall before discharge be subject to secondary treatment* or an equivalent treatment as follows:

- All discharges from agglomerations representing more than 15.000 p.e;
- All discharges from agglomerations representating between 10.000 and 15.000 p.e;
- For discharges to freshwater and estuaries from agglomerations representing between 2.000 and 10.000 p.e

2. Urban waste water discharges to waters situated in high mountain regions (over 1.500 m. above sea level) where it is difficult to apply an effective biological treatment due to low temperatures may be subjected to less stringent treatment than prescribed in paragraph 1 of this Point, provided that detailed studies indicate that such discharges do not adversely affect the environment.

3. Discharges from urban waste water treatment plants described in paragraphs 1 and 2 shall satisfy the relevant requirments of paragraph B.

4. The load expressed in p.e shall be calculated on the basis of the maximum average weekly load entering the treatment plant during the year excluding unusual situations such as those due to heavy rain.

POINT 2

1. States shall identify, for the purposes of paragraph 2, below sensitive areas.

2. States shall ensure that urban waste water entering collecting systems shall before discharge into sensitive areas be subject to more stringent treatment than that described in Point 1 for all discharges from agglomerations representative more than 10.000 p.e.

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water is reduced by at least 20% before discharge and the load of total suspended solids of the incoming waste water is reduced by at least 50%.

* Secondary treatment = treatment of urban waste water by a process, generally involving biological treatment with a secondary settlement or other process in which the value of the parameters in Table 1 are respected.

3. Discharges from urban waste water treatment plants described in paragraph 2 shall satisfy the relevant requirements of paragraph B.

4. Alternatively, requirements for individual plants set out in paragraphs 2 and 3 above do not apply in sensitive areas where it can be shown that the minimum percentage of reduction of the load for all urban waste water treatment plants in that area is at least 75% for total phosphorus and at least 75% for total nitrogen.

5. Discharges from urban waste water treatment plants which are situated in the relevant catchment areas of sensitive areas and which contribute to the pollution of these areas shall be subject to the provisions of paragraph 2,3 and 4 above.

In cases where the above catchment areas are situated wholly or partly in another State, bilateral agreements should be enforced.

6. States shall ensure that the identification of sensitive areas are reviewed at intervals of no more than 4 years.

7. States shall ensure that areas designated as sensitive following review under paragraph 6 shall within 7 years meet the above requirements.

8. State does not have to identify sensitive areas if it implements the treatment established under paragraphs 2, 3 and 4 over all its territory.

Table 1

Requirements for discarges from urban waste water treatment plants subject to Points 1 and 2. The value for concentration or the percentage of reduction shall be applied.

PARAMETERS	CONCENTRATION	MINIMUM PERCENTAGE OF REDUCTION[x]	REFERENCE METHOD OF MEASUREMENT
Biochemical oxygen demand (BOD_5 at 20°C) without nitrification [xx]	25 mg/l O_2	70-90 40 under Point 1.2	Homogenised, unfiltered, undecanted sample. Determination of dissolved oxygen before and after five-day incubation at 20°C ± 1°C, in complete darkness. Addition of a nitrification inhibitor
Chemical oxygen demand (COD)	125 mg/l O_2	75	Homogenised, unfiltered, undecanted sample. Potassium dichromate
Total suspended solids	35 mg/l[xxx] 35 under Point 1.2 (more than 10.000 p.e) 60 under Point 1.2 (2.000-10.000 p.e)	90 (xxx) 90 under Point 1.2 (more than 10.000 p.e) 70 under Point 1.2 (2.000-10.000 p.e)	- Filtering of a representative sample through a 0,45 µm filter membrane. Drying at 105°C and weighing. . Centrifuging of a representative sample (for at least 5 mins with mean acceleration of 2800 to 3.200 g) drying at 105°C weighing

Analyses concerning discharges from lagooning shall be carried out on filtered samples; however, the concentration of total suspended solids in unfiltered water samples shall not exceed 150 mg/l.

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[x] Reduction in relation to the load of the influent

[xx] The parameter can be replaced by another parameter: Total Organic Carbon (TOC) or Total Oxygen Demand (TOD) if a relationship can be established between BOD_5 and the substitute parameter

[xxx] This requirement is optional

Table 2

Requirements for discharges from urban waste water treatment plants to sensitive areas which are subject to eutrophication. One or both parameters may be applied depending of the local situation. The value for concentration or the percentage of reduction shall be applied.

PARAMETERS	CONCENTRATION	MIMIMUM PERCENTAGE OF REDUCTION [x]	REFERENCE METHOD OF MEASUREMENTS
Total Phosphorus	2 mg/l P (10.000 - 100.000 p.e.) 1 mg/l P (more than 100.000 p.e)	80	Molecular absorption Spectrophotometry
Total nitrogen [xx]	15 mg/l N (10.000-100.000 p.e) 10 mg/l N (more than 100.000 p.e) [xxx]	70-80	Molecular absorption Spectrophotometry

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[x] Reduction in relation to the load of the influent.

[xx] Total nitrogen means: the sum of total Kjeldahl-nitrogen (organic N+NH3), nitrate (NO3) - nitrogen and nitrite (NO2) - nitrogen

[xxx] Alternatively, the daily average must not exceed 20 mg/l N. This requirement refers to a water temperature of 12°C or more during the operation of the biological reactor of the waste water treatment plant. As a substitute for the condition concerning the temperature, it is possible to apply limited time of operation, which takes into account the regional climatic conditions.
This alternative applies if it can be shown that paragraph D.1 above is fulfiled.

Table 3

Series of samples taken in any year	Maximum permitted number of samples which fail to conform to numerical limits
4-7	1
8-16	2
17-28	3
29-40	4
41-53	5
54-67	6
68-81	7
82-95	8
96-110	9
111-125	10
126-140	11
141-155	12
156-171	13
172-187	14
188-203	15
204-219	16
220-235	17
236-251	18
252-268	19
269-284	20
285-300	21
301-317	22
318-334	23
335-350	24
351-365	25

5. CRITERIA FOR IDENTIFICATION OF SENSITIVE AND LESS SENSITIVE AREAS

5.1 Sensitive areas

A water body shall be identified as a sensitive area if it falls into one of the following groups:

(a) Natural freshwater lakes, other freshwater bodies, estuaries and coastal waters which are found to be eutrophic or which in the near future may become eutrophic if protective action is not taken.

The following elements might be taken into account when considering which nutrient should be reduced by further treatment:

(i) Lakes and streams reaching lakes/reservoirs/closed bays which are found to have a poor water exchange, whereby accumulation may take place. In these areas, the removal of phosphorus should be included unless it can be demonstrated that the removal will have no effect on the level of eutrophication. Where discharges from large agglomerations are made, the removal of nitrogen may also be considered.

(ii) Estuaries, bays and other coastal waters which are found to have a poor water exchange, or which receive large quantities of nutrients. Discharges from small agglomerations are usually of minor importance in those areas, but for large agglomerations, the removal of phosphorus and/or nitrogen should be included unless it can be demonstrated that the removal will have no effect on the level of eutrophication.

(b) Surface freshwaters intended for the abstraction of drinking water which could contain more than the concentration of nitrate laid down according to the relevant provisions if action is not taken.

(c) Areas where further treatment than that prescribed in Point 1 is necessary to fulfil relevant provisions

5.2 Less sensitive areas

A marine water body or area can be identified as a less sensitive area if the discharge of waste water does not adversely affect the environment due to morphology, hydrology or specific hydraulic conditions which exist in that area.

When identifying less sensitive areas, competent authorities shall take into account the risk that the discharged load may be transferred to adjacent areas where it can cause detrimental environmental effects. Competent authorities shall recognise the presence of sensitive areas outside their national jurisdiction.

The following elements shall be taken into consideration when identifying less sensitive areas:
Open bays, estuaries and other coastal waters with a good water exchange and not subject to eutrophication or oxygen depletion or which are considered unlikely to become euthrophic or to develop oxygen depletion due to the discharge of urban waste water.

ANNEX 2

INDUSTRIAL EFFLUENTS

A. GENERAL

For compliance monitoring purposes in industrial effluents, a representative example concerning industrial sectors, limit values, time limits and verification frequencies and procedures for discharges, is given below for cadmium.

This informaion came out of Council Directive 83/513/EC of 26 September 1983 on limit values and quality objectives for cadmium discharges. This example depicts the difficulties for compliance monitoring and does not necessarily mean that has to be proposed for future adaptation by the Member States.

Limit values, time limits and verification frequencies and procedures for discharges of cadmium.

1. Limit values and time limits

Industrial sector (1)	Unit of measurement	Limit values which must be complied with as from	
		1.1.1986	1.1.1989(2)
1. Zinc mining, lead and zinc refining, cadmium metal and non-ferrous metal industry	Miligrams of cadmium per litre of discharge	0.3(3)	0.2(3)
2. Manufacture of cadmium compounds	Milligrams of cadmium per litre of discharge	0.5(3)	0.2(3)
	Grams of cadmium discharged per kilogram of cadmium handled	0.5(4)	(5)
3. Manufacture of pigments	Milligrams of cadmium per litre of discharge	0.5(3)	0.2(3)
	Grams of cadmium discharged per kilogram of cadmium handled	0.3(4)	(5)
4. Manufacture of stabilizers	Milligrams of cadmium per litre of discharge	0.5(3)	0.2(3)
	Grams of cadmium discharged per kilogram of cadmium handled	0.5(4)	(5)
5. Fanufacture of primary and secondary batteries	Milligrams of cadmium per litre of discharge	0.5(3)	0.2(3)
	Grams of cadmium discharged per kilogram of cadmium handled	1.5(4)	(5)
6. Electroplating (6)	Milligrams of cadmium per litre of discharge	0.5(3)	0.2(3)

	Grams of cadmium discharged per kilogram of cadmium handled	0.3(4)	(5)
7. Manufacture of phosphoric acid and/or phosphatic fertilizer from phosphatic rock		(7)	(7)

(1) Limit values for industrial sectors not mentioned in this table will, if necessary, be fixed at a later stage. In the meantime the Member States will fix emission standards for cadmium discharges autonomously. Such standards must take into account the best technical means available and must not be less stringent than the most nearly comparable limit value in this table.

(2) On the basis of experience gained in implementing these limits the proposals for fixing more restrictive limit values with a view to their coming into force by 1992 will be submitted.

(3) Monthly flow-weighted average concentration of total cadmium

(4) Monthly average

(5) It is impossible for the moment to fix limit values expressed as load. If limit values will not be fixed, the values expressed as load given in column «1.1.1986» will be kept.

(6) Member States may suspend application of the limit values until 1 January 1989 in the case of plants which discharge less than 10 kg of cadmium a year and in which the total volume of the electroplating tanks is less than 1.5 m³, if technical or administrative considerations make such a step absolutely necessary.

(7) At present there are no economically feasible technical methods for systematically extracting cadmium from discharges arising from the production of phosphoric acid and/or phosphatic fertilizers from phosphatic rock. No limit values have therefore been fixed for such discharges. The absence of such limit values does not release the Member States from their obligation to fix emission standards for these discharges.

2. Limit values expressed as concentrations which in principle must not be exceeded are given in the above table for the industrial sectors 2,3,4,5 and 6. In no instance may limit values expressed as maximum concentrations be greater than those expressed as maximum quantities divided by water requirements per kilogram of cadmium handled. However, because the concentration of cadmium in effluents depends on the volume of water involved, which differs for different processes and plants, the limit values, expressed in terms of the quantity of cadmium discharged in relation to the quantity of cadmium handled, in the above table must be complied with in all cases.

3. *The daily average limit values are twice the corresponding monthly average limit* values given in the above table.

4. A monitoring procedure must be instituted to check whether the discharges comply with the emission standards which have been fixed in accordance with the limit values laid down.

   This procedure must provide for the taking and analysis of samples and for measurement of the flow of the discharge and the quantity of cadmium handled.

   Should the quantity of cadmium handled be impossible to determine, the monitoring procedure may be based on the quantity of cadmium that may be used in the light of the production capacity on which the authorization was based.

5. A sample representative of the discharge over a period of 24 hours will be taken. The quantity of cadmium discharged over a month must be calculated on the basis of the daily quantities of cadmium discharged.

However, a simplified monitoring procedure may be instituted in the case of industrial plants which do not discharge more than 10 kg of cadmium per annum. In the case of industrial electroplanting plants, a simplified monitoring procedure, may only be instituted if the total volume of the electroplating tanks is less than 1.5 m^3.

B. QUALITY OBJECTIVES

The competent authority shall determine the area affected in each case and shall select from among the quality objectives listed in paragraph 1 the objective or objectives that it deems appropriate having regard to the intended use of the area affected, while taking account of the fact that the purpose is to eliminate all pollution.

1. The following quality objectives[*] which will be measured sufficiently close to the point of discharge, are fixed, with the object of eliminating pollution

   1.1 The total cadmium concentration in inland surface waters affected by discharges must not exceed 5 µg/litre.
   1.2 The concentration of dissolved cadmium in estuary waters affected by discharges must not exceed 5 µg/litre.

   1.3 The concentration of dissolved cadmium in territorial waters and in internal coastal waters other than estuary waters affected by discharges must not exceed 2.5 µg/litre.

2. In addition to the above requirements, cadmium concentrations must be determined by national networks and the results compared with the following concentrations.

   2.1 In the case of inland surface waters, a total cadmium concentration of 1 µg/litre.

   2.2 In the case of estuary waters, a dissolved cadmium concentration of 1 µg/litre.

   2.3 In the case of territorial and internal coastal waters, other than estuary waters, a dissolved cadmium concentration of 0.5 µg/litre.

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[*] The cadmium concentrations indicated in 1.1, 1.2 and 1.3 are the minimum requirements necessary to protect aquatic life.

If these concentrations are not complied with at any one of the points on the national network, the reasons must be reported.

3. The concentration of cadmium in sediments and/or shellfish, if possible of the species *Mytilus edulis,* must not increase significantly with time.

4. Where several quality objectives are supplied to waters in an area, the quality of the waters must be sufficient to comply with each of those objectives.

C. REFERENCE METHODS OF MEASUREMENT

1. The reference method of analysis used for determining the cadmium content of waters, sediments and shellfish is atomic absorption spectrophotometry after preservation and suitable treatment of the sample.

   The limits of detection must be such that the cadmium concentration can be measured to an accuracy of ±30% and at a precision of ±30% at the following concentrations:

   1.1 in the case of discharges, one- tenth of the maximum permitted concentration of cadmium specified in the authorization,

   1.2 in the case of surface water, 0.1 µg/litre of one-tenth of the cadmium concentration specified in the quality objective, whichever is the greater,

   1.3 in the case of shellfish, 0.1 mg/kg, wet weight,

   1.4 in the case of sediments, one-tenth of the cadmium concentration in the sample or 0.1 mg/kg, dry weight, with drying being carried out between 105 and 110°C at constant weight, whichever value is the greater.

2. Flow measurements must be carried out to an accuracy of ± 20%

D. MONITORING PROCEDURE FOR QUALITY OBJECTIVES

1. For each authorization granted the competent authority will specify the restrictions, monitoring procedure and time limits for ensuring compliance with the quality objective(s) concerned.

2. The Member State will, for each quality objective chosen and applied, report on:

   2.1 the points of discharge and the means of dispersal,
   2.2 the area in which the quality objective is applied,
   2.3 the location of sampling points,
   2.4 the frequency of sampling,
   2.5 the methods of sampling and measurement,
   2.6 the results obtained

ANNEX 2

INSPECTION [*]

1. Introduction

Pollution sources vary in complexity and difficulty to inspect depending on facility size, process operations and variety of pollution programs involved (e.g. air, water, solid waste, toxic substances).

The primary responsibility of inspectors is to gather information that will be used to determine facility compliance with applicable regulations, rules and other requirements. Inspectors represent the government in dealing with regulated industry and municipalities and with the public.

Any act or failure to act by an inspector motivated by reason of private gain is illegal, and any actions which may be construed as influencing the performance of governmental duties should be avoided.

Inspectors should possess a good working knowledge of the various environmental pollution control statutes and understand rules, regulations, and other provisions including permits, registrations, authorizations, limitations, monitoring requirements, etc, as they pertain to a specific facility. The inspector should possess sufficient knowledge of manufacturing and production processes, modern-day pollution control technology, and the nature of popllution problems and possible solutions, including available treatment and controls.

Inspectors must properly handle information for which confidentiality is claimed or requested to prevent disclosure to unauthorized persons.

Collection and analysis of available background information on the facility are essential to the effective planning and overall sucess of a compliance inspection. A properly conducted background review should consider both the legal and technical information sought and the available information sources.

2. Technical Information Sought

Facility Background

- Maps showing facility location and environmental (i.e discharge pipes) and geographic features.
- Names, titles, phone numbers of responsible company officials
- Process flow charts
- Production levels - past, present and future
- Geology/hydrogeology of the area
- Changes in plant conditions since previous inspection
- Available aerial photographs

Inspection Reports, Records and Files

- Compliance files
- Correspondence between Company and inspecting authorities
- Citizen's complaints

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[*] U.S.EPA, 1984

- Previous inspection records
- Self-monitoring data
- Annual reports by Company (e.g. PCB reports)

Waste Generation, Control, Treatment and Disposal Systems

- Description and design data for each appropriate pollution control system and process operation
- Sources and characterization of waste discharge.
- Type and amount of waste discharged
- Waste storage areas
- Available bypasses or diversions and spill containment facilities
- Industrial processes, pollution control, treatment and disposal methods, monitoring systems.

2. Legal Information Sought

Requirements, Regulations, Limitations

- Copies of permit application, draft or existing permits, registrations, regulations, and requirements, restrictions placed on dishcarges, emissions, and disposal practices, compliance schedules, monitoring and reporting requirements, available monitoring stations, and analytical methods used by the company.
- Special exemptions and waivers if any
- Receiving ambient water quality standards, protected uses

Enforcement History

- Status of current and pending litigation against Company
- Previous deficiency notices issued to facility and responses by company
- Status of Administrative Orders, Consent Decrees, or other regulatory corrective actions, if any, and compliance by company.

Compliance inspections can be announced or unannounced. Notification is not desired when illegal discharges or emissions or improper records are suspected.

The inspectors, upon arrival at the facility, identify themselves to the owner, agent in charge, or other responsible person; present their official agency credentials to the facility, whether requested or not; and state the authorities under which the inspection is being conducted. Arrival at the facility should be made during normal working hours.

The inspectors need to have a general understanding of the physical plant under investigation and the process or processes in use at that facility. This knowledge is necessary to aid in the determinations of substances present at the facility and where these may be released as pollutants into the environment.

The compliance inspection team should do the following: Determine the production necessary to evaluate pollutants which could be present or discharged. Validate flow diagrams, process descriptions, raw materials, intermediates, products and byproducts, and determine whether processes are continuous, batch, and seasonal. Determine current operating levels, how they compare to design, if any change is significant, and whether production status is considered normal or abnormal. Information on production is essential if pollution control limits are based on production rates or products; information on production is desirable at all other times to aid evaluation of types and possible quantities of pollutants. Process modifications may have changed the types and loads of pollutants emitted, discharged, or disposed of. Different production levels may have caused higher emission mass loadings or gas flow rates. Use of raw materials, including fuels, may have increased, affecting emission characteristics. Process equiment may have deteriorated, or different operating conditions may be creating more difficult pollutant collection and control problems.

Identify those processes or physical elements of the facility which may contribute to a source of pollution (air, water, solid/hazardous waste). Identify feed inputs to the process and the sources, characterization, flow rates, etc. at all points where wastewater, gaseous emissions, and solid wastes leave each process. Determine the fate of those wastes (e.g, do they discharge or emit directly to the environment or do they discharge or emit to a treatment facility). Determine the types and amount of pollutants present or potentially present.

Determine the types of controls on the process. For example, determine if process rates remain consistent or are constantly changing, or if there is a large or small amount of variability in the raw material.

After the inspectors have determined what type of waste sources are generated by each process, they should identify the type of treatment provided and the ultimate fate of wastes, and evaluate sampling locations as to collection of representative samples. They should also identify recycle or dilution streams or other flow disturbances and where they are in reference to sampling locations.

Inspection is a complex and difficult to be implemented procedure, depending to a great extend on the type of industry and therefore a special document needs to be developed.

ANNEX 3

A CATALOGUE OF REFERENCE METHODS (UNEP/IAEA/IOC,1990)

1. Sanitary quality of coastal recreational and shellfish-growing waters

No.1	UNEP/WHO: Guidelines for monitoring the quality of coastal recreational and shellfish-growing waters.	1988
No.2	UNEP/WHO: Determination of total coliforms in sea water by the membrane filtration culture method.	1983
No.3	UNEP/WHO: Determination of faecal coliforms in sea water by the membrane filtration culture method.	1983
No.4	UNEP/WHO: Determination of faecal streptococci in sea water by the membrane fultration culture method	1983
No.5	UNEP/WHO: Determination of faecal coliforms in bivalves by multiple test tube method.	1983
No.21	UNEP/WHO/IAEA: Determinaion of total coliforms in sea water by multiple test tube (MPN) method.	1985
No.22	UNEP/WHO/IAEA: Determination of faecal coliforms in sea water by multiple test tube (MPN) method.	1985
No.23	UNEP/WHO/IAEA: Determination of faecal streptococci in sea water by multiple test tube (MPN) method	1985
No.28	UNEP/WHO/IAEA: Determination of staphylococcus aureus in sea water and sewage by the membrane filtration culture method.	1986
No.29	UNEP/WHO/IAEA: Determination of pseudomonas aeruginosa in sea-water and sewage by the membrane filtration culture method.	1986
No.30	UNEP/WHO/IAEA: Isolation/enumeration of salmonella from sea water and sewage.	1986

No.47	UNEP/WHO/IAEA: Determination of faecal coliforms in estuarine waters, suspended matter and sediments.	1991
No.55	UNEP/WHO/IAEA: Statistical methods for the evaluation of results from monitoring the quality of coastal recreational and shellfish-growing waters.	1989
«AC»	UNEP/WHO/IAEA: Determination of selected neurotoxins in marine organisms.	in preparation

2. Chemical contaminants in marine organisms

No.6	UNEP/FAO/IOC/IAEA: Guidelines for monitoring chemical contaminants in marine organisms.	1990
No.7	UNEP/FAO/IOC/IAEA: Sampling of selected marine organisms and sample preparation for trace metal analysis	1984
No.8	UNEP/FAO/IOC/IAEA: Determination of total mercury in selected marine organisms by cold vapour atomic absorption spectrophotometry.	1984
No.9	UNEP/FAO/IAEA: Determination of total arsenic in selected marine organisms by hydride generation atomic absorption spectrophotometry.	1985
No.10	UNEP/FAO/IAEA: Determination of total selenium in selected marine organisms by hydride generation atomic absorption spectrophotometry.	1984
No.11	UNEP/FAO/IOC/IAEA: Determination of total cadmium, zinc, lead and copper in selected marine organisms by flameless atomic absorption spectrophotometry.	1984
No.12	UNEP/FAO/IAEA: Sampling of selected marine organisms and sample preparation for the analysis of chlorinated hydrocarbons.	1984
No.13	UNEP/FAO/IAEA: Determinaion of methylmercury in selected marine organisms by gas chromatography.	1984

No.14	UNEP/FAO/IOC/IAEA: Determination of DDTs and PCBs in selected marine organisms by packed column gas chromatography.	1986
«AM»	UNEP/IOC/IAEA: Determination of chlorinated hydrocarbons in marine organisms: Sample extraction and clean-up.	in preparation
No.40	UNEP/IOC/IAEA: Determination of DDTs and PCBs in selected marine organisms by capillary column gas chromatography.	1988
«AI»	UNEP/IOC/IAEA/FAO: Determination of petroleum hydrocarbons in selected marine organisms.	in preparation
«U»	UNEP/IAEA/IOC/FAO: Determination of organotin compounds and total tin in selected marine organisms.	in preparation

3. Chemical contaminants in sea water

No.56	UNEP/IOC/IAEA: Determination of dissolved/dispersed hydrocarbons in marine waters.	1990
No.59	UNEP/IAEA/IOC: Determination of butyltin compounds in coastal waters.	1990

4. Chemical contaminants in marine sediments and suspended matter

No.58	Guidelines for the use of sediments for marine pollution monitoring programmes.	1990
«R»	Guidelines on the sampling and preparation of sediments of marine pollution monitoring.	in preparation
«AN»	UNEP/IOC/IAEA: Determinaion of chlorinated hydrocarbons in marine sediments: Sample extraction and clean-up.	in preparation
No.20	UNEP/IOC/IAEA: The determination of petroleum hydrocarbons in sediments.	1990-1991
«AE»	UNEP/IOC/IAEA: Determination of organophosphorus compounds in marine sediments.	in preparation
No.26	UNEP/IAEA: Determination of total mercury in marine sediments and suspended solids by cold vapour atomic absorption spectrophotometry.	1985

No.27	UNEP/IAEA: Determination of total cadmium in marine sediments by flameless atomic absorption spectrophotometry.	1985
No.31	UNEP/IAEA: Determination of total chromium in marine sediments by flameless atomic absorption spectrophotometry.	1985
No.32	UNEP/IAEA: Determination of total cobalt in marine sediments by flameless atomic absorption spectrophotometry.	1985
No.33	UNEP/IAEA: Determination of total copper in marine sediments by flamelles atomic absorption spectrophotometry.	1985
No.34	UNEP/IAEA: Determination of total lead in marine sediments by flameless atomic absorption spectrophotometry.	1985
No.35	UNEP/IAEA: Determination of total nickel in marine sediments by flameless atomic absorption spectrophotometry.	1985
No.36	UNEP/IAEA: Determination of total vanadium in marine sediments by flameless atomic absorption spectrophotometry.	1985
No.37	UNEP/IAEA: Determination of total iron in marine sediments by flame atomic absorption spectrophotometry.	1985
No.38	UNEP/IAEA: Determination of total manganese in marine sediments by flame atomic absorption spectrophotometry.	1986
No.39	UNEP/IAEA: Determination of total zinc in marine sediments by flame atomic absorption spectrophotometry.	1986
«Z»	UNEP/IOC/IAEA: Determination of aluminium in sediments.	in preparation

5. Chemical contaminants in estuarine waters and suspended matter

«C»	UNEP/IOC/IAEA: Guidelines for collecting and interprenting data on estuaries.	1990
No.41	UNEP/IOC/IAEA: Guidelines for the determination of riverine inputs of contaminants to estuaries.	1987

No.19	UNEP/IOC/IAEA: Determination of total mercury in estuarine waters and suspended sediment by cold vapour atomic absorption spectrophotometry.	1985
No.52	UNEP/WHO/IOC/IAEA: Determination of phosphorus in suspended matter and sediments.	in preparation
No.53	UNEP/WHO/IAEA: Determination of nitrogen in suspended matter and sediments.	in preparation
G	UNEP/WHO/IOC/IAEA: Determination of BOD_5 and COD in estuarine waters.	in preparation
I	UNEP/IOC/IAEA: Determination of total cadmium in estuarine waters and suspended matter.	in preparation

6. Chemical contaminants floating or on beaches

No.15	UNEP/IOC/IAEA: Monitoring of tar on marine beaches.	1985
«X»	UNEP/IOC/IAEA: Guidelines for quantifying persistant synthetic materials which may float, sink or remain in suspension.	in preparation

7. Atmospheric chemical contaminants

No.24	UNEP/WMO/IAEA: Sampling of aerosols and wet precipitation for analysis of chemical pollutants.	1985
No.42	UNEP/IAEA/WMO: Guidelines for the determination of selected trace metals in aerosols and in wet precipitation.	1988
P	UNEP/IOC/IAEA: Determination of halogenated hydrocarbons in aerosols and in wet precipitation.	in preparation
Q	UNEP/WMO/IOC/IAEA: Sampling of dry deposition.	in preparation

8. Effects on marine organisms and ecosystems

No.43	UNEP/FAO/IAEA: Test of acute lethal toxicity of pollutants to marine fish and invertrebrates.	1989
No.44	UNEP/FAO/IAEA: Estimation of the toxicity of pollutants to marine phytoplaktonic and zooplanktonic organisms.	1989

No.45	UNEP/FAO/IAEA: Comparative toxicity test of water-accommodated fractions of oils and oil dispersants to marine organisms.	1989
«JA»	UNEP/IOC/FAO/IAEA: Statistical analysis and interpretation of marine community data.	in preparation
«JB»	UNEP/IOC/FAO/IMO/IAEA: Hepatic mixed function oxidase induction in fish as an environmental monitoring technique.	in preparation
«JC»	UNEP/IOC/FAO/IMO/IAEA: Scope for growth determinations in marine bivalve molluscs.	in preparation
«AG»	UNEP/IOC/IAEA: Guidelines for evaluating the effects of thermal discharges on the marine environment.	in preparation
«AH»	UNEP/IOC/IAEA: Guidelines for detecting and monitoring eutrophication in the marine environment.	in preparation

9. Standard physical, chemical and meteorological observations

No.48	UNEP/IOC/IAEA: Principles and guidelines for the determination of physical oceanographic parameters.	in preparation
No.49	UNEP/IOC/WMO/IAEA: Guidelines for observation of meteorological parameters for marine pollution monitoring.	1989
No.50	UNEP/IOC/IAEA: Standard chemical methods for marine environmental monitoring.	1988

10. Quality assurance procedures

No.57	UNEP/IOC/IAEA/FAO: Contaminant monitoring programmes using marine organisms: Quality Assurance and Good Laboratory Practice.	1989
«OB»	UNEP/IOC/IAEA: Quality Assurance and Good Laboratory Practice for the measurement of contaminants in marine sediments.	in preparation

11. Miscellaneous methods

No.0	UNEP/IAEA: Guidelines for the use of Reference Methods in marine pollution studies.	1990

«AD»	UNEP/IOC/IAEA: Guidelines for monitoring the presence of used lubricating oils in the marine environment.	in preparation
«AK»	UNEP/IOC/IMO/IAEA: Guideline for monitoring marine dumpsites.	in preparation
«AL»	UNEP/IOC/FAO/IAEA: Guidelines for assessing the impact of point sources.	in preparation
«AF»	UNEP/IOC/IAEA: Reagent and laboratory ware clean-up procedures for low-level contaminant monitoring.	in preparation
No.46	UNEP/WHO/IAEA: Determination of methylmercury, total mercury and selenium in human hair.	1987

ANNEX 3

Table 1

Recommendation for sampling and preservation of samples according to measurement (Anon.,1969)

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time (6)
Acidity	100	P,G[2]	Cool, 4°C	24 Hrs
Alkalinity	100	P,G	Cool, 4°C	24 Hrs
Arsenic	100	P,G	HNO_3 to pH <2	6 Mos
BOD	1000	P,G	Cool, 4°C	6 Hrs[3]
Bromide	100	P,G	Cool, 4°C	24 Hrs
COD	50	P,G	H_2SO_4 to pH<2	7 Days
Chloride	50	P,G	None Req.	7 Days
Chlorine Req.	50	P,G	Det. on site	No Holding
Color	50	P,G	Cool, 4°C	24 Hrs.
Cyanides	500	P,G	Cool, 4°C NaOH to pH 12	24 Hrs
Dissolved Oxygen				
Probe	300	G only	Det.on site	No Holding
Winkler	300	G only	Fix on site	4-8 Hours
Fluoride	300	P,G	Cool,4°C	7 Days
Hardness	100	P,G	Cool,4°C HNO_3 to pH<2	7 Days
Iodide	100	P,G	Cool, 4°C	24 Hrs
MBAS	250	p,G	Cool, 4°C	24 Hrs

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time (6)
Metals				
Dissolved	200	P,G	Filter on site HNO_3 to pH<2	6 Mos
Suspended			Filter on site	6 Mos
Total	100		HNO_3 to pH<2	6 Mos
Mercury				
Dissolved	100	P,G	Filter HNO_3 to pH<2	38 Days (Glass) 13 Days (Hard Plastic)
Total	100	P,G	HNO_3 to pH<2	38 Days (Glass) 13 Days (Hard Plastic)
Nitrogen				
Ammonia	400	P,G	Cool, 4°C H_2SO_4 to pH<2	24 Hrs$^{(4)}$
Kjeldahl, total	500	P,G	Cool, 4°C H_2SO_4 to pH<2	7 Days
Nitrate	100	P,G	Cool, 4°C H_2SO_4 to pH<2	24 Hrs$^{(4)}$
Nitrite	50	P,G	Cool, 4°C	24 Hrs$^{(4)}$
NTA	50	P,G	Cool, 4°C	24 Hrs
Oil & Grease	1000	G only	Cool, 4°C H_2SO_4 or Hcl to pH < 2	24 Hrs
Organic Carbon	25	P,G	Cool, 4°C H_2SO_4 to pH<2	24 Hrs

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time (6)
pH	25	P,G	Cool, 4°C Det. on site	6 Hrs(3)
Phenolics	500	G only	Cool, 4°C H_3PO_4 to pH <4 1.0 g $CuSO_4$/l	24 Hrs
Phosphorus				
Ortho-phosphate, Dissolved	50	P,G	Filter on site Cool, 4°C	24Hrs(4)
Hydrolyzable	50	P,G	Cool, 4° C H_2SO_4 to pH<2	24 Hrs(4))
Total	50	P,G	Cool, 4° C	7 Days
Total, Dissoled	50	P,G	Filter on site Cool, 4°C	24 Hrs(4)
Residue				
Filterable	100	P,G	Cool, 4° C	7 Days
Non-Filterable	100	P,G	Cool, 4° C	7 Days
Total	100	P,G	Cool, 4° C	7 Days
Volatile	100	P,G	Cool, 4° C	7 Days
Settleable Matter	1000	P,G	None Req.	24 Hrs
Selenium	50	P,G	HNO_3 to pH<2	6 Mos
Silica	50	P only	Cool, 4° C	7 Days

Measurement	Vol. Req. (ml)	Container	Preservative	Holding Time (6)
Specific Conductance	100	P,G	Cool, 4° C	24 Hrs(5)
Sulfate	50	P,G	Cool, 4°C	7 Days
Sulfide	500	P,G	2ml zinc acetate	24 Hrs
Sulfite	50	P,G	Det. on site	No Holding
Temperature	1000	P,G	Det. on site	No Holding
Threshold Odor	200	G only	Cool, 4° C	24 Hrs
Turbidity	100	P,G	Cool, 4° C	7 Days

1. More specific instructions for preservation and sampling for water and wastewater may be found in ASTM, Part 23, p.7291 (1973).

2. Plastic or Glass

3. If samples cannot be returned to the laboratory in less than 6 hours and holding time exceeds this limit, the final reported data should indicate the actual holding time.

4. Mercuric chloride may be used as an alternate preservative at a concentration of 40 mg/l, especially if a longer holding time is required. However, the use of mercuric chloride is discouraged whenever possible.

5. If the sample is stabilized by cooling, it should be warmed to 25°C for reading, or temperature correction made and results reported at 25°C.

6. It has been shown that samples properly preserved may be held for extended periods beyond the recommended holding time.

ANNEX 4

QUESTIONNAIRES*

MUNICIPAL DISCHARGES

Country: ....

City: ....

1. Permanent population .... (last census taken) ....)

2. Average seasonal increase ....

(months of tourist season) ....)

3. Population served by municipal sewer system ....

4. Main industries (individual or group) served by municipal sewer system:

4.1. Name and type of activity and size (if many, use table at the end)

5. Sewage treatment plant: 5.1 Existent .... since when

5.2 Non-existent ....

5.3 Planned to be constructed on ....

6. Wastewater flow to the treatment plant .... (m³/day)

(When more than one exists, specify for each one) ....(m³/day)

6.1 Type of final treatment before discharge:

- Primary .... (YES or NO)
- Secondary .... (YES or NO)
- Tertiary .... (YES or NO)

7. Total wastewater treated .... (m³/day)

8. Total wastewater discharged (into the marine environment)
for the entire city)

8.1 Treated .... (m³/day)
8.2 Untreated .... (m³/day)

9. Type and location of discharge: (when more than one, specify for each one)
....

---

* WHO/UNEP,1997

10. Pollution loads at the discharge point:

10.1 BOD$_5$ .... (t/y)

10.2 COD .... (t/y)

10.3 Total-N .... (t/y)

10.4 Total-P .... (t/y)

10.5 TSS .... (t/y)

10.6 Oil (Petroleum Hydrocarbons) .... (t/y)

10.7 Heavy metals

10.7.1 .... (kg/y)

10.7.2 .... (kg/y)

10.7.3 .... (kg/y)

10.8 Organochlorines

10.8.1 .... (kg/y)

10.8.2 .... (kg/y)

10.9 Faecal coliforms .... (col/100 mL)

11. Quality of receiving environment (water, sediments and biota)

11.1 Total-N .... (mg/L)

11.2 Total-P .... (mg/L)

11.3 TSS .... (mg/L)

11.4 Oil (Petroleum Hydrocarbons) .... (mg/L)

11.5 Heavy metals

11.5.1 .... (µg/L)

11.5.2 .... (µg/L)

11.5.3 .... (µg/L)

11.6 Organochlorines

11.6.1 .... (µg/L)

11.6.2 .... (µg/L)

11.7 Faecal coliforms .... (col/100 mL)

11.8 PCBs .... (µg/L)

11.9 Radioactive Substances (if applicable)

11.10 Any other relevant information

12. When a sewage treatment plant and/or sewer system are non-existent, give estimation of the cost needed for the construction (secondary treatment will be included):

....

13. Additional information regarding the disposal of solid wastes that may affect the receiving waters:

....

....

....

14. Any other remarks:

....

....

....

Table

To be used in connection to point 4.1

Name of enterprise	Type of activity	Size	Population equivalent*

* Population equivalent will be estimated by using conventional references

INDUSTRIAL DISCHARGES DIRECTLY INTO THE SEA

Country: ....

Name of Company : ....

1. Discharge site (geographical polition) ....

....

3. Industrial wastewater treatment ....

(if YES, please specify type of treatment):

....

....

....

....

°Petroleum refining
° The paper and paper-pulp industry
° Cement production
° The tanning industry
° The metal industry
° The shipbuilding and repairing industry
° The textile industry
° The electronic industry
° The recycling industry
° Other sectors of the organic chemical industry
° Other sectors of the inorganic chemical industry
° Food processing
° Treatment and disposal of hazardous wastes
° The waste management industry

4. Way of discharge:

4.1. By outfall (YES or NO) ....

4.2. On shore (YES or NO) ....

5. Total wastewater treated .... (m^3/dday)

6. Total wastewater discharge: 6.1. Treated .... (m^3/day)

6.2 Untreated .... (m^3/day)

7. Wastewater quality and pollution loads at point of discharge:

Wastewater Quality **Pollution Loads**

7.1 BOD_5 .... (mg/L) .... (t/y)

7.2 COD .... (mg/L) .... (t/y)

7.3 Total-N .... (mg/L) .... (t/y)

7.4 Total-P .... (mg/L) .... (t/y)

7.5 TSS .... (mg/L) .... (t/y)

7.6 Heavy metals .... (µg/L) .... (kg/y)

7.6.1 .... (µg/L) .... (kg/y)

7.6.2 .... (µg/L) .... (kg/y)

7.6.3 .... (µg/L) .... (Kg/y)

7.7 Persistent Organic Pollutants:

7.7.1 PCBs
.... (µg/L) .... (kg/y)

7.7.2 .... (µg/L) .... (kg/y)

7.7.4 .... (µg/L) .... (kg/y)

7.8 Oil (petroleum hydrocarbons) .... (t/y)

8. Indirect evaluation of pollution (to be filled in when 5,6 and 7 are not answered):

PRODUCTION FIGURES

Type of Product	Unit	Annual Production
....	....	....
....	....	....
....	....	....
....	....	....

RAW MATERIALS IN USE

Type of Raw Material	Unit	Annual Consumption
....	....	....
....	....	....
....	....	....
....	....	....

ESTIMATED POLLUTION LOAD		
Pollution loads discharged into received waters	mg/L	t/y
....	....	....
....	....	....
....	....	....
....	....	....

9. Any other remarks:

....

....

....

....

10. Selected remedial measures (including preventive and end-of-pipe treatment methods) and cost estimates:

....

....

11. Air emission loads (if any): ....

....

12. When power plants above 200 MW (including nuclear) and cement industries are existing in the coastal zone, specify their emission loads: ....

....

....

13. Solid and hazardous wastes with water pollution potential (if any): ....

....

....

DISCHARGES FROM RIVERS AND CANALS INTO THE SEA

Country: ....

Name of River/Canal: ....

1. Discharge site (geographical position) ....

....

2. Average daily flow: .... (m³/day)

3. River water quality and pollution loads at point of discharge:

		River Water Quality		Pollution Loads	
3.1.	BOD$_5$	....	(mg/L)	....	(t/y)
3.2	COD	....	(mg/L)	....	(t/y)
3.3	Total-N	....	(mg/L)	....	(t/y)
3.4	Total-P	....	(mg/L)	....	(t/y)
3.5	TSS	....	(mg/L)	....	(t/y)
3.6	Heavy metals	....	(µg/L)	....	(Kg/y)
	3.6.1	....	(µg/L)	....	(Kg/y)
	3.6.2	....	(µg/L)	....	(Kg/y)
	3.6.3	....	(µg/L)	....	(Kg/y)
3.7	Persistent Organic Pollutants:				
	3.7.1	PCBs	(µg/L)	....	(Kg/y)
	3.7.2	....	(µg/L)	....	(Kg/y)
	4.7.3	....	(µg/L)	....	(Kg/y)
	4.7.4	....	(µg/L)	....	(Kg/y)
3.8	Oil (petroleum hydrocarbons)		....		(t/y)

4. Any other remarks: ....

....

EXPLANATION FOR THE COMPLETION OF THE QUESTIONNAIRES

The questionnaires have been formulated in such a way so as to provide only the necessary information in order to identify the hot spots, the source of the pollution and the necessary action for the improvement of the situation by limiting their input of pollutants into the Mediterranean.

Lagoons directly connected with the sea are considered as reveiving waters.

In order to fill in the questionnaires, the following explanation will facilitate the task:

Municipal Discharges

In the first page, on the upper right, indicate the name of the country you are dealing with and the name of the city which according to the permanent population is considered as contributing to the pollution of the sea. In the case of an urban coastal agglomerate which means an extended coastal zone, populated intensively and comprising more than one municipality and/or community, indicate the name of the municipality and/or community.

1. Indicate the permanent population giving also information on the year when the last census was taken and which you are referring to.

2. Indicate the average increase due to tourists, considering the total number of tourists that stay in the city during the peak season, giving also information on the duration of the tourist season in months.

3. Indicate the number of inhabitants that are connected with the municipal sewer system. If such a system does not exist answer «NO».

4. Indicate the name of the main industries, their types of activity and, if the industry is connected with the sewerage system, their size (e.g. number of employees). If a lot of small industries are connected with the swewer, then refer to them as a group of similar industries (for example, if ten small-sized tanneries are connected with the sewer, then refer to them as: «a group of 10 tanneries»). For this purpose use the table at the end of the questionnaire.

5. This part of the questionnaire concerns the sewage treatment plant and there is a need to provide more informaion on whether or not such a plant exists and, in the event that it is non-existent, indicate when construction is planned.

6. Indicate the flow of wastewater to the treatment plant in m^3/day if the treatment plant exists. If no data are available, please make an estimation based on the daily average water consumption *per capita* multiplied by the number of inhabitants. Where more than one treatment plant exists, specify the daily wastewater flow for each one.

6.1. Depending on the type of final treatment of the wastewater plant, specify if there is primary, secondary and tertiary treatment.

7. Indicate the total wastewater treated per day, taking into consideration that, if there is only the treatment plant, the answer would be identical to 6 above. If there is more than one treatment plant, then the sum of the wastewater treated for each one should be provided.

8.1 Indicate the total treated wastewater discharged into the marine environment.

8.2 If the treatment plant serves part of the city and there is wastewater which has not been treated but discharged into the marine environment, then indicate here the untreated flow in cubic metres per day.

9. Indicate the type of discharge giving additional information if this is the case, e.g. discharge through marine outfall, 200 metres from the shore. Indicate also the name of the location which could be the name of a bay or whatever you feel will be appropriate for easily identifying the position of the eventual hot spot.

10. Indicate the pollution loads per year which are expressed either in BOD_5 or COD and total N, total P etc. at the discharge point using any available data.

11. When no available data exist for filling in No.10 above, then give any information and data on the quality of the receiving waters, on the quality of sediments and/or bioa using the parameters listed from 11.1 to 11.10, so as to facilitate the decision or whether, because of its quality, the marine environment can be considered as a hot spot or a sensitive area.

12. Give an estimation of the funds needed for the constrution of the sewer system and/or the sewage treatment plant if they are non-existent. The estimation could be based on information on costs incurred for other works of similar or different size. If the latter is the case, then a gross estimation of the cost per inhabitant would provide an indicative amount.

13. Provide additional information regarding the disposal of solid wastes, so as to provide information and data on the eventual impact they may represent for the receiving waters. For example a landfill close to the sea could significantly contribute to the non satisfactory quality of the waters.

14. Give any other comments that you think may help to decide whether the examined city contributes to increased levels of pollution and constitutes a hot spot or a sensitive area.

Industrial Discharges

This questionnaire will serve for the identification of a hot spot or a sensitive area that is due to direct industrial discharges into the sea. Main industrial facilities of the indicated list will be considered.

1. Indicate the name of the geographical position where the considered industrial facility is located.

2. Indicate the type of industry which falls under the indicated list of activities, giving, if needed, a specification on the type of industry.

3. Write «No» if no treatment exists prior to discharge and, if there is a treatment plant, specify the treatment e.g. neutralization, coagulation or whatever is considered necessary to give a more precise picture of the situation.

4.1 and 4.2 Specify the type of discharge into the marine environment either by a submarine outfall or on shore or specify other means existing.

5. Indicate the total wastewater treated in cubic metres per day, if there is treatment.

6.1 and 6.2 If part of the wastewater is treated then indicate the discharge volumes of the treated wastewater and untreated wastewater.

7. Fill in whatever you find available in order to give a precise picture of the situation. Therefore if data exist for the wastewater quality and for the parameters listed from 7.1-7.8, fill in the first column. If, on the contrary, no data are available for the wastewater quality, and data on the pollution loads affecting the receiving waters exist, then complete points 7.1-7.8 in the second column.

8. In case there is no information on points 5,6 and 7, an indirect evaluation of the pollution will be needed and therefore only if 5,6 and 7 are not answered, if will be necessary to fill in either the **production figures,** or the **raw materials used,** according to the type of industry. For the production figures, indicate the type of product (e.g. for Dairies that produce milk, butter cheese, write the 3 types of products), the unit referred to (e.g. tn or kg), and the figure of the annual production. For the raw materials in use, indicate the type of raw material (e.g. apricots, for canning of apricots), and the figure of the annuan consumption. The above information will permit the evaluation of the pollution load, using appropriate conversion factors, and the results will appear in the third table of point 8.

9. Give any other comments that will contribute to a better understanding of the situation.

10. If there is no treatment, give a cost estimation of the most appropriate remedial measure including both preventive as well as end-of-pipe methods.

11. For any other emission loads from the industrial activity, give all available information.

12. if the industrial activity also produces solid and hazardous wastes which are treated or disposed of in a way that could affect the quality of the receiving waters, then provide any relevant available data.

Discharges from rivers and canals into the sea

This questionnaire concerns well identified rivers in every country and eventually canals that may transport pollution loads into the sea.

1. Indicate the geographical position of the «discharge site» namely the site where the mouth of the river is.

2. Indicate the average daily flow of the river in cubic metres per day.

3. Fill in whatever you find available in order to give a precise picture of the situation. Therefore if data exist for the river water quality and for the parameters listed from 3.1-3.8, fill in the first column. If on the contrary, no data are available for the river water quality and data on the pollution loads affecting the receiving waters exist, then complete points 3.1-3.8 in the second column.

4. Give any other comments that will contribute to a better understanding of the situation.

FORMAT FOR COUNTRY REPORTS

The country report to be prepared should be structured in the following way:

1. Introduction about the current situation and the modalities of conducting the survey (problems encountered, acknowledgements, etc).

2. Approach followed in defining hot spots and sensitive areas in the particular country.

3. Contribution of different sources to the defined hot spots or sensitive areas (see table)* . For each of the main sources e.g. municipal, industrial, etc it will be necessary to provide information using the questionnaires, which will be attached to the report as an annex.

4. Priority hot spots and sensitive areas will be presented in a table using ranking system, mentioned before, and presented as an example.

5. Identification of main gaps and constraints (including lack of information, reliability of information, contemporary validity of data related to dates when data were collected).

6. Proposed option for remedial actions (in order of priority and with justification for prioritization, together with information on the economic cost elements).

7. Annex containing the questionnaires.

Hot spots (or sensitive Areas)	Main sources of pollution	Principal supporting data extracted from the questionnaires
	- domestic - industrial -	

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* Table (to be used when referring to 3)

ANNEX 5

THE ANALYTICAL VALUE[*]

1. Significant Figures

The term significant figure is used rather loosely to describe some judgment of the number of reportable digits in a result. Often the judgment is not soundly based and meaningful digits are lost or meaningless digits are accepted.

Proper use of significant figures gives and indication of the reliability of the analytical method used. The following definitions and rules are suggested for retention of significant figures:

A number is an expression of quantity. A figure or digit is any of the characters 0,1,2,3,4,5,6,7,8,9 which, alone or in combination, serves to express a number. A significant figure is a digit that denotes the amount of the quantity in the place in which it stands.

Reported values should contain only significant figures. A value is made up of significant figures when it contains all digits known to be true and one last digit in doubt. For example, if a value is reported as 18.8 mg/l, the «18» must be firm values while the «0.8» is somewhat uncertain and may be «7» or «9».

The number zero may or may be a significant figure:

a. Final zeros after a decimal point are always significant figures. For example 9.8 grams to the nearest mg is reported as 9.800 grams.

b. Zeros before a decimal point with other preceding digits are significant. With no other preceding digit, a zero before the decimal point is not significant.

c. If there are no digits preceding a decimal point, the zeros after the decimal point but preceding other digits are not significant. These zeros only indicate the position of the decimal point.

d. Final zeros in a whole number may or may not be significant. In a conductivity measurement of 1000 μmhos/cm, there is no implication that the conductivity is 1000± 1 μmho. Rather, the zeros only indicate the magnitude of the number.

Once the number of significant figures is established for a type of analysis, data resulting from such analyses are reduced according to set rules for rounding off.

2. Rounding Off Numbers

Rounding of numbers is a necessary operation in all analytical areas. It is automatically applied by the limits of measurement of every instrument and all glassware. However, it is often applied in chemical calculations incorrectly by blind rule or prematurely, and in these instances, can seriously affect the final results. Rounding off should normally be applied only as follows:

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[*] U.S.EPA. 1973

2.1 Rounding-Off Rules

a. If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example: 11.443 is rounded off to 11.44

b. If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example: 11.446 is rounded off to 11.45

c. When the figure following those to be retained is 5, and there are no figures other than zeros beyond the 5, the figure is dropped, and the last place figure retained is increased by 1 if it is an odd number, or it is kept unchanged if an even number. As an example: 11.435 rounded off to 11.44, while 11.425 is rounded off to 11.42

2.2 Rounding Off Single Arithmetic Operations

a. Addition: When adding a series of numbers, the sum should be rounded off to the same numbers of decimal places as the addend with the smallest number of places. However, the operation is completed with all decimal places intact and rounding off is done afterward. As an example:

11.1
12.12
11.13
_____
33.35 The sum is rounded off to 33.4

b. Subtraction: When subtracting one number from another, rounding off should be completed before the subtraction operation, to avoid invalidation of the whole operation.

c. Multiplication: When two numbers of unequal digits are to be multiplied, all digits are carried through the operation, then the product is rounded off to the number of significant digits of the less accurate number.

d. Division: When two numbers of unequal digits are to be divided, the division is carried out on the two numbers using all digits. Then the quotient is rounded off to the number of digits of the less accurate of the divisor or divident.

e. Powers and Roots: When a number contains _n_ significant digits, its root can be relied on for _n_ digits, but its power can rarely be relied on for _n_ digits.

2.3 Rounding Off the Results of a Series of Arithmetic Operations

The rules for rounding off are reasonable for simple calculations, however, when dealing with two nearly equal numbers, there is a danger of loss of all significance when applied to a series of computations which rely on a relatively small difference in two values. Examples are calculation of variance and standard deviation. The recommended procedure is to carry several extra figures through the calculation and then to round off the final answer to the proper number of significant figures.

3. Glossary of Terms

To clarify the meanings of reports and evaluations of data, the following terms are defined.

3.1 Accuracy Data

Measurements which relate to the difference between the average test results and the true result when the latter is known or assumed. The following measures apply:

Bias is defined as error in a method which systematically distorts results. The term is used interchangeably with accuracy in that bias is a measure of inaccuracy.

Relative error is the mean error of a series of test results as a percentage of the true result.

3.2 Average

In ordinary usage, the arithmetic mean. The arithmetic mean of a set on *n* values is the sum of the values divided by *n*.

3.3 Characteristic

A property that can serve to differentiate between items. The differentiation may be either quantitative (by variables), or qualitative (by attributes).

3.4 Error

The difference between an observed value and its true value

3.5 Mean

The sum of a series test results divided by the number in the series. Arithmetic mean is understood (X).

3.6 Population

Same as Universe.

3.7 Precision

Degree of mutual agreement among individual measurements. Relative to a method of test, precision is the degree of mutual agreement among individual measurements made under prescribed, like conditions.

3.8 Precision Data

Measurements which relate to the variation among the test results themselves, i.e., the scatter or dispersion of a series of test results, without assumption of any prior informaion. The following measures apply:

a. Standard Deviation (σ). The square root of the variance.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} x_1^2}{n} - \bar{X}^2}$$

b. Standard Deviation, estimate of universe (s).

$$s = \sqrt{\frac{\sum_{i=1}^{n} x_1^2 \frac{\left[\sum_{i=1}^{n} x_1\right]^2}{n}}{n-1}}$$

c. Coefficient of Variance (V). The ratio of the standard deviation (s) of a set of numbers, <u>n</u>, to their average $\bar{X}$, expressed as a percentage:

$$V = \frac{S}{X}$$

d. Range. The difference between the largest and smallest values in a set.

e. 95% Confidence Limits. The interval within which one estimates a given population parameter to lie, 95% of the time.

3.9 Sample

A group of units, or portion of material, taken from a larger collection of units, or quantity of material, which serves to provide information that can be used as a basis for judging the quality of the larger quantity as a basis for action on the larger quantity or on the production process. Also used in the sence of a «sample of observations».

3.10 Series

A number ot test results which posses common properties that identify them uniquely.

3.11 Skewness (k)

A measure of the lopsidedness or anymmetry of a frequency distribution defined by the expression:

$$\frac{(X_i - \bar{X})^3}{n\,\sigma^3}$$

This measure is a pure signed number. If the data are perfectly symmetrical, the skewness is zero. If k is negative, the long tail of the distribution is to the left. If k is positive, the long tail extends to the right.

3.12 Unit

The totality of the set of items, units, measurements, etc., real or conceptual, that is under consideration

3.13 Variable

A term used to designate a method of testing, whereby units are measured to determine, and to record for each unit, the numerical magnitude of the characteristics under consideration. This involves reading a scale of some kind.

4. Report Forms

The analytical information reported should include the parameter, the details of the analysis such as burette readings, absorbance, wavelength, normalities of reagents, correction factors, blanks, and finally the reported value.

To reduce errors in manipulation of numbers; a good general rule is to keep data transposition to an absolute minimum. If this were pursued, the ideal report form would include all preliminary information of the analysis, yet it would be possible to use the same form through to the final reporting of data into a computer or other storage device. However, the ideal report form is not usually in use. Rather, a variety of methods are used to record data. They are:

4.1 Loose Sheets

Reporting of data onto loose or ring-binder forms is an older, but much used means of recording data. It does allow easy addition of new sheets, removal of older data, or collection of specific data segments. However, the easy facility for addition or removal also permits easy loss or misplacement of sheets, mix-ups as to date sequence, and questionable status in formal display, or for presentation as evidence.

4.2 Bound Books

An improvement in data recording is use of bound books which force the sequence of data insertion. Modification beyond a simple lined book improves its effectiveness with little additional effort. Numbering of pages encourages use in sequence and aids also in referencing data, through a table of contents, according to time, type of analysis, kind of sample, analyst, etc.

Validation can be easily accomplished by requiring the analyst to date and sign each analysis on the day completed. This validation can be strengthened further by providing space for the laboratory supervisor to sign off as to the date and acceptability of the analysis.

4.3 Pre - Printed Report Forms

Most field laboratories or other installations doing repetitive analyses for any parameters day in and day out, develop their own system of recording and tabulating laboratory data. This may include bound notebooks; but a vehicle for forwarding data is also required. In many instances, laboratory units tailor a form to fit a specific group of analyses, or to report a single type of analysis for series of samples, with as much information as possible preprinted to simplify use of the form. With loose-sheet multicopy forms (use of carbon or NCR paper) information can be forwarded daily, weekly, or on whatever schedule is necessary, while allowing retention of all data in the laboratory. Still, the most common record is an internal bench sheet, or bound book, for recording of all data in rough form.

4.4 Digital Read-out

Instrumental analyses, including automated, wet-chemistry instruments, such as Technicon AutoAnalyzer, atomic absorption spectrophotometer, pH meter, selective electrode meter, etc., now can provide direct digital readout of concentration, which can be recorded directly onto report sheets without further calculation. Electronics manufacturers now produce computer-calculators that will construct best-fit curves, integrate curves, and/or perform a pre-set series of calculations required to obtain the final report value for recording by the analyst.

5. Computerized Storage and Retrieval of Water Quality Data

The use of computers with their almost unlimited ability to record, store, retrieve, and manipulate huge amounts of data is a natural outgrowth of demands for meaningful interpretation of the great masses of data generated in almost any technical activity.

6. A Consolidated Data Reporting and Evaluation System

Information systems have been developed to bridge the gap between the analyst and his raw data, and a complex data storage and control system. These systems include preprinted report forms, computerized verification, and evaluation of data and data storage.