



**MEDITERRANEAN ACTION PLAN
MED POL**

UNITED NATIONS ENVIRONMENT PROGRAMME



FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

**DESIGNING OF MONITORING PROGRAMMES AND MANAGEMENT OF DATA
CONCERNING CHEMICAL CONTAMINANTS IN MARINE ORGANISMS**

MAP Technical Reports Series No. 77

In cooperation with



IAEA

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This volume is the seventy-seventh issue of the Mediterranean Action Plan Technical Reports Series.

This series contains selected reports resulting from the various activities performed within the framework of the components of the Mediterranean Action Plan: Pollution Monitoring and Research Programme (MED POL), Blue Plan, Priority Actions Programme, Specially Protected Areas and Regional Marine Pollution Emergency Response Centre for the Mediterranean.

PREFACE

The United Nations Environment Programme (UNEP) convened an Intergovernmental Meeting on the Protection of the Mediterranean (Barcelona), 28 January - 4 February 1975), which was attended by representatives of 16 States bordering on the Mediterranean Sea. The meeting discussed the various measures necessary for the prevention and control of pollution of the Mediterranean Sea, and concluded by adopting an Action Plan consisting of three substantive components:

- Integrated planning of the development and management of the resources of the Mediterranean Basin (management component);
- Co-ordinated programme for research, monitoring and exchange of information and assessment of the state of pollution and of protection measures (assessment component);
- Framework convention and related protocols with their technical annexes for the protection of the Mediterranean environment (legal component).

All components of the Action Plan are interdependent and provide a framework for comprehensive action to promote both the protection and the continued development of the Mediterranean ecoregion. No component is an end in itself. The Action Plan is intended to assist the Mediterranean Governments in formulating their national policies related to the continuous development and protection of the Mediterranean area and to improve their ability to identify various options for alternative patterns of development and to make choices and appropriate allocations of resources.

The Co-ordinated Mediterranean Research and Monitoring Programme (MED POL) was approved as the assessment (scientific/technical) component of the Action Plan.

The general objectives of its pilot phase (MED POL - Phase I), which evolved through a series of expert and intergovernmental meetings, were:

- to formulate and carry out a co-ordinated pollution monitoring and research programme taking into account the goals of the Mediterranean Action Plan and the capabilities of the Mediterranean research centres to participate in it;
- to assist national research centres in developing their capabilities to participate in the programme;
- to analyse the sources, amounts, levels, pathways, trends and effects of pollutants relevant to the Mediterranean Sea;
- to provide the scientific/technical information needed by the Governments of the Mediterranean States and the EEC for the negotiation and implementation of the Convention for the Protection of the Mediterranean Sea against Pollution and its related protocols;
- to build up consistent time-series of data on the sources, pathways, levels and effects of pollutants in the Mediterranean Sea and thus to contribute to the scientific knowledge of the Mediterranean Sea.

MED POL-Phase I initially consisted of seven pilot projects and baseline studies on the monitoring of oil, petroleum hydrocarbons and microbial pollution in sea water, heavy metals and chlorinated hydrocarbons in marine organisms as well as research on the effects of pollutants on organisms, populations, communities and ecosystems. In addition, four related projects were also included to broaden the scope of the programme or to provide ancillary support.

Based on the recommendations made at various expert and intergovernmental meetings, a draft Long-term (1981-1990) Programme for pollution monitoring and Research in the Mediterranean (MED POL-Phase II) was formulated by the Secretariat of the Barcelona Convention (UNEP), in co-operation with the United Nations Agencies which were responsible for the technical implementation of MED POL-Phase I, and it was formally approved by the Second Meeting of the Contracting Parties of the Mediterranean Sea against pollution and its related protocols and Intergovernmental Review Meeting of Mediterranean Coastal States of the Action Plan held in Cannes, 2-7 March 1981.

The general long-term objectives of MED POL-Phase II were to further the goals of the Barcelona Convention by assisting the Parties to prevent, abate and combat pollution of the Mediterranean Sea area and to protect and enhance the marine environment of the area. The specific objectives were designed to provide, on a continuous basis, the Parties to the Barcelona Convention and its related protocols with:

- information required for the implementation of the Convention and the protocols;
- indicators and evaluation of the effectiveness of the pollution prevention measures taken under the Convention and the protocols;
- scientific information which may lead to eventual revisions and amendments of the relevant provisions of the Convention and the protocols and for the formulation of additional protocols;
- information which could be used in formulating environmentally sound national, bilateral and multilateral management decisions essential for the continuous socio-economic development of the Mediterranean region on a sustainable basis;
- periodic assessment of the state of pollution of the Mediterranean Sea.

The monitoring of, and research on, pollutants affecting the Mediterranean marine environment reflects primarily the immediate and long-term requirements of the Barcelona Convention and its protocols, but also takes into account factors needed for the understanding of the relationship between the socio-economic development of the region and the pollution of the Mediterranean Sea.

Individual and collective training is provided for scientists and technicians in techniques (methods) required for their effective participation in monitoring and research envisaged in the framework of MED POL - PHASE II. This assistance is in the form of fellowships, experts,

workshops, seminars, grants for attendance to meetings, etc., and covers training in analytical and sampling techniques, data processing, interpretation of results and various research topics.

As in MED POL-Phase I, the overall co-ordination and guidance for MED POL-Phase II is provided by UNEP as the secretariat of the Mediterranean Action Plan (MAP). Co-operating specialized United Nations Agencies (FAO, UNESCO, WHO, WMO, IAEA, IOC) are responsible for the technical implementation and day-to-day co-ordination of the work of national centres participating in monitoring and research.

The seventy-seventh volume of the MAP Technical Reports Series contains the lecture notes which have been prepared for the FAO/UNEP/IAEA Training Workshop on the design of monitoring programmes and management of data concerning chemical contaminants in marine organisms (Athens, Greece, 22-26 June 1993).

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INTRODUCTORY PAPER ON BACKGROUND AND SCOPE

by

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1. INTRODUCTION

Pollution monitoring, in one form or another, started in the late sixties and early seventies. It was really an attempt to detect various contaminants in the marine environment and establish their levels. However, the data collected showed, in many cases, big variations which attracted the interest of research scientists. The variations studied, as far as biota are concerned, included those relevant to contaminant concentration with the animal's age, length, weight, sex, and to sampling season and location. Data quality assurance (QA) programmes were initiated to minimise variations that could be attributed to sampling techniques, sample handling and chemical analyses. Early inter-calibration exercises for halogenated hydrocarbons showed variations of up to 1000%. Another interesting fact was that the concentrations of total mercury reported for seawater decreased through the years. This did not indicate a reduction in pollution but an improvement in the analytical procedures which paid more attention to sample contamination. Eventhough analytical quality programmes are now implemented in all monitoring programmes the minute contaminant concentrations present in the marine environment still pose a problem.

By the end of the 1970's a large number of papers were published indicating the existing levels of pollution and possible variations of contaminants' concentrations in the marine environment. The generation of all these data helped to convince Governments that action was necessary but could not be used to justify specific action, especially when difficult managerial decisions had to be taken and thus Governments thought they were not getting their money's worth. One of the first questions that scientists had to respond to, was whether the situation, as regards marine pollution, was improving or deteriorating. A positive answer would indicate that the measures taken by Governments were effective. However, an attempt to analyse the data statistically in order to provide a scientifically-based response to such a question brought to surface a number of problems which were not anticipated in advance. The major problem was that the real differences which scientists tried to observe were masked by natural and anthropogenic variations and that little effort was made to minimise the former ones. Consequently, monitoring programmes had to be re-designed on a different basis.

2. OBJECTIVES

By far the most important step in designing monitoring programmes is the strict definition of the objectives of the programmes concerned. The purpose of marine pollution

onitoring has been defined by a U.S. interagency marine pollution committee as ".....to obtain time-series data for detecting significant changes.....to provide timely warning and other advice to management so that appropriate actions may be taken". However, most historical marine pollution programmes have proven useless in a management context (Segar and Stamman, 1986).

According to the Advisory Committee on Marine Pollution (ACMP) of the International Council for the Exploration of the Sea (ICES), "the ultimate purpose of monitoring is the control of exposure of the organism of interest, most likely to be first affected to the activity or contaminant in question, whether this target be Man or some specified element of the marine resource. Basically, monitoring looks at changes in the marine environment, and in practice, falls into one of the following three categories:

- monitoring for compliance purposes
- monitoring patterns and trends, or
- monitoring for research purposes

It should be noted that research purpose monitoring is generally the first and major step in establishing appropriate and efficient techniques for monitoring patterns and trends, and that in many cases the latter provides information that will be useful in the interpretation of compliance monitoring results" (ICES, 1988).

According to GESAMP (1991) the design of any monitoring programme should be based on clearly defined objectives and the formulation of testable hypotheses. Since monitoring is costly, data should only be collected that (a) are required to satisfy the objectives (b) are amenable to meaningful interpretation, and (c) have known precision and accuracy. Otherwise, technical and financial resources will be wasted and, in the case of compliance monitoring, the production of data of doubtful quality may limit their legal acceptance.

Compliance monitoring pre-supposes the existence of limits, legal or otherwise. These could be the maximum permissible level of a contaminant in seafood (protection of public health) or its concentration in an effluent (reduce inputs) or in the marine environment (any compartment or area). As stated above, monitoring for research purposes is essential in order to obtain the information necessary for designing programmes for management purposes. Programmes for such purposes should provide the manager with information that can enable him to (a) ensure that human health is not threatened, (b) ensure that unacceptable harm is not done to the marine ecosystem or resources, and (c) make informed decisions concerning continued, reduced, or expanded use of the sea for waste disposal and other activities.

Usually the common objectives set are one or more of the following:

- a) **the assessment of risks to human health** or the protection of human health. This is known as health-related monitoring and is normally carried out by national or local health services in a country. This could include monitoring of beaches and bathing waters for microbial pollution and monitoring of seafood for microbial and chemical pollution. In this case, fish samples are obtained from the market rather than sampled directly from the sea. The contaminant levels are normally

compared to some standards legally adopted or not. Research oceanographic institutions do not normally show an interest in such activities; however, any biota samples analysed for other objectives and indicating contaminant concentrations higher than the accepted health limits are reported to the relevant authorities.

- b) **the assessment of the effectiveness or efficiency of measures taken to reduce pollution.** Measures taken to reduce the level of marine pollution are primarily directed at the control and reduction of inputs of contaminants. This objective is therefore directly linked with objective (d) which monitors inputs. It is also necessary to control the quality of the marine environment with time and therefore trend monitoring has to be implemented.
- c) **the assessment of damage to marine life** or the protection of marine life. Biological effects monitoring in a systematic manner is a relatively new activity. It can provide a measurement of the direct effect of adverse water and sediment quality on marine organisms. The basis of such monitoring is measuring the extent to which a specific biological response deviates from a normal value. There are reactions at the cellular level which are specific to certain groups of chemicals. Responses such as the induction of mixed-function oxygenases (MFOs) by organic compounds and of metallothioneins by heavy metals have the potential to be very sensitive and therefore act as "early warning" indicators. It is essential that biological monitoring should be integrated with chemical monitoring, so that the extent to which the measured effects can be ascribed to specific chemicals, can be established (GESAMP, 1991).
- d) **the assessment of the inputs of contaminants** into the marine environment from various sources. This is known as load monitoring and is directly linked with objective (b). The main inputs are from land-based discharges, riverine sources, the atmosphere, and direct dumping.
- e) **the assessment of the existing level of marine pollution** as a timely warning system. For this objective, water, sediments as well as organisms have to be monitored.

All objectives are inter-dependent and a careful programme design can satisfy them all. The Oslo and Paris Commissions have decided on a Joint Monitoring Programme with the following objectives:

- a) the assessment of possible hazards to human health
- b) the assessment of harm to living resources and marine life (ecosystems)
- c) the earliest possible assessment of the existing level of marine pollution

- d) the assessment of the effectiveness of measures taken for the reduction of marine pollution in the framework of the Conventions.

The Cooperative Monitoring Programme of ICES includes only analysis of fish and shellfish and has the following three objectives:

- a) the provision of a continuing assurance of the quality of marine foodstuffs with respect to human health
- b) the provision over a wide geographical area of an indication of the health of the marine environment in the entire ICES North Atlantic area
- c) to provide an analysis of trends over time in pollutant concentrations in selected areas, especially in relation to the assessment of the efficacy of control measures

The second stage, after defining the objectives, is to decide on the methodology to achieve them and thus design a suitable programme.

3. PROGRAMME DESIGN

There are a number of factors to be considered in the planning of a monitoring programme to meet specific objectives. Some of these are:

- a) which contaminants should be measured;
- b) in which matrices should they be measured;
- c) where should the samples be collected;
- d) when should the sampling be done and how frequently;

If biota are going to be analysed, which species and tissue; also what size and how many individuals should be collected. If sediment is the matrix, then sampling technique, grain size and extraction method have to be decided.

The selection of contaminants depends on the objectives of the monitoring programme, the likely sources and the analytical capabilities of the participating laboratories. Matrices should be selected accordingly having also in mind where a contaminant would be predominantly associated. For example, one should not look for chlorobiphenyls in water since the octanol: water partition coefficient indicates otherwise.

At any rate, I do not intend to expand on these issues since the papers which follow will cover these in detail.

4. THE MED POL PROGRAMME

The MED POL programme was initiated in 1975. Phase I, which ended in 1981, consisted of baseline studies and pilot projects. The Food and Agriculture Organization of the United Nations, through its General Fisheries Council for the Mediterranean, was responsible for the technical co-ordination of the following:

- a) Baseline studies and monitoring of metals, particularly mercury and cadmium, in marine organisms
- b) Baseline studies and monitoring of DDT, PCB's and other chlorinated hydrocarbons in marine organisms
- c) Research on the effects of pollutants on marine organisms and their populations
- d) Research on the effects of pollutants on marine communities and ecosystems.

When approving MED POL - Phase II the Contracting Parties decided that its specific objectives are designed to provide them with:

- information required for the implementation of the Convention and the protocols;
- indicators and evaluation of the effectiveness of the pollution prevention measures taken under the Convention and the protocols;
- scientific information which may lead to eventual revisions and amendments of the relevant provisions of the Convention and the protocols and for the formulation of additional protocols;
- information which could be used in formulating environmentally sound national, bilateral and multilateral management decisions essential for the continuous socio-economic development of the Mediterranean region on a sustainable basis;
- periodic assessment of the state of pollution of the Mediterranean Sea.

MED POL Phase II is organised on four levels:

- (a) monitoring of sources of pollution providing information on the type and amount of pollutants released directly into the environment;
- (b) monitoring of nearshore areas, including estuaries, under the direct influence of pollutants from identifiable primary (outfalls, discharge and coastal dumping points or secondary (rivers) sources;
- (c) monitoring of offshore areas (reference areas) providing information on the general trends in the level of pollution in the Mediterranean;
- (d) monitoring of the transport of pollutants to the Mediterranean through the atmosphere, providing additional information on the pollution load reaching the Mediterranean Sea.

Monitoring type (a) includes pollutants discharged directly into the coastal waters from land-based sources, pollutants dumped directly into the sea, pollutants dumped in emergency

or released accidentally into the sea and substances reaching the sea through natural (weathering, hydrothermal etc.) processes from land-based (coastal) or maritime sources. Substances to be monitored are generally those listed in the Annexes to the protocols.

Monitoring types (a) and (d) assess pollution loads from land-based sources and those reaching the sea through the atmosphere respectively, while types (b) and (c) refer to levels in the environment. In fact, the four types indicate that the programme is interested in load monitoring and in the establishment of pollution levels.

For general monitoring purposes of coastal waters the following priority parameters were initially indicated:

- total mercury in organisms and sediments;
- cadmium in organisms;
- high-molecular weight halogenated hydrocarbons in organisms and sediments;
- petroleum hydrocarbons in water, sediments and oil residues (tar balls) on sea-shores;
- faecal coliforms in recreational waters and edible bivalves;
- basic oceanographic and meteorological conditions.

It was envisaged that after 3 years the following additional parameters would be added to the list:

- cadmium in sediments;
- organic mercury in organisms and sediments;
- total arsenic in organisms;
- selenium in organisms;
- lead in organisms;
- polynuclear aromatic hydrocarbons in organisms;
- additional organics (such as carcinogenic compounds) in organisms;
- radionuclides in organisms;
- faecal coliforms in sediments;
- pathogens in waters, sediments and bivalves;
- ecological parameters, such as productivity and community structure.

On the basis of the experience gained during the first five years of implementation of the monitoring component of MED POL Phase II, it was proposed to continue with the above parameters but with minor changes as follows:

Category I parameters:

- Total mercury in organisms and sediments
- Organic mercury in organisms
- Cadmium in organisms and sediments
- High molecular weight halogenated hydrocarbons in organisms and sediments
- Faecal coliforms in recreational waters and bivalves

Category II parameters:

- Basic oceanographic and meteorological parameters (e.g. salinity, oxygen, temperature, chlorophyll, wind)
- Floating tar balls and tar balls on beaches
- Total arsenic in organisms
- Radionuclides in organisms
- Pathogenic microorganisms
- Polynuclear aromatic hydrocarbons in organisms

The species recommended for monitoring purposes represented different ecotypes:

a) Bivalves

Mytilus galloprovincialis (MG), or Mytilus edulis (ME), or Perna perna (PP) or Donax trunculus (DT).

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 (MB), or Mullus surmuletus (MS), or Upeneus molluccensis (UM).

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 (TT), or Thunnus alalunga (TA), or Xiphias gladius (XG).

d) Pelagic plankton feeding fish

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

e) Shrimps

Parapenaeus longirostris (PL), or Nephrops norvegicus (NN), or Penaeus kerathurus (PK).

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

5. REFERENCES

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MONITORING; ITS STRATEGIES, TACTICS AND OPERATIONAL PLANS

by

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1. INTRODUCTION

The aim of this paper is to make the course participant or reader familiar with some well established monitoring programmes, some of their results, their strong and weak sides as well as giving an illustration on where these programmes are moving in their further development.

The first few headlines are addressing basic questions in a provocative manner to set the scene for the further presentation and discussion of this theme. Therefore, the main text of the paper is kept short since this presentation relies primarily on the material in the different annexes.

2. WHAT IS MONITORING?

Given different cultural backgrounds the word "monitor" may have different meanings: to supervise, to overview or to watch etc.

In a more environmental sense the word, in its more positive and active understanding, means "to act as a watchdog" that detects changes in the environment, regardless if these changes are positive or negative.

One of several widely accepted definitions is that **monitoring is the repeated measurement of an activity or of a contaminant or of its effects, whether direct or indirect, in the marine environment.**

3. IS POLLUTION AND CONTAMINATION THE SAME THING?

These two words are used in such a way that they overlap. In some cases they also seem to be used with no discrimination between them. This paper operates on the definition that:

Contamination means the introduction to the environment of a substance, or energy, so that background values are exceeded, and

Pollution means that the contamination has reached a level where adverse or deleterious effects, or even damage, occur.

4. WHY, AND WHAT, DO WE NEED TO MONITOR?

The environment is constantly changing. Most of these changes are certainly natural but Man and Man's activities cause several adverse changes as well as they may considerably change the speed and direction of many natural processes. Therefore, it is essential to review and describe the environmental status of an area and detect negative changes as early as possible in order to introduce corrective measures as early as possible. Another reason for monitoring is that when measures have been decided and introduced it is essential to follow the result and detect and report on the possible improvements. An example of the latter is the decision by ministerial conferences within the North Sea and Baltic Sea communities to reduce by 50%, before the end of 1995, the discharges of nutrients and certain inorganic and organic contaminants.

Due to the high variability in the natural systems it may be very difficult to prove, or even to demonstrate, changes of that size. However, by setting realistic goals and objectives for our monitoring programmes we will be in a position to report results.

What do we need to monitor? Obviously we need to monitor those human activities that threaten the quality of the marine environment. This means nutrients and contaminants according to what is known about discharges of these substances.

However, measuring concentrations of contaminants does not tell us anything about their effects in a direct sense. In some cases we know at what contaminant concentration level we can expect a more or less dramatic effect in Nature but more often this dose-response relationship is not known. Therefore, it is essential that a good programme also includes monitoring of biological effects although it may be very difficult to link an observed effect with a certain concentration level of a certain contaminant.

In addition to this, there is a need to have "a monitoring of the unknown." WHY ? there is a very simple answer to that! We certainly do not know the composition and content of all Man's discharges to the environment. Consequently, by definition, we do not know if we are monitoring all contaminants we should (most probably we are not) or if we are always looking for effects where they may or will occur.

Therefore, in addition to the biological effects monitoring mentioned above, in a good programme there should be a willingness and readiness to spend resources on surveys or studies having the potential of disclosing or revealing the unknown or the unexpected.

It is understandable if this cannot be done because resources are not available, but it is a mistake to deliberately exclude this "watch-dog component" on the belief that we know exactly what should be monitored.

A classical example of this is the discovery of PCB in the environment. In the (gas chromatographic) analysis of DDT in biota samples some strange and unexplained information (peaks in the chromatogram) appeared. The professional curiosity of one chemist led to retrospective analyses of archived biological samples from the Museum of Natural History (in Stockholm). Since all samples had an adequate historical record it was possible to trace

back in time when these substances first appeared. With more detective work on industrial production, the PCBs came into focus and further analyses confirmed that the presence of PCBs was indeed the explanation for the peaks! Nobody would deny that PCBs have been, and still are, substances of great environmental concern.

5. THIS CALLS FOR A STRATEGY - BUT WHAT EXACTLY IS A STRATEGY?

Let us take it from the beginning! There is no unified way to define "strategy"! The word means different things to different people because they work in different organisations with different cultures!

The usual situation is that there is no clear distinction between "strategy" and "tactics."

In Figure 1 you can find one attempt (of several possible) to compare the thinking on this subject within the commercial business and the environment monitoring sector.

The figure shows a pyramid with building blocks in three levels: strategy, tactics and operational plans.

In the commercial business sector one makes an important decision in setting up a company or starting a new activity, e.g. "We are going to be the biggest Volvo car supplier in Brazil." This statement is the business idea and it contains three crucial elements "Selling what" (Volvo cars), "How much" (the biggest car supplier) and "Where" (in Brazil).

This business idea is actually the strategy of the company! Their tactics will consist of such elements as whether they will set up offices and shops in all the places where they want to be present; or if they should work through local existing companies in a franchise system; whether they should offer leasing schemes or not; whether they should offer differentiated prices to different customer groups etc.

Their operational plans will describe in detail how to accomplish all this plus many other things as e.g.; how to influence the market by advertising; how to deal with customer complaints etc.

In the field of monitoring a strategy could be "We must protect our national population from consuming shellfish that could cause shellfish poisoning." The tactics could include such elements as: is it sufficient to take samples from the catch that will be put on the market? should one sample some randomly selected areas or should one sample all areas where they fish plus all installations for shellfish aquaculture? Again, the operational plans would have to tackle practicalities such as frequency of sampling, methods for sampling, analysis and data reporting etc.

As international monitoring programmes are established by representatives from different administrations in different countries having different "cultural background" concerning language and management it is not at all surprising that the picture is less clear on how the words "strategy" and "tactics" are used. This is certainly not a criticism! The logical conclusion is that when these words are used it is advisable to find out what they stand for in the programme that is being discussed!

The International Council for the Exploration of the Sea (ICES), being a scientific advisory body to the Helsinki Commission and the Oslo and Paris Commissions, and a partner with the latter commissions within the North Sea Task Force, has worked out a monitoring strategy. The strategy is presented in detail in Annex 1. One may note in Figure 1 that the ICES strategy overlaps the areas of strategy and tactics and also that the operational plans of the Commissions (Guidelines) overlap the areas of tactics and operational plans. Again, this is not a criticism but rather a note that "the monitoring scheme" can be presented in different ways. There is no given answer to the question "which is the best or the correct way". The important point is that monitoring must be part of a system with a holistic view as described in Figure 2. Here, we can see that monitoring becomes useful when its results are assessed and subsequently used as a basis for management decisions. Then, monitoring is needed to follow the results of these decisions. Therefore, it is natural to see this as a series of steps with feed-back in between them. Presented as a cyclic system it is natural to put research as "the hub of the wheel" as research is needed to design each step in an optimal way. It should also be pointed out (although it does not appear in the figure) that the different steps also can provide valuable input to the research.

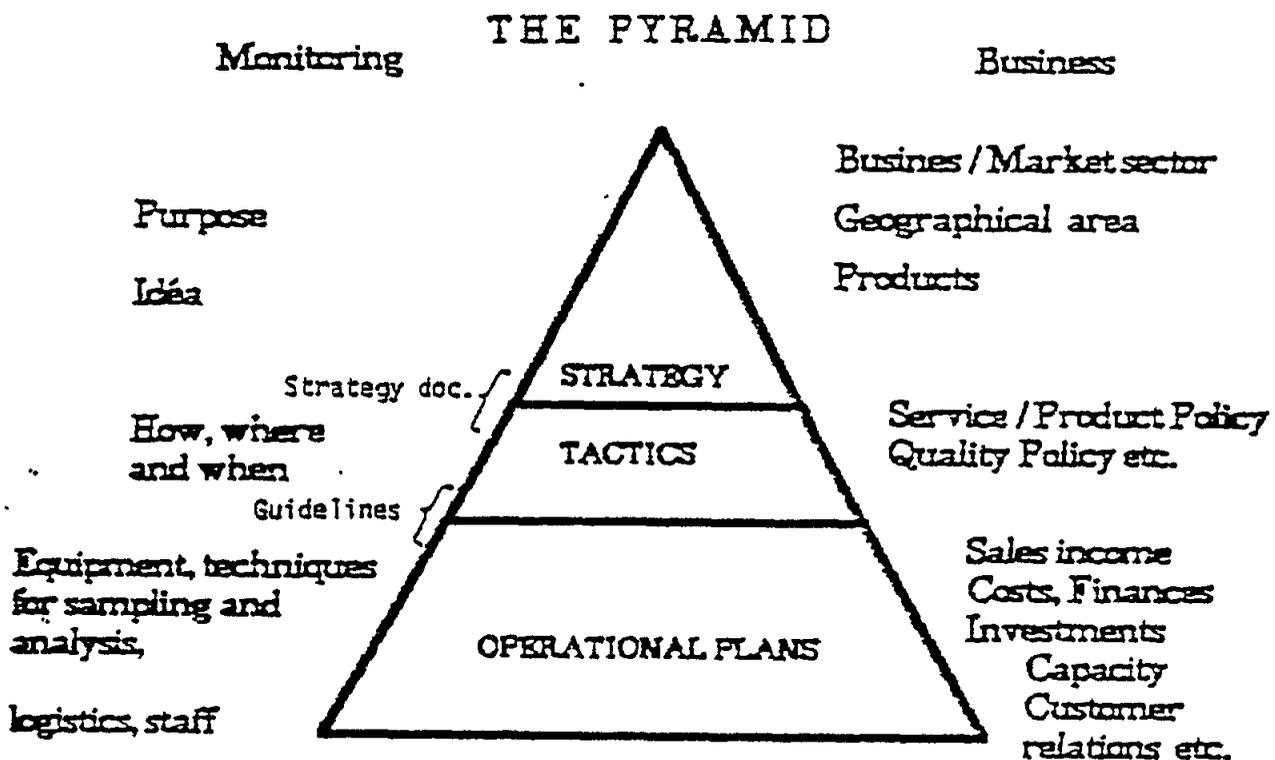


Figure indicating strategy, tactics and operational plans

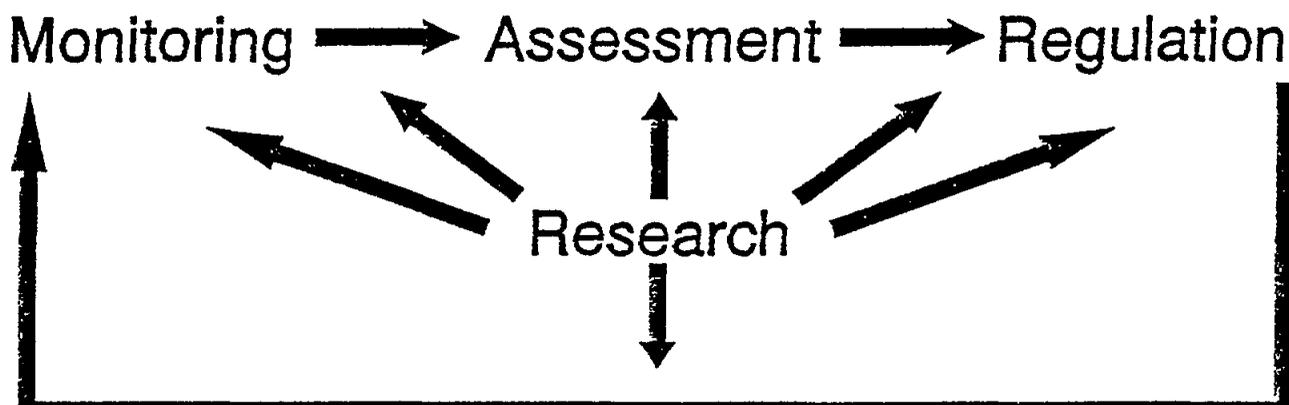


Fig. 2 The monitoring is linked in a management system and the importance of research for the management is underlined

6. A COMPARISON OF SOME WELL ESTABLISHED MONITORING PROGRAMMES

6.1 The Joint Monitoring Programme of the Oslo and Paris Commissions

The Joint Monitoring Programme (JMP) of the Oslo and Paris Commissions (OSPARCOM) has been active since the principles of the programme were elaborated by the Joint Monitoring Group (JMG) in 1978.

The objectives of the JMP are as follows:

It is the duty of both the Oslo and Paris commissions to examine the condition of the seas covered by the Conventions and the effectiveness of measures adopted. The JMP of the Oslo and Paris Commissions focuses on three compartments: marine organisms, seawater and sediments. Monitoring is carried out in more than sixty JMP areas for the following purposes:

- (a) the assessment of possible hazards to human health;
- (b) the assessment of harm to living resources and marine life (ecosystems);
- (c) the assessment of the existing level of marine pollution (spatial distribution) and
- (d) the assessment of the effectiveness of measures taken for the reduction of marine pollution in the framework of the Conventions (temporal trend assessment).

Purposes (a) and (b) are applicable only to marine organisms. For purpose (c), all three compartments are monitored; whereas for purpose (d) only organisms and sediments are monitored as a general rule.

In addition to these assessments, the JMG is also charged with the evaluation of the monitoring of dumping grounds for industrial wastes, sewage sludge and dredged spoils. Another task of the Group is the evaluation of inputs to the marine environment from land-based sources.

Assessment of monitoring data for the various purposes is carried out in a regular way. Several assessment reports have been produced, either as internal documents for the OSPARCOM or as open publications.

6.2 The Monitoring Master Plan of the North Sea Task Force

The North Sea Task Force (NSTF) originates from a German political initiative to accelerate the work of the OSPARCOM, or more precisely, the work of the Commission as carried out for the North Sea area. A Ministerial Conference was arranged and one of the results was that OSPARCOM and ICES joined forces in 1988 and became equal partners in NSTF.

The Monitoring Master Plan (MMP) was designed with one overruling objective in mind; the 1993 Quality Status Report (QSR) of the North Sea as decided upon by the Ministerial Conference. The MMP focuses upon providing supplementary information to that collected under the JMP so that the QSR could give a complete description of the environmental situation in the North Sea. The MMP, therefore, was designed to: a) collect information on the distribution of well researched contaminants in areas normally not sampled, and, b) the occurrence and distribution of less well researched contaminants.

One example from the structure of the MMP is given in Annex 2. The example shows a systematic way of deciding where, or rather in which compartments of the marine environment to monitor the different contaminants. The table is based on considerations of cost-benefit of monitoring. It must be underlined that the table should never be used without due consideration of the relevant text! The first assessment is the QSR that will be published in late 1993 as a preparation for the ministerial conference in 1994.

6.3 The Baltic Monitoring Programme of the Helsinki Commission

This programme was launched in 1979. There are two very interesting principles that makes this programme different from e.g. the JMP. **The BMP Guidelines point out that for the understanding of the results of the environmental monitoring it is absolutely essential to understand the natural variations in the system.** Therefore, such investigations are included in the monitoring (although partly on a voluntary basis).

The aim of the baltic Monitoring Programme (BMP) is to follow the long-term (annual and long periods) change (trends) of selected determinants in the Baltic ecosystem.

Monitoring data form a part of the background information for an appropriate assessment of the state of the marine environment and for a

forecast of possible man-induced changes. In order to register such man-induced changes, the natural changes of different elements of the ecosystem must be known. Therefore, monitoring will often include registration of more or less "natural" conditions. In its more restricted sense, the term is applied to the regular measurement of contaminant levels in relation to set standards or in order to judge the effectiveness of a system of regulation and control. Monitoring does not encompass experimental laboratory studies and scientific investigations, which, nevertheless, may be of importance in the planning of future monitoring activities.

In this way the aim of the BMP is defined in a very soft or vague way. Although the text points out trends at various time scales nothing is said about which determinants (contaminants) should be monitored or how small trends the programme should be able to detect.

Furthermore, it is stated that although all contracting parties are invited to contribute by monitoring in all subregions of the Baltic, **there is a principle of strict regional responsibility. This puts the burden on identified countries to produce enough data from each subregion.**

The programme has produced one very extensive scientific assessment of the status of the Baltic marine environment published in 1981 and after that two periodic assessments (in 1986 and 1990). A third periodic assessment is being organised.

7. STRENGTHS AND WEAKNESSES IN THE PROGRAMMES

The programmes bring Contracting Parties (member countries) and their institutions together in a cooperation within a coordinated plan. This is cost effective in the sense that the undeniably high costs for marine environmental monitoring is shared by all parties. Furthermore, it offers the possibility to collect more data from a large sea area than a single country normally could afford to do.

The fact that assessments of the quality of the marine environment are carried out jointly has both practical, scientific and political advantages. When an agreed assessment is ready it serves as a common management instrument for further regulations e.g. discharge reductions etc.

As pointed out above, all three monitoring programmes have produced, or are producing, useful assessments.

However, one should not deny that there are weak sides as well. The weaknesses are both in programme structure and in their execution. If they are not identified at an early stage they certainly become obvious in the assessment work. Therefore, it is important to create and maintain the feedback so that conclusions from the assessments are used also to improve the monitoring programmes and their plans.

Generally there are insufficient data to allow an adequate assessment and essential information on inputs is often missing. Some of the major reasons are that the agreed monitoring plans are often not carried out completely and often monitoring guidelines are not followed. This means e.g. that mandatory determinands are not measured and/or too few stations are sampled. Furthermore, information on the very necessary 'supporting parameters' (e.g., salinity, fat content) is often missing. As neither the JMP

nor the MMP provide biological monitoring data, except for benthos, it would be recommendable to encourage the expansion of these monitoring programmes to cover also birds and mammals.

A strong point of the MMP is that, often for the first time, data were collected in areas far enough from local pollution sources to be used as potential reference areas.

The advantage of applying biological effect techniques is the fact that they integrate the effects of a wide range of stress factors, so they can provide information on the effects of substances that are not measured in the chemical monitoring programme. However, the application of certain techniques (EROD, fish diseases and oyster larvae bioassays) is still under development and we will, therefore, have to wait some more years before they will be widely used on a routine basis.

8. WHERE DO WE GO FROM HERE?

The existing Oslo and Paris Commissions have been re-negotiated by their contracting parties. The new "Convention for the Protection of the Marine Environment of the North-East Atlantic" has been signed in October 1992 and it is expected that the Convention will come into force within the next few years. However, it is too early to describe at this point how the JMP will be changed.

Also the Helsinki Convention has been re-negotiated. The Environment Committee of HELCOM has decided that all monitoring activities of the HELCOM should be joined under one umbrella, called the Cooperative Monitoring in the Baltic Marine Environment or COMBINE. This will result in an improved coordination and easier management of more strict quality assurance procedures. Annex 3 describes the objectives of COMBINE and its subparts. Although the text is still preliminary it is interesting to see that now the objectives are more clearly defined.

ANNEX 1

THE ICES monitoring strategy

This text is an extract from the Report of the ICES Advisory Committee on Marine Pollution (ACMP) 1988. (Coop.Res.Rep. No 160).

4. MONITORING STRATEGIES

Based on the report of the Working Group on Environmental Assessments and Monitoring Strategies (WGEAMS), the ACMP reviewed guidelines on the Philosophy, Principles, and Strategy of Monitoring, issued as an annex to the WGEAMS report. On the basis of this paper, the ACMP has prepared the following guidance on this topic.

4.1 Philosophy, Principles and Strategy of Monitoring

4.1.1 Introduction

This paper is a revised and extended version of the previous advice on the question of monitoring in relation to the marine environment given by ACMP in its 1978 report (Cooperative Research Report No. 84, Annex 1).

4.1.2 Definition

In the context of assessing and regulating environmental and human health impacts of anthropogenic activities, specifically the introduction of wastes, monitoring is the repeated measurement of an activity or of a contaminant or of its effects, whether direct or indirect, in the marine environment.

4.1.3 Objectives

The ultimate purpose of monitoring is the control of exposure of the organism of interest, most likely to be first affected, to the activity or contaminant in question, whether this target be Man or some specified element of the marine resource. Basically, monitoring looks at changes in the marine environment, and in practice, falls into one of the following categories:

- monitoring for compliance purposes,
- monitoring patterns and trends, or
- monitoring for research purposes.

It should be noted that purpose monitoring is generally the first and major step in establishing patterns and trends, and that in many cases the latter provides information that will be useful in the interpretation of compliance monitoring results.

4.1.4 Strategies

All too often monitoring programmes continue unchanged long after they have ceased to produce useful data in the context of the original objective.

It is essential that monitoring should have a clearly defined objective, that the measurements made are designed so as to be usable in meeting that objective, and that the results be reviewed at regular intervals in relation to that objective. The monitoring scheme should then be continued, revised or even terminated, as appropriate.

Then, before any programme is drawn up and any measurements are made, the following questions should be addressed:

- 1) What exactly do we wish to measure?
- 2) Why do we wish to monitor a particular variable, contaminant or biological effect?
- 3) How can that measurement be achieved and is monitoring the most appropriate approach?
- 4) In what compartment or at which locations can measurements most effectively be made?
- 5) For how long do we need to continue measurements in order to meet the originally defined aim?

Although much is now known about the marine environment, there is still a lack of basic knowledge and adequate description of the marine ecosystem as a whole. In order to be able to assess the quality and health of the environment, there is a need to be able to determinate natural variability and corresponding induced effects. This can only be achieved through monitoring programmes that include biological effects or produce data that can be compared to known and agreed effects levels, i.e., environmental quality standards.

Since the environment is subject to natural changes, e.g., climatic, it is important that an understanding is established of these natural changes and the way they might affect either contaminant levels or biological characteristics. This implies longterm data sets on parameters which establish the basic characteristics of the marine media, e.g., water temperature and salinity, transparency, chlorophyll levels, and nutrient concentrations.

There is also a fundamental need to recognise the requirements of decision-makers. It is especially necessary to recognise that they will require the results on finite time scales and that they will expect the results to be presented in a readily interpretable form. Thus, in common with the formulation of a regional assessment, part of which will be based on monitoring data, a basic requirement of monitoring is that it yields accurate data. These data, in turn, will provide the basis of sound, reliable advice to administrators on the need for environmental protection measures or the effectiveness of protection measures already introduced.

It is apparent that the responsibility to undertake monitoring programmes rests with organisations having interests in the nature and scale of particular areas and problems. From the single effluent outfall or river, to estuaries and shelf seas, through to the open ocean, there is a gradation of responsibility from local authorities to international organisations. However, with

respect to the protection of the environment, global consideration are of primary importance and, as far as possible, they should be taken into account in developing standards and scientifically based quality criteria.

With these strategic considerations as background, the following illustrates a practical approach to the planning of monitoring programmes.

It is first essential to identify the resource at risk and then the substances or activities most likely to threaten the resource it is desired to protect. This obviously requires, at an early stage, a fairly thorough assessment of what activities are already in progress and which substances are likely to enter the area in question and via which routes. Alternatively, information on inputs can be used to focus environmental monitoring effort on those substances or effects which are most likely to be encountered at levels considered to be significant. An understanding of input fluxes to the marine environment will frequently permit even sharper focussing of the monitoring effort.

The next step assumes the existence of maximum acceptable levels of inputs or effects in order to protect the resource in question. This requires an understanding of working relationship between rates of input and environmental concentrations, ideally via a model of exposure pathways, and the effects it is desired to avoid. It also assumes that a maximum acceptable level has been set or can be derived. Standards do not always exist and it is often argued that they cannot be defined. However, the use of simple data, even data from acute toxicity tests, can be used to derive preliminary quality objectives which will, if they incorporate appropriate safety factors, suffice pending the derivation of more accurate standards from more thorough biological testing.

4.1.5 Guidelines

The following general guidelines should provide some assistance in selecting the most appropriate monitoring techniques for the problem in question. Detailed guidelines on monitoring using marine organisms, sediments and sea water have been provided in past ACMP reports and are currently under review; details will be published separately as soon as the reviews are complete. If the following guidelines are followed, it is hoped that some of the effort currently devoted to routine monitoring can be deployed to research programmes designed to establish a better understanding of the marine environment and what constitutes a pollution problem.

4.1.5.1 Contaminants

In the past, the selection of contaminants has been based largely on the black and grey lists of the various pollution prevention conventions. It is now apparent that some of those originally listed substances do not present serious pollution risks in a marine context, whereas other substances not identified in the lists probably do. This illustrates the need to review monitoring activities from time to time in order to assess the need for their continuation.

It is, therefore, recommended that the choice of which contaminants need to be monitored should depend primarily upon the perceived aim, i.e., why there may be concern, and

secondly, on whether there is real reason for concern in the area in question, i.e., is there an input of sufficient scale and is there a target likely to be affected. One certainly should not have to monitor regularly for all contaminants at all sites and it should not be necessary to use more than one substrate or effect to meet each aim. Thus, for example, if it is possible to analyse samples of fish liver for a range of metals and establish trends over time, it is not necessary also to measure any of these same contaminants in sea water for the same purpose. Matrix tables could be provided to cover the various options available and indicate the most appropriate choice.

The following table is given as an illustration.

Table 1

Marine matrix selection for contaminants monitoring in relation to the protection of human health.

Matrix	Contaminant									
	PCB	Lindane	Hg	Cd	Cu	Zn	As	Cr	Ni	Pb
Water										
Sediments										
Shellfish	+	+	+	+			4			+
Fish muscle			+				4			
Fish liver	x ²	x ²		x ¹	3	3		3	3	

+ = primary matrix
x = secondary matrix

Notes and Qualifications:

- 1 If fish liver is not a consumed fisheries product, ignore entry.
- 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 concern in respect to the consumption of fisheries products.
- 4 While arsenic exists in significant amounts, e.g., in plaice muscle and crustaceans, its chemical form makes it of little concern in respect to fish consumption and human health.

4.1.5.2 Biological Effects

At present, there is a wide variety of techniques available that are capable of demonstrating whether or not an effect occurs. Some are simple to conduct, others more

complex, and not all are readily amenable to use in the field. A difficulty in many cases is that although an effect is clearly detectable, its significance is unclear in terms of the well-being of the organism or species in question. Such techniques are not suitable for routine application to monitoring programmes and are probably best regarded at present as research techniques. From the standpoint of monitoring as defined in this document, the most useful biological effects are those that can be interpreted as being likely to affect adversely the ability of the species to survive, grow normally or reproduce. Ideally, the effect should be linked to a particular contaminant or source of contamination, but the fundamental requirement is that the effect is liable to have harmful consequences. Experience suggests that no one technique is likely to suit all situations.

4.1.5.3 Data Quality

Whilst it is obvious that good quality data are necessary at all times, attention should be paid to the level of accuracy and precision required. This can only be judged in relation to the aim. For example, if one is looking for trends at the $\pm 20\%$ level, a high degree of precision will be called for (accuracy of data will also be important, in particular where several laboratories are to be used and data are referred to an agreed standard). However, if, on the other hand, one is demonstrating compliance with a standard which is several times higher than the concentrations actually being encountered, the level of precision (and accuracy) required is lower. There may be occasions when it is extremely difficult to measure accurately the parameter of interest, e.g., river inputs. In such situations, the limitations of the data must be clearly stated and, if comparisons are made between data from different sources, it is essential that the data compared be collected according to a common pattern, so as to eliminate differences related to procedures. Equally important is the statistical reliability of the original sampling design and the interpretation of the results.

In cooperative programmes involving several laboratories, it will of course be necessary to ensure that all participants are producing comparable data. For new contaminants this may not initially be possible and it may, therefore, be appropriate to allow a single laboratory with proven capability to conduct preliminary measurements in order to demonstrate the scale of a problem. If further measurements are considered necessary on a wider basis, it is almost certain that national authorities would wish to assure themselves of access to the data at the earliest possible opportunity. This would necessitate measures to assure the comparability of data produced by the different organizations in the different countries but the principle of having lead laboratories for particular contaminants, at least one per country, would facilitate achieving this end. The use of quality assurance procedures is strongly recommended.

4.1.5.4 Reporting Data

Once the monitoring programme is underway, it will be necessary from time to time to report the data to some coordinating centre so that they can be reviewed and assessed relative to the originally stated aim and/or established standards or criteria. It is essential that the data be reported in adequate detail to meet this requirement. In this context, however, it should be noted that although it is now relatively easy to transmit data from centre to centre by tape, diskette or electronically, collecting and recording data involves effort and costs money. What is collected and transmitted should, therefore, be tailored to the need and be the minimum necessary to meet that need.

ANNEX 2

Examples from the structure of the NSTF/MMP

Extract from the North Sea Task Force Monitoring Master Plan (NSTF/MMP). (North Sea Environment Report No 3).

1.1.3 The assessment of the existing level of marine pollution (JMP purpose (c) - Table 2)

Water

A distinction is to be made between nearshore and offshore waters. In the Former, marked salinity gradients occur, and contaminant distribution is more likely to be influenced by riverine or land-based inputs. In the latter, which is more from the above-mentioned inputs of contaminants, gradients are normally substantially less marked.

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. However, considerable efforts are still required to improve the comparability of analytical performance among laboratories engaged in sea water analysis in member countries. The requirements for precision and accuracy of analysis at low concentrations limit the number of determinands that can be considered in offshore waters to mercury, cadmium, copper, zinc, lead and lindane, all at secondary matrix level. Even in these cases, it would be essential for each laboratory to establish in-house quality control procedures, and for rigorous attempts to be made to establish comparability between laboratories, with particular attention being paid to lead.

In nearshore waters subject to anthropogenic influences, concentrations may be somewhat more variable, and chromium and nickel analyses might be added to the above list. The same quality assurance precautions would be needed. In nearshore 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 octanol: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.

There are some sheltered bays or lagoons in which the inputs of contaminants are sufficiently large to cause marked elevation of contaminant concentrations in sea water, or which changes in concentrations can be expected. As agreed by the Commissions, in such areas it might be appropriate for national authorities to give more prominence to water analysis in monitoring programmes, but this should not be regarded as general recommendation.

Sediments

There is very considerable emphasis laid on the use of surficial sediments as primary matrix for most of the contaminants. Participating laboratories should take full account of the most recent advice on the selection of sampling locations and methods (see, e.g., Section 15, 1986 ACMP Report (Coop.Res.Rep. No 142); Annex 2, 1983 ACMP Report (Coop. Res.Rep. No. 124); Annex 2, 1984 ACMP Report (Coop.Res.Rep. No. 132)). Areas of high sedimentation and low bioturbation rates are particularly favourable. It is also necessary to subject the samples or data to appropriate normalisation procedures to compensate for the natural distribution of contaminants in relation to the texture, provenance and grain-size of the sediment.

Biota

Both sediment and shellfish are indicated as primary monitoring matrices for tributyl-tin (TBT). Whilst the main area of concern over TBT is its effects on shellfish, particularly molluscs, for example, oysters and dogwhelk, these organisms are by nature of limited geographical distribution. TBT, and its derivatives DBT (dibutyl-tin) and MBT (monobutyl-tin), can be found in sediments, especially near shipyards and busy shipping lanes, in harbours and marinas and, at least until recently, in the vicinity of some mariculture operations. The monitoring of sediment for these compounds would allow the use of a single matrix in a wider range of environment (e.g., into low salinity areas of estuaries) than would be possible using a single molluscan species.

Matrix Table 2

In relation to the assessment of the existing level of marine pollution
(i.e., contamination [JMP Purpose (c)])
(This matrix table must not be considered independently of the preceding text)
(see also extensions to this table, from the 1990 Report of the ACMP, p. 36)

Matrix	Contaminant										
	PCB/CBs	Y-HCH	Hg	Cd	Cu	Zn	As	Cr	Ni	Pb	TBT
Nearshore water		P	P ¹	P ¹	P ¹	P ¹		P ¹	P ¹	P ¹	S
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
Shellfish	S ³	S ³	S ¹	S ¹		S ¹				S ¹	P
Fish muscle			T ^{1,4}				S ^{1,4}				
Fish liver	S ⁴		T ^{1,4}							T ^{1,4}	

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 organic carbon measurements and appropriate normalisation procedures, following the most recent ICES guidelines for monitoring contaminants in sediments.
 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.
- CBs: Chlorobiphenyls on an individual basis, congener Nos. 28, 52, 101, 118, 138, 153 and 180.

ANNEX 3

Aims of the Cooperative Monitoring in the Baltic Marine Environment (COMBINE) of the Helsinki Commission

To identify and quantify the effects of existing anthropogenic discharges/activities in the Baltic Sea, in the context of the natural variations in the system, and to identify and quantify the improvements in the environment as a result of regulatory actions.

More specifically this means:

1. For the open sea and coastal area monitoring:

1.1 Hydrographic variations

To set the background for all other measurements related to the identification and quantification of the effects of anthropogenic discharges/activities, the parameters providing an indication of natural fluctuations in the hydrographic regime of the Baltic Sea must be monitored on a continuous basis.

To this end, at a minimum the following must be measured: temperature, salinity, oxygen and hydrogen sulphide.

1.2 Problems related to eutrophication

To determine the extent and the effects of anthropogenic inputs of nutrients on marine biota, the following must be measured as a minimum:

- a) Concentrations of nutrients: phosphate, total phosphorus, ammonia, nitrite, nitrate, total nitrogen and silicate, to quantify the increases above natural levels.
- b) The response of the different biological compartments:
 - chlorophyll-a, as an equivalent of the standing stock of phytoplankton;
 - primary production (together with pH, alkalinity/carbon dioxide): to measure the increase in the rate of production, i.e., the first response of phytoplankton to increased nutrient load.
 - phytoplankton biomass, to indicate increases in the stock, and species composition, to indicate a response in the system as a possible change in the food chain composition (e.g., an increase in some species of phytoplankton that are not consumed by zooplankton could lead to decreased oxygen concentrations in bottom waters following sedimentation of unconsumed phytoplankton) or an increase in toxic species that are harmful to other organisms.

- zooplankton biomass and species composition, as changes can result from changes in phytoplankton biomass and species composition.
- zoobenthos biomass (increase in biomass indicates eutrophication) and species composition (reduced species diversity). Excessive levels of eutrophication can result in low concentrations of oxygen in the bottom waters, resulting in damage to or death of zoobenthos.

1.3 For contaminants in biota

To compare the level of contaminants in selected species of biota (including different parts of their tissues) from different geographical regions of the Baltic Sea in order to detect possible contamination patterns, including areas of special concern (usually known as 'hot spots').

To measure levels of contaminants in selected species of biota at specific locations over time in order to detect whether levels are changing in response to the changes in inputs of contaminants to the Baltic Sea.

To measure levels of contaminants in selected species of biota at different locations within the Baltic Sea, particularly in areas of special concern, in order to assess whether the levels pose a threat to these species and/or to higher trophic levels, including marine mammals and seabirds.

1.4 For the effects of contaminants

To carry out biological effects measurements at selected locations in the Baltic Sea, particularly at sites of special concern, in order to assess whether the levels of contaminants in sea water and/or suspended particulate matter and/or sediments and/or in the organisms themselves are causing detrimental effects on biota (e.g., changes in community structure).

2. For monitoring of radioactive substances

The HELCOM expert group on monitoring of radioactive substances will draft this section at their forthcoming meeting.

3. For monitoring of airborne pollutants

To provide data that enable estimates of dry and wet deposition and their variation in time and space over the Baltic Sea to be made. This is undertaken for anthropogenic pollutants that may cause eutrophication or bioaccumulation of persistent toxic compounds.

To measure concentrations in air and precipitation of the following components:

- with regard to possible eutrophication:
NO₂ sum of [HNO₃(gas) and NO₃ (part.)], sum of [NH₃(gas) and NH₄⁺ (part.)], NO₃⁻ (prec.), NH₄⁺ (prec.) as the main nitrogen-containing compounds in air and precipitation

- with regard to possible bioaccumulation of persistent toxic compounds:
- trace metals in precipitation and in particulate matter (Pb, Cd, Cu, Zn, Cr, Ni, As, Hg);
- persistent organic compounds in air and precipitation:
 - Carbontetrachloride
 - Trichloroethylene
 - Tetrachloroethylene
 - Trichlorobenzene
 - Trichloroethane 1,1,1-
 - Xylenes
 - Hexachlorobenzene
 - Dioxins
 - PAH
 - Pentachlorophenol
 - Hexachlorocyclohexane

To use and encourage the development of atmospheric transport models to obtain atmospheric deposition estimates covering also the open sea for which no measurements exist.

To participate in and encourage the collection of information on emissions from sources both inside and outside the Convention Area that contribute to this deposition and thus are needed as input to the models.

**WATER, SEDIMENTS AND FISH;
IN WHICH MEDIA SHOULD I LOOK FOR THE CONTAMINANTS ?**

by

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1. INTRODUCTION

The greater part of the inorganic contaminants discharged to the marine environment from various sources are also available in Nature as natural compounds. This is essential to underline since it has some important consequences from a monitoring perspective:

- there are certain natural concentration levels (background levels)
- there are established mechanisms for their distribution
- there are established mechanisms for their interaction with biological processes
- organisms have in many cases developed a tolerance to a certain degree (e.g. a certain concentration) to these substances

On the other hand, the major part of the organic contaminants discharged are synthetic which means that they are unknown in Nature. From a monitoring perspective this means that:

- there are no natural concentration levels (background levels)
- there are sometimes no established mechanisms for their distribution
- they often interfere with natural processes in organisms
- organisms have in some cases a natural or developed a tolerance to a certain degree (e.g. a certain concentration) to these substances
- in many cases they are extremely toxic to organisms.

2. SOME PROPERTIES OF INORGANIC CONTAMINANTS, MAINLY METALS

A short repetition of some well known facts of relevance:

- most of the pure metals are practically insoluble in water
- many inorganic metal salts have a moderate to high solubility in water, whereas others are almost insoluble
- some organic metal salts have at least a moderate solubility in water

- once the metal is in solution it will not evaporate but it will undergo various chemical reactions.

3. DISTRIBUTION OF METALS, ACCUMULATION AND INTERACTION WITH BIOLOGICAL PROCESSES

A metal that is discharged to a water area in its non-dissolved state simply comes as a particle e.g. as mineral particles from mining. The particle will settle to the sea bottom usually within a rather short distance. If the particle is very small it may become adsorbed on organic material such as humic substances or ingested by organisms together with their food. From its position on the sea floor or in the organism it may then undergo chemical reactions that bring the metal into solution. If the particle has sedimented it usually will dissolve only very slowly. Therefore, metals concentrate in sediments and, if the sedimentation rate is sufficiently high and no or little resuspension occurs, sediments can provide an excellent record of contaminants input over shorter or longer periods.

A metal discharged as a dissolved substance will interact with the chemical environment in the water in different ways. The metal may react chemically and form an insoluble compound. When e.g. a waste water containing cadmium is discharged in an area where the bottom water is stagnant and contains hydrogen sulphide, insoluble cadmium sulphide will form when the two water masses are mixed. The cadmium sulphide will precipitate and, while it may be carried some distance by water currents, it will eventually sediment to the bottom.

A dissolved metal that does not precipitate will not stay as a "naked" positively charged ion but will form various complexes with the negative ions in the water. This will in many cases increase the solubility of the metal. Furthermore, different complexes of the same metal may have different (degree of) biological effects.

The dissolved metal, or the metal adsorbed to organic particles and ingested by organisms such as zooplankton, may interact with biochemical reactions e.g. in enzymatic processes. Metals may also become linked to proteins and accumulate in certain tissues as e.g. in filter feeding mussels or in fish liver.

The concentration of a metal (or rather its complexes!) may certainly increase in the water if there is a major discharge. However, since the water masses are in almost constant motion it is unlikely that metal concentrations will become high with the exception of near the discharge point and in very local areas with limited water exchange.

It is important to underline that the examples given are parts of a system that is dynamic. Although the processes have different speeds the metal may pass from one compartment of the environment to the other, and often in a reversible way. Refer to Figure 1 for a principal presentation and to Figure 2 for a more detailed illustration.

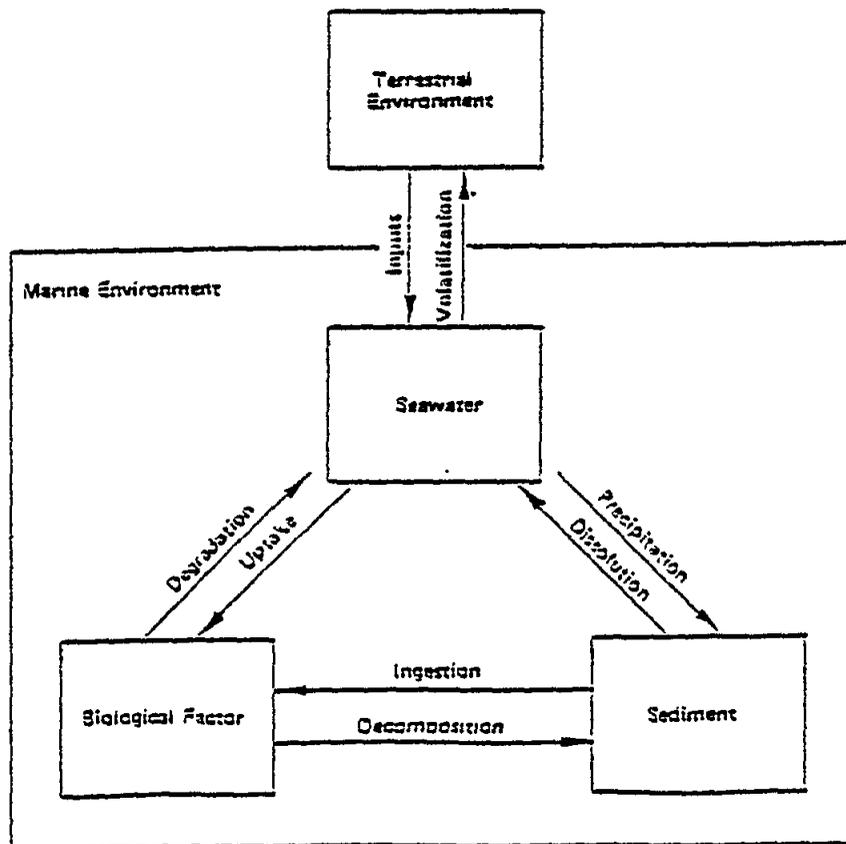


Fig. 1 A general presentation of processes influencing the distribution of contaminants in the environment

4. SOME PROPERTIES OF ORGANIC SUBSTANCES

A short repetition of some well known facts of relevance:

- organic substances range widely in solubility in water (consider such extremes as alcohol and DDT)
- most organic substances do not dissociate in water which, together with the low solubility, make their reactions slow in the water phase
- many organic substances have a high volatility and they may therefore evaporate to a high degree
- most of the organic contaminants of concern for the marine environment are lipophilic which means that they do not dissolve in water but can readily dissolve in lipids or in organic solvents.

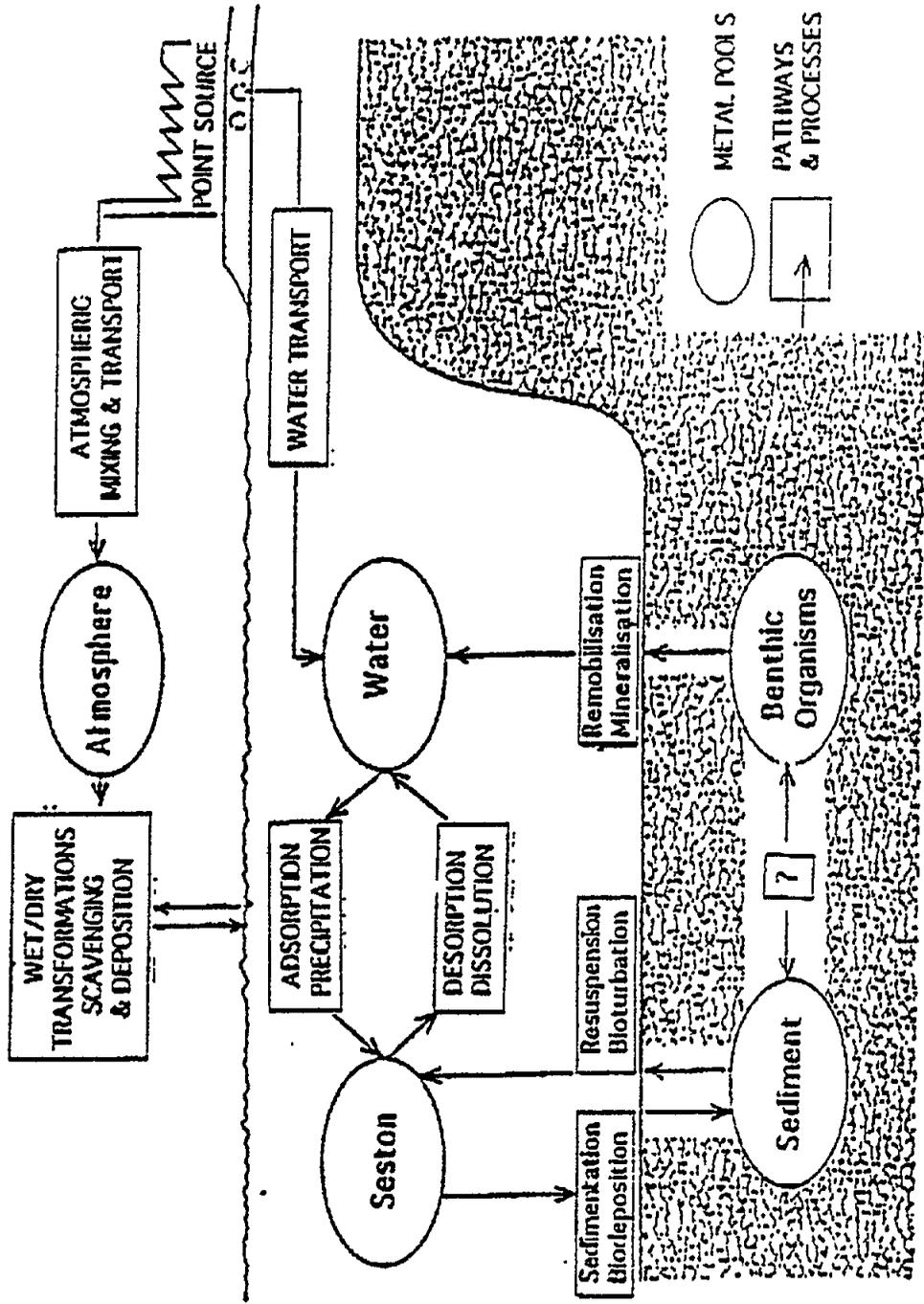


Fig. 2 A more detailed presentation of processes influencing the distribution of contaminants in the environment

5. DISTRIBUTION OF ORGANIC SUBSTANCES, ACCUMULATION AND INTERACTION WITH BIOLOGICAL PROCESSES

An organic substance such as ethanol, that immediately dissolves in water, will be quickly mixed into the water and become dispersed and transported in the same way as many inorganic substances. High concentrations in the water phase will therefore be only a temporary phenomenon. Evaporation to the atmosphere can occur if there is a large spill of the substance, but since the dissolution is quick the major part of the discharged amount may still go into the water phase. Such organic substances will not enter organisms by dissolution in fatty tissues to any significant degree.

If there is a major spill or discharge of oil (mineral oil or vegetabilic oil), or a substance or mixture of substances behaving like an oil, the physical processes may be of very significant importance for the removal and modification of the discharged material. Evaporation from e.g. a crude mineral oil may actually be, quantitatively, the most important process involved in removing the oil from the sea! After evaporation of the most volatile parts of the oil the remaining part may have a density higher than water and will therefore sink to the bottom and be incorporated in the sediment. Refer to Figure 3 for further details.

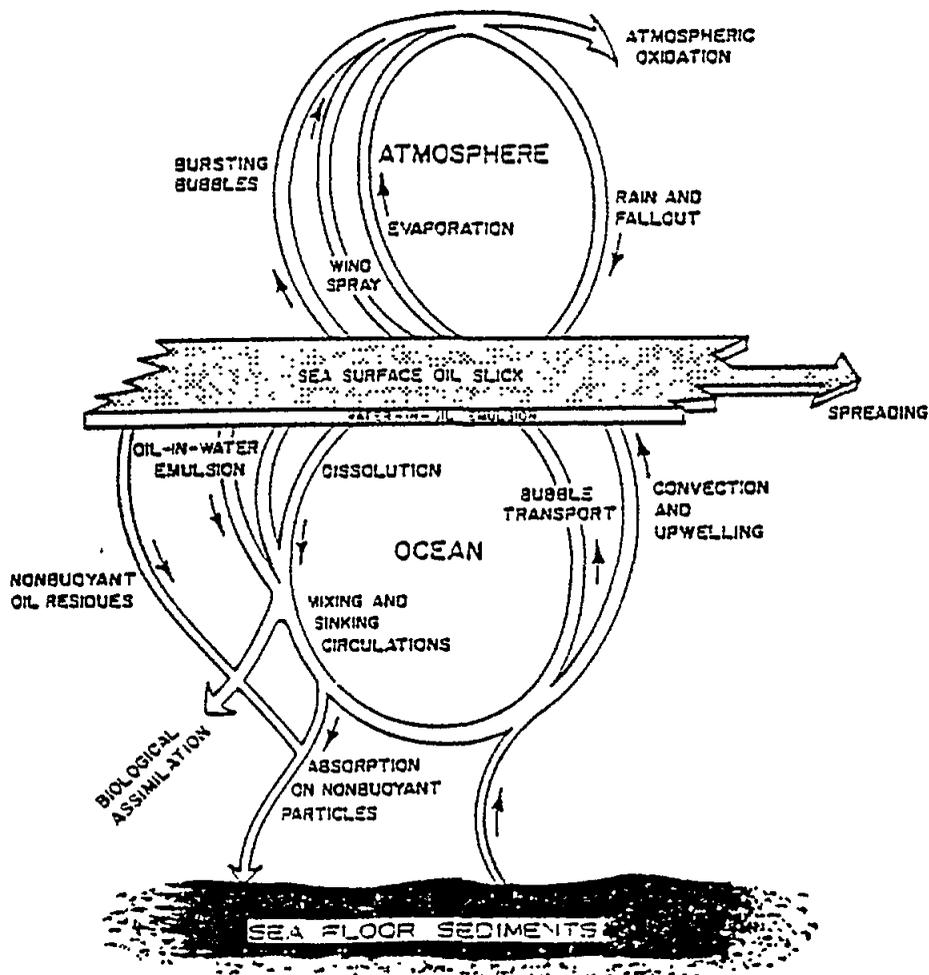


Fig. 3 A general presentation of processes influencing the distribution of mineral oil in the environment

The most important properties of the organic contaminants of concern for the marine environment are, from a monitoring perspective, their lipophilicity and the fact that when they undergo chemical modification by various biotic or abiotic reactions. The reaction products are often as harmful as the parent substance.

Because of their lipophilicity these substances may easily become adsorbed or absorbed to organic particles such as humic substances or phyto- and zooplankton in the water. Via these particles the contaminants then continue into the food web and into higher organisms (mussels, fish, birds and mammals).

These lipid soluble contaminants accumulate in biota in two ways. Firstly, they enter and accumulate in the fatty tissues of the "first" organism e.g. a mussel. As the organism grows the concentrations of the contaminant increases in the specimen. This is called bioconcentration. Then the mussel is consumed by the "second" organism, which may be a fish. Since a single fish consumes a great number of mussels, all having their content of the contaminant, the fish receives a higher body burden of the contaminant. This way of accumulation through the various levels in the food web is called biomagnification.

6. WHERE TO MONITOR; IN WATER, IN SEDIMENTS OR IN BIOTA?

In principle, the simplest general answer to the question is: go for the best signal-to-noise ratio!

In all quantitative chemical analyses there is a certain signal (noise) from the detector in the measurement instrument as soon as it is ready for operation. If one analyses a sample with a very low concentration of the contaminant it may actually be difficult to quantify - or even to detect the presence of - the contaminant! This is a low signal-to-noise ratio. Consequently, from a strict analytical standpoint, one should try to focus on analysing those samples where one could expect the highest concentrations of the contaminant. This means samples taken near the source and samples where the contaminant has been concentrating. This does not necessarily mean that the concentrations are high!

Obviously, there are several other factors to consider when deciding on how the contaminant monitoring should be done.

The first thing is to consider the aim of the monitoring! Consider the human health monitoring of DDT or PCB. It would be a waste of resources to make sampling of water and sediments a general part of such a programme. The concentrations of DDT and PCB in the water are extremely low since these substances are strongly lipophilic. They may accumulate in sediments, but since human beings are in very limited contact with sediments this would be of concern in very extreme cases only. Consequently, monitoring of DDT and PCB in edible fish and shellfish is the logical design of the programme.

In general, trend monitoring of contaminants (including nutrients) in the water of open sea areas is very difficult because of the high variability (patchiness) in time and space. For a study of regional distribution at a certain point in time such sampling can be useful, although there are certainly difficulties involved.

Therefore, in general, sediments and biota are the most relevant compartments (matrices) for contaminant monitoring in the marine environment! However, this does not exclude difficulties relating to variability in space and time!

Advantages with sediments are not only that they accumulate but also that the sample, or rather the material, is stationary from one sampling occasion to the next. Therefore repeated sampling for trend studies are possible. Preconditions for this is of course that localities that should be monitored have sufficient accumulation rates. If sediments are resuspended or frequently eroded they are not suitable for monitoring. The same thing is true if there is a high degree of bioperturbation that disturbs the stratification of the sediment.

Advantages with biota sampling is not only their bioconcentration and biomagnification properties but also e.g. that they offer possibilities to study relationship between contaminant concentrations and their biological effects. Disadvantages are i.a. that seasonal biological cycles influence the contaminant concentrations in the specimens. It is therefore essential that sampling is carried out in a consistent way, which means sampling should always be carried out at the same phase of the biological cycle.

There are several other factors in favour of and against sediments and biota. They will not be analysed here, but rather described in some of the following lectures.

**WHICH CONTAMINANTS DO I NEED TO MONITOR,
AND WHERE SHOULD I LOOK FOR THEM ?**

by

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1. WHICH CONTAMINANTS SHOULD BE MONITORED?

It would be rather convenient to base a monitoring programme on a fixed, and not too long, list of contaminants to be monitored. This would make planning and implementation easier, particularly concerning chemical analyses and assessments. However, in the light of increased knowledge regarding various contaminants and the introduction of new substances of concern, priorities change and new entries are added to the lists of substances to be monitored.

Therefore, this paper cannot, and will not, present a recipe which would tell you exactly what to monitor and where.

The aim of this paper is to review the work undertaken by various international organizations regarding the selection of the substances to be monitored and where (in which compartments) they should be monitored. The paper will also present some approaches on how to identify (new) substances that should be monitored. Finally, some advice is provided to help you decide in which compartments of the marine environment one should monitor these substances.

The examples are taken from various international conventions, working groups etc. The material is presented as a suite of annexes.

1.1 Substances regulated under the Barcelona Convention

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 environment. 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, persistence 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 is normally referred to as the "Black List" although the term is not used in the convention text itself. 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 is 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 Annex 1 to this paper) where substances are listed.

1.2 Substances regulated under the Paris Convention (PARCOM)

The Convention for the Prevention of Marine Pollution from Land-Based Sources, better known as the Paris Convention, came into force in 1978. Here, already in the text of the Convention, we find the type of detailed regulation included in the LBS protocol of the Barcelona Convention. Articles 4 and 5, along with *Annex A*, contain the necessary specifications. (Please refer to Annex 2 of this paper). As can be seen, the selection of substances is rather similar to that under the Barcelona Convention, but the Paris Convention has defined more stringent criteria for the identification of substances to be included in the lists.

However, as requirements change the Conventions are revised. The Paris Convention has been re-negotiated and the new "Convention for the Protection of the Marine Environment of the North-East Atlantic" was signed in October 1992. The Convention is expected to come into force within the next four to five years. Already now preparations are under way to change the monitoring and assessment systems in order to adjust to the new requirements.

Some examples of this are given in Annex 3. Here, one can see the relevant regulations in Articles 3, 4 and 5 of the Convention, its *Annex 1* and its *Appendix 2*. The important difference, from a monitoring perspective, is that the text is now more of a framework than a specific list. *It specifies rather few substances but concentrates on groups of substances.* Furthermore, *it specifies a much wider set of criteria for the selection of substances to regulate* and requires the Contracting Parties to take these into consideration when they design their programmes and measures for the protection of the marine environment!

1.3 Substances regulated under the Helsinki Convention (HELCOM)

Also this Convention has been re-negotiated. The Convention for the Protection of the Environment of the Baltic Sea Area was signed in April 1992 and it is expected to come into force within the next few years.

As can be seen in Annex 4 to this paper there are large similarities with the new Paris Convention. The extended lists of criteria for the identification of substances (or groups of substances) to regulate are rather similar in the two conventions. It should be noted, however, that due to the concern for the very vulnerable environment of the Baltic Sea the new Convention has a list of substances that are actually banned, as well as a list of pesticides the use of which should be minimised.

2. HOW CAN WE IDENTIFY WHICH SUBSTANCES TO MONITOR?

As presented in a previous paper 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 defensible 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. Some examples of substances that are being discussed for inclusion in monitoring programmes are brominated flame retardants, simazine, atrazine and the planar chlorobiphenyls (planar CBs), chlordanes and polychlorinated camphenes (PCC).

However, as 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. This is further described below.

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 contaminants on Man, living resources and amenities.

During a couple of years the ICES Working Group on Environmental Assessments and Monitoring Strategies developed its advice. The deliberations of the Group are contained in Annexes 5 and 6.

3. EXAMPLES RELATED TO IN WHICH MEDIA VARIOUS 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 is included here as Annex 7.

It is important to stress that the information contained in the tables in Annex 7 should not be used alone but always be combined with the explanatory text!

ANNEX 1

Selected regulations under the Barcelona Convention

This annex contains selected material from the "Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources" of the Barcelona Convention

Article 5

1. The Parties undertake to eliminate pollution of the Protocol Area from land-based sources by substances listed in annex I to this Protocol.
2. To this end they shall elaborate and implement, jointly or individually, as appropriate, the necessary programmes and measures.
3. These programmes and measures shall include, in particular, common emission standards and standards for use.
4. The standards and the time-tables for the implementation of the programmes and measures aimed at eliminating pollution from land-based sources shall be fixed by the Parties and periodically reviewed, if necessary every two years, for each of the substances listed in annex I, in accordance with the provisions of article 15 of this Protocol.

Article 6

1. The Parties shall strictly limit pollution from land-based sources in the Protocol Area by substances or sources listed in annex II to this Protocol.
2. To this end they shall elaborate and implement, jointly or individually, as appropriate, suitable programmes and measures.
3. Discharges shall be strictly subject to the issue, by the competent national authorities, of an authorization taking due account of the provisions of annex III to this Protocol.

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.¹
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.
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 purposes 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 processes and therefore generally affect more limited coastal areas.

1. The following elements and their compounds:

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

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

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 indirectly, 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.

ANNEX 2

Selected regulations under the Oslo and Paris Conventions

This annex contains selected material from "The Convention for the Prevention of Marine Pollution from Land-Based Sources"

ARTICLE 4

1. The Contracting Parties undertake:
 - a. to eliminate, if necessary by stages, pollution of the maritime area from land-based sources by substances listed in Part I of Annex A to the present Convention;
 - b. to limit strictly pollution of the maritime area from land-based sources by substances listed in Part II of Annex A to the present Convention.
2. In order to carry out the undertaking in paragraph 1 of this Article, the Contracting Parties, jointly or individually as appropriate, shall implement programmes and measures:
 - a. for the elimination, as a matter of urgency, of pollution of the maritime area from land-based sources by substances listed in Part I of Annex A to the present Convention;
 - b. for the reduction or, as appropriate, elimination of pollution of the maritime area from land-based sources by substances listed in Part II of Annex A to the present Convention. These substances shall be discharged only after approval has been granted by the appropriate authorities within each Contracting State. Such approval shall be periodically reviewed.
3. The programmes and measures adopted under paragraph 2 of this Article shall include, as appropriate, specific regulations or standards governing the quality of the environment, discharges into the maritime area, such discharges into watercourses and emissions into the atmosphere as affect the maritime area, and the composition and use of substances and products. These programmes and measures shall take into account the latest technical developments.

The programmes shall contain time-limits for their completion.
4. The Contracting Parties may, furthermore, jointly or individually as appropriate, implement programmes or measures to forestall, reduce or eliminate pollution of the maritime area from land-based sources by a substance not then listed in Annex A to the present Convention, if scientific evidence has established that a serious hazard may be created in the maritime area by that substance and if urgent action is necessary.

ARTICLE 5

1. The Contracting Parties undertake to adopt measures to forestall and, as appropriate, eliminate pollution of the maritime area from land-based sources by radio-active substances referred to in Part III of Annex A of the present Convention.

2. Without prejudice to their obligations under other treaties and conventions, in implementing this undertaking the Contracting Parties shall:

a. take full account of the recommendations of the appropriate international organizations and agencies;

b. take account of the monitoring procedures recommended by these international organizations and agencies;

c. coordinate their monitoring and study of radio-active substances in accordance with Articles 10 and 11 of the present Convention.

annex A

The allocation of substances to Parts I, II and III below takes account of the following criteria:

a. persistences;

b. toxicity or other noxious properties;

c. tendency to bio-accumulation;

These criteria are not necessarily of equal importance for a particular substance or group of substances, and other factors, such as the location and quantities of the discharge, may need to be considered.

PART I

The following substances are included in this Part

i. because they are not readily degradable or rendered harmless by natural processes; and

ii. because they may either:

a. give rise to dangerous accumulation of harmful material in the food chain, or

b. endanger the welfare of living organisms causing undesirable change in the marine eco-systems, or

c. interfere seriously with the harvesting of sea foods or with other legitimate uses of the sea; and

- iii. because it is considered that pollution by these substances necessitates urgent action:
1. Organohalogen compounds and substances which may form such compounds in the marine environment, excluding those which are biologically harmless, or which are rapidly converted in the sea into substances which are biologically harmless.
 2. Mercury and mercury compounds.
 3. Cadmium and cadmium compounds.
 4. Persistent synthetic materials which may float, remain in suspension or sink, and which may seriously interfere with any legitimate use of the sea.
 5. Persistent oils and hydrocarbons of petroleum origin.

PART II

The following substances are included in this Part because, although exhibiting similar characteristics to the substances in Part I and requiring strict control, they seem less noxious or are more readily rendered harmless by natural processes:

1. Organic compounds of phosphorus, silicon and tin, and substances which may form such compounds in the marine environment, excluding those which are biologically harmless, or which are rapidly converted in the sea into substances which are biologically harmless.
2. Elemental phosphorus.
3. Non-persistent oils and hydrocarbons of petroleum origin.
4. The following elements and their compounds:
Arsenic Lead
Chromium Nickel
Copper Zinc
5. Substances which have been agreed by the Commission as having a deleterious effect on the taste and/or smell of products derived from the marine environment for human consumption.

PART III

The following substances are include din this Part because, although they display characteristics similar to those of substances listed in Part I and should be subject to stringent controls with the aim of preventing and, as appropriate, eliminating the pollution which they cause, they are already the subject of research, recommendations and, in some cases, measures under the auspices of several international organizations and institutions; those substances are subject to the provisions of Article 5:

- Radioactive substances, including wastes.

ANNEX 3

Selected regulations under the new Paris Convention

This annex contains selected material from "The Convention for the Protection of the Marine Environment of the North-East Atlantic." (The OSPAR Convention).

ARTICLE 3 POLLUTION FROM LAND-BASED SOURCES

The Contracting Parties shall take, individually and jointly, all possible steps to prevent and eliminate pollution from land-based sources in accordance with the provisions of the Convention, in particular as provided for in Annex I.

ARTICLE 4 POLLUTION BY DUMPING OR INCINERATION

The Contracting Parties shall take, individually and jointly, all possible steps to prevent and eliminate pollution by dumping or incineration of wastes or other matter in accordance with the provisions of the Convention, in particular as provided for in Annex II.

ARTICLE 5 POLLUTION FROM OFFSHORE SOURCES

The Contracting Parties shall take, individually and jointly, all possible steps to prevent and eliminate pollution from offshore sources in accordance with the provisions of the Convention, in particular as provided for in Annex III.

Annex I ON THE PREVENTION AND ELIMINATION OF POLLUTION FROM LAND-BASED SOURCES

ARTICLE 1

1. When adopting programmes and measures for the purpose of this Annex, the Contracting Parties shall require, either individually or jointly, the use of:
 - best available techniques for point sources
 - best environmental practice for point and diffuse sources

including, where appropriate, clean technology.

2. When setting priorities and in assessing the nature and extent of the programmes and measures and their time scales, the Contracting Parties shall use the criteria given in Appendix 2.
3. The Contracting Parties shall take preventive measures to minimise the risk of pollution caused by accidents.
4. When adopting programmes and measures in relation to radioactive substances, including waste, the Contracting Parties shall also take account of:
 - (a) the recommendations of the other appropriate international organisations and agencies;
 - (b) the monitoring procedures recommended by these international organisations and agencies.

ARTICLE 2

1. Point source discharges to the maritime area, and releases into water *or air* which reach and may affect the maritime area, shall be strictly subject to authorisation or regulation by the competent authorities of the Contracting Parties. Such authorisation or regulation shall, in particular, implement relevant decisions of the Commission which bind the relevant Contracting Party.

2. The Contracting Parties shall provide for a system of regular monitoring and inspection by their competent authorities to assess compliance with authorisations and regulations of releases into water *or air*.

ARTICLE 3

For the purpose of this Annex, it shall, *inter alia*, be the duty of the Commission to draw up:

- (a) plans for the reduction and phasing out of substances that are toxic, persistent and liable to bioaccumulate arising from land-based sources;
- (b) when appropriate, programmes and measures for the reduction of inputs of nutrients from urban, municipal, industrial, agricultural and other sources.

Appendix 2

CRITERIA MENTIONED IN PARAGRAPH 2 OF ARTICLE 1 OF ANNEX I AND IN PARAGRAPH 2 OF ARTICLE 2 OF ANNEX III

1. When setting priorities and in assessing the nature and extent of the programmes and measures and their time scales, the Contracting Parties shall use the criteria given below:
 - (a) persistency;
 - (b) toxicity or other noxious properties;
 - (c) tendency to bioaccumulation;
 - (d) radioactivity;

- (e) the ratio between observed or (where the results of observations are not yet available) predicted concentrations and no observed effect concentrations;
 - (f) anthropogenically caused risk of eutrophication;
 - (g) transboundary significance;
 - (h) risk of undesirable changes in the marine ecosystem and irreversibility or durability of effects;
 - (i) interference with harvesting of sea-foods or with other legitimate uses of the sea;
 - (j) effects on the taste and/or smell of products for human consumption from the sea, or effects on smell, colour, transparency or other characteristics of the water in the marine environment;
 - (k) distribution pattern (i.e., quantities involved, use pattern and liability to reach the marine environment);
 - (l) non-fulfillment of environmental quality objectives.
2. These criteria are not necessarily of equal importance for the consideration of a particular substance or group of substances.
3. The above criteria indicate that substances which shall be subject to programmes and measures include:
- (a) heavy metals and their compounds;
 - (b) organohalogen compounds (and substances which may form such compounds in the marine environment);
 - (c) organic compounds of phosphorus and silicon;
 - (d) biocides such as pesticides, fungicides, herbicides, insecticides, slimicides and chemicals used, *inter alia*, for the preservation of wood, timber, wood pulp, cellulose, paper, hides and textiles;
 - (e) oils and hydrocarbons of petroleum origin;
 - (f) nitrogen and phosphorus compounds;
 - (g) radioactive substances, including wastes;
 - (h) persistent synthetic materials which may float, remain in suspension or sink.

ANNEX 4

Selected regulations under the new Helsinki Convention

This annex contains selected material from "The Convention on the Protection of the Marine Environment of the Baltic Sea Area, 1992."

Article 5 Harmful substances

The Contracting Parties undertake to prevent and eliminate pollution of the marine environment of the Baltic Sea Area caused by harmful substances from all sources, according to the provisions of this Convention and, to this end, to implement the procedures and measures of Annex I.

Annex I Harmful substances

PART I GENERAL PRINCIPLES

1.0 Introduction

In order to fulfil the requirements of relevant parts of this Convention the following procedure shall be used by the Contracting Parties in identifying and evaluating harmful substances, as defined in Article 2, paragraph 7.

1.1 Criteria on the allocation of substances

The identification and evaluation of substances shall be based on the intrinsic properties of substances, namely:

- persistency;
- toxicity or other noxious properties;
- tendency to bio-accumulation,

as well as on characteristics liable to cause pollution, such as

- the ratio between observed concentrations and concentrations having no observed effect;
- anthropogenically or long-range significance;
- transboundary or long-range significance;
- risk of undesirable changes in the marine ecosystem and irreversibility or durability of effects;
- radioactivity;
- serious interference with harvesting of sea-foods or with other legitimate uses of the sea;
- distribution pattern (i.e. quantities involved, use pattern and liability to reach the marine environment);
- proven carcinogenic, teratogenic or mutagenic properties in or through the marine environment.

These characteristics are not necessarily of equal importance for the identification and evaluation of a particular substance or group of substances.

1.2 Priority groups of harmful substances

The Contracting Parties shall, in their preventive measures, give priority to the following groups of substances which are generally recognised as harmful substances:

- a) heavy metals and their compounds;
- b) organohalogen compounds;
- c) organic compounds of phosphorus and tin;
- d) pesticides, such as fungicides, herbicides, insecticides, slimicides and chemicals used for the preservation of wood, timber, wood pulp, cellulose, paper, hides and textiles;
- e) oils and hydrocarbons of petroleum origin;
- f) other organic compounds especially harmful to the marine environment;
- g) nitrogen and phosphorus compounds;
- h) radioactive substances, including wastes;
- i) persistent materials which may float, remain in suspension or sink;
- j) substances which cause serious effects on taste and/or smell of products for human consumption from the sea, or effects on taste, smell, colour, transparency or other characteristics of the water.

PART 2 BANNED SUBSTANCES

In order to protect the Baltic Sea Area from hazardous substances, the Contracting Parties shall prohibit, totally or partially, the use of the following substances or groups of substances in the Baltic Sea Area and its catchment area:

2.1 Substances banned for all final uses, except for drugs

DDT (1,1,1-trichloro-2,2-bis-(chlorophenyl)-ethane) and its derivatives DDE and DDD;

2.2 Substances banned for all uses, except in existing closed system equipment until the end of service life or for research, development and analytical purposes

- a) PCB's (polychlorinated biphenyls);
- b) PCT's (polychlorinated terphenyls).

2.3 Substances banned for certain applications

Organotin compounds for antifouling paints for pleasure craft under 25 m and fish net cages.

PART 3 PESTICIDES

In order to protect the Baltic Sea Area from hazardous substances, the Contracting Parties shall endeavour to minimize and, whenever possible, to ban the use of the following substances as pesticides in the Baltic Sea Area and its catchment area:

	<u>CAS-number</u>
Acrylonitrile	107131
Aldrin	309002
Aramite	140578
Cadmium-compounds	-
Chlordane	57749
Chlordecone	143500
Chlordimeform	6164983
Chloroform	67663
1,2-Dibromoethane	106934
Dieldrin	60571
Endrin	72208
Fluoroacetic acid and derivatives	7664393, 144490
Heptachlor	76448
Isobenzane	297789
Isodrin	465736
Kelevan	4234791
Lead-compounds	-
Mercury-compounds	-
Morfamquat	4636833
Nitrophen	1836755
Pentachlorophenol	87865
Polychlorinated terpenes	8001501
Quintozene	82688
Selenium-compounds	-
2,4,5-T	93765
Toxaphene	8001352

ANNEX 5

Identification of "new" contaminants; Part I

This annex contains selected material from the Report of the (ICES) Working Group on Environmental Assessments and Monitoring Strategies (1990).

6. CONSIDER AND REPORT ON SYSTEMATIC PROCEDURES TO ASSESS THE HAZARDS OF POTENTIALLY TOXIC SUBSTANCES AS A MEANS OF IDENTIFYING PRIORITY MARINE CONTAMINANTS (IN THE CONTEXT OF ACMP'S ENVIRONMENTAL MANAGEMENT PRINCIPLES), TAKING INTO ACCOUNT THE MCWG COMMENTS AND RELEVANT NORTH SEA TASK FORCE PAPERS

This item was introduced as a continuation of the 1989 meeting discussion on mechanisms for the identification of "new" contaminants presenting particular hazards to the environment. In addition, ICES had been asked by HELCOM for assistance in developing a general scheme for the identification of chemical substances with possible harmful properties towards the marine environment based on toxicity, chemical properties, etc., and to provide guidance for its use relevant to the Baltic Sea.

Discussion centered upon methods for identifying "new" contaminants of significance to the sea. There was normally a long chain of events from the design of a new product or substance, through testing, licensing, etc. to production and use. It would be preferable to intervene in this system at an early enough stage, if it appears that significant environmental risks would be involved.

The term "new" contaminant could be understood in several ways; referring 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 which newly came to our attention (eg., intentional or unintentional by-products of industrial processes).

It was generally felt that the hazard posed by individual compounds was more rapidly assessed than that of complex mixtures. Inventories of chemical usage by individual factories could give information on possible major components of wastes. National licensing or, to some extent, patenting schemes could give leads on the types of new compounds which may be released to the aquatic environment. If the nature of the substances is known, chemical and biological testing, QSAR studies, and risk assessment can be undertaken.

Assessment of the risk associated with mixed complex wastes of indeterminate composition cannot be approached in the same way. Examples were given, including the occurrence of haemolytic anemia in salmon in a Scottish river, and various effects outside some Swedish pulp mills. In both cases, the investigations had been generated by observations of biological effects. The effects stimulated research to identify chemically the biologically active components of the waste giving rise to the effects. This suggested two general approaches that might be adopted. Firstly, it might be possible to characterize, in a fairly complete way, the chemical composition

of a complex contaminant source (e.g., effluent or river), or the suite of chemicals accumulated by some animals at a high trophic level. These approaches would place different emphases on such properties as persistence or bioaccumulation.

An alternative approach might be through exploring the toxicity of effluent streams, rivers, sediment extracts, etc., and subsequently attempting to identify the chemical components responsible for any observed biological effect. This approach might allow regulatory action to be taken to limit the impact before the precise chemical cause has been identified. There were proposals in hand to test the toxicity of water and sediment extracts from the Skagerrak and the Rhine to bacterial strains (e.g., Microton system). The association of a biological effect with a particular effluent stream may be sufficient to call for controls. It was noted that there was a general tendency in several countries for regulatory authorities to require dischargers to characterize their wastes more completely in both chemical and biological senses. Biological effluent treatment was becoming more common, although it was noted that particularly significant components resistant to biological decomposition might be unaffected by this system. It was noted that, e.g, in France, dischargers had to make payments related to the solids content and toxicity to Daphnia magna of their effluent, and this encouraged the adoption of improved waste control or the best available technology (known as BAT in the work of the various commissions for the marine environment).

It was noted that within the work of HELCOM, and in parallel with the Paris Commission's TWG (Technical Working Group), efforts were being made to address the control of complex mixed wastes through consideration of each industry in a generic manner. For example, within HELCOM the iron and steel industries had been catalogued and assessed, and attention was now moving to the chemical industries. The latter was proving more complicated, and needed to be treated in various sub-divisions according to the nature of the operations being carried out. Other possible generic classifications were petrochemicals, textiles, sewage, etc.

The Working Group recommended in relation to complex discharges that:

- a) Work to prepare inventories of chemicals used by various industries should continue.
- b) Biological tests in mesocosms should be encouraged, in order to identify the potential biological effects of complex wastes, and fractions of complex wastes.
- c) Efforts should be made to chemically characterize the substances causing effects noted in b) above.
- d) There should be intensification of field monitoring and research programmes to address the appropriate effects and chemicals identified in b) and c), above. These programmes should be undertaken in areas where impacts would be predicted, and these may include both coastal and off-shore waters.
- e) A system of biological specimen banking should be established to allow retrospective analyses, for example, of new contaminants.

ANNEX 6

Identification of "new" contaminants; Part II

This annex contains selected material from the Report of the (ICES) Working Group on Environmental Assessments and Monitoring Strategies (1991).

REVIEW OF SOME APPROACHES TO THE SELECTION OF SUBSTANCES OF PARTICULAR HAZARD TO THE ENVIRONMENT

A. Introduction

This short review paper has been prepared in response to the task defined at the 1990 meeting of WGEAMS, and describes some systematic procedures which have been employed for the assessment of the hazards of potentially toxic substances, as an approach to the identification of priority contaminants for control measures. A recent GESAMP report (No. 45, Global Strategies for Marine Environmental Protection) clearly points out the need for defined goals in environmental protection, and emphasizes the need for key scientific elements in a comprehensive strategy. These elements include information on such factors as sources, transport, transformation, and fate of contaminants, and of their effects on man, living resources and amenities. A primary goal of this work is hazard assessment of activities and chemicals, and subsequently risk assessment and management. The development of the schemes that are described below mainly has had as an objective the ability to identify substances posing particularly high risk in the marine environment using relatively simple and available data, and thus to focus subsequent management actions.

Selection schemes for the identification of priority aquatic pollutants have recently been extensively reviewed by Jackson and Peterson in a report to the EC on study contract B 6612/290/89. They noted that selection schemes are mainly based either on decision/logic trees (as in the UK scheme described below) or on a system of ranking based on values or scores for selected parameters.

The logic tree schemes require the selection of trigger values for various parameters to determine the progression of compounds through the tree. The selection of these values is of critical importance to the final decision on any compound. Similarly, the scoring schemes used in ranking systems control the relative weight given to particular properties of the substances under consideration, and therefore can be used to reflect the relative importance of properties as assessed by the designers of the scheme.

A fundamental problem with selection schemes is that to be useful they must be able to operate on the relatively limited data that are available for many compounds of potential interest to regulators and, at the same time, produce lists of priority substances that are not unmanageably long. This means that the schemes must eliminate large numbers of substances to arrive at a short final list, but in doing so must be reliable. Users of the scheme must have some

confidence that hazardous substances have not inadvertently been eliminated during the selection process. There may, therefore, be a conflict between simplicity and universality of operation with reliability of selection (avoiding false non-selection).

B. Types of Selection Schemes

Examples of various types of schemes will now be described.

1. A simple scheme based on trigger values for a limited number of properties. This type of scheme may be particularly useful for the initial screening of large numbers of compounds, for which very detailed information is not available.

In 1990, GESAMP published report No. 42, "Review of potentially harmful substances: Choosing priority organochlorines for marine hazard assessment". This document sets out to develop a scheme for the identification of those members of the broad group of chlorinated hydrocarbons which warranted particularly stringent controls on their use and disposal. The assessment scheme is shown in Appendix 1.

The group recognised that the limited amount of data available for many of the compounds made it necessary to adopt a very simple screening procedure. The initial analysis excluded all pesticides, PCBs, dioxins and furans, but considered about 720 other compounds. The group considered that the most critical parameters were the octanol/water partition coefficient ($\log K_{o/w}$) (as an index of likely bioaccumulation), persistence, and toxicity. Trigger values were as follows:

Parameter	Trigger value	Comments
$\log K_{o/w}$	>3	From literature or calculated from the molecular structure (QSAR)
Persistence	>1 week	In water
Toxicity (LC50, EC50)	<10 mg/l	

A fourth factor, the production and use of the chemical, was also sometimes considered.

The scheme considered a chemical to have been selected if it met two or more of the trigger values (or was very similar in structure to others which did so). Chemicals were not selected if they did not meet any of the trigger values, and other chemicals could not be assessed through lack of data.

The scheme identified 77 compounds which were considered to be in need of further more detailed assessment to ascertain the true level of risk. It therefore can be considered a preliminary screening scheme as a precursor to more rigorous assessment. The scheme was not applied to pesticides, PCBs, dioxins or furans because it was clear that they would all meet at least one of the criteria, and that a different form of assessment would be needed.

The list of compounds selected is shown in Appendix 1.

In applying this scheme, the authors found that the data were limited for many substances. Environmental criteria are needed for an ever-increasing number of chemicals, and it was necessary to adopt a QSAR approach to the problem. The authors do not describe in detail the QSAR methods that they used, but in employing the method they recognised that QSAR assessments can provide at least a guide to the likely physico-chemical and biological properties of a wide range of substances.

2. A logic tree scheme, which seeks to avoid making judgements on the relative importance of, say, toxicity and carcinogenicity, by assessing types of impact through different logic trees.

A systematic procedure has been adopted by the UK as a contribution to the deliberations of the International Conferences on the Protection of the North Sea. The initial candidate substances were derived from candidate List 1 substances (from the EC Dangerous Substances Directive) and form substances included in the Third North Sea Conference reference list. This priority-setting scheme was used by the UK to develop a "Red List" of priority substances, and would be applicable to other chemicals in the future as necessary, provided that the required physical, chemical, and biological data (or most of them) are available.

The scheme is described in detail in Appendix 2, and consists of four decision trees, which address the possibilities of acute aquatic toxicity, chronic toxicity, bioaccumulation*, and carcinogenicity. It attempts to assess the relative hazard through each of these routes, taking into account the likelihood that the substance being assessed will enter the aquatic environment. For a substance to be recognised as a priority substance, and therefore be included on the Red List, it was necessary for it to qualify through one or more of the decision trees. It did not have to qualify through all trees, and therefore the scheme did not seek to define the relative importance of, say, bioaccumulation versus acute toxicity.

3. As an example of a ranking or scoring system, a scheme developed by the Ontario Ministry of the Environment is described. The description is taken from Jackson and Peterson, and is presented in Appendix 3. (The scoring system is not included here in great detail because it is voluminous).

C. Discussion

There are, therefore, a number of approaches that have been taken to priority chemical selection, and to the details of individual schemes within these approaches. As has been noted above, the choices of both the assessment parameters and the trigger values or scorings associated with them can greatly influence the final list of chemicals. Jackson and Peterson tabulated the parameters that appear in 14 selection schemes (see Table 1). It can be seen that the complexity of the schemes varies greatly, with schemes using between 2 and 11 parameters, out of a range of 16. The most commonly used parameters are acute aquatic toxicity, persistence, and bioaccumulation potential ($K_{o/w}$). In a second group are carcinogenicity, acute mammalian toxicity, and physico-chemical properties.

* Only this example is included in this paper

Surprisingly little use is made of chronic toxicity data (possibly reflecting their relative scarcity) and production or use tonnage (which must influence, but not control, the amount of the substance entering the marine environment).

There is similarly great variability in the trigger values (see Table 2) used in different schemes. In most parameters, there seems to be a range of about 100 in the selected values of many of the triggers. For example, triggers on acute toxicity vary from 0.1 to 10 mg/l, and bioaccumulation factors from 2100 to 15,000.

The IEE, IEA and EIW organised a seminar on "The setting of a common selection scheme of dangerous substances", with reference to EC Directive 76/464 (Dangerous Substances) and the North Sea Declaration (March 1990) in July 1990, in Como, Italy. The purpose of the seminar was to develop a framework within which a selection scheme should be developed. The seminar did not come to a conclusion as to the type of scheme which should be adopted, but indicated that trigger values, etc., should reflect standards and other values already applied in EC Directives, bearing in mind the Precautionary Principle where necessary, and that any scheme should be thoroughly tested using substances for which good data were available.

It can be concluded that there is some measure of agreement as to the possible structures of the more detailed selection schemes, and that they may be classified as scoring/ranking schemes and logic tree schemes, and that some parameters which describe either the exposure of an organism to a compound or the response of that organism should be included. These basic parameters include toxicity, persistence, bioaccumulation potential, and preferably parameters concerned with input to and behaviour in the environment. However, there is as yet no clear agreement on the range of parameters that should be used, or on the scorings/trigger values that should be applied.

KEY TO TABLES 1 AND 2 (from Jackson and Peterson, 1989)

United Kingdom:	Hedgcock and Copper, 1991 Dept of the Environment, 1988 Dept of the Environment, 1989 Byrne, C.D., 1988 Agy and Zable, 1990 Zabel and Jennings, 1987
Italy:	Sampaolo and Bientti, 1984, 1989
SRI:	Stamford Research Institute, 1980
XI/85/001:	CEC, 1985
XI/730/89:	CEC, 1989
North Sea:	Second International Conference on Protection of the North Sea, 1987 Third International Conference on Protection of the North Sea, 1989, 1990
Netherlands:	Working Group on Criteria for the assessment of motor pollution (BCW) 1989
CEFIC:	CEFIC, 1987
ICI:	ICI water and liquid effluent panel, 1988
Korte <u>et al.</u> :	Korte <u>et al.</u> , 1986
BMU:	Advisory Council to the Federal Ministry for the Environment, 1987
GDCL BUA:	Gesellschaft Deutscher Chemipa, 1989a, 1989b
France:	Commission D'Evaluation de l'ecotoxicité des substances chimiques, 1986
Ontario:	Environment Ontario, 1989

Table 1

Use of parameters.

	U n i t e d K i n g d o m	#	#	#	N e t h e r l a n d s	C E F I C	K o r t e I C I	B M U	G D C h B U A	F r a n c e	O n t a r i o
Ranking/scoring	*	*						*	*		*
Logic tree	*				*	*	*	*			
Appearance on other lists	(*)	(*)				(*)	(*)		*	(*)	
Teratogenicity		*									*
Mutagenicity		*			*				*		*
Carcinogenicity	*	*			*	*	*		*	*	*
Chronic mammal toxicity		*	*							*	
Acute mammal toxicity	*	*	*	*				*	*		*
Chronic aquatic toxicity	*		*			*					*
Acute aquatic toxicity	*	*	*	*	*	*	*	*	*	*	*
Models			*	*	*		*				
Bioaccumulation/ K_{ow}	*	*	*	*	*	*	*	*	(*)	*	*
Persistence	*	*	*	*	*	*	*	*	(*)	*	*
Persistence	*	*	*	*	*		*	(*)		*	*
Point/Diffuse	*		*								
Presence in environment					*	*			*		
Use tonnage	*		*		*						
Production tonnage	*	*	*		*	*			(*)		

Italy - Sampaolo and Binetti
France - Mission du Contrôle

Note - The way in which parameters are used in different schemes may not be comparable

model-based exposure assessments

(*) may not be integral part of priority setting

Table 2

Comparison of Trigger Values in Different Schemes.

Scheme/ Parameter	U.K.	ICI	CEFIC	Netherlands	Mission du Contrôle France	Scoring system GDCh Germany	6th amendment CEC XI/85/001	Scoring system Canada	Scoring system Italy	North Sea
Acute toxicity mg/l fish 96h, LC ₅₀	<1.0 >100	<1.0 >10	<0.1 >1.0	<0.01	<0.1 >1.0	<1.0 >100	<0.1 >10	<0.1	<10 >1,000	<1.0 (>100)
Chronic toxicity mg/l	<0.01 >1.0			<0.01 + <60% degradation in four days						
Persistence half life, days	>100 2.10	>100 <10	>100 <30	Degradation <10% in 28d	>40	Included	Not readily degradable	>100	>30 <1 hour	<u>BOD</u> <0.5 COD
Bioaccumulation factor (Log K _{ow})	>1,000(>3.5) <100(<2)	>1,000	>1,000	Not yet included	>100(>3)	>100 <100	>300(>3.5)	>15,000	(>3) (<0)	>100
Higher organism LD ₅₀ mg/kg	<50 >500					<25	<25	<0.5		
Production and use, tonnes/year	>10,000 <1,000			>100					>100,000 <1	
Solubility in water mg/l	>1,000 <1									
Volatility, Pascals	>0.133 <0.000133				1½ <1 hour				>500 <10	
Carcinogenicity	Yes	Yes		Yes (1½ >1 day)	Yes	Yes		Yes	Yes	
Occurrence, mg/l				In Rhine		>1		Yes		

Note - these figures are not directly comparable - see text
 Bold type indicates high value
 Normal type indicates low value

Appendix 1
(from GESAMP, 1990)

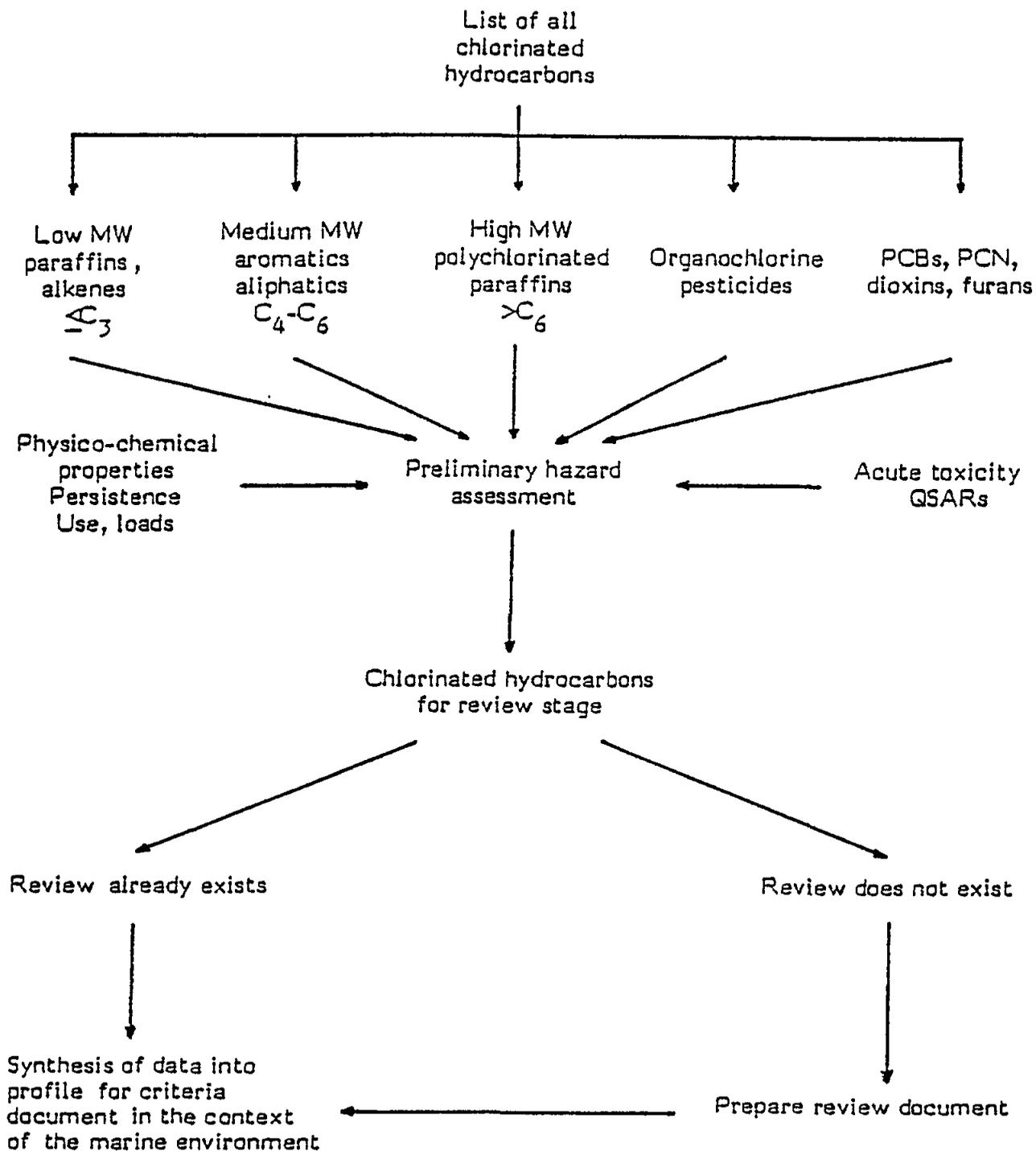


Figure 1. Recommended procedure for reviewing organochlorine compounds

List of Potentially Harmful Organochlorine Substances Selected on the Basis of Data Examined

Substances of Group 1: C₁ to C₃ Compounds

1,1,2,2-Tetrachloroethane	Hexachloroethane
1,1,2-Tetrachloroethylene	Vinylchloride
1,1,2-Trichloroethane	Methylchloride
1,1,2-Trichloroethylene	Pentachloroethane
Chloroform	Tetrachloroethene
Dichloromethane	Tetrachloromethane
Epichlorohydrin	

Substances of Group 2: C₄ to C₆ Compounds

1,1,2,3,4,4-Hexachloro-1,3-butadiene	2-Chloro-1,3-butadiene
1,2,3,4-Tetrachlorobenzene	3,4,6-Trichlorocatechol
1,2,3,5-Tetrachlorobenzene	Chlorobenzene
1,2,3-Trichlorobenzene	Hexachlorobenzene
1,2,4,5-Tetrachlorobenzene	Hexachlorocyclohexane
1,2,4-Trichlorobenzene	Hexachlorocyclopentadiene
1,3,5-Trichlorobenzene	3-chlorophenol
1-Chloro-2-nitrobenzene	1,3-Dichlorobenzene
1-Chloro-3-nitrobenzene	2-Chlorophenol
1-Chloro-4-nitrobenzene	1,2-Dichlorobenzene
1-Chlorobutane	4-Chloroaniline
2,3,4,5-Tetrachlorophenol	4-Chlorophenol
2,3,4,6-Tetrachlorophenol	1,4-Dichlorobenzene
2,3,5,6-Tetrachlorophenol	Pentachlorobenzene
2,3-Dichlorophenol	Pentachlorophenol
2,5-Dichlorophenol	Pentachloropyridine
2,4-Dichlorophenol	Tetrachlorocatechol

Substances of Group 3: Compounds with more than C₆

DL-3-(a-Acetyl-p-chloro-benzyl)-benzylchloride	
1-(o-Chlorophenyl)-1-(p-chlorophenyl)-2,2-dichloroethane (o,p'-DDD)	
1,1'(Dichloroethylidene)-bis[4-Chlorobenzene] (p,p'-DDE)	
1-(o-Chlorophenyl)-1-(p-chlorophenyl)-2,2,2-Trichloroethane (p,p'-DDT)	
2,4,5-Trichlorophenoxy acetic acid	2,3-Dichlorotoluene
2,4,5-Trichlorotoluene	2,4-Dichlorotoluene
2,4-Dichloroacetophenone	2,5-Dichlorotoluene
2,6-Dichlorobenzonitrile	2,6-Dichlorotoluene
2-Chloro-4-nitrotoluene	3,4-Dichlorotoluene
2-Chlorotoluene	Tetrachloroguaiacol
3-Chlorotoluene	3,4,5-Trichloroguaiacol
4-Chlorotoluene	4,5,6-Trichloroguaiacol
Benzotrichloride	4-Chlorostyrene
Octachlorostyrene	á,á,2,6-Tetrachlorotoluene

Group 4: PCBs, PCDD/PCDF

Total of 209 PCB isomers

Commercial mixtures of PCBs: Aroclors, Kaneclors, Chlophens, etc.

Total of 210 PCDD/PCDF isomers
of these 17 "toxic" isomers (=2,3,7,8-Cl substituted PCDD/PCDF)

Appendix 2
(from Hedgecote and Cooper, 1991)

SECTION 4 - LOGIC FOR THE SELECTION PROCEDURE

4.1 SCENARIOS FOR PRIORITY CANDIDATE SELECTION

The selection procedure consists of four decision trees, or scenarios, which will select those substances which pose the greatest hazard to the aquatic environment on the basis of a combination of their toxicity, bioaccumulation, carcinogenicity, persistence and likelihood of entering water. The four scenarios are summarised below and in Figures 1-4. Where reference is made in the Figures to 'high' or 'low' values, such as 'high' acute toxicity, the definition of 'high' and 'low' can be obtained from the threshold values presented in Table 6. These threshold values have been selected by the DoE, but they may be changed for any particular run as described under Item 7 of Section 5.2.

Table 6

Numerical values for high and low thresholds for chemical property or toxic end points.

Property	Toxic end point or parameter	Unit	High	Low	Insignificant
Acute aquatic toxicity	96 hr LC50 (fish) or 48 hr EC50/LC50 (invert)	mg/l	<1.0	>100	-
Sub chronic or chronic aquatic toxicity	NOEC	mg/l	<0.01	>1	-
Persistence in the aquatic environment	Half life	days	>100	<10	<2
Bioaccumulation potential	Bioconcentration factor	-	>1000	<100	-
	Log Kow	-	>3.5	<2	-
Toxicity to higher organisms	Significant toxic effect or oral LD50	mg/kg	<50	>500	-
Production and use		tonnes/ year	>10000	<1000	-
Solubility in water		mg/l	>1000	<1	-
Volatility		Pascals	>0.133	<0.000133	-

4.1.1 The food chain scenario (bioaccumulation)

This considers whether the substance is likely to reach a level at which toxicity will occur in higher organisms as a result of bioconcentration through the food chain (see Figure 3).

The decision is based on the substance's estimated level of input, its persistence in surface waters, its bioaccumulation in aquatic organisms and its toxicity to higher organisms (mammals). Substances may be considered as priority candidates if they meet the criteria outlined in Figure 1. It is recognised that the use of a rat (or other mammalian) acute oral LD50 as a toxic endpoint for higher organisms is less than ideal, but no other more suitable value is consistently reported in the literature.

Appendix 3 (from Jackson and Peterson, 1989)

10. Canada

Ontario Ministry of the Environment scoring system

Summary

A scoring system which gives score values to effects parameters. The series of scores is considered by expert judgement and if any one exceeds guideline limits, the substance is subject to exposure assessment. Substances of high exposure are then priority listed for more information and monitoring.

- | | |
|----------------|--|
| Advantages: | - guidelines for scores relating to fixed parameter values |
| | - easy to use and flexible - uses available data |
| | - inclusion of carcinogenicity, teratogenicity, genotoxicity |
| | - potential inclusion of both human and environmental impacts |
| Disadvantages: | - Priority listing may be by one characteristic only and so different individual characteristics may lead to listing of different substances |

Ontario Ministry of the Environment

The Municipal/Industrial Strategy for Abatement (MISA) of the Canadian Ontario Ministry of the Environment uses an Effluent Monitoring Priority Pollutants List (EMPPL) of substances which require more extensive information and monitoring because of their hazard to the environment (Environment Ontario 1989). The listing process is based upon the substance's environmental persistence, bioaccumulation potential, acute and sublethal toxicity to biota and presence in discharges to surface waters.

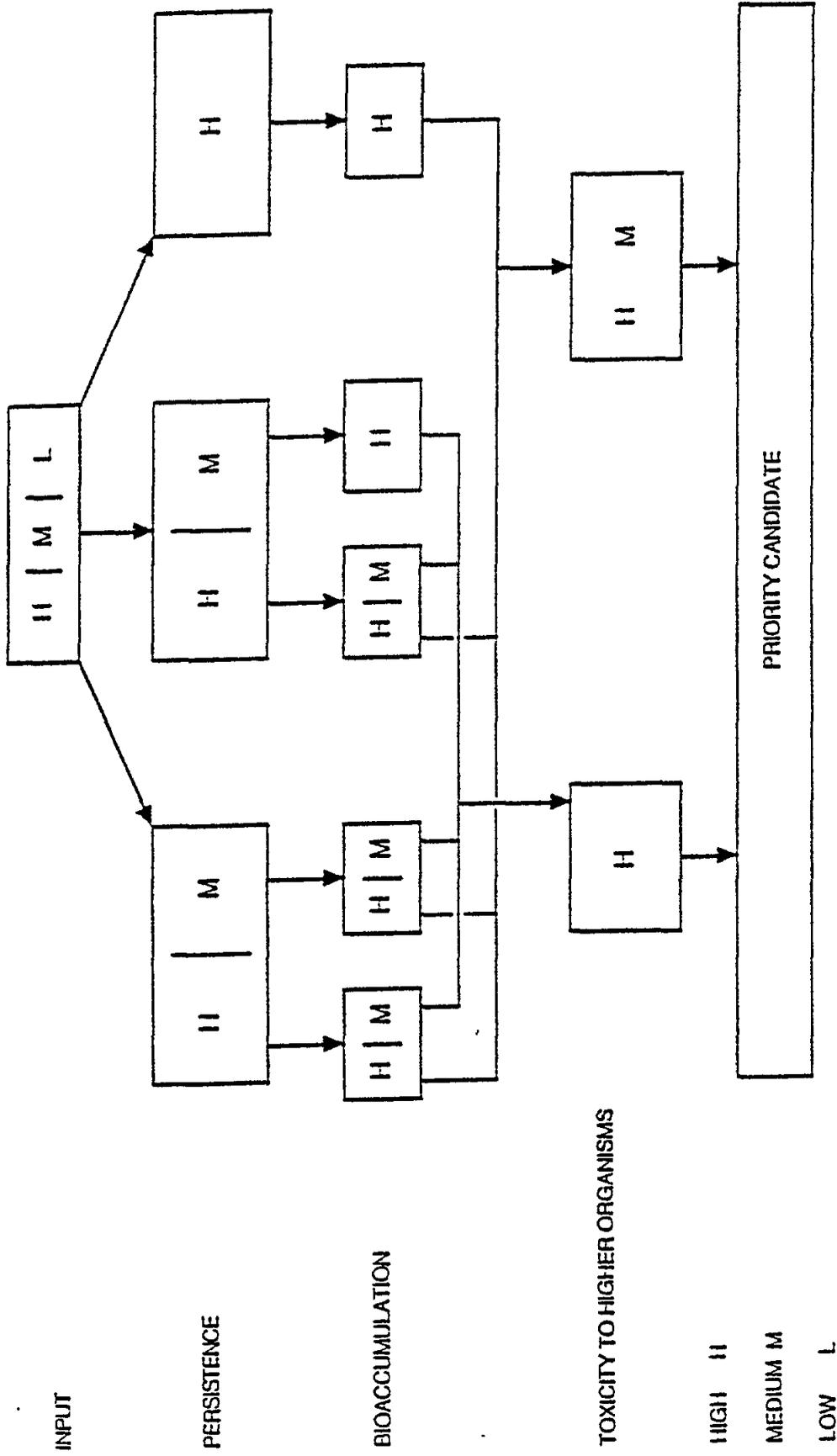


Figure 3 Bioaccumulation (Food Chain Scenario)

The first stage of the process is chemical identification - the development of a comprehensive list of candidate substances which are placed in one of two groups. The primary group consists of chemicals detected in effluents and surface waters and the secondary group of chemicals which have not yet been detected but which would be of concern if they were found. Chemicals are chosen from these groups by the MISA office (for the 1988 update, chemicals from organic chemical, iron and steel, mining, electric power generation and pulp paper industries) which are then subject to a preliminary hazard assessment process.

The hazard assessment process uses an effects and fate scoring system with exposure assessment criteria in order to place chemicals on the EMPPL. The scoring system (Environment Ontario undated) gives scores for environmental behaviour parameters:

- a. Environmental transport
- b. Environmental persistence
- c. Bioaccumulation

and for toxicity parameters:

- a. Acute lethality
- b. Sub-lethal effects on non-mammals
- c. Sub-lethal effects on plants
- d. Sub-lethal effects on mammals
- e. Teratogenicity
- f. Genotoxicity
- g. Carcinogenicity

Values for each of these parameters are given score values on a scale of 0-10 according to predetermined criteria.

ANNEX 7

Contaminants monitoring in different media

This annex contains selected material from the Report of the (ICES) Working Group on Environmental Assessments and Monitoring Strategies (1990).

OPTIMISATION OF MONITORING MARINE CONTAMINANTS WITH RESPECT TO MARINE MATRIX

ICES has been requested to supplement its advice on appropriate marine matrices for monitoring contaminants for the purposes of the Joint Monitoring Programme (JMP) by the addition of a number of new contaminants identified by the North Sea Task Force in its Monitoring Master Plan, which is intended as a supplement to the JMP in the North Sea. This document contains the information supplied by the Working Group on Environmental Assessments and Monitoring Strategies in its 1989 report, with the addition of material covering the new contaminants.

The matrices considered included sea water, sediments, and biota, as are included in the current JMP. The matrices 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. More complete explanations of individual cases are given below.

In many cases, primary and secondary choices of matrix are given and, in some cases, tertiary choices. These choices should be viewed as alternatives, or complementary choices, but the Working Group considered that, if circumstances permitted, a primary matrix should be preferentially selected for analysis, as this would provide the greatest amount of information relevant to the particular monitoring purpose. The Working Group recognised that suitable primary matrices may not be available in all monitoring locations, and in such cases, secondary or tertiary matrices should be used. It was fully appreciated that, in some cases (particularly in relation to Purpose c), the assessment of the existing level of marine pollution) a more comprehensive assessment might be obtained by the analysis of the contaminant in all matrices. However, the priority selections of matrices were made with the aim of providing the most useful scientific information for assessing distributions of contaminants, and focussing attention of those matrices that might enable the most consistent picture of distributions over wide areas to be obtained through the collective efforts of a number of laboratories and countries.

It was also recognised that in some cases matrices will be chosen on the basis of pre-existing local information and on-going monitoring programmes. The advice in the following sections should not be taken as denigrating the continuation of existing monitoring programmes designed in the context of local conditions that are yielding useful information, even if they do not wholly match the selections advocated here.

The Working Group wished to remind JMG that, in all circumstances, 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, pre-concentration, analysis, standardisation and interpretation). Participating laboratories should be required to adopt appropriate procedures in this area.

Purpose A: The assessment of possible hazards to human health (Table 1)

The Working Group recognised that, in the generality of the area covered by JMG, none of the contaminants considered presented a widespread serious hazard to human health through the consumption of marine foodstuffs. In some cases (e.g., copper, zinc, arsenic, chromium, and nickel), the contaminants were not normally of concern with respect to fisheries products. Equally, the monitoring of contaminants in sea water or sediment would not have any direct applicability to human health risk, and these considerations are reflected in Matrix Table 1. This table, therefore, 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.

The Working Group also recognised that 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 1 in relation to broader scale surveys. For example, in some areas there may be concern over the concentrations of CBs in the muscle of lipid-rich fish species, such as herring or mackerel, and in such circumstance it would be appropriate to analyse herring or mackerel muscle.

Purpose C: The assessment of the existing level of marine pollution (Table 2)

Water

In designing Table 2 (and Table 3), the Working Group took note of the JMG recommendation (JMG 14/15/1, Annex 8) that "seawater analysis should not, as a rule, be used for purpose (d) - trend monitoring (OSPAR 10/11/1, § 2.12). Although the Commissions agreed that seawater analyses were not the most appropriate compartment for detecting true statistical trends in time (purpose (d)), the Commissions nevertheless acknowledged that 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 (OSPAR 10/11/1, § 2.13).

In discussing sea water analysis, the Working Group drew a distinction 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.

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. However, the Working Group recognised the considerable efforts being made by the Marine Chemistry Working Group to improve the comparability of analytical performance among laboratories engaged in sea water analysis in member states. 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 essential 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.

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.

The Working Group recognised that 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. As agreed by the commissions, in such areas it might be appropriate for national authorities to give more prominence to water analysis in monitoring programmes.

Sediments

There is very considerable emphasis laid on the use of surficial sediments as a primary matrix for most of the contaminants. Participating laboratories should take full account of the most recent advice on the selection of sampling locations and methods (see, e.g., Section 15, Coop.Res.Rep. No. 142 (1987); Annex 2, Coop.Res.Rep. No. 124 (1983); Annex 2,

Coop.Res.Rep. No. 132 (1984)). Areas of high sedimentation and low bioturbation rates are particularly favourable. It is also necessary to subject the samples or data to appropriate normalisation procedures to allow, particularly, for grain size variations.

Biota

Both sediment and shellfish are indicated as primary monitoring matrices for TBT. Whilst the main area of concern over TBT is its effects on shellfish, particularly molluscs (oyster, dogwhelk, etc.), these organisms are by nature of limited geographical distribution. TBT, and its derivatives DBT and MBT, can be found in sediment, especially near shipyards, harbours and areas of extensive shipping and mariculture, and the monitoring of sediment should allow the use of a single matrix in a wider range of environments (e.g., into low salinity areas of estuaries) than would be possible using one mollusc species.

In preparing advice in relation to this monitoring purpose, the Working Group interpreted the purpose as referring to marine contamination, rather than marine pollution (as stated in the purpose). It must be emphasised that this advice has no relation to effects of contaminants on biota. Biological effects monitoring is, in the view of the Working Group, covered by JMG Purpose (b). The Working Group envisaged that once biological effects monitoring was established, it would be accompanied by appropriate chemical measurements of the active contaminant or contaminants. It may be possible subsequently to make inferences of the likely extent and intensity of biological effects from the results of Purpose (c) monitoring, by application of correlations between effects and contaminant concentrations derived from Purpose (b) monitoring.

Purpose D: Assessment of the effectiveness of measures taken for the reduction of marine pollution with the framework of the conventions (Table 3)

Measures taken within the framework of the Conventions to reduce the level of marine pollution are primarily directed at the control and reduction of inputs of contaminants. The main inputs are from riverine sources, land-based discharges, the atmosphere, and by direct dumping. The most efficient way to assess the effectiveness of the measures taken to reduce inputs is therefore to monitor the inputs, and JMG should take note of efforts already being made within the Commissions to assess the levels and trends of inputs. JMG may wish to take note of the comments in the 1988 ACMP report on the estimation of gross and net riverine inputs, and on atmospheric inputs. The monitoring of inputs can give detailed information on the effects of control measures on individual or localised groups of contaminant sources, and can therefore be particularly useful in regulatory procedures. It is likely that more and larger responses will be obtained when monitoring is conducted closer to the sources being regulated. Thus, for example, for land discharges, rivers and streams will generally yield higher signal-to-noise ratios than the marine environment.

It is also necessary to assess the effectiveness of the control measures in improving the quality of the marine environment. It is this aspect of trend monitoring that is covered by the Working Group advice in Table 3.

The Working Group noted that monitoring for the assessment of temporal trends of contaminants in the marine environment is very much less developed than monitoring for Purposes (a) and (c). There is an ICES Working Group on Statistical Aspects of Trend Monitoring (WGSATM) which is primarily addressing questions in this area. The advice in Table 3 represents the combinations of matrices and contaminants which WGEAMS feels have so far demonstrated the potential to display temporal trends, or which (e.g., shellfish) are likely to be usable in the near future. The table, therefore, represents a statement of the current "state of the art", and JMG should be aware that, as the subject is developed, additional combinations may become appropriate. With these considerations in mind, most of the recommendations are indicated as primary matrices, to reflect that they are very much alternatives.

When considering monitoring for temporal trends, it is necessary to consider the likely length of time which may elapse before any change in input may be reflected in the monitoring matrix. This length of time will be a complex function of environmental factors and processes, the magnitude and rate of changes in inputs, analytical factors, and data analysis procedures, with particular emphasis on the variance of each of the contributory media and processes. This may have particular importance in relation to the frequency with which JMG may wish to assess the effectiveness of measures taken by the Commissions, or the frequency of regional assessment exercises (e.g., in the North Sea area).

The WGSATM has conducted a simplistic assessment of trend monitoring data on the mercury content of fish muscle and liver made available to ICES, and estimated from these data that fish muscle analyses could detect (with at least 0.95 probability) changes of at least 30% over a period of 10 years, whilst fish liver analyses could only detect changes of 50% or more. Such observations should be taken into account by JMG when assessing the potential usefulness of temporal trend monitoring, bearing in mind that the data set analysed, whilst selected as representing the "best available case" in terms of data quality and quantity, was limited in respect to both of these.

Biota

In relation to the use of biota in trend monitoring, the WGSATM pointed out that the detection of trends in contaminant concentrations in biota may not necessarily imply that environmental levels or inputs have changed. Circumstances are quite conceivable in which other environmental factors, for example leading to a change in type or availability of prey species, could give rise to changes in the degree of exposure of the predator species to the contaminants concerned.

Sediments

Table 3 particularly emphasises the potential of down-core analysis of sediments in trend monitoring for a wide range of contaminants. As noted with respect to Purpose (c), and in footnote 5 to Table 3, it is particularly important to pay attention to the site selection and data normalisation procedures discussed in other ICES documents. Arsenic and chromium analyses are not recommended as it is as yet unclear how the distribution of these elements may be affected by changes in redox potential in anoxic sediments.

The JMG should take note of comments in the 1989 report of the Working Group on Marine Sediments in Relation to Pollution on the influence of sedimentation rate and bioturbation intensity on the ability of sediment core samples to reflect changes in input to the sediment. It is also likely that sediment core analyses will reflect general basin conditions, rather than changes in single sources or types of input.

Water

Water analysis is not recommended for trend monitoring (except for lindane). However, in circumstances of marked contamination and where changes are expected, as discussed for Purpose (c), contaminant monitoring in sea water may be appropriate, provided that statistical considerations indicate that such analyses could reliably reflect the effects of control measures.

The comments above on the relationship between contaminant monitoring and biological effects monitoring apply equally to monitoring for Purpose (d).

Clarification of contaminants included in the following Matrix tables:

A) Chlorinated biphenyls (CBs).

CBs on an individual basis: CB nos. 28, 31, 52, 101, 105, 118, 138, 153, 156 and 180. This list is the same as that of the ICES/IOC/OSPARCOM intercalibration exercise and involves all three mono-ortho-C1 substituted CBs considered to be of environmental concern

B) Chlordanes

Cis-chlordane, trans-nonachlor, trans-chlordane, oxychlordane

C) Planar chlorobiphenyls: CBs-77, 126, and 169

D) Polychlorinated dibenzodioxins and dibenzofurans (PCDD/PCDF)

All seventeen 2,3,7,8-polychlorinated dibenzo-*para*-dioxins and dibenzofurans

E) DDT

Only p,p'-DDT, p,p'-DDE and p,p'-DDD (TDE)

F) Polycyclic aromatic hydrocarbons

PAHs selected: Naphthalene and C1-, C2- and C3-alkyl derivatives; Phenanthrene and C1- and C2-alkyl derivatives; Anthracene; Dibenzothiophene and C1- and C2-alkyl derivatives; Fluoranthene; Pyrene; Benz[a]anthracene; Chrysene (+ triphenylene); Benzofluoranthenes; Benzo[e]pyrene, Benzo[a]pyrene; Perylene; Benzo[ghi]perylene; Indeno[1,2,3-*cd*]pyrene and Dibenz[a,h]anthracene

G) Polychlorinated camphenes (PCC)

For quantification purposes it has to be borne in mind that this extremely complex mixture can only be quantified on the basis of technical mixture equivalents (e.g., toxaphene).

H) Triazines

Simazine and Atrazine are the major compounds of importance

I) Polybrominated diphenyl ethers (PBDE)

2,4,2',4'-tetrabromodiphenylether and 2,4,5,2',4'-pentabromodiphenylether as representatives of the brominated fire retardants

J) Polybrominated biphenyls (PBB)

Matrix Table 1

In relation to the assessment of possible hazards to human health
(JMP Purpose a)

Matrix	Contaminant																					
	CBs	α-HCH	Hg ⁵	Cd	Cu ³	Zn ³	As ⁴	Cr ³	Ni ³	Pb	MeHg	TBT ³	Chlor- dane ³	Planar CB	PCDD/PCDF	DDT ³	Diel- drin	PAH	PCC	Tri- azines ³	PBDE ⁶	PBB ³
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 ¹										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 concern in respect to the consumption 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 health.
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.

Matrix Table 2

In relation to the assessment of the existing level of marine pollution (i.e., contamination)
(JMP Purpose c)

Matrix	Contaminant																						
	CBs	α-HCH	Hg	Cd	Cu	Zn	As	Cr	Ni	Pb	TBT	MeHg	Chlor-dane	Planar CB	PCDD/PCDF	DDT	Diel-drin	PAH	PCC	Tri-azines	PBDE	PBB	
Nearshore water		P	P ¹	P ¹	P ¹	P ¹		P ¹	P ¹	P ¹	S ¹												
Offshore water		S	S ¹	S ¹	S ¹	S ¹				S ¹													P
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						
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					

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 relation to the assessment of the effectiveness of measures taken for the reduction of marine pollution
(i.e., contamination) in the framework of the Conventions
(JMP Purpose a)

Matrix	Contaminant																						
	CBs	α-HCH	Hg	Cd	Cu ⁴	Zn	As ⁶	Cr ⁷	Ni ⁴	Pb	TBT	MeHg	Chlor- dane	Planar CB	PCDD/PCDF	DDT	Diel- drin	PAH	PCC ⁷	Tri- azines	PBDE	PBB	
Water		P ²									P										P		
Sediment profiles ^{5,8}	P	P	P	P	P	P			P	P			P	P	P		P					P	P
Shellfish Fish muscle			P	P	P	P				P	P		P										
Fish liver	P ^{1,3}		P ^{1,3}										P ^{1,3}	P ^{1,3}	P ^{1,3}		P ^{1,3}	P ^{1,3}				P ^{1,3}	P ^{1,3}

P: primary matrix
S: secondary matrix

Notes and Qualifications:

1. Considerable care has to be taken with species selection and availability, sampling protocol, and statistical aspects of data analysis.
2. Considerably greater effort is required, in respect to sampling and analytical frequency, if measurements are made in water, but the potential signal-to-noise ratio for trends is greater than that in sediments.
3. Sedentary species should be selected.
4. Highly unlikely that any trend signal related to anthropogenic influences will be detected.
5. Care should be taken in selecting favourable areas of high sedimentation rate, and limited bioturbation, following the latest ICES Guidelines for monitoring contaminants in sediments, including organic carbon measurements and appropriate normalisation procedures. Care should be taken to avoid contamination of subsurface sediment during sampling.
6. No recommendation can yet be made, except that As should not be measured in sediment profiles.
7. No recommendation can yet be made.
8. Care should be taken to avoid sub-surface contamination of sediment profiles.

CORRECT SAMPLING - WHAT IS THAT ?

by

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ABSTRACT

The material presented in this paper illustrates the influence of natural biological cycles in organisms on the monitoring of contaminants. The concentration in e.g. fish muscle or fish liver from one and the same specimen can vary quite considerably depending on when during the annual cycle the sample is taken. Also, problems related to i.a. sampling frequency and pooling of samples are illustrated.

1. INTRODUCTION

Biological variation such as within and between populations, seasonal variation and short-term fluctuation by chance are often neglected when interpreting data, whether the aim is to study spatial distribution or to study variation of the pollution over time. Even with the most sophisticated chemical analyses, where all kind of analytical errors are minimized, the results of one single or a few biological samples will not provide more information than the samples permit from a biological point of view.

It is therefore essential that sampling programmes for contaminant monitoring are designed in order to take into account as many biological factors as possible of those which can influence, and thereby disturb, the interpretation of the contaminant analysis. This is normally formalised by the issuing of detailed guidelines to be followed by all participants in the monitoring programme. It has been the sad experience for many scientists assessing monitoring data, that in several cases participants did not follow the guidelines concerning sampling, analytical procedures or protocols for reporting. It is the aim of this paper to give examples of undesired effects that are introduced if the programme is poorly planned or executed. It should be underlined, however, that the examples are taken from the scientific literature. The examples are of high quality, and have been selected to illustrate important principles.

2. PROBLEMS

The following problems are related to various biological processes and are therefore relevant for the scope of this paper. In order to avoid overlap with other papers in this document the physiological processes will not be discussed in any detail. The aim is to focus on how the contaminant monitoring results can be influenced and, consequently, also misinterpreted.

- a) Seasonal variation of contaminants' concentrations depending on reproduction cycle.
- b) Variation in contaminants' concentrations depending on length or age of the indicator organism.
- c) Variation in contaminants' concentrations depending on fat content.
- d) The effect of pooling of samples.
- e) The effect of frequency of sampling.

Example 1: Seasonal variation of contaminants' concentrations depending on reproduction cycle

The first example is from Claisse (1993) using data from the French "Mussel Watch" programme (National Monitoring Network for the Quality of the Marine Environment, RNO).

The programme has relied on four samplings per year since 1979 at a number of sites along the French coastline providing data for comparisons between the degree of contamination of different sites and time trend studies for each site. However, thanks to the high sampling frequency, the results offer a unique possibility to demonstrate the influence of the annual reproduction cycle in the mussels (blue mussels, *Mytilus edulis*).

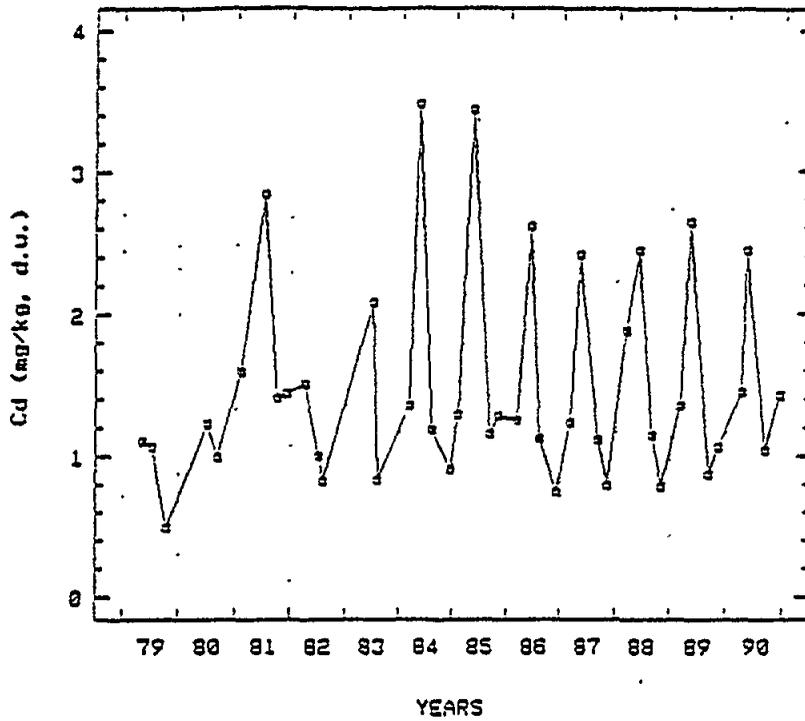
Figure 1 shows the long-term variation between 1979 and 1990 of cadmium and PAH at two sites. The results are expressed as mg contaminant per kg of dry weight of the mussel tissue. The variations are very big but it is easily seen that the variations within (every) year is far greater than between the start and the end of the time series.

In Figure 2 the corresponding data are presented as monthly means. The number at each data point shows how many times each month is represented in the data series. The pattern is rather similar for both contaminants. The concentrations are relatively low during winter when the gametes are built up as a preparation for the spawning period. During the spawning the animals loose body weight but the contaminant remains relatively unchanged and, therefore, the concentration of contaminant increases. After spawning the animal becomes sexually dormant and the body weight is again increasing and the contaminant concentrations decrease and reach a minimum during the autumn. Clearly these variations in contaminant concentrations are related to the biological cycle of the indicator organism.

It is very resource demanding to sample and analyse organisms several times every year. It is normal that sampling for contaminant monitoring is carried out only once every year (or even less frequent as described below). From this example it is clear that sampling must be made during the same phase of the biological cycle every year if the results should form a consistent data set that could allow statistical analysis of time trends. Breeding periods are linked to changes in the physical environment of the mussels, mainly variations in water temperature. If data from different sampling sites should be comparable it is essential to know the timing between the reproduction cycles at all these sites so that samples are taken at correct occasions. Finally, it is obvious that when results of monitoring are to be

CADMIUM / BAYE DE MARENNES OLERON

Mussels



PAH / SEINE

Mussels

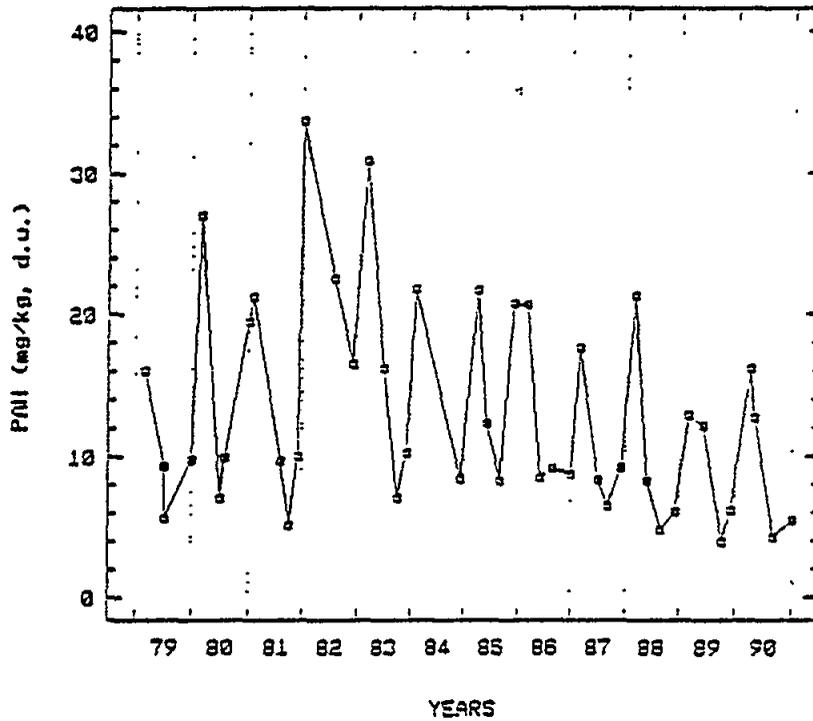


Fig. 1 Seasonal variations in mussels for cadmium in the bay of Marennes-Oléron (Atlantic coast) and for PAH in the Seine estuary (Channel coast) (From Claisse, 1993)

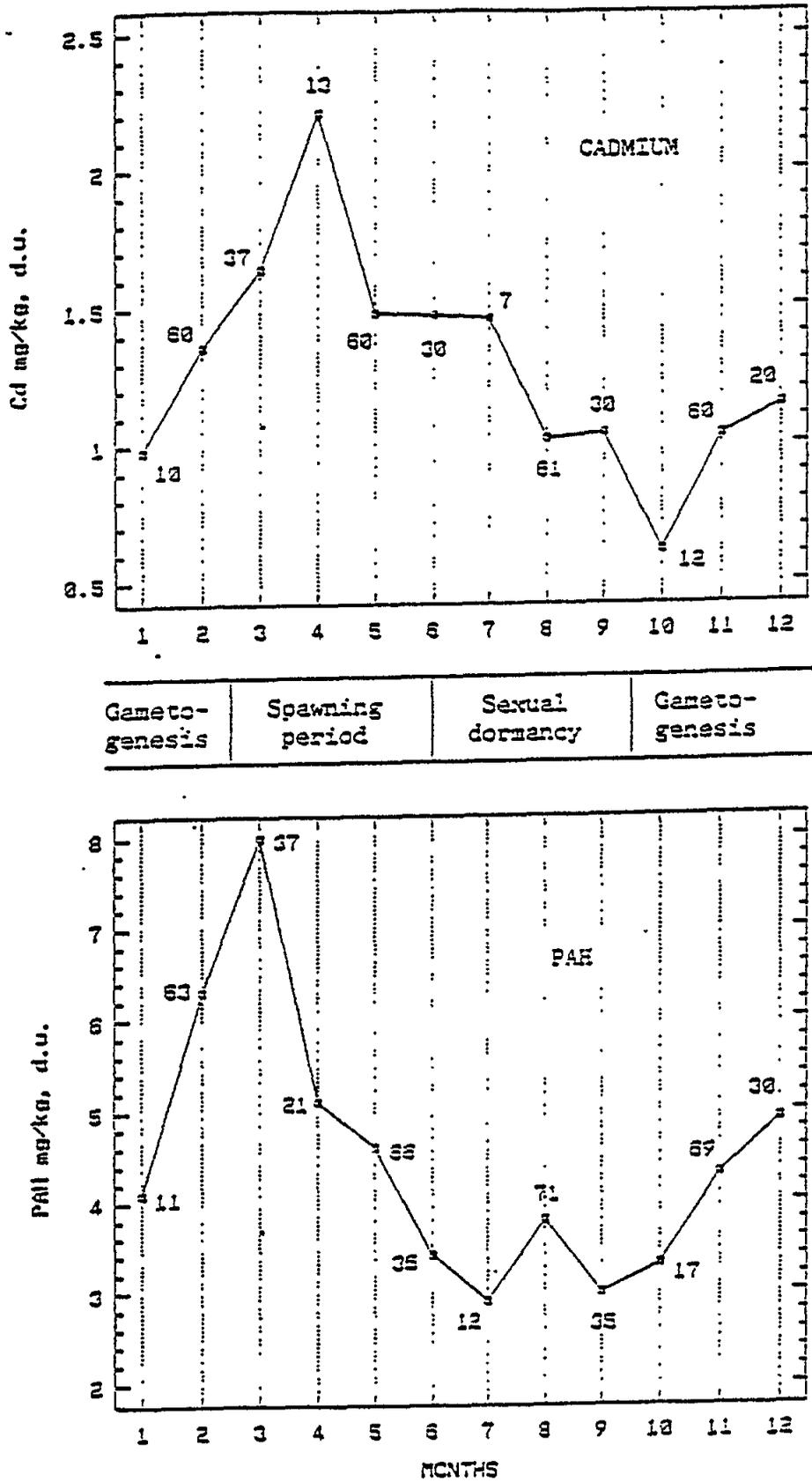


Fig. 2 Monthly mean variations in mussels for cadmium in the bay of Marennes-Oléron (Atlantic coast) and for PAH in the Seine estuary (Channel coast) (From Claisse, 1993)

compared with criteria and standards it is essential to stipulate when sampling must be done. Based on the results from the RNO programme it was possible to demonstrate that concentrations of various organic and inorganic contaminants could vary with a factor of 1-3 between different months. As an example, a site along the Loire river could be classified either as low or moderately contaminated by cadmium depending on whether the samples were taken in September-October or in March-April respectively!

The second example is from Bignert et al. (1993). A study of DDT compounds in Baltic herring (Clupea harengus) is presented in Figure 3. The concentrations are expressed as mg DDTs per kg of lipid. The data sets in (c) and (d) represent the breeding season April - June and the non-breeding season July - March respectively. The variation within the two samples is substantial and there is no clear significant difference between them if the 95% confidence interval of the mean values is taken into account. Then the data sets were divided into age groups; one for fish 1-3 years old and one for the fish older than 3 years. In (e) and (f) the results of the breeding and non-breeding fish older than three years, are shown. There seems to be a tendency to higher concentrations in the breeders (e) but again the difference is not significant. Concerning the breeders (g) and the non-breeders (h) aged 1-3 the situation changes. Here the difference is significant and the samples taken in the non-breeding period show the lower concentrations. Why the older fish do not show the same pattern? The explanation, or at least part of it, is probably that the older herrings migrate whereas the younger specimens do not. Thus the younger ones represent better the situation at one specific location and the older fish integrate over a wider geographical area.

Example 2: Variation in contaminants' concentrations depending on length or age of the indicator organism

Depending on the mechanisms for uptake and elimination of contaminants in organisms there is often a relation between contaminant concentration in the organism and the length or the age or the organism. This correlation can either be positive or negative as will be demonstrated by some examples.

Stronkhorst (1992) studied organic and inorganic contaminants in blue mussels (Mytilus edulis) in the Ems-Dollard and Western Scheldt estuaries in the Netherlands. Some results of the mussel study are presented.

His results are very well represented in the seven plots which appear in Figure 4. The results are expressed as mg of the various contaminants per kg wet weight of the mussel tissue. The mussels are graded in size classes which, needless to say, indirectly represent different ages of the animals. No effort was made to determine the actual age of the individual mussels.

In several cases the contaminant concentrations decrease with size (age) of the mussel. This was found for chromium, nickel, PCB and PAH. On the other hand cadmium, copper, mercury and lead showed different trends in the two estuaries. In the case of cadmium in mussels from the Western Scheldt there was an increase with length but for zinc, arsenic, dieldrin, lindane and pp'-DDE there was no linear length-effect relationship.

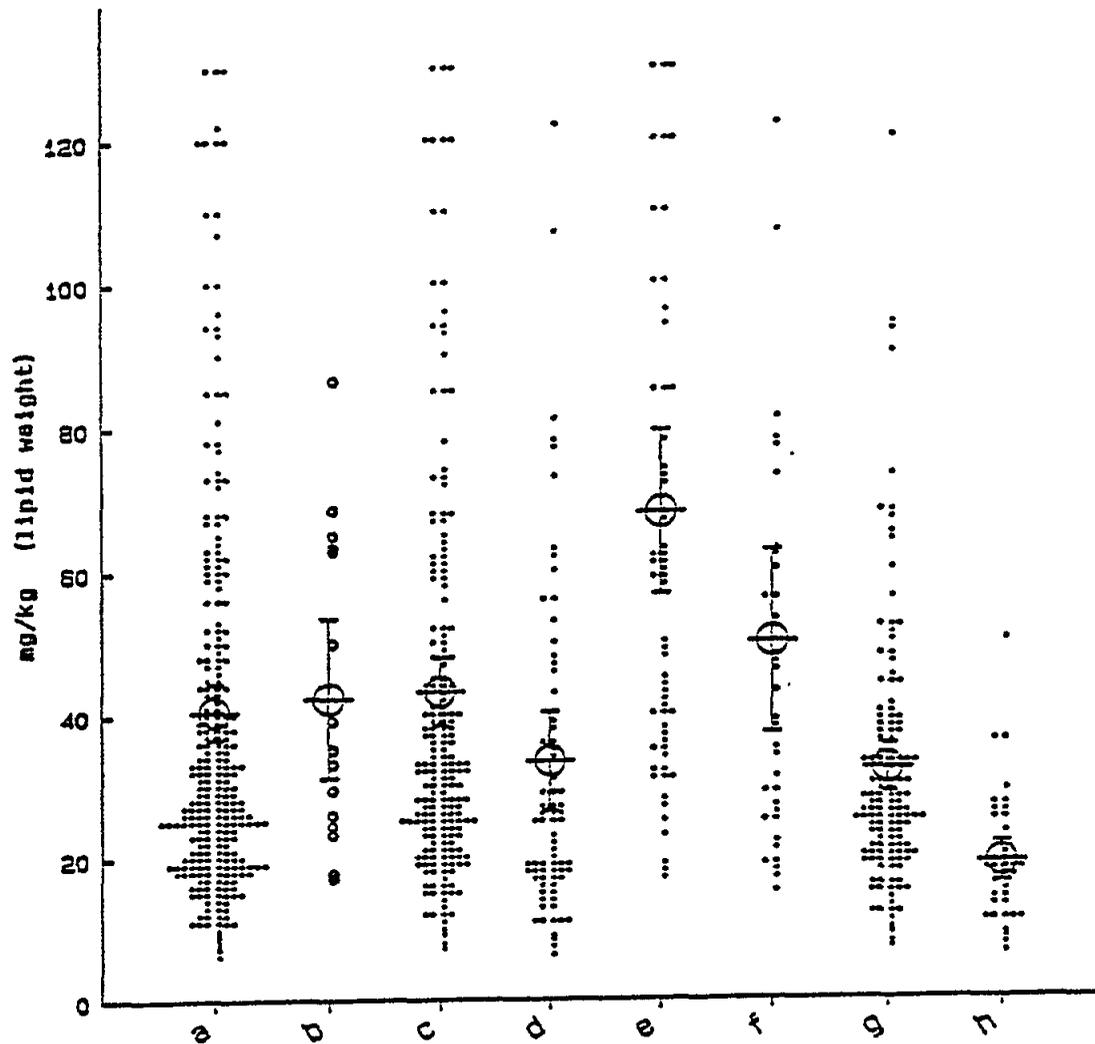


Fig. 3 Concentrations of DDT compounds (mg kg^{-1} lipid weight) in herrings collected during 1969-1970 in the southern Baltic. (a) individual concentrations of all herrings; (b) pooled samples of each catch; (c) the breeding season; (d) the non-breeding period; (e) breeding season, older than 3 years old; (f) non-breeding period, older than 3 years old; (g) breeding season, 1-3 years old; (h) non-breeding period, 1-3 years old. \bar{x} , arithmetic mean values. Vertical bars indicate 95% confidence interval of mean. (Five values greater than 140 mg kg^{-1} are excluded in Fig. 3 but are included in the estimation of the confidence intervals) (From Bignert *et al.*, 1993)

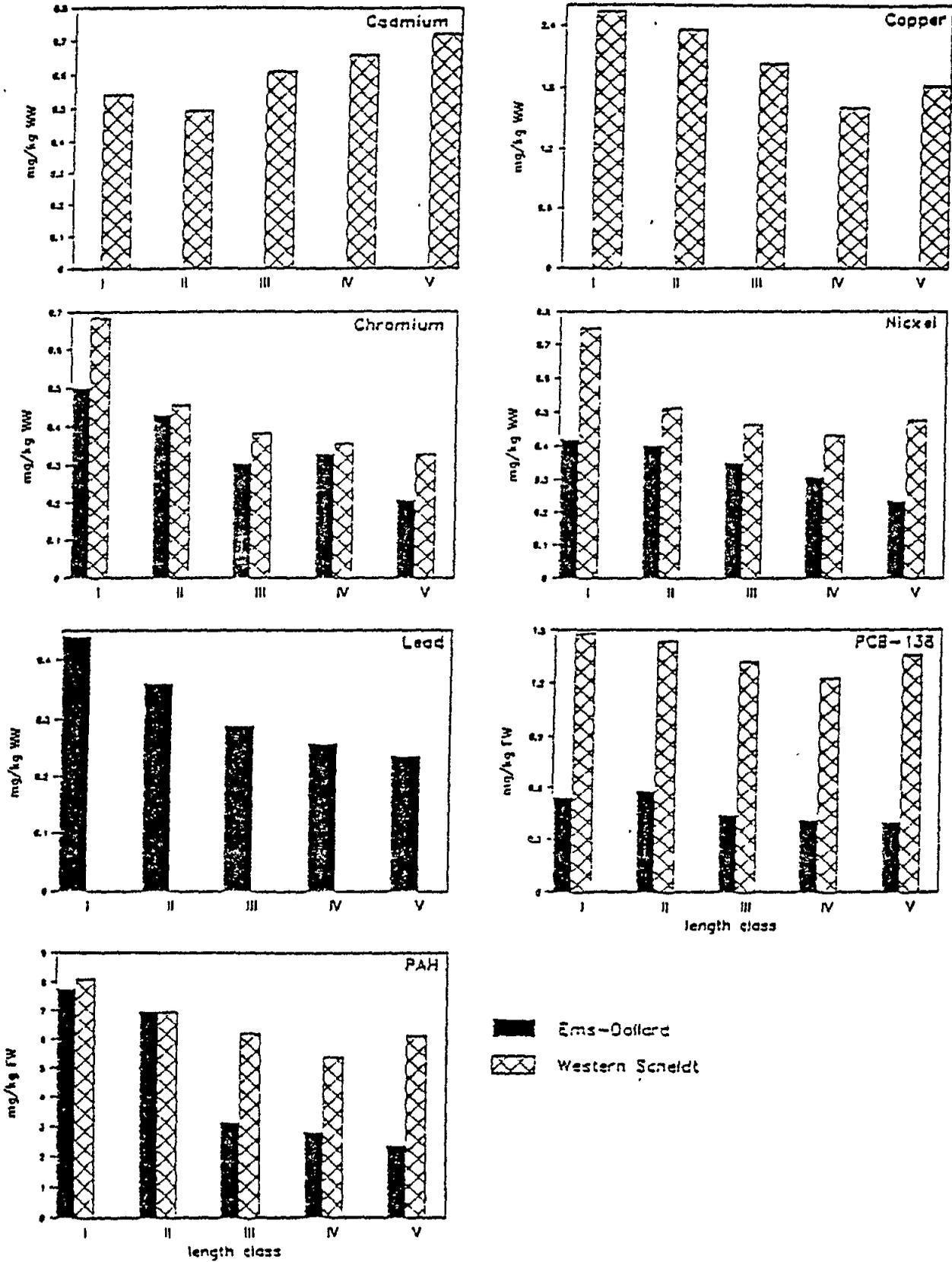


Fig. 4 Geometric mean concentrations of cadmium, copper, zinc, chromium, arsenic, nickel, lead and mercury per length class in mussels from Ems Dollard and Western Scheldt (I=25-30mm; II=31-37mm; III=38-46mm; IV=47-56mm; V=57-70mm) (From Stronkhorst, 1992)

One would perhaps expect that the contaminant concentrations would increase over time in the animal since we are dealing with substances that bio-accumulate. However, larger mussels tend to pump less water through their body per unit of body weight and this reduces the uptake rate over time. Furthermore, as the mussel grows the contaminant is "diluted" in the body and the concentration figure is decreasing since it is expressed as mg kg^{-1} .

One would also expect that substances of similar nature, e.g. heavy metals, would behave in a similar way. It should be kept in mind that the explanatory factors for the variations do not need to be identical or even similar for substances which from a chemical point of view, normally can be considered as similar.

A second example is taken from Bignert *et al.* (1993) and their study, referred to above, concerning the Baltic herring. Figure 5 shows the results of DDTs (mg kg^{-1} lipid) for fish of different age sampled in spawning and non-spawning periods. The authors argue that, particularly for the non-spawning fish, there is for the age 1-3 years no significant difference between concentrations of DDTs at different age. When the fish grow older and start migrating the concentrations seem to increase with age but the differences increase drastically between specimens in the same age group as can be seen from the vast increase of the 95% confidence intervals. This reduces the certainty in calculations of concentration differences between age groups. This can be further argued depending on whether conclusions are based on pooled or non-pooled samples, but that will be discussed later. The authors drew the conclusion that herring 1-3 year old, and sampled in the non-breeding season, were to be preferred for trend studies of the DDTs.

Example 3: Variation in contaminants' concentrations depending on (liver) fat content

As seen above, contaminant concentrations are often reported on (or normalised to) a lipid weight basis (e.g. mg kg^{-1} lipid). This has been chosen for various reasons e.g. it levels out differences in water content between mussels, and it also simply gives more convenient (higher) numbers when e.g. trace concentrations of organic contaminants in fish are reported as compared with using the wet body weight of the fish as a standard. However, there are some disadvantages in using lipid weight as the basis for normalising and reporting as will be shown in two examples.

The first example is from the paper by Stronkhorst (1992) who studied not only blue mussels but also flounder (*Platichthys flesus*) in the two Dutch Estuaries. Figure 6 deals with PCB congener 158 and how the results are influenced by changes in the fat content of the fish liver. Figure 6a seems to indicate that, although there is rather much variation between the years, there is an increase from 1985 to 1990 of the contaminant concentration (note the logarithmic scale) expressed as mg kg^{-1} fat weight.

However, during the same period the fat content (in per cent) of the flounder livers decreased markedly as is shown in Figure 6b. Since the amount of PCB-158 was contained in a decreasing amount of fat the concentrations of PCB-158 increased. If the actual figures for the PCB congener were instead

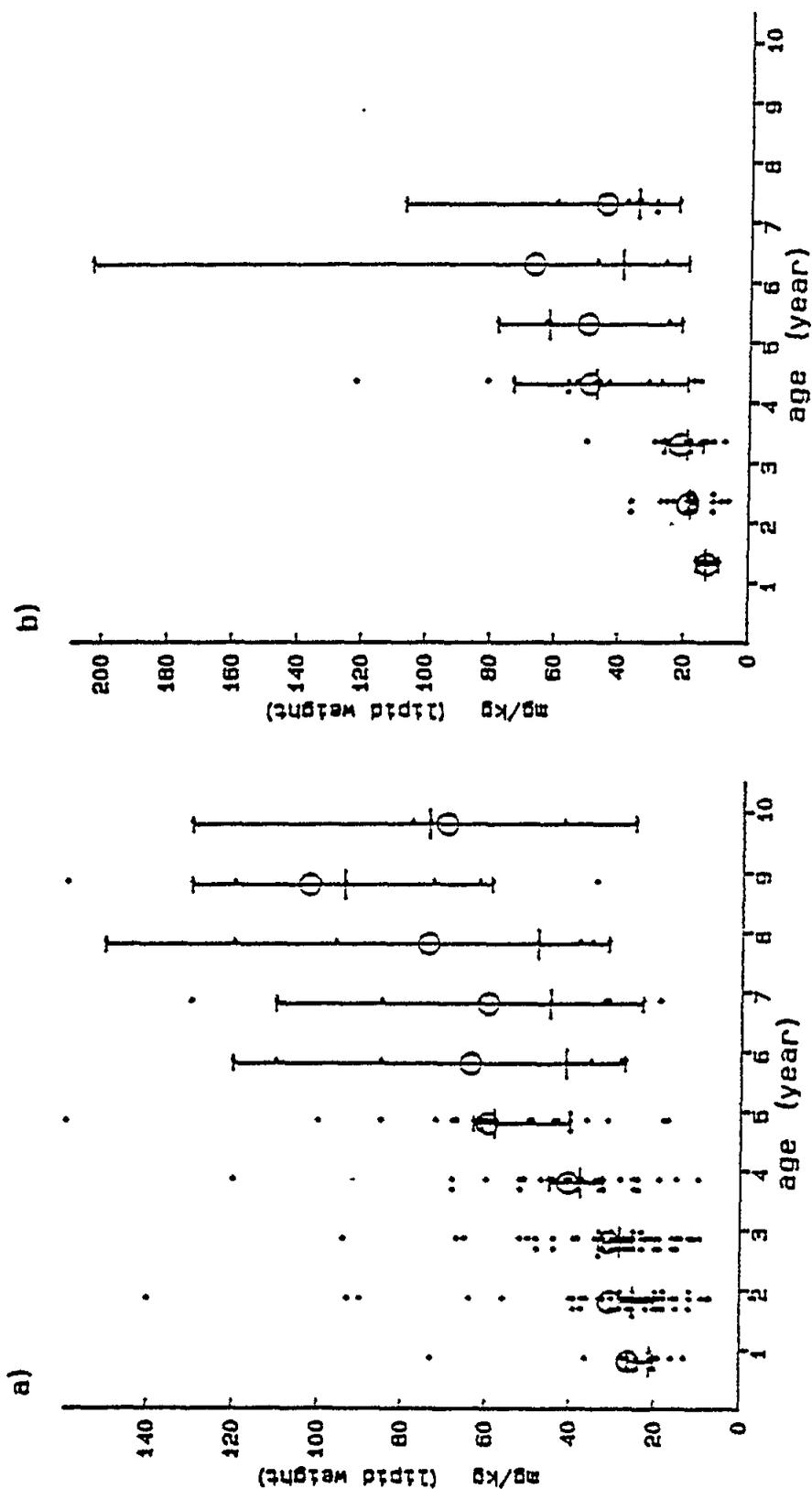


Fig. 5

Concentrations of DDT compounds (mg kg^{-1} lipid weight) in herrings collected in the southern Baltic during (a) the breeding season; (b) the non-breeding period. The material is divided into age classes. \circ , arithmetic mean; —, median. Vertical bars indicate 95% confidence interval of median. (Two values greater than 160 mg kg^{-1} are excluded in Fig. 5a but are included in the estimation of the confidence intervals) (From Bignert *et al.*, 1993)

expressed per kg of wet weight of the fish, as in Figure 6c, it is rather evident that during the period the body burden of PCB-158 per kilogram of fish actually decreased.

However, the question of normalisation to fat weight basis is more complicated than that. Different laboratories apply different methods for the fat weight determinations and also this may have consequences for the interpretation of the results!

An example is selected from the paper by Hummel *et al.* (1990) in their study of PCB content of blue mussels in some estuaries in the Netherlands. They included a comparison of two different fat determinations in their study. In the first instance the mussels were extracted with n-pentane. In the second instance a set of mussels were extracted according to the Bligh and Dyer (1959) method. Whereas the n-pentane extracts mainly non-polar material, the other procedure with its mixture of chloroform and methanol also extracts polar compounds such as phospholipids. Consequently the Bligh and Dyer extracts more material. The results of the n-pentane extraction is further below referred to as the fat content and the result of the chloroform-methanol extraction is referred to as lipids!

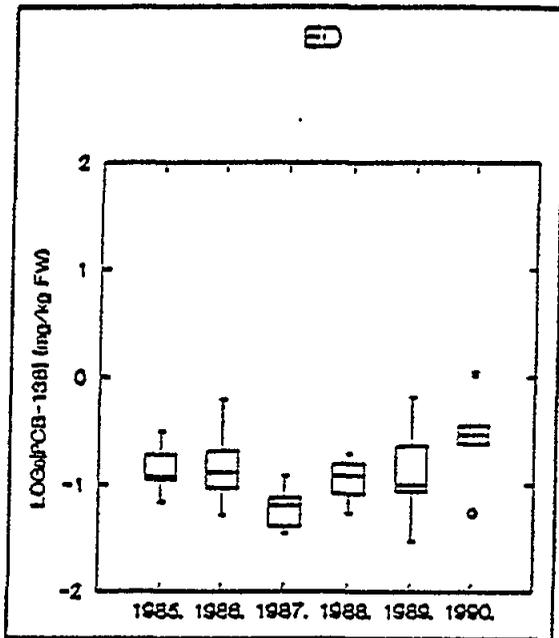
Figure 7 summarises some of their findings in this respect. Figure 7a shows the PCB content of mussels in ppm on a dry weight basis at 10 sampling stations and for the months of November, February, May and August. It is rather obvious, at least for the more contaminated stations, that after a peak concentration in February there would be a minimum in May followed by a certain increase in August. If the results were expressed on a fat weight basis (Figure 7b) the increase in August would never occur! The reason is found in Figure 7d where there is an obvious increase in fat content in the mussels during August. Thus, PCBs simply get diluted in the fat content and this explains why the concentrations on a fat weight basis remain almost constant from May to August.

It is worth pointing out that in Figure 7e the lipid content of the mussels is shown as a contrast to the fat content in Figure 7d. Two conclusions can be drawn from comparing these two figures. Since the numerical values of the fat and lipid content are rather different, analytical results of e.g. PCB concentrations would be very different when expressed on a fat basis and lipid basis respectively. This is very important to keep in mind when results from different laboratories are assessed together in joint programmes, or when results are compared with e.g. regulatory standards! Furthermore, there is very little seasonal variation in lipid content in the mussels and, therefore, the seasonal PCB pattern shown in Figure 7b would be very different if results were presented on a lipid basis!

Example 4: The effect of pooling of samples

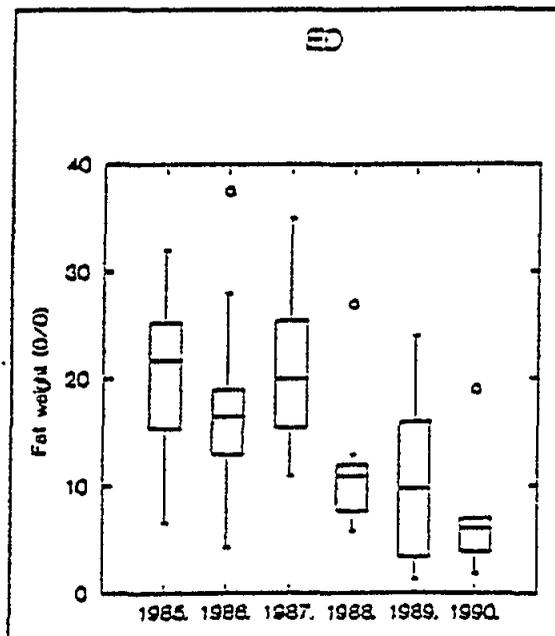
This subject is probably also mentioned in the papers on statistical aspects of sampling and analysis, but it may still be relevant to give some examples here.

Bignert *et al.* (1993) discuss at great length the problems related to interpretation of pooled samples. One aspect of this is indicated in Figure 3. Figure 3a shows the results when all herring samples in all the catches were analysed individually. The full span of the results can be seen from the lowest to the highest individual concentration for each fish. Furthermore,



6a

6b



6c

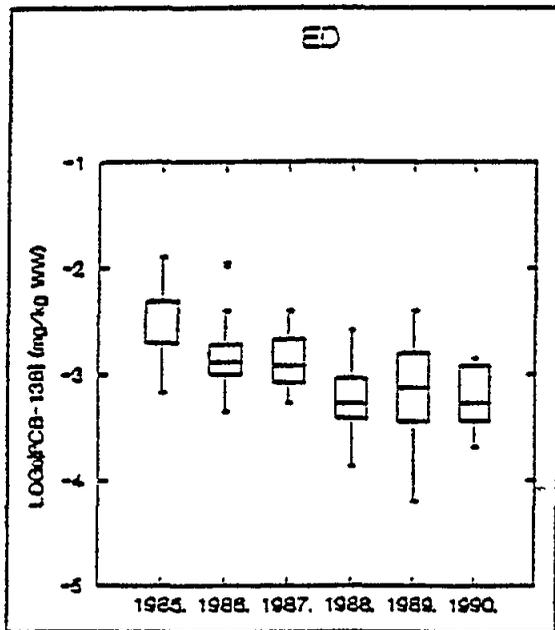


Fig. 6 Box and whisker plots of PCB-158 concentrations on a fat wet weight basis (6a), wet weight basis (6c) as well as the percentage fat weight in the livers (6b) of flounders from the Ems Dollard, 1985-90 (From Stronkhorst, 1992)

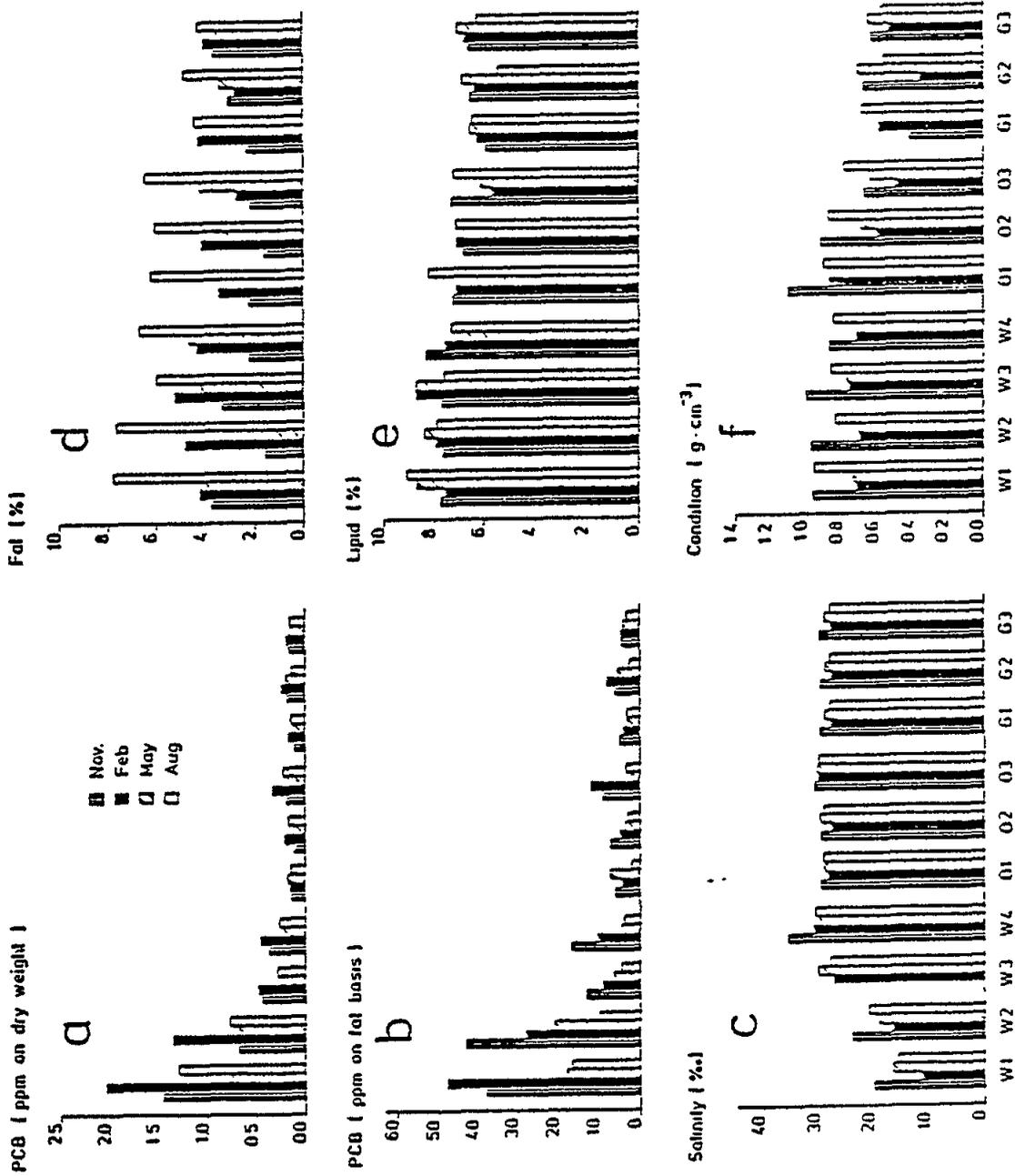


Fig. 7 The concentration of PCBs in mussels on the basis of (a) dry weight and (b) fat in mussels; (c) the salinity of the ambient water; (d) the fat, (e) lipid content and (f) condition of the mussels at the 10 sampling stations (From Hummel *et al.*, 1990)

for each concentration level one can see how many individual fishes are represented. Thus, we know a lot about the biological variation of the material. In Figure 3b the results from each catch have been used to calculate a mean value, thus simulating what happens when several fish are pooled into one sample for analysis. The arithmetic mean values in the two cases do not differ significantly but certainly in this latter case we know a lot less about the biological variation of the population we are sampling.

In Figure 5 Bignert et al. (1993) demonstrate that this knowledge is essential. If the study of DDT concentrations versus age of fish would have been based on pooled samples only (i.e. the arithmetic means in the figure) a linear regression analysis would show an increase of DDT by fish age. However, based on the knowledge of the biological variation of the fish populations (the median values and its 95% confidence interval) it is obvious that for the fish aged 1-3 years there is no age effect and for the older fish the variation within each age group masks any possible relation between contaminant concentration and age!

Example 5: The effect of frequency of sampling

This last example will illustrate how short term fluctuations of a few years, combined with the effect of different sampling frequencies, can influence the results of a long term monitoring.

Again the example is taken from the work of Bignert et al. (1993). In Figure 8 the results of PCB in young herring for the period 1972-1988 are presented. All results based on annual samplings and analyses of individual herrings are included. It is obvious that over the entire period there is a decrease in the PCB concentrations by a factor of 2-3.

In Figure 9 some simulations are shown to demonstrate the effect that could occur if the monitoring programme has to be reduced, e.g. for financial reasons, to sampling every three years, starting in 1972, 1973 and 1974 respectively. Furthermore, pooling of samples is again simulated as described earlier. In the first two simulations the decrease in PCB levels is again visible. However, in the third simulation the overall picture is an increase in the recent years and it would indeed be impossible to know if there is really a decrease in the first part of the monitoring period, or, if the high concentrations found in 1974 are just odd results of dubious significance!

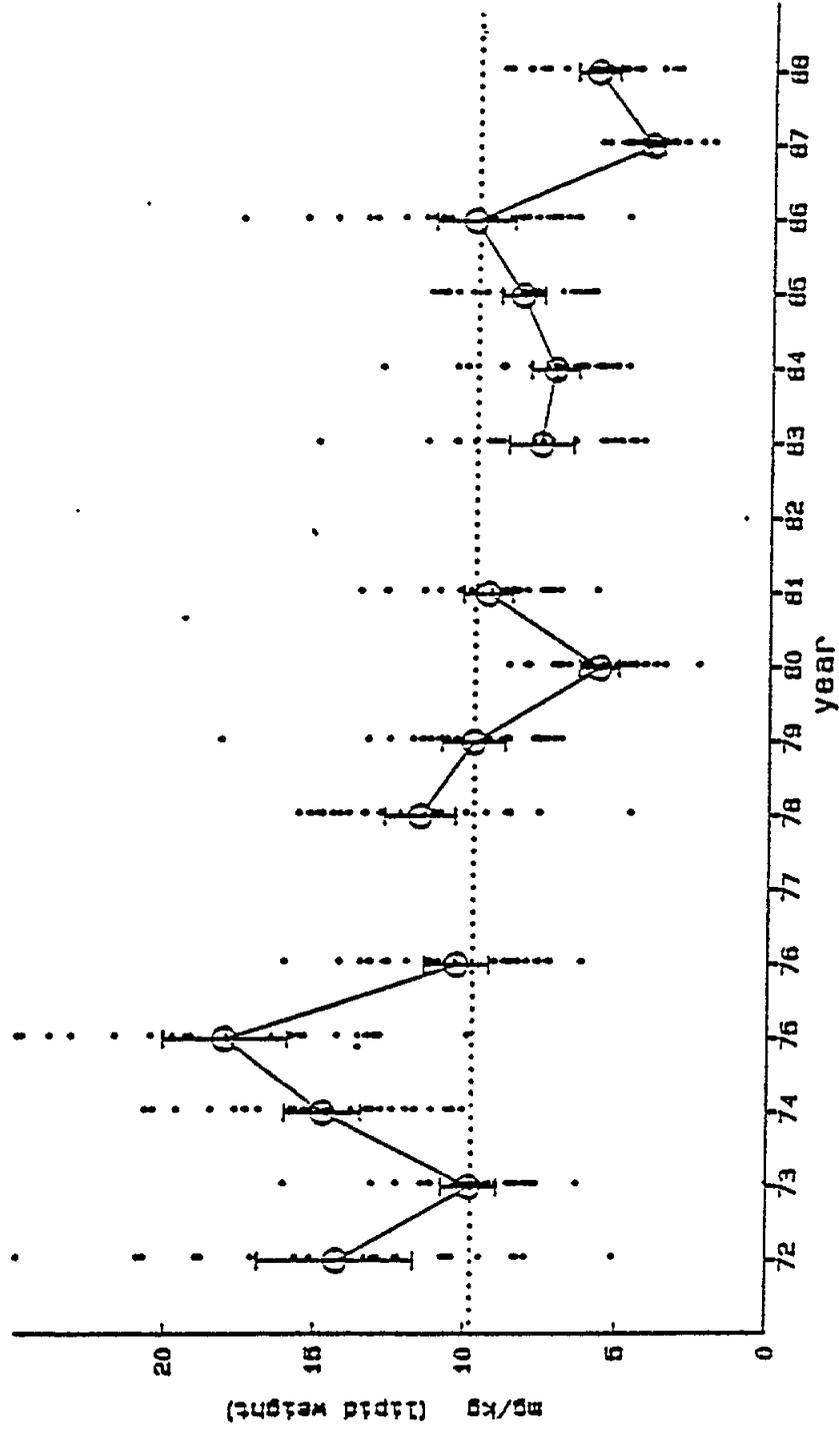


Fig. 8 Concentration of total PCB (mg kg^{-1} lipid weight) in young herrings collected during the breeding season 1972-1988 in the Karlskrona archipelago. O, arithmetic mean. Vertical bars indicate 95% confidence interval of mean (From Bignert *et al.*, 1993)

ADEQUATE BIOLOGICAL SAMPLING IN ECOTOXICOLOGICAL INVESTIGATIONS

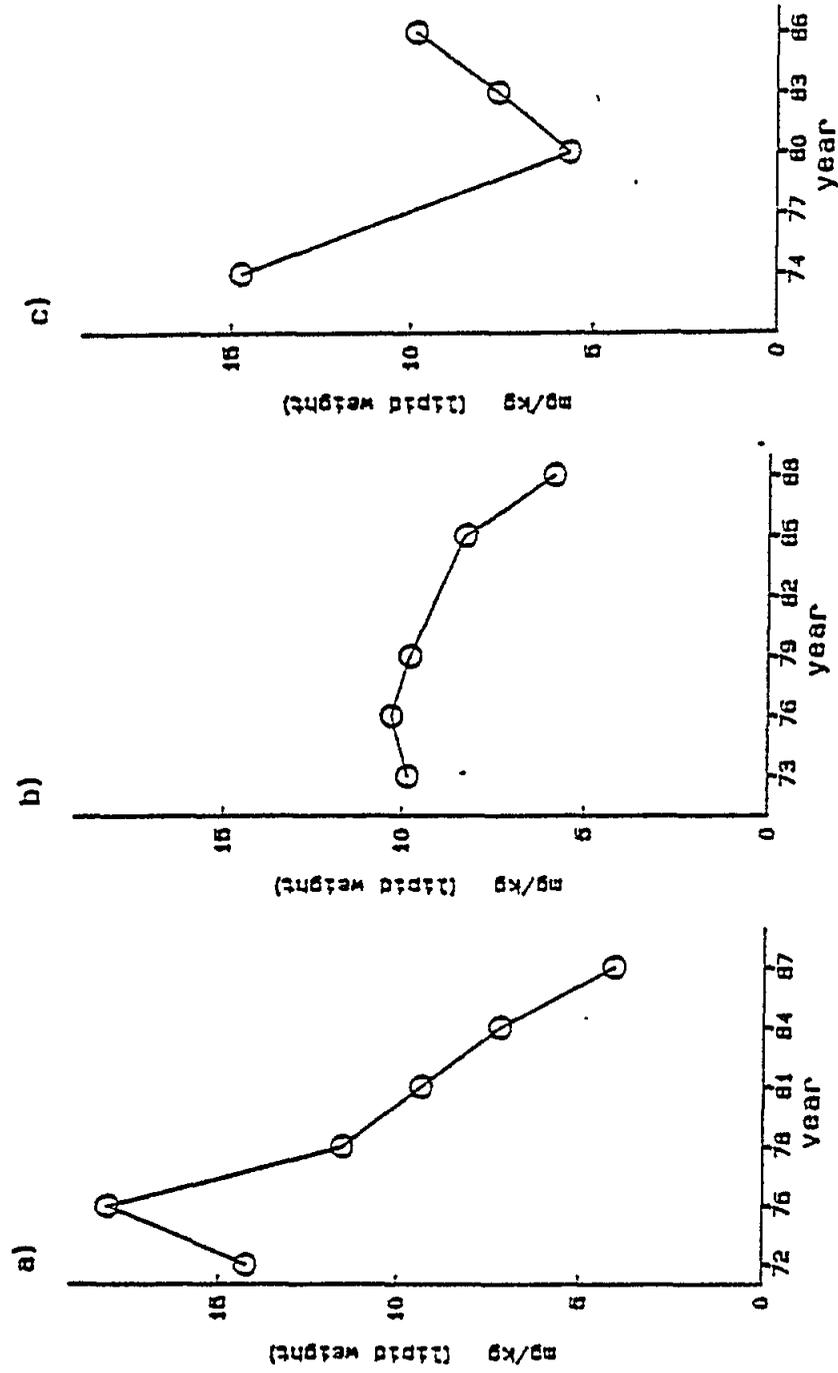


Fig. 9 Annual mean concentration of total PCB (mg kg⁻¹ lipid weight) in young herring collected during the breeding season in the archipelago of Karlskrona. The three examples demonstrate the time-series that would be obtained if sampling were performed every 3 years starting in 1972, 1973 and 1974, respectively (From Bignert et al., 1993)

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**UPTAKE, STORAGE AND ELIMINATION OF CHEMICAL CONTAMINANTS
(METALS, ORGANOCHLORINE COMPOUNDS, RADIONUCLIDES)
IN MARINE BIOTA**

by

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Chemical contaminants are ubiquitous. Metals occur naturally as ions, compounds and complexes and can be natural components of sea water and sediments. Many of them are extracted, purified and processed for industrial use and then released to the environment again. Therefore metals can build up to high concentrations and may then represent a risk to marine life and human consumers of seafood. Organochlorine compounds do not naturally occur in the environment. These synthetic compounds, particularly pesticides (e.g. DDT) and certain industrial chemicals (e.g. PCBs) which are produced and used in large quantities are now widely distributed in the environment. Being fat-soluble, persistent and largely non-biodegradable, they accumulate in sediments and in the lipids of organisms. Their build-up in top predators, particularly marine mammals and birds, causes damage to them while their presence in seafood can make it toxic for human consumption.

As a result of a general redistribution, living organisms can be exposed to these toxic components, through respiration, tegument contact and consumption. Some of them are among the most widely distributed chemical contaminants of large-scale pollution of the world ocean (Tables 1 and 2).

The ability of aquatic organisms to concentrate and to integrate chemical contaminants is named *bioaccumulation* or *bioconcentration*. *The concentration factor* is defined by the following ratio:

$$\frac{\text{contaminant concentration within the organism}}{\text{contaminant concentration within ambient water}}$$

When the concentration factor for a given contaminant increases, in a food chain, from the lower trophic levels to the higher trophic levels, this is named *biomagnification*.

Certain metals are, besides having negative effects in high doses, essential for organisms in small doses. Organisms need at least 11 essential trace elements: iron (Fe), copper (Cu), zinc (Zn), cobalt (Co), manganese (Mn), chromium (Cr), molybdenum (Mo), vanadium (V), selenium (Se) nickel (Ni) and tin (Sn). these are important for enzyme metabolism. Accumulation mechanisms were developed by organisms to enrich these essential elements from the extreme dissolution in seawater. but at the same time, non essential and extremely toxic elements like mercury, cadmium and lead are also absorbed from

seawater by organisms which use the same mechanisms as for essential elements. For instance chromium is necessary but is also poisonous in higher concentrations.

No biochemical reactions are known in which mercury, cadmium and lead play a positive role; therefore, these elements even in very small concentrations are basically toxic: they have always a negative effect on physiological processes.

Table 1

The most widely distributed toxic components of large-scale pollution of the world ocean (modified after Patin, 1982).

Groups and components of pollution	Priority ^(a)	Degrees of biological danger ^(b)	Prevalence
Radionuclides			
⁹⁰ Strontium	1	+	Global
¹³⁷ Caesium	1	++	Global
²³⁹ Plutonium	-	++	Global
Tritium	-	+	Global
¹⁴⁴ Cerium	-	+	Global
Organochlorine toxicants			
DDT and its metabolites	2	++	Global
Polychlorinated biphenyls	2	++	Global
Aldrin	2	++	Global
Dieldrin	2	++	Local
Lindane	2	++	Local
Metals			
Methyl mercury	1	++	Global
Cadmium	3	++	Global
Mercury	4	++	Global
Lead	4	++	Global
Zinc	-	+	Local
Copper	-	+	Regional
Arsenic	6	(+)	Regional
Chromium	-	++	Local
Iron	-	-	Local
Manganese	-	-	Local
Petroleum and petroleum products	5	(+)	Global
Detergents	-	?	Regional

Note: (a) Indicators of priority from the point of view of danger to man are shown in conformity to the recommendations of the United Nations Environment Programme (UNEP, 1974); (b) degree of danger for marine organisms: ++ strong; + considerable; (+) weak; ? not determined; - insignificant (GESAMP-IMCO/FAO/WMO/WHO/IAEA/UN, 1973).

Table 2

Anthropogenic inputs of trace metals into the aquatic ecosystems (10^6 kg yr^{-1}) (Nriagu and Pacyna, 1988).

Source category	Annual global discharge (10^9 m^3)	As	Cd	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
Domestic wastewater†														
- Central	90	1.8-8.1	0.18-1.8	8.1-36	4.5-18	0-0.18	18-81	0-2.7	9.0-54	0.9-7.2	0-2.7	0-4.5	0-2.7	9.0-45
- Non-central	60	1.2-7.2	0.3-1.2	6.0-42	4.2-30	0-0.42	30-90	0-1.8	12-48	0.6-4.8	0-1.8	0-3.0	0-1.8	6.0-36
Steam electric	6	2.4-14	0.01-0.24	3.0-8.4	3.6-23	0-3.6	4.8-18	0.1-1.2	3.0-18	0.24-1.2	0-0.36	6.0-30	0-0.6	6.0-30
Base metal mining and dressing	0.5	0-0.75	0-0.3	0-0.7	0.1-9	0-0.15	0.8-12	0-0.6	0.01-0.5	0.25-2.5	0.04-0.35	0.25-1.0	-	0.02-6
Smelting and refining														
- Iron and steel	7						14-36			1.4-2.8				5.6-24
- Non-ferrous metals	2	1.0-13	0.01-3.6	3-20	2.4-17	0-0.04	2.0-15	0.01-0.4	2.0-24	1.0-6.0	0.08-7.2	3.0-20	0-1.2	2.0-20
Manufacturing processes														
- Metals	25	0.25-1.5	0.5-1.8	15-58	10-38	0-0.75	2.5-20	0.5-5.0	0.2-7.5	2.5-22	2.8-15	0-5.0	0-0.75	25-138
- Chemicals	5	0.6-7.0	0.1-2.5	2.5-24	1.0-18	0.02-1.5	2.0-15	0-3.0	1.0-6.0	0.4-3.0	0.1-0.4	0.02-2.5	0-0.35	0.2-5.0
- Pulp and paper	3	0.36-4.2	-	0.01-1.5	0.03-0.39	-	0.03-1.5	-	0-0.12	0.01-0.9	0-0.27	0.01-0.9	-	0.09-1.5
- Petroleum products	0.3	0-0.06	-	0-0.21	0-0.06	0-0.02	-	-	0-0.06	0-0.12	0-0.03	0-0.09	-	0-0.24
Atmospheric fallout‡		3.6-7.7	0.9-3.6	2.2-16	6.0-15	0.22-1.8	3.2-20	0.2-1.7	4.6-16	87-113	0.44-1.7	0.54-1.1	1.4-9.1	21-58
Dumping of sewage sludge§	[$6 \times 10^9 \text{ kg}$]	0.4-6.7	0.08-1.3	5.8-32	2.9-22	0.01-0.31	32-1.06	0.98-4.8	1.3-20	2.9-16	0.18-2.9	0.26-3.8	0.72-4.3	2.6-31
Total input, water		12-70	2.1-17	45-239	35-90	0.3-8.8	109-414	1.8-21	33-194	97-180	3.9-33	10-72	2.1-21	77-375
Median value		41	9.4	142	112	4.6	262	11	113	138	18	41	12	226

* The discharges given represent contaminated process waters, and do not include cooling waters.

† The wastewater production figure corresponds to about $60 \text{ m}^3 \text{ capita}^{-1} \text{ yr}^{-1}$ multiplied by the 2.4×10^9 residents in urban and rural areas of the world. The other discharge figures likewise have been derived from the reported water demand per unit tonne of metal smelted or good manufactured.

‡ We have assumed that 70% of each metal emitted to the atmosphere is deposited on land and the remaining 30% in the aquatic environments.

§ Worldwide sewage sludge production is estimated to be 30 million tonnes, assuming average sludge production rate of $30 \text{ g capita}^{-1} \text{ day}^{-1}$ in urban and rural communities. It is believed that 20% of the municipal sludge is directly discharged or dumped into aquatic ecosystems, about 10% is incinerated and the rest is deposited on land.

That organisms continue to survive in the sea despite these negative effects is due to the fact that they tolerate the toxicity of these trace elements not only at the low concentrations that occur naturally in seawater, but also in the higher concentrations which organisms inevitably accumulate in their tissues. Uptake mechanisms cause more trace elements to be absorbed than the organism needs (Bryan, 1976). If excretion is not sufficient, toxic trace elements may be transformed into a non toxic compounds and stored away in the digestive gland, the kidneys or the shell of molluscs. As long as excretion and storage mechanisms are effective, sensitive tissues like the brain are protected from accumulating too high concentrations of toxic elements which might be harmful to physiological processes (Gerlach, 1981).

In detail, physiological and biochemical strategies for uptake, storage and elimination of toxic elements may differ widely. Various mechanisms are involved in these processes, depending on the element and organism.

It is generally accepted that the first effects of a chemical on an organism will be at the cellular and subcellular level (Fig. 1). If the reactions which occur at that level are damaging enough, they will affect organ function. but if the reactions are adaptive, they will not produce a harmful effect at a higher level of cellular and tissue organization.

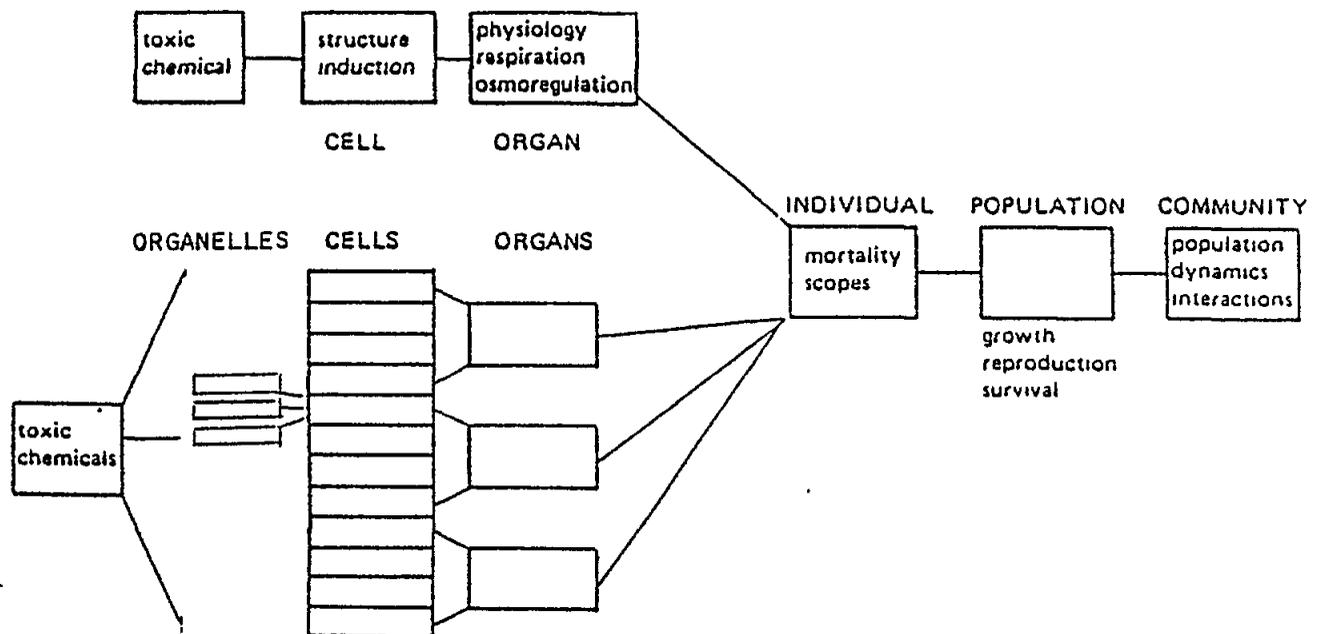


Fig. 1 Progressive effects of pollutants at different levels of biological organization (modified from Lloyd, 1991 who modified it from Haux and Forlin, 1988)

Therefore, direct chemical analysis of the metal content of the organelles, cells, organs and tissues, using very sensitive, reproducible and precise microanalytical methods are informative of environmental contamination (Chassard-Bouchaud, 1991). Figure 2 presents the main characteristics of the different methods which can be used.

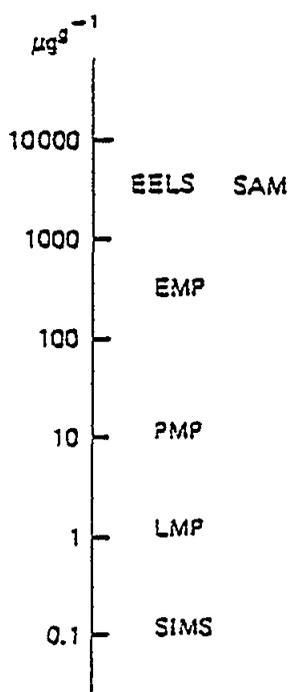
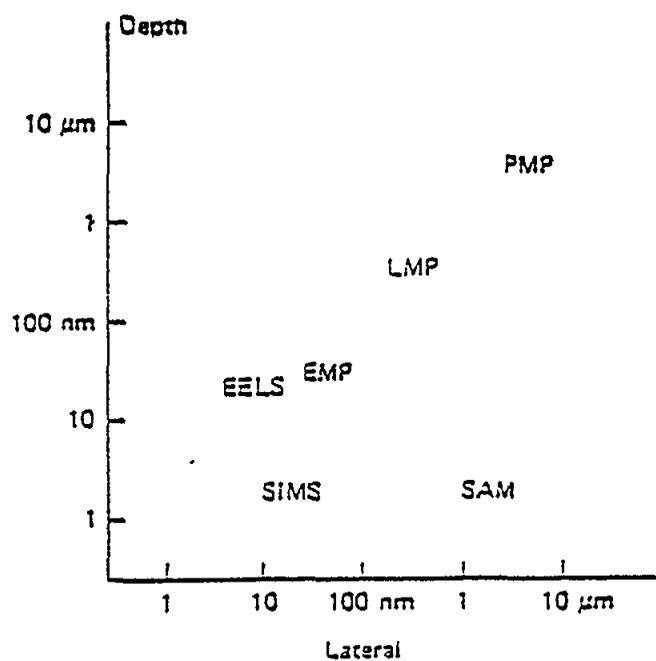


Fig. 2 a. Lateral and depth resolution of microanalytical techniques. Modified after Roomans *et al.* (1988). EELS: electron energy loss spectrometry. EMP: electron microprobe (=electron probe X-ray microanalysis). LMP: laser microprobe. PMP: proton microprobe. SAM: scanning Auger microanalysis. SIMS: secondary ion mass spectrometry (from Chassard-Bouchaud, 1991)

b. Sensitivity of microanalytical techniques. Modified after Roomans *et al.* (1988). EELS: electron energy loss spectrometry. EMP: electron microprobe (=electron probe X-ray microanalysis). LMP: laser microprobe. PMP: proton microprobe. SAM: scanning Auger microanalysis. SIMS: secondary ion mass spectrometry (from Chassard-Bouchaud, 1991)

Moreover, using the photon microscope, it is easy to observe if the tissues and organs are damaged and using the transmission electron microscope it is easy to observe the ultrastructural abnormalities.

But what happens at the organism level? Concerning chemical contaminants, the following processes have to be considered: uptake, storage and elimination.

Uptake of toxicants from seawater follows several different ways which are partly combined: uptake happens via gills, digestive tract and tegument epithelium. *Elimination* may happen via some of these routes and obligatory through excretion organs. *Storage* happens in a great variety of tissue and organs which are called *target tissue* or *target organs* of bioaccumulation: they differ widely depending on the elements, taxonomic groups and even on the species belonging to the same taxonomic group. They may be the following:

- muscles which are the edible parts in fish, crustaceans etc....
- digestive gland of bivalves, crustaceans etc...
- fish liver
- shells and byssal threads of bivalves
- exoskeletons of crustaceans
- reproductive organs
- certain types of cells such as amoebocytes, macrophages...

Moreover, for a given chemical, in a given species and in a given organ, bioaccumulation may differ depending on *several ecological factors*:

- *abiotic factors*:
 - chemical form (valency state....)
 - pH
 - salinity
 - temperature: an example is given with cadmium which is more poisonous at high temperatures and low salinity (Fig. 3).
- *biological factors*:
 - age and size: usually small and young organisms may accumulate at a higher level partly due to a higher metabolism in young than in adults.
 - sex and sexual maturity: in the crab Cancer pagurus, the digestive gland concentrates more plutonium in the female than in the male. Some trace elements such as Zn, Mn, Co, Cu concentrate at a higher level in the ovary than in the testis of Carcinus maenas.
 - moult and moulting cycle: in crustaceans some elements may be accumulated more before moulting than after (Co). The example of crustaceans will be developed further on.
 - food supply

To summarize, Fig. 4 represents the exchange processes existing between a marine organism and its environment concerning the pathways of uptake, storage and elimination of chemicals.

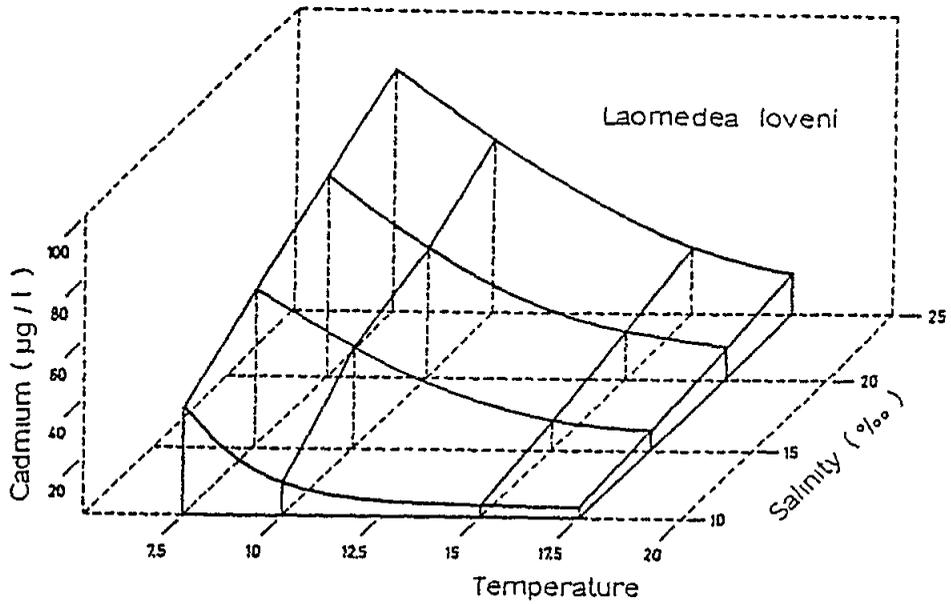


Fig. 3 Experimental animals react differently to poisons, depending on the ecological conditions under which they have been kept. The diagram shows the cadmium concentration at which half the number of polyps in a colony of hydroid polyps (*Laomedea loveni*) is reduced, after 7 experimental days (7 d LC₅₀). At below 20 µg l⁻¹, cadmium is most poisonous at high temperatures and low salinity (Theede *et al.*, 1979 in Gerlach, 1981)

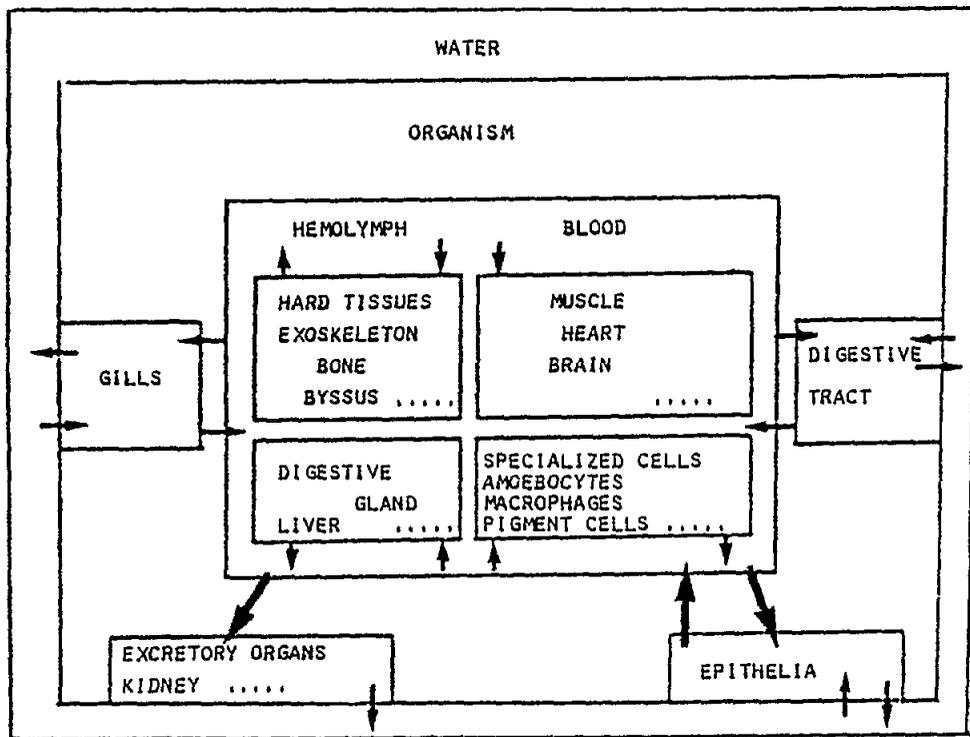


Fig. 4 Exchange pathways between marine organism and its environment

Conversely, pollutants have several impacts on ecosystems (Fig. 5).

Among chemical contaminants, it is very important to take into account radioactive elements. They enter the sea from both natural and anthropogenic sources at variable concentrations which may pose a threat to marine organisms. The main input from man is from wastes and accidental releases. In normal conditions the largest quantities of radionuclides are derived from nuclear reprocessing plants. Most of the power stations are located alongside freshwaters and their effluents are transported to the sea via river systems.

Since many organisms accumulate metal contaminants from water and sediments into their body, they are called "indicator species": they act as sentinels in providing the chemical composition of their environment: refer to the other paper entitled "Criteria for the selection of organisms for monitoring purposes". These types of indicators belong mainly to bivalve molluscs (particularly to filter feeders), crustaceans and fish.

We present some examples of species belonging to bivalves (the marine common mussel Mytilus sp.), crustaceans (crab: Liocarcinus puber) and very briefly Teleost fish.

RADIONUCLIDES

Marine organisms at different trophic levels are capable of concentrating radionuclides relative to the amounts present in the water. Fig. 6 presents the concentration factors of plutonium at the different trophic levels: the highest levels are detected in primary producers and then they decrease in primary consumers, secondary consumers and at the end tertiary consumers which exhibit the lowest levels. This is due to the fact that lower organisms feed on sediment which is able to concentrate radioactivity; higher organisms then feed on the lower ones. Some concentration factors for selected radionuclides are given in Table 3. For marine foodstuffs, species other than fish must be considered, because the lower organisms are eaten by man and they may also form part of the food chain to fish.

Table 3

Concentration factors for specified radionuclides
(CEC, 1979 in Galle and Masse, 1982).

Radionuclides	Marine concentration factors					Fresh water concentration factors	
	Fish	Crustacea	Molluscs	Sediments	Seaweed	Sediments	Fish
H-3	1	1	1	0	1	0	1
C-14	5000	5000	5000	100	4000	2000	5000
Sr-90	1	10	10	500	10	2000	30
I-131	10	100	100	100	1000	200	30
Cs-137	50	30	30	500	30	30000	1000
Pu-239	10	100	1000	50000	1000	30000	10
Am-241	10	200	2000	50000	2000	30000	30

Concentration factor = $\frac{\text{activity/unit wet weight of edible material/or unit dry weight of sediment}}{\text{activity/unit volume of filtered water (in Bq tonne}^{-1} \text{ per BQ m}^{-3})}$

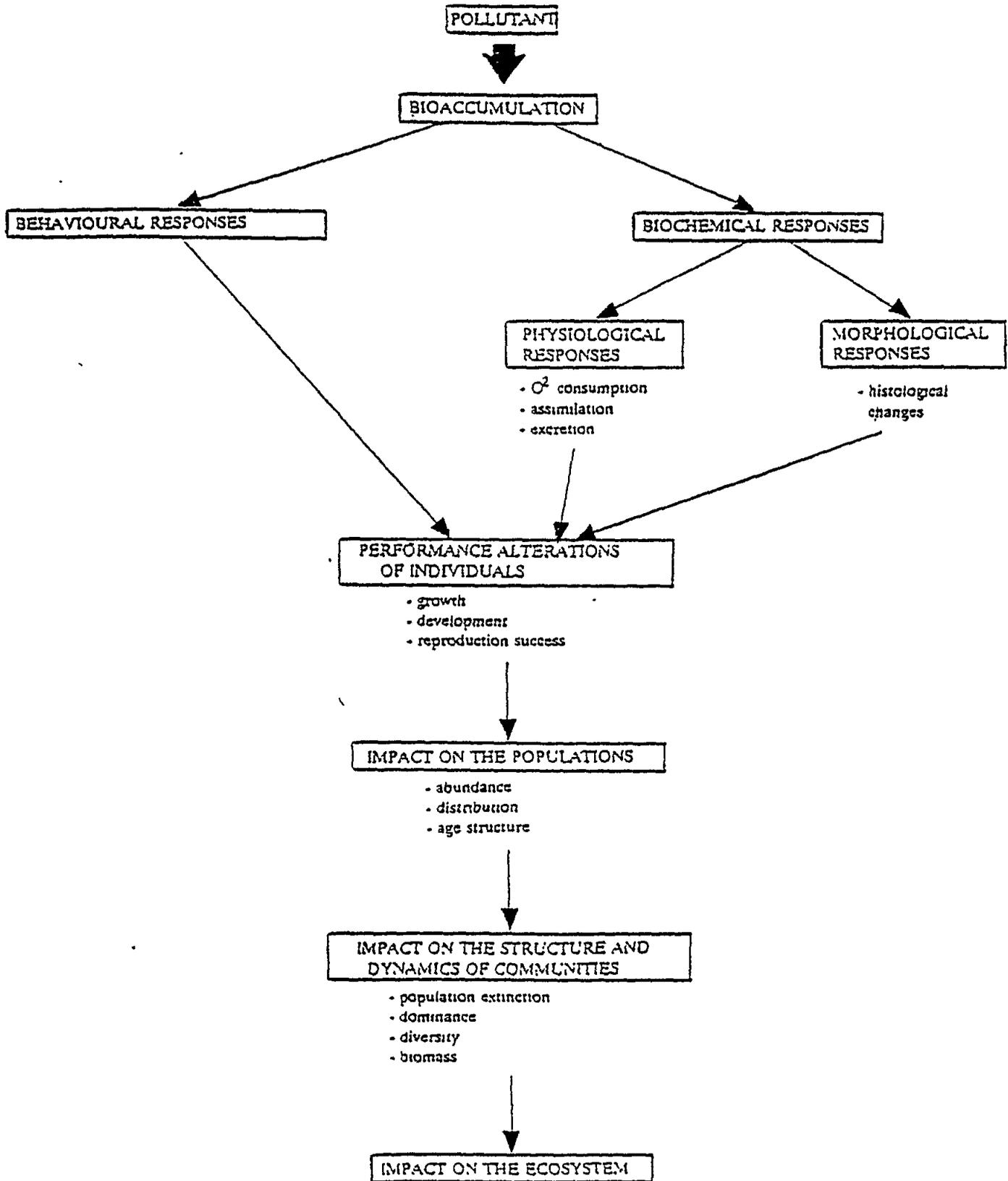


Fig. 5 Sequence of impact induced by a pollutant within an ecosystem (Caquet *et al.*, 1989)

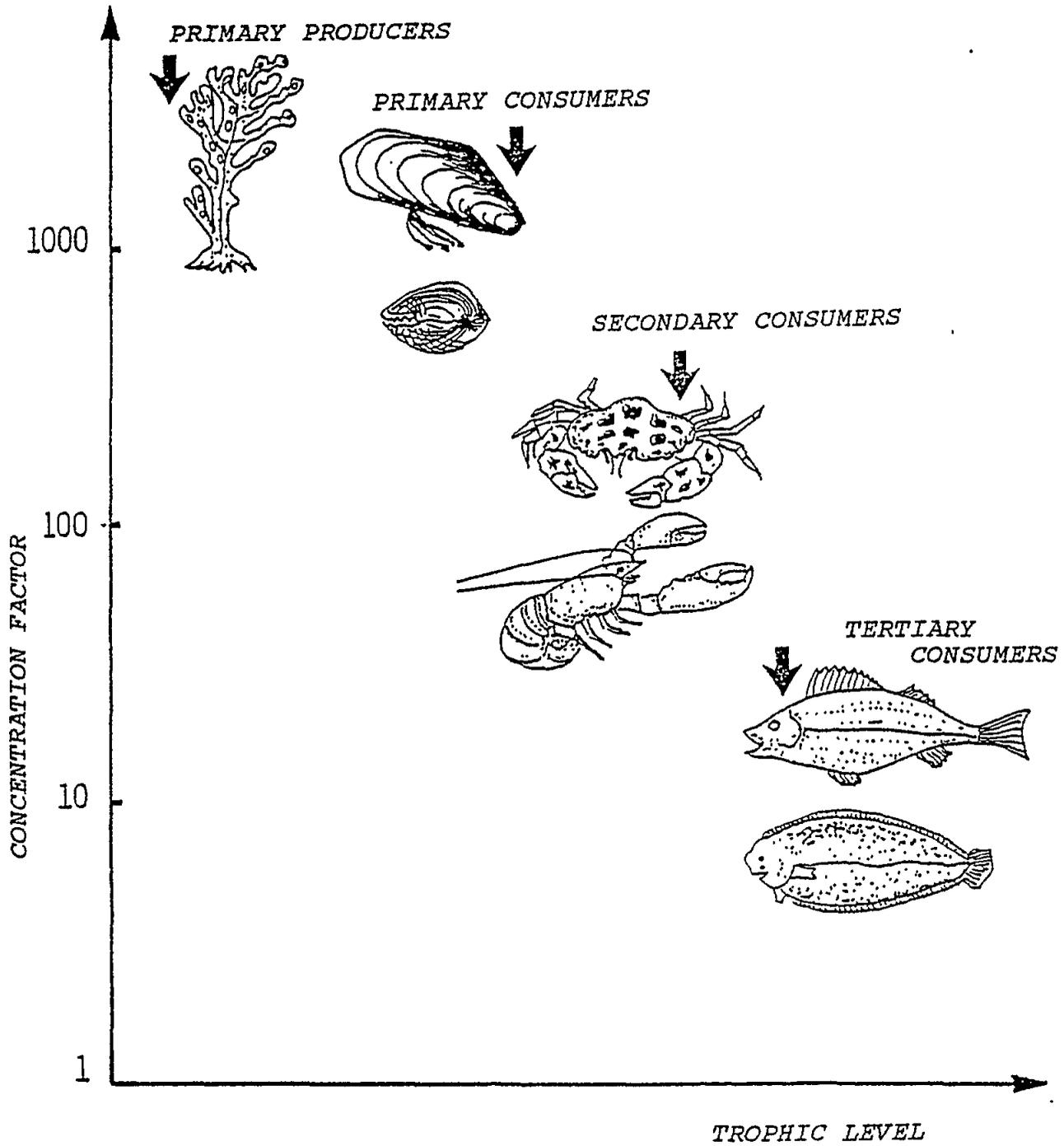


Fig. 6 Concentration factors of plutonium at the different trophic levels

- elements belonging to the same column of the table of element classification, such as lanthanides and actinides behave in the same manner. This is also valuable for other elements such as aluminium and indium for instance. This similar behaviour is due to the electron components of the atoms.
- This preference of contaminants to certain organs provides useful information: the main target organ in an indicator species is the one which has to be investigated first.

ORGANOCHLORINE COMPOUNDS

These substances include a variety of constituents (DDT, aldrin, lindane and other chloro-organic poisons, polychlorinated biphenyls: PCBs) (see Table 4). They are distinguished by:

- the presence of chlorine-containing groups in the molecule
- a high environmental stability
- an extreme toxicity.

The toxic properties of individual compounds in this group are different and a mutual comparison is difficult. Figure 11 presents the different pathways of these compounds within the aquatic ecosystems. It has to be pointed out that chloro-organic substances are more toxic than any other organic pollutants. Toxicity effects on the principal species of marine organisms begin in the concentration range of between 10^{-5} and 10^{-2} mg l⁻¹. The sensitivity increases in the sequence: molluscs, fish, crustacea. Fig. 12 presents an example of an insecticide, dieldrin, and the mechanism of its bioaccumulation within a marine food chain. The concentration of this toxicant is increasing from the low trophic levels (in phytoplankton a few ppb) up to the upper levels (in birds such as cormorant: more than 1 ppm). This progressive concentration within the different steps of the trophic chain is an example of biomagnification.

Concentrations of these toxicants are particularly high in littoral areas where industrial wastes are discharged by factories. Mytilus edulis collected from a harbour in the Baltic was shown to contain 28,000 ppm of PCBs. The concentration factor of PCBs in the mussel Mytilus galloprovincialis collected from the littoral waters of the Marseille area, was shown to reach 690,000.

Table 5 shows results obtained by several authors concerning the different sites of metal storage. From these data, considering the column "comment", it has to be emphasized that tissues have to be investigated also at the structural and ultrastructural levels. In some of our previous investigations (Chassard-Bouchaud et al., 1992) we were able to point out the important role played by special types of cells such as hemocytes macrophages (named in that table as "wandering cells") and by target organelles of bioaccumulation such as lysosomes and spherocrystals (named in the table as "granules").

In conclusion, this paper demonstrates, using a few examples how the processes involved in the uptake, storage and elimination of chemical contaminants are different from one species to another for a given element,

with in addition, variations due to abiotic and biological factors. When the main target organ of bioaccumulation of a given element has been determined in a given species, it can be recommended to investigate and analyse only this target tissue.

Table 4

Principal organohalogen compounds.

<p>ORGANOCHLORINE INSECTICIDES</p> <ul style="list-style-type: none">• DDT (dichloro-diphenyl-trichlorethane) and its metabolites• LINDANE• CHLORINATED CYCLOPENTADIENES - Chlordane<ul style="list-style-type: none">AldrinDieldrinEndrinHeptachlorEndosulfan• TOXAPHENE• DICYCLOBUTADIENES : Mirex<ul style="list-style-type: none">Kepone <p>High toxicity insecticides Widespread contamination of the aquatic environments Considerable persistence Very toxic to the aquatic Arthropods: Crustaceans, zooplankton, copepod larvae</p>
<p>POLYCHLOROBIPHENYLS: PCBs</p> <p>A mixture of chlorinated biphenyl isomers and homologues Use: electric transformers, plastics, paints, etc Widespread contamination of the aquatic environments Very toxic to the aquatic Arthropods: Crustaceans, zooplankton, copepod larvae</p>
<p>DIOXINS</p> <p>Could be present as impurities in the herbicides. They are formed spontaneously during the combustion of organochlorine molecules. They are the most dangerous contaminants in the environment</p>
<p>CHLOROFLUOROCARBONS - FREONS</p> <p>Cryogenic liquid Propulsion gas for aerosols Degrade the ozone layer</p>

Table 5

Different sites for metal storage (in Lockwood, 1976).

Species	Metals	Tissue	Comment	Reference
Fish <u>Makaira ampla</u> (Pacific blue marlin) <u>Sebastes caurinus</u> (rock fish)	Hg Cd	Liver, muscle Liver	Low promotion methylmercury-demethylation? Induced Cd-metallothionein	Rivers <u>et al.</u> (1972) Olafson & Thompson (1974)
Crustaceans <u>Procambarus clarkii</u> (freshwater crayfish) <u>Homarus vulgaris</u> (lobster) <u>Crangon vulgaris</u> (shrimp) <u>Lysmata seticaudata</u> (shrimp)	Cu, Fe Mn Cu Cd	Hepatopancreas exoskeleton Hepatopancreas Exoskeleton	Large granules in Fe and Cu cells Excess Cu stored as granules* 50% total body Cd lost at moult	Ogura (1959) Bryan & Ward (1965) Djangmah (1970) Fowler & Benayoun (1974)
Molluscs <u>Biomphalaria glabrata</u> (freshwater pulmonate) <u>Oncomelania formosana</u> (freshwater prosobranch) <u>Ostrea edulis</u> (oyster) <u>Pecten maximus</u> (scallop) <u>Octopus vulgaris</u> (octopus)	Cu Cu Cu, Zn Zn, Mn, Pb, Ag, Cd, Cu Hg	Leucocytes Connective tissue Leucocytes Kidney Digestive gland Digestive gland	Phagocytosis of excess Cu Crystals of carbonate deposited by wandering cells* Phago- or pinocytosis of excess metals Large (5µm) granules inside cells May occur in granules* Especially in contaminated conditions	Cheng & Sullivan (1974) Winkler & Chi (1967) Boyce & Herdman (1898) Bryan (1973) Bryan (1973) Renzoni <u>et al.</u> (1973)
Polychaete <u>Nereis diversicolor</u> (ragworm)	Cu, Pb	Epidermis	Fine granules in high-metal worms	Bryan (1974)

* cf comment in the text

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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.

"Biomonitoring are organisms which can be used for the recognition and quantitative determination of anthropogenically induced environmental factors" (Bick, 1982). 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 biomonitoring is now a well-accepted terminology.

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

2.1 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.

2.2 Toxicity testing

It is used to obtain basic 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 such as:

- Is the material lethal to the test organism and at what concentration?
- What are the effects on an organism exposed to sublethal concentrations of toxicant for part or all of its life cycle?
- Which organism is most sensitive?
- Under which conditions are contaminants most toxic?
- What are the short-term effects of episodic waste discharges?

Various toxicity tests exist to answer these 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 organisms 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 regulation of effluent discharge.

3. SELECTION OF CONTAMINANTS

Among the many possible chemical species which could be considered, the bioaccumulation of heavy metals has been studied most extensively. The chemical substances mostly investigated are given in Table 1. 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;
- 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.

Table 1

Chemical substances usually measured in marine organisms for monitoring purposes.

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, Heptachlor 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)

total mercury
organic mercury
cadmium
halogenated hydrocarbons

category II (optional)

total arsenic
radionuclides
polynuclear aromatic hydrocarbons

4. SELECTION OF ORGANISMS

How to choose the test organisms?

The choice 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 organism 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 organism 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.

5. LIST OF SUGGESTED ORGANISMS TO BE USED FOR MONITORING CHEMICAL CONTAMINANTS

5.1 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 are recommended:

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.

5.2 Possible organisms for the assessment of contamination in the north Atlantic region

	Cd	Hg	Cu	Cr	Pb	Zn	HH	PHC
Rocky substrate								
<u>Mytilus edulis</u> (common mussel)	+	+	?	+	+	+	+	+
<u>Littorina littorea</u> (gastropod)	+		+	?	+	+		
<u>Patella vulgata</u> (limpet, gastropod)	+		+		+	+		

	Cd	Hg	Cu	Cr	Pb	Zn	HH	PHC
Muddy substrate								
<u>Scrobicularia plana</u> (da Costa) (peppery furrow bivalve)	+	+	?	+	+	+		
<u>Macoma balthica</u> (bivalve)	+	+	?	+	+	+		
<u>Nereis diversicolor</u> (polychaete)	+	+	+	+	+	+		

Key: + = appears to act as good indicator
 ? = doubt about use as indicator
 HH = halogenated hydrocarbons
 PHC = petroleum hydrocarbons

NOTES: The organisms listed for muddy substrates are all deposit feeders, whilst those for rocky substrates are filter feeders or herbivores. It is unlikely that contaminant levels in the tissues of the two groups will reflect contaminant levels in the same part of the marine environment.

From the species listed above, it appears that the choice for a good indicator species is becoming more and more restricted....as only Molluscs (bivalves and gastropods) and Polychaete worms remain.

5.3 Polychaetes as indicator species

Nereis diversicolor has been extensively investigated as it appears that a simple relationship exists between the heavy metal concentration in the sediment and body tissue: Figure 2 presents the results obtained by Bryan (1974).

5.4 Bivalves as indicator species

From the criteria listed in para 4.1 (How to choose the tests organism?), it appears that these characteristics restrict the useful organisms to a range of fairly large, abundant, widespread, intertidal organisms, mainly molluscs. Filter feeding molluscs are more likely to reflect contaminants in the water column whilst deposit feeders will also be influenced by sediment chemistry. Water chemistry will more rapidly respond to effluent discharges and dispersal conditions at the time of sampling.

Filter-feeders such as mussels are therefore more likely to provide the information required to fulfil the objectives of a monitoring programme concerned with water quality. Common mussels: Mytilus edulis and M. galloprovincialis that are used in global "Mussel Watch" programmes are suitable for spatial and trend monitoring programmes in coastal waters. Table 2 presents, as an example, concentrations of metals in Mytilus edulis from different areas.

Table 2

Concentrations of metals in mussels (*M. edulis*) from different areas (in Bayne, 1976).

Locality of sampling	Concentration ($\mu\text{g g}^{-1}$ dry wt)													Tissue	Author
	Fe	Mn	Co	Ni	Cd	Cu	Pb	Zn	Ag	Cr	Al	V	Mo		
South coast, England	290	3.6	0.15	2.1	0.95	2.0	0.4	0.04	0.1	-	76.0	-	-	Shell	Segar <u>et al.</u> (1971)
South coast, England	1700	3.5	1.6	3.7	5.1	9.6	9.1	91.0	0.03	1.5	1230	-	-	Soft parts	B. Brown (personal communication)
South coast, England	-	-	-	-	-	5-26	-	60-81	-	-	-	-	-	Soft parts	
East coast, England	-	-	-	-	-	9.50	-	167-312	-	-	-	5.0	-	Soft parts	
New Zealand	1960	27.0	-	7.0	10	9.0	12	91.0	1.0	16.0	-	-	0.6	Soft parts	Brooks and Rumsby (1965)
California	-	6-28	-	-	3-7	5-11	2-8	204-341	1-1.3	2.8	-	-	-	Soft parts	Graham (1972)
California	-	9.3-45.8	-	-	2.5-5.8	5.8-8.6	9-21.2	6.9-14.2	4.4-6.3	5-7	-	-	-	Shell	Graham (1972)
California	-	5.9- 7.8	-	-	2.0-4.9	9.0-303	2.2-23.4	164-310	1-5.5	1.5-7.8	-	-	-	Soft parts	Graham (1972)
California	-	8.4-14.2	-	-	2.5-9.2	8.1-18.6	9-19.4	8.6-26.5	5.0-7.9	5.7-14.2	-	-	-	Shell	Graham (1972)

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THE ROLE OF CONSISTENCY IN THE DATA COLLECTION PROCESS

by

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1. AN INTRODUCTORY EXAMPLE

The contaminant time series in Figure 1 shows contaminant measurement collected annually over a ten year period. Suppose that the measurements in years 1-5 are from area A and those in years 6-10 from area B. What can we say about the spatial distribution of contaminant levels or about temporal trends in contaminant levels?

The answer is not very much. Contaminant levels in area B between years 6-10 are clearly higher than those in area A between years 1-5. However, we can not infer that contaminant levels in area B are higher than those in area A, because we have never observed contaminant levels in both areas at the same time. Had we sampled both areas throughout the ten year period, we might have observed the contaminant time series in Figure 2 in which contaminant levels in area B are always lower than those in area A. Further, we can not infer that contaminant levels increase over the ten year period, because we have not sampled in the same place throughout the ten years. Had we done so, we might have observed the contaminant time series in Figure 3 in which contaminant levels are decreasing.

The problem with the data in Figure 1 is that they have not been collected consistently - ie different locations have been sampled at different times - so that spatial variation in contaminant levels can not be distinguished from temporal variation in contaminant levels.

This example is clearly contrived, but it does show that if contaminant data are not collected in an appropriate way, it will not be possible to answer important questions about contaminant levels in the environment.

2. CONSISTENCY

Contaminant levels can vary in many ways. For example, in addition to temporal and spatial variation, measured contaminant levels in biota can depend on the time of year, the size of the organism and the way in which the organism is treated and chemically analysed, etc. The design of a contaminant monitoring programme must take account of all these sources of variation. The generally recognised way of doing so is to remove all the sources of variation that they are not interested in, by "keeping as many things fixed" as possible.

For example, in a temporal monitoring programme, data collection should be the same from year to year, so that any observed changes in contaminant levels can be attributed to temporal variation rather than any

- individuals should be taken at the same time each year; if there are several sampling occasions each year, then these should be at the same times each year,
- individuals should be of the same species each year,
- the same number of individuals should be taken each year,
- individuals should be handled in the same way each year.

Sample preparation:

- the same tissue type should be used each year,
- the tissue should be prepared for chemical analysis in the same way each year,
- if individuals are pooled for chemical analysis, the same number of individuals should be put in each pool each year,

Chemical analysis:

- the same contaminant should be measured each year,
- the same number of replicate analyses should be made on each individual (or pool) each year,
- the same method of analysis should be used each year, backed up by an on-going analytical quality control programme.

Some of these things are a bit vague. What is meant by the 'same statistical population' and how is the 'same area' defined? These things should be specified at the start of the monitoring programme and should form part of the sampling protocol. Of course, once specified, the sampling protocol should be adhered to.

4. WHAT HAPPENS IF SAMPLING IS INCONSISTENT?

Inconsistent sampling has two main effects:

- it adds noise to the data, making it harder to identify meaningful trends in the data,
- it can lead to spurious trends in the data, which do not truly reflect changes in environmental contaminant levels.

For example, suppose that contaminant levels vary seasonally and that there is a slight downwards trend in contaminant levels over time, as shown in Figure 4. Figures 5, 6, 7 and 8 show what happens if we sample as follows:

- a) Fig. 5: Sampling at the same time (ie July 1) each year,
- b) Fig. 6: Sampling at random in the same month (ie mid June - mid July) each year,

collected at different places, at different times of year, were pooled in different ways, some contaminants were never measured in the same species more than once, etc. The contaminant data can not be used to make inferences about temporal trends in contaminant levels, because the temporal variation can not be distinguished from all the other sources of variation.

6. CONCLUSIONS

Sampling must be consistent if a monitoring programme is to be of any use, since only then can a monitoring programme address important questions about environmental contaminant levels.

Inconsistent sampling must be avoided because it reduces the effectiveness of a monitoring programme, wastes time and resources, and most seriously of all, can give misleading information about trends in environmental contaminant levels.

7. REFERENCE

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HOW MANY SAMPLES ARE NECESSARY TO DETECT IMPORTANT TRENDS?

by

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1. INTRODUCTION

How many samples are necessary to detect important trends? Unfortunately, there is no simple answer. It depends on three main things:

- The type of trend. For example, a temporal monitoring programme will generally require different numbers of samples to detect, eg.
 - a steady increase in contaminant levels,
 - a sudden transient increase in contaminant levels,
 - contaminant levels which exceed some safety threshold.
- The magnitude of the trend. For example, all other things being equal, a monitoring programme designed to detect an increase in contaminant levels of 5% per year over 5 years will require more samples than one designed to detect an increase of 20% per year over 5 years.
- The variability in the data. The more variable the data, the more samples are needed to detect a particular trend.

To choose an appropriate number of samples, we need to consider the statistical power of the monitoring programme. Power studies examine the types and magnitudes of changes that are likely to be detected by the programme. Clearly, power studies depend on the programme's objectives. Here, we shall demonstrate a power study to look at linear trends in contaminant levels over time; full details are given in Fryer and Nicholson (1993). Fryer and Nicholson (1993) also look at the power of a temporal monitoring programme to detect a sudden transient increase in contaminant levels. Nicholson and Fryer (1992) investigate the power of a temporal monitoring programme to detect any between-year variation in contaminant levels. An excellent account of statistical power is given by Cohen (1977).

2. A TEMPORAL MODEL OF CONTAMINANT LEVELS

Consider a contaminant monitoring programme in which R samples are taken at the same time in each of T successive years. Let y_{tr} be the log-concentration of the r th sample in year t and let

$$y_{tr} = \mu_t + \dot{u}_t + \hat{a}_{tr},$$

where

- μ_t is the mean log-concentration in year t ,

- \hat{u}_t is an error term representing random between-year variation in contaminant levels,
- \hat{a}_r is an error term representing random within-year variation in contaminant levels.

Assume that the errors \hat{a}_r are independent normal random variables with zero mean and constant variance σ^2 and that the errors \hat{u}_t are independent normal random variables with zero mean and constant variance σ^2 . Further, assume that the \hat{a}_r are independent of the \hat{u}_t .

Note that:

- Log-concentrations are used, because they are often found to be approximately normally distributed with homogenous within-year variances (eg Anon., 1989). In some situations, alternative transformations might be more appropriate.
- The random within-year variation σ^2 is the 'natural' variation in contaminant levels found in any population.
- The random between-year variation σ^2 represents between-year variation in contaminant levels in which there is no systematic pattern. This could arise through eg random climatic changes, random fluctuations in discharge, variations in the bias of analytical methods. Investigations of the International Council for the Exploration of the Seas (ICES) Cooperative Monitoring programme (CMP) data on heavy metals in fish muscle revealed considerable random between-year variation (Fryer and Nicholson, 1990).

Test for a linear trend

Let

$$\bar{Y}_t = \frac{1}{R} \sum_{r=1}^R Y_{tr}, \quad t = 1 \dots T,$$

be the yearly sample mean log-concentrations.

Evidence of a linear trend is assessed by regressing \bar{y}_t on t , ie by fitting the models

$$E[\bar{Y}_t] = \mu_1,$$

$$E[\bar{Y}_t] = \mu_1 + b(t-1)$$

giving residual sums of squares S_1, S_2 respectively, and then comparing the statistic

$$(T+2) \frac{S_1 + S_2}{S_2}$$

to an F-distribution on 1 and T-2 degrees of freedom (Draper and Smith, 1981).

Power

A linear change in log-concentration can be represented by

$$\mu_t = \mu_1 + (t-1) \log \left(1 + \frac{q}{100} \right)$$

where q measures the size of the trend; eg $q = 5$ corresponds to a 5% increase in concentration per year.

The power of the test for linear trend is the probability that a given trend results in a statistically significant test. Power depends on the degrees of freedom $\hat{i} = T - 2$,

and the magnitude of

$$\hat{a} = \log \left(1 + \frac{q}{100} \right)^2 \left(\frac{(T+1)T(T-1)}{12(t-2)\sigma^2/R} \right) \quad (1)$$

Strictly, power also depends on the significance level $\hat{\alpha}$, but only tests at the 5% significance level will be considered here. For a given value of \hat{i} , power increases as \hat{a} increases; ie a linear change is more likely to be detected. Thus, the power is positively related to the magnitude of the trend and the number of samples per year R and inversely related to both the within-year and between-year variances $\hat{\sigma}^2$ and $\hat{\sigma}^2$. In fact, power is also positively related to the number of years T , but this relationship is quite complicated because T affects both \hat{i} and \hat{a} .

Figure 1 shows power curves (ie the relationship between power and \hat{a}) for a range of values of \hat{i} . For example, if $q=5\%$, $T=10$, $R=10$, $\hat{\sigma}^2=0.1$, then $\hat{i}=8$, $\hat{a}=1.79$ and the probability of detecting the trend is 0.22. Table 1 shows the effect of T and R on power for different combinations of $\hat{\sigma}^2$ and $\hat{\sigma}^2$ when $q=10\%$.

3. HOW DO WE USE THE POWER CURVES?

Suppose that the objective of the monitoring programme is to detect trends of 10% per year or more over a 10 year period. How many samples per year do we need to take?

Table 1

The power to detect a linear trend of $q=10\%$ for different values of T , R and $\hat{\sigma}$. Throughout, $\hat{\sigma}^2=0.1$.

$\hat{\sigma}$	T	$R=1$	$R=5$	$R=10$	$R=25$
0	5	0.11	0.53	0.84	0.98
	10	0.67	1.00	1.00	1.00
	20	1.00	1.00	1.00	1.00
0.025	5	0.09	0.17	0.21	0.24
	10	0.56	0.94	0.98	0.99
	20	1.00	1.00	1.00	1.00
0.1	5	0.08	0.10	0.10	0.10
	10	0.40	0.59	0.63	0.65
	20	1.00	1.00	1.00	1.00
0.4	5	0.06	0.06	0.06	0.06
	10	0.19	0.22	0.22	0.22
	20	0.91	0.95	0.95	0.95

Suppose that the monitoring programme must detect, with probability greater than 0.9, trends in mercury in cod of 10% per year over 10 years. Estimates of $\hat{\sigma}^2$ and $\hat{\sigma}$ for zinc in cod are 0.102 and 0.044 respectively. Since $T=10$, we look at the power curve for $\hat{\sigma}=8$ (Figure 1) to find that, for a power greater than 0.9, $\hat{\sigma}$ must be greater than 13.8. Using equation (1) this means that R must be at least 10; ie we need to take 10 samples per year.

Now let's repeat the exercise for nickel, for which $\hat{\sigma}^2$ and $\hat{\sigma}$ are estimated to be 0.068 and 0.11 respectively. Again, $\hat{\sigma}$ must be greater than 13.8 to detect trends in nickel in cod of 10% per year over 10 years with probability greater than 0.9. Unfortunately, no value of R will do this (try it!); there is too much variation in the data to detect these types of trends. So what do we do? One option would be to redefine the objectives of the monitoring programme to detect, say, trends in nickel in cod of 20% per year over 10 years. However, if trends of 10% per year over 10 years are important, it would be necessary to consider an alternative design of monitoring programme or an alternative tissue type / species / compartment which exhibits less random variation in nickel levels (for a fuller discussion, see Fryer and Nicholson, 1993).

4. OTHER CONSIDERATIONS

Although a power study is one way of ascertaining an appropriate sampling level, other considerations must also be taken into account. In particular, it is generally advisable to take replicate samples (N.B. replicate samples, not replicate chemical analyses of the same sample) to guard against eg outside contamination of a sample.

It is important to note that a monitoring programme will usually have several objectives, each requiring a power study. In practice, the number of samples chosen will be some balance of the numbers indicated by the individual power studies.

5. EXPERIENCE WITH THE MED POL DATA OF HEAVY METALS AND HALOGENATED HYDROCARBONS IN BIOTA

In general, the power of the MED POL data of heavy metals and halogenated hydrocarbons in biota for detecting temporal trends was very poor. This was because contaminant time series were not collected over enough years or too few samples were collected each year, or both. For example, even if contaminant levels had increased by 30% per year, most of the MED POL contaminant time series would have been unlikely to have detected these trends.

6. CONCLUSIONS

- A monitoring programme should have specific objectives.
- Given estimates of the variability of contaminant data, power studies should be used to help decide the number of samples required to meet the programme's objectives.
- Different programmes will have different objectives and require different power studies.
- Sometimes, it will not be feasible (either financially, practically or statistically) to meet a programme's objectives. This information should be used to either change the programme, redefine the objectives of the programme or cancel the programme.

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COMPUTERIZATION OF MARINE POLLUTION DATA

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1. INTRODUCTION

This paper focuses on the technical concepts regarding monitoring and the characteristics of marine pollution data, each component relevant to the computerization, integration of the concepts and components involved, and finally, the formats for the transfer/exchange of data.

Experience gained through the handling of the Mediterranean pollution data as is received by MEDU from the coastal states shows that there is still more to be done in the region in order to have good, usable data archives. Some very common problems regarding data submission are emphasized herebelow.

Two manuals have been published and should be referred to in conjunction with this paper. These are:

- Computerization of MED POL Data, Volume 1, "CODES", and
- Computerization of MED POL Data, Volume 2, "DATA TRANSFER FORMATS, DTF".

The Introduction to the second document as well as the data formats for chemical contaminants in biota are reproduced in Annex. The hardware used is a PC-386 and the software is PC-ORACLE running under MSDOS 5.0.

2. MONITORING - WHAT IS IT, TECHNICALLY?

Monitoring of marine pollution starts with its design. The country, or the wide area, is subdivided into distinctive **areas**. Each area consists of specific **stations** of different **types**, **geographical co-ordinates** and other characteristics. **Samples** are to be collected from these stations from various **matrices** at certain **frequencies** (perhaps during specific **periods** only) by the designated **persons/institutes**. Each sample is then to be analyzed for the **pollution parameters**. The MED POL pollution monitoring programme is designed and carried out **yearly** by each Mediterranean country.

Does it work as smoothly as explained above? Obviously not. There are many instances which cause change to these elements. During a given year of actual work, stations, matrices, periods, frequencies, parameters, the people and institutes involved, and many other factors do not remain as they were specified in the design. How do we handle this computerization task?

Long term monitoring (carried out over a number of years) is yet another issue. Such monitoring is constantly reviewed, due to some changes in factors involved. These reviews may take place at the end of each monitoring year, or after some evaluation/assessment work. Obviously, some things -if not many- are altered and in some cases the whole programme may be reoriented. This is yet another challenge for the computer people.

3. THE WAY OUT

Suggested action is found in the following list of "initial pre-requisites":

- Talk to people involved -there will be many- ; be prepared to listen, ask questions, and then listen and listen again;
- Identify key **concepts** as clearly as possible;
- Establish **links** among the concepts;
- Make sure that main **components** are clearly distinguished;
- Find out the **relation** between the components;
- Keep the design **simple**, as simple as you can;
- Do not forget necessary provisions for the addition of modules later on;
- Go through this list more than once.

Finally, choose an approach. Realize and accept the fact that your solution may not be the perfect one. However, does it work? Does it meet the demands? Are the duplications and/or gaps minimal? Can you easily enter, manipulate, and get the information out? **Are you able to create a manageable, accurate, and reliable information database?** If the answer is "yes" or even "yes, but", then you are on the right track.

4. THE CONCEPTS

In MED POL data processing, the **design of pollution monitoring programmes and data submission** are closely linked but not identical concepts.

In the former case, we are mainly interested in specifying what we are going to do, where, how, when, how often, by whom,...etc., whereas in the latter, we mostly concentrate on the pollution data sampled and analyzed.

What are the main **linking factors**? They are areas, stations, and persons/institutes involved. An area may be in the programme design, and also in the data submitted, whereas an institute included in the programme design may not be active or may even have been replaced by another in the actual work. Similarly, a station in the design with a given geographical co-ordinate may not be sampled at all, or, its co-ordinates at each sampling may vary(!). In MED POL, problems such as in the first case are handled through the use of a specific flag. Regarding the second case, an approach of keeping geographical co-ordinates of each sample is used.

As explained above, the main element of the design of pollution monitoring programmes is the computerization of planned sampling. Yearly data submission, however, is built on the following foundations:

- **Matrix** or matrices are specified;
- **Areas/stations** are specified;
- Unique **samples** are taken from the specified matrices and stations on certain days/times; and finally
- Each sample is analyzed for one or more **pollution parameters**.

5. COMPONENTS

Each computerization project consists of many factors. We often ask many questions to be able to avoid possible future problems:

How much detail should be included? Which information is mandatory and which is not? What is the tolerable simplification level? Usability? Expected outputs? Can it be distributed? Modularity? Can it be expanded without too much complication? Expected input problems? What will be the operational data flow mechanism? How large is the backlog on data to be entered?... and many more. All these factors will be followed by scientists, managers and administrators who will ask for more and not give way with any demands. Marine pollution data is complicated, involves many people and requires doing quite a bit of homework before attempting a start (see also page 174 in Annex).

Three main components make up the MED POL marine pollution database application: codes, support information, and the actual pollution-specific information.

Codes should be kept as simple as possible and the main criterion in their development process is "usability, applicability". On the one hand, they should be able to handle the information to be computerized and be open-ended; on the other hand they should not become a collection of "huge lists". Developing MED POL codes at MEDU, we did make use of various existing coding schemes, simplifying and reducing large lists to fewer entries applicable to the Mediterranean region. (See "CODES" manual for the thirteen code lists currently under use in MED POL.)

Support information consists of countries, cities, and institutes and grows steadily ("semi-dynamic data"). These inventories do not have yearly characteristics as is the case for the design of monitoring or data submission. They help assure the accuracy of the actual pollution-specific data via cross-checks during data entry and also help to avoid duplication in the main data files.

In MED POL, actual **pollution-specific information** is divided into two subsystems:

- Monitoring agreements; and
- Data submission.

The structure of the overall system is shown on page 176 of the Annex. The technical design of the monitoring agreements is explained on pages 175, 177 and 178 (in Annex).

The design structure of the data submission subsystem is tightly locked on the station type and matrix inter-relation. A coastal station may provide samples from biota, sea water, sediment, suspended matter, or plankton, but not from air, precipitation, or effluent. Similarly, MED POL does not deal with every pollution parameter in every matrix. For example, the seashore matrix deals only with pollution parameter groups of litter, tar balls, and possibly micro-organisms, but nothing else.

Finally, what is the breakdown of this subsystem as used in MED POL? It is built upon the **pollution parameter group-matrix** relationship. For example, heavy metals in biota is one mini system, heavy metals in sea water is another. Each mini system consists of three entities: Stations (heavily controlled), samples (for each station), and data analysis (for each sample). For more detailed information, please see Annex pp. 177-182.

6. THE MAIN CHARACTERISTICS OF MARINE POLLUTION DATA

What is the core of marine pollution data? Few characteristics from the station, sample, and data analysis make up the nucleus for its completeness and accuracy. In one way or another, the data must be associated with the:

- Matrix;
- Geographical location, i.e. co-ordinates;
- Sampling and sometimes also analysis date (plus sampling time in some cases);
- Pollution parameter;
- Concentration; and
- Other mandatory supplementary information for station, sample, and data analysis which is variable from one matrix to another.

It is obvious that, without this information, the utilization of the data suffers tremendously. For more detailed information, please see two of the data transfer format tables given in Annex.

What about the information which cannot be classified easily, or is irregular? In fact, this caused some trouble in the computerization of MED POL data. The solution was found in the use of "commentary" flags, flagging each bit of information wherever necessary, and then entering the associated commentary information in separate "comment" files. It works!

7. THE DATA FLOW MECHANISM

Another major difficulty is the actual flow of marine pollution data, from sampling and analysis to evaluation and assessment. This involves people, many people. It requires good organizational skills. In MED POL, raw data goes through the following cycle:

- It is received (on paper or magnetic media such as diskettes);
- It is checked by the scientist(s), as well as by the data processing people;
- If no comments arise, it is entered into the database (after necessary refining, if applicable); if there are any comments, the

originating country/institute is contacted on the problematic data;

- It is printed and verified by data processing;
- It is verified by the scientist(s);
- It is sent to the originating country for further checking and verification (together with a map of sampling locations);
- Country confirmation, verification, and changes are received;
- The changes are carried out on the computerized data;
- The data is evaluated, either at MEDU, or through a consultant;
- The assessment documents are prepared.

8. FINAL WORD

This experience has shown that the current real necessity is **reliable and accurate data**. Mediterranean pollution data collected over a period of fifteen years, unfortunately, do have gaps and inaccuracies, as well as incomplete information. The initiative to transfer the data on magnetic media has been started mainly to avoid these problems. We feel it is of great importance for the originator to "really look" at his/her data, besides speeding up the data flow mechanism.

Finally, an inventory is as good as its basic contents - not in terms of the software being utilized. If this is assured, then one can utilize a word processing or a spreadsheet package, or even an editor to store the data.

ANNEX

INTRODUCTION

NECESSITY FOR DATA TRANSFER FORMAT USAGE

A data processing application such as the computerization of marine pollution data involves various components and their multi-level interactions. A high degree of consideration needs to be given to the analysis of data variety, contents, and size; analysis of data flow and handling; the human factor: staffing; product types for scientists and decision makers; the detail level of application, its use and distribution; and the selection of hardware and software. Frequently, each component is revised, established mechanisms reviewed, and/or new ones created.

Looking closely, it is easy to realize the complexity and size of the overall picture. Not only is the number of people involved large, but the data types and sizes are different. For example, marine pollution data groups such as heavy metals, micro-organisms, etc., show different characteristics, not to mention the variations for different matrices such as water, sediment, biota, etc.

The current PC technology does provide an easy solution for a "start-up". However, it may also create many time-consuming duplications leading to inaccuracies and a slowing down of the real work. Presently, Mediterranean countries (with the exception of three) still submit the data reports in paper form (and some, recently, as computer printouts), resulting in hundreds of pages for any given year.

The usability of this database depends on the accuracy of the monitoring programme, adherence to it, and the dynamic strategy building. On the other hand, reliability of its contents depends on the accuracy of the number of steps regularly carried out: sampling and parameter analysis; data entry and verification schemes; data refining techniques; statistical and scientific analysis; and data presentation. The whole process should involve speedy, accurate, critical yet positive interaction from people such as scientists, technicians, decision-makers, data entry operators, field staff, data analysts, computer professionals, and consultants.

Data flow, from the originator to its eventual entry into the computer, its analysis and presentation, and feedback to the data originator, draws a big circle. The cycle repeats itself annually, resulting in a constant increase in the size of data inventories. The accumulated data is then put into national or regional evaluation studies leading finally to the assessment of the state of pollution.

MED POL marine pollution inventories date back to 1974-75 with the Phase I data. Since the 1980s, the data processing activities and the potential within the Co-ordinating Unit has developed gradually. Naturally, an acceleration in the rate of marine pollution data transfer to the Unit was inevitable. Assessment of the state of pollution in the Mediterranean required more frequent sampling, more spatial coverage, additional pollution parameter groups and new matrices.

The Unit received its first magnetic data in 1986, on a PC diskette. This gave an impetus to the data processing section. After the initial tedious data and format conversions, today there are regular country contacts, exchanges of information and working relationships on the subject. As more countries are submitting data, more institutes and laboratories are joining the monitoring programme, expanding the transfer of data. This in turn has led to this document's creation.

Initial work on "Marine Pollution Data Transfer Formats" began in 1991. Its development has taken some time and involved the efforts of many people from different countries. It is intended to be a starting point for regional data exchange using magnetic media.

A BRIEF LOOK AT THE MED POL DATABASE

The computerization of MED POL data has passed through different stages over the last decade. Similarly, equipment usage has also changed from a mainframe approach to PCs:

- 1980 to 1983 Use of International Computing Centre (ICC)/Geneva, FAO Computer Centre/Rome mainframe facilities;
- 1983 to 1986 MAP VS/80 minicomputer facilities;
- 1986 to 1989 PC/AT and dBase III; and
- 1989 to present PC/386 and ORACLE.

The present system is based on the PC-ORACLE database development package. Other packages could be used or even developed provided certain data characteristics can be handled efficiently. Two such examples are a) scientific number handling (e.g. 1.996545E12) due to the large variation of concentration values of different parameters (e.g. the micro-organism count in effluent versus heavy metal in air), and b) "no data" handling (should not be taken as zero for numeric data).

Figure 1 represents the block diagram of the MED POL database, together with the menus, submenus, and forms. In the figure, each box represents a menu. Selections leading to a submenu appear in upper case, forms in lower case. ("Comment" menus are not included.)

This application was intended to be open-ended: It is continuously being reviewed and new subsystems added. Data inventories are:

- a. Codes, background information (matrices, station types, pollution parameters, species, tissues, etc.) (See Volume I, "CODES", for a full list);
- b. Supportive information (cities, institutes, intercalibration exercises, etc.);

- c. Monitoring areas and stations with related specific parameters; institutes/persons participating in the programme, entered on a yearly basis;
- d. Expected yearly monitoring agreement programmes (sampling agreements);
- e. Annual actual data reports (data samples and analysis results); and
- f. Unspecified and/or irregular information, remarks on data (Comments).

The foundations of the overall system are based on the codes (a). Codes employed in MED POL are a compromise between the existing huge lists and practicality, their applicability in the Mediterranean region. Ideally, codes need to be established only once with new additions only after some serious discussion ("relatively static data").

Supportive information (b) data inventory would grow steadily, as updating becomes necessary ("semi-dynamic data").

The monitoring areas and stations as well as the participating institutes and persons (c) would be specified in accordance with the monitoring programme design. Due to possible -sometimes frequent - yearly changes in the programme, this data is entered every year. The areas and stations, institutes and persons are firstly marked with a flag as "TO BE MONITORED/AGREED TO MONITOR", respectively.

Sampling agreements (d) constitute:

"Which pollution parameter (or group of parameters) will be measured? Where? In which matrix or matrices? How? At which frequency? By whom?" Again, this information is entered yearly.

Actual pollution data report (e) consists of:

- Location data (area/station information);
- Sample data (sampling date, depth,...etc.); and
- Pollution parameter analysis data (no. of analysis, concentration, standard deviation,...etc.).

This approach of breaking down a pollution data record into STATION, SAMPLE, and DATA ANALYSIS was employed throughout the design and implementation process (with the exception of airborne pollution).

As the data arrives, area/station and institute/person information is checked against the monitoring programme agreement. Subsequently, this is followed by an update of the already stored information as follows:

- Agreed to be monitored, and WAS MONITORED (AREAS/STATIONS);
- Agreed to monitor, and MONITORED (INSTITUTES/PERSONS);
- Not agreed to be monitored, but WAS MONITORED (AREAS/STATIONS);
- Not agreed to monitor, but MONITORED (INSTITUTES/PERSONS).

Marine pollution data sample and parameter analysis characteristics differ from one matrix to another. For example, there are different structures of halogenated hydrocarbon data in biota and in water). This is handled with a matrixwise data organization approach that has been adopted into the MED POL database.

Additionally, different parameter groups for one unique matrix appear with different structures (for example, different structures for micro-organisms compared to the heavy metal data in sea water). These require a choice between the VERTICAL and HORIZONTAL structures. A compromise between the two leads to "X POLLUTION PARAMETER GROUP IN Y MATRIX" approach (e.g. petroleum hydrocarbons in sediment).

Lastly, each set of data may contain some useful information which may not be easily classified, or may be irregular (f). Therefore, each data record in the MED POL database contains a "tag or flag", where one can insert a 1-character code (e.g. an asterix) and then insert the remark(s) or comment(s) on a separate but correlated file. Comment items exist for each database component, and can be accessed either through the associated box, or directly from the "COMMENTS" box.

Structural Design

The following approach was used in the MED POL database design philosophy:

- COUNTRIES consists of pollution monitoring AREAS;
- AREAS comprise of STATIONS;
- Different MATRICES in the stations may be sampled;
- Matrices provide SAMPLES; and
- PARAMETER ANALYSIS are carried out on the SAMPLES.

The overall structure of the yearly data is based on this AREA, STATION, MATRIX, SAMPLE, and PARAMETER ANALYSIS binding.

Each area is identified by a key (from the following combined information):

- 2-digit numeric YEAR (monitoring year, XX for 19XX);
- 3-character COUNTRY code (see Appendix I); and
- 6-character AREA code.

Each station is identified by a code consisting of area identification plus an additional 6-character STATION code.

Areas are common to all data report subsystems. However, stations are accessed only through a screening process based on the station type code. For example, a coastal station can report heavy metal data in sediment, or micro-organism data in sea water, but not effluent data.

As explained previously, MED POL application subsystems are identified as 'X POLLUTION PARAMETER GROUP IN Y MATRIX'. This specifies the subsystem file creation principle which is based on the GROUP/MATRIX separation. For example, nutrient and micro-organism data in sea water are two different subsystems. They make use of the same area and station inventories, but both have different sample and parameter analysis files.

Sample identification needs an extra 4-digit numeric code in addition to the station identification. Generally, this numeric code is generated internally as the number of samples increase for a given station during the year.

Finally, parameter analysis identification consists of sample identification plus a 5-character pollution parameter code. The following examples illustrate the key usage:

Area key	:	"88SPABAR-10" (Year:88, Country code:SPA, and Area code:BAR110);
Station key	:	"90GRENORTH@STA1" (Year:90, Country code:GRE, Area code:NORTH, Station code:STA1)
Sample key	:	"91MATVAL@@@CC12@@8" (Year:91, Country code:MAT, Area code:VAL, station code:CC12, Sample no:8); and
Parameter analysis key	:	"85ITAEMI@@@1 @@@@2CD" (Year:85, Country code:ITA, Area code:EMI, station code:1, Sample no:2, Parameter code:CD).

ON DATA TRANSFER STEPS

Prerequisites for a proper data transfer are: a) observing the MED POL codes, and b) complying with the key structures and sizes for the area, station, sample, and parameter analysis information.

Preferably, the yearly data transfer would follow or be similar to the structure it is based upon:

- Four separate files which are common to all pollution data. These are the areas, stations, institutes, and persons files;
- Separate sample/parameter analysis file pairs for each pollution parameter group for each given matrix.

For example, if petroleum hydrocarbon (PHC) and micro-organism (MC) data in water (SW), and heavy metal (HM) in biota (BI) data are to be submitted, then ten files are needed (1. Areas, 2. Stations, 3. Institutes, 4. Persons, 5. PHC in SW sample, 6. PHC in SW parameter analysis, 7. MC in SW sample, 8. MC in SW parameter analysis, 9. HM in BI sample, and 10. HM in BI parameter analysis). All these files would be interlinked with the proper use of keys. (Please note that, as indicated previously, the airborne pollution data subsystem does not involve sample and parameter analysis files, but only an observation file.)

Unfortunately, the information transfer in the manner described above may not be possible for many data originators, largely due to their data recording, organization, or processing methods. Also, improper use of keys -if done- would create further confusion at the receiving end.

An alternative and more simpler philosophy has been adopted. This consists of "one flat file per subsystem", where area, station, sample, and parameter analysis information are included in one batch. Pollution data would be sorted in the same order (on area, station, sample and parameter codes). One should still pay attention to avoid discrepancies in the area or station information from one file to other when the codes are in fact identical. (However, due to the limited information required from the area or station data, this would not cause big problems.)

ASCII text files on a diskette are suggested. Field separation would be either columnar (strict observation of field sizes), or free format where fields are delimited with a delimiter such as a comma. If free format option is selected, then all alphanumeric fields should be enclosed in single or double quotes.

Any date format can be used, some examples are:

- DD/MM/YY (e.g. 24/01/92);
- MM/DD/YY (e.g. 01/24/92);
- YY/MM/DD (e.g. 92/01/24);
- YY/DDD (e.g. 92024); and
- DD-MMM-YY (e.g. 24-JAN-92).

The slash delimiter may be replaced with another delimiter such as period, dash, or even no delimiter option can be employed.

EXPLANATIONS ON THE FORMAT TABLES

Each format table describes the structure of a single data record of a marine pollution subsystem. With the exception of the AIR table, all are divided into three information segments:

- Area and Station;
- Sampling; and
- Parameter Analysis.

One might notice that the locational information is being associated with the sampling and not the station. This is due to experience gained over the years which has shown that sampling carried out at one station can move from one point to another during the year (the exceptions being air and precipitation stations).

These segments are later used to append the various data components - such as area, station, sample, and parameter analysis - into the respective files in the MED POL database.

Table structure is as follows:

Seq No.	Indicates field sequence number.
Column Name	Short name of the field.
Requisite?	Specifies whether the presence of data in the field is essential. If data is not provided for such a field in a record, all the record is to be discarded, because these fields constitute the minimum required information. Their absence would either result in difficulty to construct the necessary computer key(s), make the data meaningless, or the location unknown (missing co-ordinates).
Description	Detailed description of the field, including explanation of the codes -if coding is employed-, format and unit -for numeric fields-, and reference to other sources. For numeric format samples, each "9" indicates a numeric digit.
Column Type/Length	Type of the field and its length. Three types are employed: Character/alphanumeric (CHAR), numeric (NUM), and date (DATE). Number in parenthesis indicates the size. For decimal numeric fields, the first number indicates total number of digits - including the "." decimal separator -, and the second indicates the number of decimal digits. Attention should also be paid to the 10-character fields which are specified as "scientific data format" in the 'Description' column. Regarding the date-format fields, flexibility is given to the data originator; any date format (see previous paragraph) can be employed.

Data grouping should follow the order of "area-station-sample-parameter analysis" for a given year. In other words, the grouping would be all stations in one area, all samples in one station, and all parameter analyses in one sample, as the following:

Area1, Station1, Sample1, Parameter Analysis1
Area1, Station1, Sample1, Parameter Analysis2
Area1, Station1, Sample1, Parameter Analysis3
Area1, Station1, Sample2, Parameter Analysis1
Area1, Station1, Sample2, Parameter Analysis2
.
Area1, Station2, Sample1, Parameter Analysis1
Area1, Station2, Sample1, Parameter Analysis2
Area1, Station2, Sample2, Parameter Analysis1
Area1, Station2, Sample2, Parameter Analysis2
Area1, Station2, Sample2, Parameter Analysis3
Area1, Station2, Sample3, Parameter Analysis1
.

Area2, Station1, Sample1, Parameter Analysis1
Area2, Station1, Sample1, Parameter Analysis2
Area2, Station1, Sample2, Parameter Analysis1
Area2, Station1, Sample2, Parameter Analysis2
Area2, Station2, Sample1, Parameter Analysis1

Required institutional information, (see "SAMPLING INST CODE", and "ANALYZING INST CODE"), associated with the data, is explained in the Supplementary Data section.

HALOGENATED HYDROCARBONS IN BIOTA (excluding Plankton)

Filename: HHBI.ASC

Seq. No.	Column Name	Mandatory?	Description	Column Type/Length
Area & Station Information				
1	YEAR	YES	Monitoring year (Format is XX for 19XX)	NUM (2)
2	COUNTRY	YES	Monitoring country code (See country list, Appendix I)	CHAR (3)
3	AREA CODE	YES	Monitoring area code	CHAR (6)
4	AREA DESCRIPTION	-	Monitoring area description	CHAR (30)
5	STATION CODE	YES	Monitoring station code	CHAR (6)
6	STATION DESCRIPTION	-	Monitoring station description	CHAR (30)
7	STATION TYPE	YES	Station type (See Volume 1, CODES)	CHAR (1)
8	BOTTOM DEPTH	-	Bottom depth in meters (Format is 99999.9)	NUM (6,1)
Sampling Information				
9	SAMPLING DATE	YES	Date of sampling (Format is dd-mmm-yy or dd/mm/yy or mm/dd/yy)	DATE
10	LATITUDE DEGREE	YES	Latitude degree (sampling coordinate - applies to Seq. Nos. 10 - 17)	NUM (2)
11	LATITUDE MINUTE	YES	Latitude minute	NUM (2)
12	LATITUDE SECOND	YES	Latitude second	NUM (2)
13	LATITUDE POSITION	YES	Latitude position (Code N = North, S = South)	CHAR (1)
14	LONGITUDE DEGREE	YES	Longitude degree	NUM (3)
15	LONGITUDE MINUTE	YES	Longitude minute	NUM (2)
16	LONGITUDE SECOND	YES	Longitude second	NUM (2)
17	LONGITUDE POSITION	YES	Longitude position (Code W = West, E = East)	CHAR (1)
18	SAMPLING DEPTH	-	Sampling depth in meters (Format is 99999.9)	NUM (6,1)
19	SPECIES	YES	Species code (See Volume I, CODES)	CHAR (3)
20	NS	YES	Number of specimens, if the sample is composite	NUM (3)

Seq. No.	Column Name	Mandatory?	Description	Column Type/Length
21	AVERAGE LENGTH	-	Average length in centimeters (Format is 9999.99)	NUM (6,2)
22	LENGTH STD	-	Length standard deviation in centimeters for composite sample (Format is 999.99)	NUM (5,2)
23	AVERAGE WEIGHT	-	Average weight in grams (Format is 999999.9)	NUM (7,1)
24	WEIGHT STD	-	Weight standard deviation in grams for composite sample (Format is 99999.9)	NUM (6,1)
25	SEX	-	Sex code (Code F=Female, M=Male, I=Indeterminate only)	CHAR (1)
26	AGE	-	Age in years (Format is 99.9)	NUM (3,1)
27	TISSUE	YES	Tissue code (See Volume I, CODES)	CHAR (2)
28	EOM	-	Percent of extractable organic matter (Format is 99.99)	NUM (4,2)
29	DW/FW	YES	Ratio of dry weight to fresh weight in percentage (Format is 99.99)	NUM (4,2)
30	SAMPLING INST CODE	YES	Sampling institute code (See Supplementary Data section for clarification)	NUM (2)
Parameter Analysis Information				
31	PARAMETER	YES	Halogenated Hydrocarbon code (See Volume 1, CODES)	CHAR (5)
32	NA	-	Number of parameter analysis	NUM (2)
33	CONCENTRATION	YES	Concentration in scientific format (9.99999E99, see Volume I, CODES for units)	CHAR (10)
34	INEXACT	-	If concentration is inexact (Code GT=Greater, LT=Less, BL=Below detection limit only)	CHAR (2)
35	STD	-	Standard deviation if more than one analysis is made (9.99999E99, see Volume I, CODES for units)	CHAR (10)
36	FW - DW	YES	Fresh/dry weight result (Code F=Fresh, D=Dry only)	CHAR (1)
37	ANALYSIS METHOD	-	Method used (See Volume I, CODES)	CHAR (5)
38	ANALYSIS DATE	-	Date of analysis (Format is dd-mmm-yy or dd/mm/yy or mm/dd/yy)	DATE
39	ANALYZING INST CODE	-	Analyzing institute code (See Supplementary Data section for clarification)	NUM (2)

HEAVY METALS IN BIOTA (excluding Plankton)

Filename: HMBI.ASC

Seq. No.	Column Name	Mandatory ?	Description	Column Type/Length
Area & Station Information				
1	YEAR	YES	Monitoring year (Format is XX for 19XX)	NUM (2)
2	COUNTRY	YES	Monitoring country code (See country list, Appendix I)	CHAR (3)
3	AREA CODE	YES	Monitoring area code	CHAR (6)
4	AREA DESCRIPTION	-	Monitoring area description	CHAR (30)
5	STATION CODE	YES	Monitoring station code	CHAR (6)
6	STATION DESCRIPTION	-	Monitoring station description	CHAR (30)
7	STATION TYPE	YES	Station type (See Volume 1, CODES)	CHAR (1)
8	BOTTOM DEPTH	-	Bottom depth in meters (Format is 99999.9)	NUM (6,1)
Sampling Information				
9	SAMPLING DATE	YES	Date of sampling (Format is dd-mmm-yy or dd/mm/yy or mm/dd/yy)	DATE
10	LATITUDE DEGREE	YES	Latitude degree (sampling coordinate - applies to Seq. Nos. 10 - 17)	NUM (2)
11	LATITUDE MINUTE	YES	Latitude minute	NUM (2)
12	LATITUDE SECOND	YES	Latitude second	NUM (2)
13	LATITUDE POSITION	YES	Latitude position (Code N = North, S = South)	CHAR (1)
14	LONGITUDE DEGREE	YES	Longitude degree	NUM (3)
15	LONGITUDE MINUTE	YES	Longitude minute	NUM (2)
16	LONGITUDE SECOND	YES	Longitude second	NUM (2)
17	LONGITUDE POSITION	YES	Longitude position (Code W = West, E = East)	CHAR (1)
18	SAMPLING DEPTH	-	Sampling depth in meters (Format is 99999.9)	NUM (6,1)
19	SPECIES	YES	Species code (See Volume I, CODES)	CHAR (3)
20	NS	YES	Number of specimens, if the sample is composite	NUM (3)

Seq. No.	Column Name	Mandatory ?	Description	Column Type/Length
21	AVERAGE LENGTH	-	Average length in centimeters (Format is 9999.99)	NUM (6,2)
22	LENGTH STD	-	Length standard deviation in centimeters for composite sample (Format is 999.99)	NUM (5,2)
23	AVERAGE WEIGHT	-	Average weight in grams (Format is 999999.9)	NUM (7,1)
24	WEIGHT STD	-	Weight standard deviation in grams for composite sample (Format is 99999.9)	NUM (6,1)
25	SEX	-	Sex code (Code F=Female, M=Male, I=Indeterminate only)	CHAR (1)
26	AGE	-	Age in years (Format is 99.9)	NUM (3,1)
27	TISSUE	YES	Tissue code (See Volume I, CODES)	CHAR (2)
28	DW/FW	YES	Ratio of dry weight to fresh weight in percentage (Format is 99.99)	NUM (4,2)
29	SAMPLING INST CODE	YES	Sampling institute code (See Supplementary Data section for clarification)	NUM (2)
Parameter Analysis Information				
30	PARAMETER	YES	Heavy Metal code (See Volume 1, CODES)	CHAR (5)
31	NA	-	Number of parameter analysis	NUM (2)
32	CONCENTRATION	YES	Concentration in scientific format (9.99999E99, see Volume I, CODES for units)	CHAR (10)
33	INEXACT	-	If concentration is inexact (Code GT=Greater, LT=Less, BL=Below detection limit only)	CHAR (2)
34	STD	-	Standard deviation if more than one analysis is made (9.99999E99, see Volume I, CODES for units)	CHAR (10)
35	FW - DW	YES	Fresh/dry weight result (Code F=Fresh, D=Dry only)	CHAR (1)
36	ANALYSIS METHOD	-	Method used (See Volume I, CODES)	CHAR (5)
37	ANALYSIS DATE	-	Date of analysis (Format is dd-mmm-yy or dd/mm/yy or mm/dd/yy)	DATE
38	ANALYZING INST CODE	-	Analyzing institute code (See Supplementary Data section for clarification)	NUM (2)

NOTE: This document has been prepared jointly by the Intergovernmental Oceanographic Commission (IOC), the International Atomic Energy Agency (IAEA), the Food and Agriculture Organization of the United Nations (FAO) and the United Nations Environment Programme (UNEP) under project FP.5102-88-03.

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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 1989.

PREFACE

The Regional Seas Programme was initiated by UNEP in 1974. Since then the Governing Council of UNEP has repeatedly endorsed a regional approach to the control of marine pollution and the management of marine and coastal resources and has requested the development of regional action plans. The Regional Seas Programme at present includes ten regions and has over 120 coastal States participating in it. (1), (2).

One of the basic components of the action plans sponsored by UNEP in the framework of the Regional Seas Programme is the assessment of the state of the marine environment and of its resources, and of the sources and trends of the pollution, and the impact of pollution on human health, marine ecosystems and amenities. In order to assist those participating in this activity and to ensure that the data obtained through this assessment can be compared on a world-wide basis and thus contribute to the Global Environment Monitoring System (GEMS) of UNEP, a set of Reference Methods and Guidelines for marine pollution studies are being developed as part of the programme of comprehensive technical support which includes the provision of expert advice, reference methods and materials, training and data quality assurance (3). The Methods recommended to be adopted by Governments participating in the Regional Seas Programme.

The methods and guidelines are prepared in co-operation with the relevant specialized bodies of the United Nations system as well as other organizations and are tested by a number of experts competent in the field relevant to the methods described.

In the description of the methods and guidelines the style used by the International Organization for Standardization (ISO) is followed as closely as possible.

The methods and guidelines, as published in UNEP's series of Reference Methods for Marine Pollution Studies, are not considered as final. They are planned to be periodically revised taking into account the development of our understanding of the problems, as analytical instrumentation and the actual need of the users. In order to facilitate these revisions the users are invited to convey their comments and suggestions to:

Marine Environmental Studies Laboratory
IAEA Marine Environment Laboratory
19, Avenue des Castellans
MC 98000 MONACO

which is responsible for the technical co-ordination of the development, testing and intercalibration of Reference Methods.

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- (1) UNEP: Achievements and planned development of the UNEP's Regional Seas Programme and comparable programmes sponsored by other bodies. UNEP Regional Seas Reports and Studies No.1 UNEP, 1982
 - (2) P. HULM: A Strategy for the Seas. The Regional Seas Programme: Past and Future, UNEP 1983.
 - (3) UNEP/IAEA/IOC: Reference Methods and Materials: A Programme of comprehensive support for regional and global marine pollution assessments. UNEP 1990.

The present Reference Method provides guidelines for establishing Quality Assurance (QA) and Good Laboratory Practice (GLP) procedures in laboratories involved in the monitoring of contaminants in marine organisms. The guidelines are based on the experience of laboratories participating in large international monitoring programmes including those of UNEP's Regional Seas Programme, the International Council for the Exploration of the Sea (ICES) and the various regional programmes of IOC. Quality Assurance is an essential part of any monitoring programme and is the only means to guarantee comparability of data - without such procedures data reports would be meaningless.

This first edition of the Reference Method for Marine Pollution Studies No. 57 was prepared in cooperation with the Intergovernmental Oceanographic Commission (IOC), the International Atomic Energy Agency (IAEA) and the Food and Agriculture Organization of the United Nations (FAO). It includes comments received from the joint IOC/UNEP Group of Experts on Methods, Standards and Intercalibration (GEMSI) of GIPME who reviewed the guidelines. The assistance of all those who contributed to the preparation of this reference method is gratefully acknowledged.

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1. SCOPE AND FIELD OF APPLICATION

This publication provides guidelines for obtaining reliable and relevant data during monitoring programmes in which contaminants are measured in marine organisms. It describes the precautions to be taken in each of the procedural steps from planning and sampling to the publication of data reports.

2. REFERENCES

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3. INTRODUCTION

Many laboratories are actively participating in marine pollution monitoring programmes under the auspices of the United Nations Environment Programme (UNEP), the Intergovernmental Oceanographic Commission (IOC) and the Food and Agriculture Organization of the United Nations (FAO). These organizations have expressed concern about the quality of data arising from such programmes, particularly the accuracy and comparability of data produced by individual laboratories. In order to deal with this problem they have encouraged laboratories to participate in intercomparison exercises, arranged for less experienced laboratories to attend analytical workshops and have arranged for reference analytical methods to be produced and distributed to participants in the various regional seas programmes.

It should be stressed, however, that the acquisition of reliable and relevant data of the appropriate quality, for contaminants in marine samples, is not solely dependant on the production of accurate analytical measurements. The overall quality of data is also dependent on three other factors, which are:

a representative and meaningful sampling programme;

a suitable storage and pre-treatment procedure for samples following collection and prior to analysis; and,

a data assessment procedure.

Unless all four factors are given adequate consideration before and during the monitoring programme, the aims of the programme may not be wasted. The term used to describe the approach to this work is "quality assurance". Quality assurance involves all those steps which are required to guarantee the generation of data of suitable quality to address the defined aims of a monitoring programme.

The purpose of this document is to provide general guidance on quality assurance and to outline the approach that could be taken by laboratories to achieve the specific aim(s) for each marine pollution monitoring programme. Since most laboratories are currently focussing on programmes involving marine organisms, this document will be confined to this aspect.

Since quality assurance work starts from the time when a decision is taken to get involved with marine pollution monitoring it is appropriate to begin by discussing the different aims which laboratories might wish to pursue under this work.

4. AIMS OF MONITORING PROGRAMMES

Four main aims can be identified for programmes involving the collection and analysis of marine organisms for the three main groups of contaminants (metals, organochlorine compounds and petroleum hydrocarbons), these are:

- (i) The measurement of contaminant levels in edible marine organisms in relation to public health
- (ii) The identification of heavily contaminated areas of the sea ("hot spots") where levels of contaminants are at least an order of magnitude higher than levels in clean or uncontaminated areas.
- (iii) The establishment of present levels of contaminants in marine organisms (i.e., a "baseline")
- (iv) The assessment of changes in concentrations of contaminants in organisms over a period of time (trends).

Each of these programmes places a different demand on the laboratories regarding the method and care to be taken in the collection, storage and analysis of samples. These aspects are considered below in detail in the context of the main aims of each programme.

It is very important that the investigator should prepare a clear and unambiguous statement on the aims and objectives of the work before embarking on any monitoring programme. Only by doing this will it be clear what type of information will be required, and consequently what criteria should be laid down for the collection, storage and analysis of samples. Time spent on defining aims and objectives and the planning of the various parts of the field and laboratory work will always be rewarded by a more efficient and effective programme.

Good planning can avoid unnecessary sampling and analyses, i.e., it is sensible to initially aim for a programme which satisfies essential rather than desirable objectives. It is easy to expand such a programme if the necessary resources are available. Also, if plans are made in advance as to how the data to be collected is to be used, this will assist in the design of field and laboratory work. Finally, there is a need to regularly review the programme of work to assess how well the aims are being met. Such reviews might lead to a reduction of sampling and analyses, and the time gained can be usefully employed elsewhere. Equally it might identify the need to put in more effort; early warning of such extra work can allow time to plan the necessary manpower and other resources.

5. SAMPLING STRATEGY

If the sampling strategy is not designed with great care, the data from the measurements may not meet the needs of the programme. On the basis of previous experience considerable effort needs to be devoted to long-term monitoring, so it is important to ensure that this is done in the most efficient and effective way.

Good planning needs considerable time and thought; never be persuaded to rush this aspect of the work and ensure that all disciplines involved are consulted before plans are finalized.

In designing a representative and meaningful sampling programme involving marine organisms there are a number of questions which have to be considered:

- a) where should the samples be collected;
- b) which organism(s) should be selected for study;
- c) when should the sampling be done and what is the appropriate frequency of sample collection;
- d) how many individual organisms should be collected on each sampling occasion and which size(s) should be included in each sample; and,
- e) which tissue(s) of the organisms(s) should be taken for analysis.

Each of these points will be addressed below for each of the main aims referred to above, i.e., public health, hot spots, baseline and trend studies.

6. PUBLIC HEALTH

6.1 Since the aim of the programme is to assess the level of contaminants in edible species then samples should ideally be taken at the point of sale to the general public, i.e., at the fish market. Alternatively the scientist(s) can collect the fish/shellfish from the main fishing areas.

6.2 The selection of organisms will be dictated by the eating patterns of the population. These can be identified by a survey of the species sold at the market, by obtaining information from colleagues in government departments who deal with such matters or in the absence of such information, by distributing a questionnaire to a representative section of the general public.

6.3 Unless there is a seasonal fishing pattern for some species, then samples may be taken at any time of the year. Ideally all species should be sampled at the same time so that a synoptic picture can be obtained for the contaminant levels. A typical monitoring programme might be a survey every 5 years. However, available resources may allow more frequent surveys to be conducted; assuming that the results indicate that this is required (i.e., if concentrations of contaminants in foodstuffs are found to exceed permissible limits). This increased sampling should be confirmed to species "which permissible limits of contaminants are exceeded.

6.4 The size(s) of organisms to be sampled should be based on information collected at the fish market. If small and large sizes are sold to the general public, this should be reflected in the sample. The number of individual organisms in each sample may partly be influenced by the importance of the species as a foodstuff, by the availability of scientific manpower and by the need to sample sufficient of each species and of each size category to cover the range of values encountered in a typical population or catch. Generally, a sample of 5-10 individuals could be collected for each size range of fish and large shellfish (crabs, lobsters) and 50 individuals for smaller shellfish (e.g. mussels, shrimps).

6.5 Only edible tissue need be analysed for contaminants - usually this means muscle tissue for fish and large crustaceans and whole soft tissue (less viscera) for other shellfish.

6.6 Every opportunity should be taken to collect data on the size (or length) and age of the species. This may assist decision making at a later date if the programme is too focussed on a particular area and/or species.

7. HOT SPOTS

7.1 Hot spots are usually found close to estuarine and coastal areas where anthropogenic wastes are discharged. The only offshore areas where hot spots are likely to occur are those which are used for the dumping of wastes from ships (and sites where net deposition of fine material takes place).

7.2 Although one theoretically can select any type of organism to monitor hot spots, in practice the most useful organism for this purpose are the invertebrates. These species, by virtue of their feeding behaviour, can reflect levels of contamination in the soluble phase, in the suspended particulate phase and in the sediment phase (see Appendix 1 for the list of characteristics for organisms to be used in monitoring studies). It should be noted, however, that levels of lipophilic organic compounds are most considerably influenced by water: lipid distribution equilibria. This factor may be more important than feeding habits for such compounds.

It should be stated that no single organism can be used to monitor levels in the above three phases. It may be necessary to use a seaweed (macro algae) for the soluble phase, a filter feeder (e.g., mussels) for the particulate phase and a detritus feeder for the sediment phase. The investigator should therefore consult biologists to determine which species are best for the type of waste(s) and phase(s) under examination.

If a single preferred organism had to be nominated, the common mussel (*Mytilus edulis* or the equivalent local species), would be recommended.

7.3 Seasonal variations in food supply, and the spawning cycle, are known to cause changes in total body weight as well as lipid concentration and composition and consequently contaminant levels in the tissues of invertebrates. In order to minimise these variations it is suggested that sampling be undertaken at the pre-spawning period. Provided sampling covers the area under investigation in a representative manner, one survey is normally sufficient for the identification of hot spots.

7.4 Ideally the number of individuals collected should cover the size range of organisms encountered at the sampling site in order to establish the variations of contaminant levels with size. Although this approach need not be taken at each of the sampling sites, it should be carried out at least at one site in order to allow comparisons to be made with other sites where sampling should be restricted to a small size range. Depending on analytical resources, the organisms from each site can either be analysed individually or bulked. In the latter case, no information will be derived on the variation with size but in terms of the aim of the programme

the results can be used to compare data from site to site with some level of confidence (this assumes that a number of replicate analyses are performed on the bulked sample to allow differences to be detected above and beyond those produced by sample variation).

7.5 Whole soft tissue, less viscera, should be taken for analysis. N.B.

For the analysis of lipophilic contaminants it is important to measure the lipid content of each sample (e.g., n-hexane extract) in order to ensure that comparisons of data on a lipid basis can be made for different regions and times of sampling (i.e., in relation to the seasonal changes of lipid concentration in organisms).

8. BASELINE AND TRENDS

8.1 Sampling sites should include estuarine, coastal and offshore areas to ensure that both clean and contaminated areas are covered in this programme. Sampling at sea should be done by trained personnel operating from research or chartered vessels, rather than by fishermen, to ensure that contamination of the samples during and after collection is kept at an acceptable level.

8.2 Since the aim is to establish the current state of contamination of marine organisms generally, there are no restrictions on the species that can be included in such a study; other than that imposed by the resources available to the investigator. If the laboratory wishes to conduct trend monitoring or compare levels of contaminants at different sites, then it is necessary to include those organisms which will provide the data with which to achieve such aims, e.g. invertebrates.

8.3 Collections should be made over a short interval of time to ensure as synoptic a picture as possible for the baseline survey and to enable comparisons of concentrations of contaminants at different sites. This also ensures that organisms are in the same physiological state (i.e., lipid metabolism, spawning, etc.).

It is appropriate to repeat a baseline study every 5 years unless major changes in discharges occur or are anticipated in the intervening period, which are considered to influence levels of contaminants in organisms over the entire study area. In most cases the effects of increasing or decreasing inputs of contaminants are usually confined to the area in the immediate vicinity of the discharge. More frequent monitoring at these locations would fall under the category of trend studies.

For trend studies the minimum frequency of monitoring for fish and shellfish would consist of an annual sampling whereas the maximum sampling for invertebrates might be as much as 4-12 times per year.

Each laboratory will clearly establish the frequency of sampling which meets the aims of its programme. This frequency will reflect both the changes it wishes to measure over a particular period of time and the resources it has at its' disposal.

8.4 Baseline studies should attempt to cover all size ranges of the species under examination in order to produce a comprehensive picture for the state of the environment. A

sample of 5-10 individuals for each size range would be an appropriate number for each fish and major shellfish species. A sample of 25-50 individuals is usually required for smaller shellfish.

Having established the relationship of contaminant levels with size of organisms it is usual to select a particular size or size range for trend studies to reduce variability. The numbers of individuals required for each sample will be determined by the differences in contaminant levels one wishes to be able to differentiate, i.e., the smaller the difference the greater the number of individuals required for each sample. In a recent study of trace metal variability in two populations of *Mytilus californianus*, through the random sampling of organisms at two sites, Gordon *et al.* found coefficients of variation of 18-40%. They concluded that a sample of 20-100 individuals/site was required to detect a concentration difference of 20% between sites. Differences of 40% could be detected by analysing about 1/3 as many samples.

8.5 For fish muscle is the most useful tissue for all purposes. However liver and kidney tissues have been used for both baseline and trend studies. Both hepatopancreas and muscle tissue have been used in studies of large crustaceans. In general, whole soft tissue is taken for smaller shellfish.

9. STORAGE AND PRE-TREATMENT OF SAMPLES

9.1 Practical guidelines

Guidelines and recommended procedures dealing with the storage and pre-treatment of samples following their collection are given in UNEP Reference Methods for Marine Pollution Studies 7 and 12 (which deal with metals and halogenated hydrocarbons respectively).

The guidelines cover the following:

The types of storage containers to be used to avoid contamination of samples in transit and the recommended temperature for storage prior to dissection and analysis.

The precautions to be taken during the removal of soft tissue from the organism and during the preparation of the sub-sample for analysis to avoid contamination from dissection tools, reagents, laboratory environment and the person carrying out these procedures.

Analysts should ensure that adequate time and effort are allowed for this work since improper storage of samples and poor sample handling prior to analysis will lead to the production of unacceptable data irrespective of how well the subsequent analytical measurements are carried out.

9.2 Planning and management

Good planning is essential if this work is to be done efficiently and effectively. The following guidance is given in this respect:

9.2.1 Sampling

- Staff involved in sampling work should be given clear written instructions concerning the methods of collection, particularly the precautions that have to be taken to avoid contamination of samples during the transfer from the site to the storage container.
- Experienced staff should accompany new staff on their first site visit and possibly on later visits to monitor their work.
- A check list of sampling and storage equipment should be compiled for each type of sampling and this should be used before each site visit.
- Adequate time should be allocated for each site visit to ensure that unexpected delays do not cause field staff to give less attention to sampling and storage.
- Log books should be provided to record essential details of samples and any site characteristics that are considered necessary. These logs should be checked on completion of this site visit.
- On arrival at the laboratory samples should be catalogued and securely stored in order to avoid loss of samples.

9.2.2 Dissection of samples

- Ideally dissection of samples should be done on fresh material (cooled but not deep frozen). If these samples cannot be analysed within one or two days they should be deep frozen until they can be analysed.
- If the above procedure cannot be followed, the samples should be deep frozen following collection and only removed for thawing and dissection when the chemical analyses of soft tissue can be done. Repeated freezing and thawing of samples can lead to loss of body fluids and water content. This can not only effect the form and concentration of contaminants in soft tissue but can make the determination of wet to dry weight conversion factors very difficult.
- The dissection of organisms by inexperienced staff, under poorly controlled laboratory conditions, can result in the production of unrepresentative and contaminated samples of soft tissue for analysis. Staff responsible for dissection must be given proper training in dissection and sub-sampling. They must be issued with the appropriate dissection tools and must work in an area of the laboratory specially kept for this work. It is good practice to assign two people to this work - one to dissect and transfer tissue to the sub-sample container, the other to catalogue the sample and weight of tissue taken for each sub-sample.

N.B. Adequate time must be allowed for this work to avoid staff making errors.

10. ANALYTICAL QUALITY ASSURANCE

The earlier section of this document dealt with the collection of representative and meaningful samples of marine organisms and the pre-treatment and storage procedures which ensure that losses and additions of contaminants prior to chemical analysis are kept to a minimum. This section deals with the aspect of quality assurance concerned with the measurement of contaminants in biological tissue namely analytical quality control and assessment.

It is assumed that the analyst has chosen a suitable analytical procedure to provide the appropriate performance characteristics of precision, accuracy and limit of detection (see Appendix 2).

Before an analyst employs an analytical procedure on a regular basis for the measurement of contaminants in a sample of biological tissue it is essential to check its performance characteristics to ensure that the method will produce data of the required accuracy and precision. This applies equally to the Reference Methods for Marine pollution Studies published by UNEP (in cooperation with other UN Agencies) as well as to any methods developed by the laboratory or other published methods used by the laboratory.

This check on accuracy and precision is done by analysing certified reference materials (CRMs) of known matrix and composition. (A list of relevant CRMs is given in Appendix 3). In the absence of such materials the analyst should check the accuracy and precision by the method of "standard addition", i.e., the analysis of samples of the tissue to which known quantities of contaminants of interest have been added (i.e. "spikes"). Total recovery of "spikes" does not however guarantee that the method will produce accurate data for samples since the chemical form of the analyte in the sample and in the spike may not be the same or the concentration/extraction procedure may be inadequate to release the contaminant from its site in the sample. It is advisable, therefore, whenever possible, to employ CRMs for the evaluation of analytical methods since this is the only true test for accuracy of a method for the sample and analyte(s) under examination. Analysts should choose the CRM which is not only of a similar matrix to the sample but which also has a similar concentration of the analyte(s) under examination. In this respect it is often necessary to analyse two CRMs to cover the upper and lower ranges of concentrations likely to be encountered. This ensures that the method will provide accurate and precise data over the expected range of concentrations.

It must be emphasized, however, that the use of a validated method, suitable instrumentation, experienced personnel, etc. does not guarantee the regular production of reliable data. All analytical work should be done under a system of quality control (the steps taken to minimise errors) and a system of quality assessment (the procedure adopted to verify that the errors are within the acceptable limits).

10.1 Quality Control

The elements of good quality control are as follows:

- Consistent use of reliable qualified personnel, and well-maintained instrumentation.

- Appropriate calibrations and standards.
- Close supervision of all operations by senior personnel.
- Use of CRMs for evaluation methodology.
- Use of reference materials on a regular basis throughout the monitoring programme to check that analytical performance is maintained.
- Participation, encouraged by senior management, in interlaboratory checks of analytical performance (this is the only independent method available to check on a laboratory's analytical capability, see Appendix 4).

10.2 Quality Assessment

The establishment of a system of control charts is the main element of this assessment technique. Control charts are plots of the results of analyses of the same sample over a period of time (see Appendix 5). They allow analysts to check whether their results are falling within the acceptable limits of accuracy and precision.

Data for control charts may consist of the analyses of CRMs and other reference materials. The latter may include homogeneous materials based on real samples which have been prepared by the analyst (known as internal reference materials).

Regular analyses for control chart purposes are essential to avoid waste of valuable time and effort spent on analytical work. Ideally, daily analyses of such internal reference materials should be performed so that only one batch of analytical data is lost if the analysis gets out of control. Many laboratories devote about 10% of their total routine effort to quality control and assessment (see also section 9).

11. DOCUMENTATION AND REPORTING OF DATA

The adoption of the following guidelines by a laboratory should provide adequate documentation: to support any data report or decisions on the results of its monitoring programmes, and to allow it to trace samples from the collection stage to the completion of its analyses by providing a record of the appropriate data in logbooks or in computer files.

11.1 Documentation

The following documentation is necessary for a laboratory participating in pollutant monitoring activities:

- (i) Descriptions of the sampling strategy, methods of collection, procedures of storage, pre-treatment and analytical procedures.
- (ii) Sample documentation (description of organisms, numbers or individuals collected for each sample, weights of tissue taken for analysis (individual tissue or homogenate)).

(iii) Evidence of successful evaluation and testing of analytical procedures, including details of accuracy, precision and limit of detection.

(iv) The approach used for quality control and quality assessment and evidence that these procedures have been used and have provided acceptable data.

(v) Calibration details, a description of working standards used on each occasion and calculations of results.

(vi) A secure system for the long term storage of data either in logbooks or in computer files is essential. It is therefore advisable to have a duplicate set of records in case one is lost, mislaid or accidentally destroyed.

Advice should be sought on the correct method of storing computer tapes and/or discs to ensure the long-term stability of the data files.

11.2 Preliminary assessment, tabulation and storage of data

It has been shown that even the most experienced personnel can make simple arithmetic errors in calculating data. Thus a check should be made for such errors before compiling tables of results. Once this check has been carried out it is appropriate to carry out a preliminary assessment of the quality of the data, prior to its evaluation and publication, to ensure that no erroneous results are included in the data set. This assessment can include a comparison of the results with existing data (i.e., data previously collected by the laboratory or data published in the literature for the study area). Before consigning data to long term storage a final check should be made to ensure that no transcriptional errors have been made in transferring the data (i.e., the re-typing of data sets by typists or data processors can sometimes lead to such errors).

11.3 Publication of data

Data held in logbooks or on a computer which has not been published is effectively lost to the scientific community. Every effort should be made to evaluate and publish these results, even in the simple form of a report. In addition to the results, the contents of a data report would normally include a statement on the aims of the work, a description of the methods used to collect and analyse samples together with a statement on findings and conclusions.

In general it is inadvisable to supply a third party with a copy of your raw data, unless:

(a) it is accompanied by information on its accuracy, precision and limits of determination and details of the sampling record;

or,

(b) it is accompanied by a report from the analyst or principal investigator in which the results have been evaluated.

APPENDIX 1

SELECTION OF ORGANISMS FOR MONITORING PURPOSES

The ideal characteristics of organisms for use as indicators of marine contamination are:

- The organism should accumulate the contaminant without being affected by the levels encountered.
- The organism should be sedentary in order to be representative of the area of collection.
- The organism should be abundant in the study region.
- The organism should be sufficiently long-lived to allow sampling of more than one year class if desired.
- The organism should be of a reasonable size, given adequate tissue for analysis.
- The organism should be easy to sample and hardy enough to survive in the laboratory, allowing (if desired) defecation before analysis and laboratory studies of uptake of contaminants.
- The organism should tolerate brackish water.
- The organism should exhibit high concentration factors allowing direct analysis without pre-concentration.
- A simple relationship should exist between contamination residues in the organisms and the average concentration in the surrounding seawater.

These conditions restrict the useful organisms to a range of fairly large, abundant, widespread, inter-tidal organisms, mainly macro-algae and molluscs.

Filter-feeding molluscs are more likely to reflect conditions in the water column, whilst deposit feeders will respond to sediment chemistry. The concentration of contaminants in the water column, however, will largely reflect effluent discharges and dispersal conditions at the moment of sampling. Filter-feeders are therefore more likely to provide the information required to fulfill the objectives of the monitoring programme.

If a single preferred organism had to be nominated, the common mussel, *Mytilus edulis*, would be recommended. Other bivalves (particularly mussels and oysters) may also fulfill the criteria indicated. Care must be taken with species identification as concentration factors of some contaminants vary widely between species.

All the measurements are biased since the mean values of all three procedures do not coincide with the true value. However, it should be noted that most of the results for measurement "A" will be more accurate than those of "B" or "C", due to precision considerations.

2. Bias

There are four possible sources of bias in analytical measurements:

- (i) Inability to determine the appropriate forms of the analyte in the sample.
- (ii) The effects of other substances present in the sample (interferences)

These are the two most common sources of bias. However, it may not be possible for a routine analytical laboratory to devote the necessary time and effort to conduct all the tests required to check the sources of variation. In view of this, analysts should minimise these sources of error by adopting analytical procedures which have been recommended by either an expert group or an expert laboratory.

- (iii) A biased calibration

Provided that care is taken in preparing any standards required for calibration purposes this source of error should be minimal. The purchase of standards from a reputable company will usually guarantee the accuracy of the stock standards. The accuracy of working standards (dilutions of the stock standards) will however be determined by the ability of the analyst to carefully carry out the necessary preparatory work, particularly with respect to the cleanliness of operations. Inattention to this aspect can lead to contaminated standards and therefore inaccurate calibrations.

N.B. Remember to double check dilutions of stock standards since simple errors (using the wrong size of pipette or making a mistake in the calculation of the dilution required) can lead to inaccurate standards.

If analytical instruments are not well maintained and serviced regularly the response of them will vary with time thus affecting calibrations.

- (iv) A biased blank correction

In theory, a blank correction involves the analysis of a sample which contains negligible concentrations of the analytes in a matrix similar to the samples being analysed. This ideal situation is difficult to achieve in practice since "field blanks" are not easily obtained. Whenever possible, however, such blanks should be used and processed in exactly the same way as samples. The reduction or minimisation of a blank value and its variability can be achieved by:

- a. ensuring that only high quality reagents and labware are used in the analytical procedure;

and

b. ensuring that all operations are conducted with rigorously cleaned labware and in laboratories which are free from sources of contamination.

3. Precision

Precision, which is defined as the random variability of the measurement procedure, can vary within and between batches of analyses. An estimate of precision from only one batch of analyses can therefore give an over-optimistic estimate of subsequent routine analytical results. Precision should be estimated from a series of analyses, on the same material, conducted over a period of time. This approach enables the total random error to be separated into the error arising from variations within and between batches of analyses. This information can be useful in identifying the location and magnitude of sources of errors. e.g., a large value for between-batch standard deviation may indicate a changing calibration. Similarly a large value for within - batch standard deviation may indicate a contamination problem.

Since the precision of analytical results often depends on the concentration of the analyte, it is necessary to analyse samples which cover the upper and lower limits of the analytical method. This can be done by choosing the appropriate CRMs (see Appendix 3) to cover the range or by analysing spiked samples of different concentrations.

4. Limit of detection

Limit of detection (LOD) is that concentration at which the analyte can be quantified to a given accuracy with an agreed degree of confidence. The LOD of an analytical procedure can be calculated as follows:

$$St = Sb + \text{constant} \cdot v = Sb + K v$$

LOD is based on the relationship between the gross analytical signal (St), the field blank (Sb) and the variability in the field blank (v) measurements.

(Field blanks are samples that contain the analyte(s) at levels below the LOD. These are difficult to obtain so in most instances analysts substitute reagent blanks for them).

In practice most analysts define LOD using a K of 3.

$$\text{i.e., } LOD = Sb + 3v$$

Measurements below $3v$ should be reported as not detected (nd) with the limit of detection given in parenthesis. In the region $3v - 10v$ measurements should be reported as detected, again with the LOD being given in parenthesis.

APPENDIX 3

REFERENCE MATERIALS (RMs)

A comprehensive list of marine RMs can be found in the latest edition of "Standards and Reference Materials for use in Marine Science (NOAA Technical Memorandum NOS OMA 51)**" which is produced by the U.S. National Oceanic and Atmospheric Administration in cooperation with the IOC/IAEA/UNEP Group of Experts on Standards and Reference Materials (GESREM). In this document a description is given of each RM (its preparation, its composition and in the case of CRMs the values for the analyte(s) in question) together with the name and address of the organisation from which the RM(s) can be purchased.

At the time of preparing this document there are five major organisations which are actively involved in the production of marine RMs for contaminants in biological tissue. They are:

National Institute of Science and Technology (NIST), Office of Standard Reference Materials, Gaithersburg, MD 20899 USA.

National Research Council of Canada (NRCC), Division of Chemistry, Montreal Rd., Ottawa, Canada K1A 0R6.

National Institute for Environmental Studies (NIES), Yatabe-machi, Tsukuba, Ibarake 305, Japan.

International Atomic Energy Agency (IAEA), International Laboratory of Marine Radioactivity, Stade Louis II, 19 Avenue des Castellans, MC 98000, Principality of Monaco.

Community Bureau of Reference (BCR), Community of European Communities, 200 rue de la Loi, B-1049 Brussels, Belgium.

Some commonly used marine RMs are listed below together with the organisation that supply them.

<u>Material</u>	<u>Matrix</u>	<u>Analyte(s)</u>	<u>Supplier</u>
TORT-1 LUTS-1	Lobster hepatopancreas	Metals (high conc)	NRCC
DORM-1	dogfish muscle	Metals (low conc)	NRCC

* Document available from: Office of Oceanography and Marine Assessment,
National Ocean Service National Oceanic and
Atmospheric Admin. U.S. Department of Commerce
6001 Executive Blvd., Room 323
Rockville, MD 20852, U.S.A.

<u>Material</u>	<u>Matrix</u>	<u>Analyte(s)</u>	<u>Supplier</u>
DOLT-1	dogfish liver dogfish liver oil	Metals (intermediate conc) Chlorobiphenyls (CBs)	NRCC NRCC
CLB-1-A	Iso octane solution CLB-1-D	CBs standards	NRCC
CRM 279	Sea lettuce	Metals	BCR
CRM 349	Cod liver oil	CBs (IUPAC Nos. 28,52,101,118,138,153,180)	BCR
CRM 350	Mackerel oil	CBs (as above)	BCR
MA-A-1/TM	Copepod	Metals	IAEA
MA-A-2/TM	Fish Muscle	Metals	IAEA
MA-B-3/TM	Baltic fish	Metals	IAEA
IAEA-350	Tuna fish	Metals	IAEA
MA-A-1/OC	Copepod	PCBs (1242 and 1254) and selected pesticides	IAEA
MA-A-2/OC	Fish Muscle	PCBs (1254 and 1260) and selected pesticides	IAEA
MA-M-2/OC	Mussel homogenate	as above	IAEA
MA-B-3/OC	Baltic fish	selected pesticides and selected PCB congeners	IAEA
IAEA-351	Tuna fish	as above	IAEA
SRM 1566	Oyster tissue	trace elements	NIST
NIES No.6	Mussel powder	metals	NIES
NIES No.9	Sargassum	metals	NIES

Analysts who wish to ensure that their analytical data are accurate and precise should purchase one or more of these RMs for use in their evaluation of analytical methods and in their routine quality control work. Although the cost of such materials may appear prohibitive it is sound judgement to allocate funds to the provision of such materials in order to ensure that time and effort are used constructively and productively. Time devoted to quality assurance work (ca 10% of an analysts time) is time that is well invested.

N.B. Analysts should not use non-marine RMs for validating analytical methods and quality control work associated with marine monitoring programmes. They should choose RM(s) which have matrices which are either identical, or very similar, to the samples under study and which cover the upper and lower range of concentration of contaminants being measured. Further information on the correct use of Reference Materials may be obtained from the literature cited in section 2 of these guidelines.

APPENDIX 4

INTERCOMPARISON EXERCISES

These exercises provide analysts with an opportunity to obtain an independent assessment of the quality of analytical data produced by them. They also allow others, including coordinators of multi-laboratory monitoring programmes, to assess the comparability (and in some cases accuracy) of the data being produced by participants in these programmes. They provide a stimulus to improve methodology and encouragement to adopt state-of-the-art methodology. Whenever possible analysts should participate, and be encouraged to participate by their line managers, in such exercises.

The exercises are normally conducted using blind samples - homogenous substances which contain unknown concentrations of the analyte in a matrix identical, or similar, to that normally examined in the associated monitoring programme. Occasionally, analysts receive samples which contain known (but undisclosed to them) concentrations of analyte(s). In all cases these materials are specially prepared for such exercises.

Participants in such exercises are usually asked to analyse the materials by the analytical method(s) used in their normal monitoring work. Coordinators of exercises accept that the results submitted by participants will be the best data produced by them, since experience has shown that greater than usual care is taken by analysts during the analysis of such materials. Well designed exercises will usually include several materials to cover the range of concentrations of analytes and different matrices normally encountered in monitoring programmes in order to assess differences in analytical performance at the upper and lower ranges of concentration. Coordinators of exercises will try to ensure that a sufficient number of experts participate to provide some degree of standardisation or validation for the exercise. The absence of experts automatically means that the results from participants can only be compared rather than assessed for bias.

It is essential that the quality of analytical work is maintained during and in between exercises. Only the analyst can ensure that this actually happens.

For further information on specific exercises, please contact the addresses given on the inside back cover of this document.

- (i) Select the RM to be analysed with samples on a regular basis.
- (ii) Analyse the RM at least 10 times for the analyte(s) under examination. These analyses should not be done on the same day but spread out over a period of time in an attempt to ensure that the full range of random errors within and between batch analyses are covered.
- (iii) Calculate the mean value (\bar{X}), and the standard deviation (s) and then plot the following values on a blank control chart: \bar{X} , $\bar{X} + 2s$ (UCL), $\bar{X} + 3s$ (UWL), $\bar{X} - 2s$ (LCL) and $\bar{X} - 3s$ (LWL).

3. Using an AQCC

Assuming that the analytical measurements for RM(s) follow a normal distribution, 95% of them (19 in every 20) should fall within the area between UWL (upper warning limit) and LWL (lower warning limit). Similarly 99.7% of the results should fall within the area between UCL (upper control limit) and LCL (lower control limit).

The analyst should plot the results of the analysis of RM(s) after each batch of analyses to check where the data lies in relation to these limits. An example of such a plot is given in Fig. 2.

The following guidelines can be used to assess whether the data for the RM(s) and consequently the data for the samples are of acceptable quality, i.e., are the analyses under control.

- (a) The mere fact that one result falls outside the warning limits need not require the analyst to doubt the result or take any action provided that the next result falls within the warning limits.
- (b) If the results fall outside the warning limits too frequently, particularly if the same warning limit has been crossed more than once on consecutive results, then the analyst needs to assess the source of this systematic error.
- (c) If the results on more than 10 successive occasions fall on the same side of the \bar{X} line (either between \bar{X} and UWL or \bar{X} and LWL) then the analyst needs to check the analytical procedure to determine the cause of this error.
- (d) If the result falls outside the UCL or LCL lines then the analyst should check the analytical procedure to determine the cause of this source of error.

If any of the above cases occur the analyst should reject the results of the analysis of the particular batch of samples and should not carry out any further analysis of samples until the source(s) of the errors have been identified and he/she is satisfied that future analyses will be under control.

4. Use of Internal Reference Materials

The accuracy of a method can only be checked with an SRM or a CRM for which the mean values and standard deviations are well documented. Analysts who choose to use their own specially prepared RM (i.e., an internal RM, IRM)

for quality control purposes should note that they are primarily checking the precision of measurements and not their accuracy. These IRMs are very convenient however, for analyses where large quantities of materials are required for each determination (e.g., analyses for organic contaminants) and where the cost of these materials for QC charts would be prohibitive. Full instructions on the preparation and calibration of IRMs will be given in another publication in the present series.

5. Further information

The relevant publications listed in Section 2 of these guidelines contain valuable information on the correct use of reference materials and the application of QC charts. They should form part of every analytical laboratory's reference collection.

ALTERNATIVE MEANS OF ASSESSING DATA

by

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1. INTRODUCTION

In contaminant monitoring issues there are usually two main purposes to be addressed: levels of contaminant concentrations and whether these levels are increasing or decreasing. Even though detailed guidelines may exist (a rare occurrence) and these are followed very carefully (even rarer) there is no given method of assessing the results. Even with the spatial and temporal trend evaluation methods recognized by ICES (1988, 1989, 1991) there still remains considerable need for evaluation by experts. It would appear that each data has its own individuality that requires the close attention of the assessor.

2. ASSUMPTIONS

In this brief review we will assume that the appropriate guidelines have been followed to meet the monitoring targets in question. Furthermore, we will assume that there is no question about the quality of data, in other words that good laboratory practice (GLP) has been followed and the laboratories involved have participated successfully in appropriate intercalibration exercises. From the assessor's standpoint it is important that the data are readily available to verify these assumptions, especially the results from analyses of certified reference material (CRM) determined at the time of the data series in question.

3. LEVELS

Determining whether the concentrations of a contaminant in a given medium is high or low, is relative to the basis of comparison. For example, levels were assessed using the data collected during the 1985 ICES baseline study of contaminants in fish and shellfish of the North Atlantic. The assessors here used **upper quartiles** (the concentration above which 25% of the values were found), among other techniques, to distinguish areas of elevated levels. The results may be presented in box-and-whisker plots or maps (Fig. 1 and 2, ICES, 1988; JST, 1992). It is apparent that the value of this approach is better the better the geographical coverage is. Monitoring 'hot spot' areas or not doing so will bias the results. For example, the upper 25% of mercury concentrations in 66 samples of cod liver were above 67 ppb w.w. (0.067 mg kg⁻¹ wet weight). The samples were fairly evenly distributed around the British Isles, North Sea and southern Baltic Sea, but these samples were only from a relatively narrow belt of latitude of the convention area (50E to 61EN). Are the concentrations of mercury found in cod liver north or south of this area or from the western Atlantic, significantly different?

Table 1

Concentrations of metals (ppm d.w.) in the blue mussel (ME Mytilus edulis) and Mediterranean mussel (MG Mytilus galloprovincialis). Also shown are various limits to assess levels of contamination. The originating country is given: Norway (N), Netherlands (NL), Denmark (DK), Finland (SF), I (Ireland), Great Britain (GB), France (F), United States of America (USA) and Sweden (S). The average daily consumption rates of shellfish is given for 'risk' assessment of two populations in Norway. Where necessary, values were converted using a wet/dry weight ratio of 6.

	Cd	Cu	Hg	Pb	Zn	Reference
Mediterranean:						
MG-mean	0.72	7.8	1.38	4.8	162	Jeftić <i>et al.</i> , 1990
MG-max.	6.36	36	42	96.6	586	Jeftić <i>et al.</i> , 1990
North Sea baseline:						
ME-85 mean	1.03	7.9	0.10	1.7	95.7	ICES, 1988
ME-85 Q ₇₅	1.8	9.9	0.19	3.5	130	ICES, 1988
Classification (N):						
ME-class 1	<2		<0.2	<5	<200	Knutzen, 1992
ME-class 2	2-5		0.2-0.5	5-20	200-400	Knutzen, 1992
ME-class 3	5-20		0.5-1.5	20-50	400-1000	Knutzen, 1992
ME-class 4	20-40		1.5-4	50-100	1000-2500	Knutzen, 1992
ME-class 5	>40		>4	>100	>2500	Knutzen, 1992
Ecotoxicological:						
MRL (NL)	0.07		0.04			Jonkers & Everts, 1992
"Health" limits:						
DK "action limit"	3		1.8	6		FAO, 1989
NL	6		6	12		JMG, 1992
SF	3		6			PNUN, 1987
I				12		FAO, 1989
GB				60		FAO, 1989
F			3			FAO, 1989
USA			6			FAO, 1989
S			6	6		PNUN, 1987
'Risk' limits (N):						
Rural 0.5 g/d	348		408	4014		Green, 1987
Urban 1.6 g/d	126		132	1290		Green, 1987

Another approach in assessment is the use of **ecotoxicological reference values**. These are largely based on experimental studies and theoretical coupling to the 'real' environment. Jonkers and Everts (1992) have done some useful work in this area for the Netherlands authorities. Their goal is to establish a concentration of maximum permissible risk level (MRL) of a substance at which 95% of all the species potentially present in the ecosystem plus all 'characteristic species' in certain areas are afforded complete protection in the sense of their chronic No Observed Effect Concentration (NOEC) not being exceeded. It is assumed that the negligible risk level (NRL) of a substance provides complete protection for an ecosystem and it is generally taken as 1% of the MRL. Risk assessment is based on (sub-) chronic toxicity data. However, they often have used an equilibrium partitioning method or extrapolation techniques due to the scarcity of data. The MRL's for cadmium and mercury for mussels are shown in Table 1 and are well below the upper limits for 'Class 1'. For so low concentrations of cadmium one can question the usefulness of the NRL.

There are not a great number of studies in the field where contaminants alone have been shown to have detrimental effects on organisms. The exceptions being generally cases of extreme contaminant emissions. It is worth mentioning that soft bottom or benthos surveys have been useful in reflecting moderate levels of metals in sediment (Rygg, 1984).

The use of **health limits** is a further method of assessing levels. Risk assessment for the consumption of seafood generally has guidelines quite different from spatial or trend assessment guidelines and often those assessing such data are in a separate governmental body than the other assessors. Hence, the combined assessment of health, spatial distribution and trends is not always feasible. Just the same, it may be useful in cases of extreme contamination to relate the concentrations found to the human consumption viewpoint. Table 1 shows examples of various health limits employed by various countries. These are not usually legally binding but represent guidelines on which the respective health authorities can act. Note that the limits are based on a fixed consumption rate and do not reflect local dietary conditions. If we were to calculate the local consumption rates of selected 'rural' and 'urban' communities in Norway the hazardous concentration levels would be considerably higher (cf., Table 1).

Comparison of contaminant concentrations to various limits give a rough assessment of the levels concerned. However, several barriers remain. There are many contaminants for which limits have not been established not to mention lack of international agreement for those contaminants where limits have been used. Moreover, where concentrations exceed given limits there has been a tendency to avoid classifying the degree of contamination both with regards to overconcentrations or the ecological consequences. There also might be some improvement by normalizing the data with respect to covariables that influence uptake (e.g. length, sex) before comparisons are made.

4. TEMPORAL TRENDS

So far we have looked at comparing two concentrations, a measured value against a reference value (quartiles, 'background', health) to assess the level of contamination. But we can not progress far in determining the significance of the difference without considering statistics. The same principles apply whether one is looking at temporal trends or spatial gradients. Consider two data sets A and B (Fig. 3, first case). The means may be far apart but an F-test from analysis of variance (ANOVA) show that they are not significantly different. because of the spread of data about the mean. This spread is often illustrated by calculating the 95% **confidence intervals** (CI) for the data set (see e.g., Elliot, 1977). Usually when the CI's overlap, the two data sets are not significantly different but as shown in Figure 3 there are exceptions. As an alternative, Nicholson (1985) suggests using **confidence bands** where, if the bands overlap, the two data sets are always not significantly different regardless of variation in sample count. If they do not overlap then you can be certain they are significantly different if the count in each sample is the same. If the confidence limits do not overlap, the samples are always significantly different.

- significant differences exist in the slopes of linear relationships between contaminant and biological variables
- mean concentrations adjusted for biological effects differ between years
- there is evidence of a linear trend
- if yes, the linear trend is a reasonable summary of the between year difference in the adjusted mean log concentrations

The results from the three model approach may be presented in tables giving some of the most important information on data quality, trends/ fluctuations, residual standard deviation etc. (Table 2, ICES, 1991) or in figures for specific stations (Fig. 5, ICES, 1991) or summary-trends for large regions (JMG, 1991). The six model approach has been done on ICES fish muscle contaminant data up to and including 1985 (Fig. 6, ICES 1989).

Though these approaches are robust and a good means for initial approach to assessment there remains some relevant criticism. The approaches do not take into account the possible synergistic/antagonistic effects of other contaminants, a problem repeatedly discussed at WGSAEM but as yet without a viable alternative. Also, in long term studies the trends are seldom linear. Are the changes measured reflecting natural variation in the fish due to unknown/unmeasured factors or variation in anthropogenic loads?. Furthermore, in practice there is often difficulty to interpret fish length-concentration relationships even when length stratified requirements are met. WGSAEM has recently considered doing the assessment on 'large' and 'small' fish in order to avoid this problem (in other words remove length as a covariate).

5. MORE EXAMPLES

The Ranfjord is a 70 km long and narrow fjord in the north of Norway (14EE, 66.3EN). It has several basins varying in depth between 200-500 m. Undersea landslides and consequent turbidity currents are not uncommon along the steep rim of these basins. Tidal amplitude is normally 1-2 m. The freshwater discharge into the head of the fjord has an annual mean of about 300 m³/s but often reaches about 600 m³/s during the spring thaw. Surface water (0-5 m) of the inner fjord has a salinity normally about 3-15. The underlying seawater salinity varies between 30 and 34. Surface temperatures during the winter are near or below freezing and during the summer can vary between 10-15EC.

The major anthropogenic perturbances are contaminant pollution (PAH and metals) and discharge of inert mining trailings (recently about 2 million tons annually) from mining/smelter industries during the past 3-6 decades. The municipal discharge from about 25000 residents in Moi Rana may cause some eutrophication at the head of the fjord.

The closing of the smelter works and some mining industries by 1989-90 resulted in a 70-90% reduction of contaminant discharge.

Table 2

Example of results from a three-model approach to temporal trend assessment -
summary of results of statistical analysis of mercury data (ICES, 1991).

Mercury					Yearly geometric means (mg kg ⁻¹ wet weight)											Trend evaluation results				
SPEC	IAREA	JMPAR EA	CTRY	TIS	78	79	80	81	82	83	84	85	86	87	88	QLF	TRND	FLC	RLSD %	Notes
GADU	31F2	J01	B	L						0.039	0.019	0.032	0.044	0.055	0.032		-	yes	34.7	
PLAT	31F2	J01	B	L						0.121	0.116	0.160	0.101	0.154	0.144	1	-	-	44.6	
MYTI	27E9X	J10	FR	W				0.045	0.039	0.039	0.052	0.036	0.040	0.049	0.060		-	-	21.2	
MYTI	27F0X	J10	FR	W		0.056	0.026	0.042	0.045	0.047	0.039	0.036	0.036	0.038	0.036		-	yes	13.6	
MYTI	31F2	J01	B	W		0.021	0.067	0.058	0.035	0.030	0.037	0.037	0.024	0.047	0.047		-	yes	16.3	1
MYTI	31F3	J22 2 2	NL	W								0.040	0.047	0.025	0.038	1	-	yes	18.7	
MYTI	35F6	J12	FRG	W							0.038			0.125	0.028	1	-	yes	27.8	1
MYTI	36F6	J25 2 2	NL	W								0.030	0.036	0.017	0.043	1	-	yes	26.3	1
MYTI	36F8	J13 2	FRG	W									0.142	0.142	0.225	1	up	-	25.4	
MYTI	47F99	J26 71A	N	W					0.069	0.048	0.039	0.049	0.047	0.018	0.037		down	yes	20.0	
MYTI	47G04	J26 35A	N	W				0.040	0.024	0.018	0.014	0.017	0.026	0.010	0.036		-	yes	34.8	
MYTI	47G06	J26 36A	N	W				0.030		0.012	0.009	0.019	0.026	0.011	0.026	1	-	yes	28.2	
MYTI	48G06	J26 31A	N	W				0.035		0.015	0.024	0.020	0.031	0.011	0.022	1	-	yes	19.9	
MYTI	48G07	J26 30A	N	W							0.021	0.016	0.028	0.011	0.029		-	yes	31.4	
MYTI	55F97	J65 84A	N	W							0.011	0.018	0.017	0.009	0.030		-	-	44.6	
MYTI	55G01	J65 82A	N	W							0.009	0.021	0.026	0.011	0.030	1	-	yes	15.3	1
MYTI	43G1	J34	S	W				0.015	0.012	0.017	0.017	0.017		0.010	0.014		down	yes	29.1	
MYTI	46G1	J33	S	W			0.009	0.022	0.017	0.024	0.021	0.057	0.009	0.022	0.020	1	up	yes	36.8	

Table 3

Example of experimental study that show overconcentrations (relative to control) of aromatic hydrocarbons (THC in water and PAH in mussels) and copper in seawater and blue mussels (from Widdows and Johnson, 1988).

concentration	seawater		blue mussels	
	THC	Cu	PAH	Cu
control	1	1	1	1
low	2.1	1.6	5.6	2.2
medium	10.5	10	20.7	3.7
high	41.5	40	9.7	8.1

Table 4

Overconcentrations of metals in seawater (unfiltered) and mussel (from Knutzen and Skei, 1991).

matrix	station	Hg	Cd	Pb	Zn	Cu
seawater	B2	50	240	260	3200	50
	B4	2	22	24	230	9
	B7	1.5	16	14	180	7
blue mussel	B2	7	26	17	3.5	<1
	B4	3.5	23	11	4	<1
	B7	2	18	7	3	<1

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ANNEX

Raw data and statistics for illustrating the use of confidence intervals or confidence bands.

ROW	A	B	B*4	B*16	B+0.02	B+0.10
1	0.06	0.07	0.07	0.07	0.09	0.13
2	0.05	0.12	0.12	0.12	0.14	0.18
3	0.07	0.02	0.02	0.02	0.04	0.08
4	0.01	0.18	0.18	0.18	0.20	0.24
5	0.06	0.11	0.11	0.11	0.13	0.17
6			0.07	0.07		
7			0.12	0.12		
8			0.02	0.02		
9			0.18	0.18		
10			0.11	0.11		
11			0.07	0.07		
12			0.12	0.12		
13			0.02	0.02		
14			0.18	0.18		
15			0.11	0.11		
16			0.07	0.07		
17			0.12	0.12		
18			0.02	0.02		
19			0.18	0.18		
20			0.11	0.11		
21				0.07		
22				0.12		
23				0.02		
24				0.18		
25				0.11		
26				0.07		
27				0.12		
28				0.02		
29				0.18		
30				0.11		
31				0.07		
32				0.12		
33				0.02		
34				0.18		
35				0.11		
36				0.07		
37				0.12		
38				0.02		
39				0.18		
40				0.11		

	N	MEAN	MEDIAN	TRMEAN	STDEV	SEMEAN
A	5	0.0500	0.0600	0.0500	0.0235	0.0105
B	5	0.1000	0.1100	0.1000	0.0596	0.0266
X	5	0.1600	0.1700	0.1600	0.0596	0.0266
B*4	20	0.1000	0.1100	0.1000	0.0547	0.0122
B*16	40	0.10000	0.11000	0.10000	0.05397	0.00853
B+0.02	5	0.1200	0.1300	0.1200	0.0596	0.0266
B+0.10	5	0.1600	0.1700	0.1600	0.0596	0.0266
	MIN	MAX	Q1	Q3		
A	0.0100	0.0700	0.0300	0.0650		
B	0.0200	0.1800	0.0450	0.1500		
X	0.0800	0.2400	0.1050	0.2100		
B*4	0.0200	0.1800	0.0700	0.1200		
B*16	0.02000	0.18000	0.07000	0.12000		
B+0.02	0.0400	0.2000	0.0650	0.1700		
B+0.10	0.0800	0.2400	0.1050	0.2100		

AND SO... WHAT ACTION DO WE TAKE?

by

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1. REGULATORY ACTION

Most of the regulatory action is issued by the Norwegian Pollution Control Authority (SFT). Examples of recent action are given in Table 1. Even though action has been taken it has not always been effective. This has been revealed through monitoring. For example DDT has been prohibited since 1970 but still high concentrations are found in the Sør fjord region (Fig. 1). DDT containing insecticide was commonly used in the fruit orchard farms of the fjord area. Are the farmers still using the prohibited chemical? Is there still large quantities in the soil that gradually are being leached into the sea?

Restriction on the use of TBT have been applied since 1989, however, a team of Scottish scientists using imposex registration in dog whelk (*Nucella lapillus*) found signs of elevated levels (Fig. 2). TBT has been prohibited since 1989 with the exceptions of boats over 25m, aluminum boats, or light metal structures below the water line. Is the legislation not strict enough? Is it too early to see the effects? Is there any question as to the validity of the tests?

The concentrations of certain contaminants in nine fjord areas are so high that the Norwegian Food Control Authority (SNT) have issued restrictions on the **sale** and **warnings** on the consumption of certain seafoods in these areas (pers.comm., K.Færder, SNT). For example, the warnings for Sør fjord and adjacent Hardanger fjord are: not to eat mussels or flounder liver from the Sør fjord, eat only "moderate" quantities of mussels from the Hardanger fjord, do not eat more than two meals of "bottom dwelling" fish per week and not more than one meal per week of cod liver from Sør fjord.

2. REMEDIAL ACTION

Skei (1992) argues that as the discharge of contaminants is reduced (through legislative control, increased public awareness, etc.) there will be a greater problem of secondary pollution, i.e. the flux of contaminants from contaminated sediment/waste-deposits into the water column.

There are five primary ways in dealing with this (cf., Skei, 1992):

- **dredging** and disposal of the dredged material in a confined area;
- **incineration** (in cases of small amount and high toxicity);
- various **capping** techniques (sand, fly ash, cement, membranes, etc.);

- **fixation** by adding of chemical (chemical immobilization/solidification);
- **reduction of mobility** of critical compounds by changes of pH/redox conditions.

Table 1

Examples of action taken by the Norwegian State Pollution Control Authority (SFT) for certain contaminants (revised from SFT, 1992).

Contaminant	Source/product	Action taken
Hg	Amalgam, thermometers, batteries	Obligatory amalgam-cleaning treatment at dental offices by 1992. Sale of mercury thermometers prohibited
Cd	Corrosion inhibiting anodes on sea structures, batteries, plastic stabilizers and dyes, artificial fertilizers	Controlled deposit of wasted rechargeable cadmium-batteries. Reduce the use of cadmium in plastic products.
Cu	Antifouling paints and treatment of fishing nets	Regulation of use and discharge
Zn	Sea structure anodes,	Prohibited use of zinc-containing anodes by 1995
Pb	Traffic, batteries, gun-shot	Considering increase tax on lead-containing gasoline. Improve control of deposit of wasted batteries. Restrictions on use of lead-shot
TBT	Antifouling paint and fishing nets and wood treatment products.	Reduce discharge of TBT compounds
DDT	insecticides	Prohibited since 1970

Each method has its pros and cons. In the Minamata Bay where 150 tonnes of mercury was discharged during the 40's, the dredging alternative was chosen at a cost of 92 million US dollars (1978) of which the polluter was obliged to pay 65% of the cost (Ishikawa and Ikegaki, 1980).

The actual process of dredging may only aggravate the problem by mobilizing contaminants, at least on a short term scale (Förstner, 1987). Furthermore, there is a risk of seepage of contaminants into the water table or sea at the relocation dump site. In the Sørfjorden, West Norway, the capping alternative was chosen (Skei, 1992). The inner fjord seabed had concentrations exceeding 10% Zn and 0.9% Pb. The capping incorporated three techniques: a permeable membrane, a 30cm layer of shell sand and a piled wall

enclosing the most contaminated area. The permeable membrane would theoretically allow some diffusion of gases and, hence prevent gas formation, but would not lead to a large flux of contaminants. The shell sand layer would allow for diffusion better than more clayey material, and it is thick enough to allow normal recolonization of the area, protect the membrane and serve as an absorption zone for any contaminants that might have leaked through the membrane. The wall protects the cap from erosion by storms or wave action.

3. PRECAUTIONARY PRINCIPLE

The current debate around the precautionary principle strikes at the heart of the enigma for improved local and global environmental quality. The traditional approach to pollution control has been not to impose regulation without sufficient scientific evidence that the emissions are harmful. The precautionary approach is to impose regulation without sufficient evidence of harmful effects. An important example of the latter was the agreement for 50% reduction in nutrient inputs to the North Sea agreed at the Ministerial Conference for the North Sea in 1987 and reconfirmed in 1990. This political decision has limited scientific foundation but obviously infers large consequences especially to industries, farmers and municipalities.

Peterman and M'Gonigle (1992) liken these approaches to the judicial equivalents that a man is innocent until proven guilty (the traditional approach) or he is guilty until proven innocent (the precautionary principle). In the former case we attempt to reduce the number of innocent imprisoned but face the problem that more guilty people go free. The statistical parallel of this is minimizing the chance of committing a Type I error (rejecting null hypothesis when it is true). But with a reduction in the chance of committing a Type I error there is a corresponding increase in the chance of committing a Type II error (accepting the null hypothesis when it is false). We can not have one without the other. Hence, in more extreme applications of the precautionary principle we maximize a Type I error and minimize a Type II error which would have the consequence of putting considerable burden on industry to show proof of innocence. Whereas, in the traditional approach "environmentalists" have often enormous problems to show proof of guilt even though the effects may seem evident to almost everyone. The traditional approach has lead to what Peterman and M'Gonigle have termed a **permissive regulatory system**. By enhancing the chances of committing a Type II error we may experience detrimental and perhaps irreversible effects far more serious and more encompassing than the original problem.

Peterman and M'Gonigle (1992) further argue that the problems encountered by these approaches underline the need for improved regulatory procedures. This is especially relevant considering the increasing number and severity of surprise effects of human activities and difficulty in demonstrating causal effects scientifically which undermines possible legal action. One alternative, they point out, is the reduction in the use of potentially harmful wastes. Examples of this are the Oslo Commission's 'Prior Justification Procedure' and the American 'Massachusetts Toxics Use Reduction Act' which are remedies more oriented towards the production processes than end-of-pipe emissions. This new alternative they term **preventative design**.

But monitoring programmes focus on end-of-pipe effects and hence, it is important that investigators (scientist and policy makers alike) have a clear concept of the statistical power of the methods they employ. They should know what is the minimum change that is detectable by the method chosen. Peterman and M'Gonigle (1992) point out that conclusions about safety or no effect are associated with an agreed level of statistical power.

4. IMPROVEMENT OF MONITORING DESIGN

During the course of this workshop there has been considerable emphasis placed on the importance of selecting goals, agreeing on and following guidelines and rational approach to assessment of the data material.

It is evident that we do not have the resources to monitor just for the sake of monitoring. There is an ever increasing competition for limited funds compounded by the increasing costs of fieldwork and chemical analyses in order to obtain high quality data. It is paramount that we have a clear grasp of the purposes of the work and realize the statistical power of our methods in order to know what changes are detectable. It is perhaps important at this point to review some positive aspects of monitoring. Monitoring can be:

- Related to known/accepted limits such as for health risk or "reference"
- Related to known changes in inputs (eg. local discharges)
- Related to other matrices (sediment, seawater)
- Used to trace a source of contamination by establishing a gradient
- Used to create a basis for immediate action
- Give authorities important feedback on consequences of remedial action.

Improved monitoring is needed and the guiding light should be **KISS** - Keep It Simple (Stupid)!. It is my impression that the ambition level of many monitoring programmes generally far exceeds the ability to reach the goals. This goes for the North Sea area as well as the Mediterranean. A simple robust programme carried out by all participating countries not only provides a good data base (high quality, easier assessments) but while doing so necessitates an improved infrastructure into which all countries can actively participate.

One step to simplify spatial distribution of contaminants would be to reduce the monitoring species to a few that are widely distributed such as the Mediterranean mussel (*Mytilus galloprovincialis*) and red mullet (*Mullus barbatus*). It is self evident that the large number of species monitored as shown in Table 2 only make the problem of assessment more complex. However, with just a few selected species some areas may go unmonitored.

Table 2

Some Mediterranean organisms used in contaminant monitoring (from Jeftić *et al.*, 1990). H=Hg (Tab.19), P=PCB, D=DDT or derivatives (Tab.24). Monitoring organisms used in MED POL Phase II are shown in bold print (Jeftić *et al.*, 1990; UNEP, 1989). The different regions of the Mediterranean are indicated in roman numerals.

Species		I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
<u>Engraulis encrasicolus</u> (European anchovy)	fish		H		H		H						
<u>Mullus barbatus</u> (red mullet)	fish		HPD	H	HPD	HPD	H	H	HPD	HPD	PD		H
<u>Mullus surmuletus</u> (striped red mullet)	fish		H		PD	PD				H		H	
<u>Mytilus galloprovincialis</u> (Mediterranean mussel)	biv.		HPD		HPD	HPD	H		HPD	H		H	H
<u>Nephrops norvegicus</u> (Norwegian lobster)	crus.		H		HP		H						
<u>Sarda sarda</u> (atlantic bonito)			H										
<u>Thunnus thynnus</u> (tuna)	fish		HD		H				HD			H	
<u>Xiphias gladius</u> (swordfish)	fish		H	H					H				
<u>Perna perna</u>													
<u>Thunnus alalunga</u> (albacore)	fish						H						
<u>Lithophaga lithophaga</u>	biv.							H					
<u>Trachurus mediterraneus</u> (Med. horse mackerel)	fish							H	H		H		H
<u>Carcinus mediterraneus</u>	crus.		PD			PD			HD	D	PD		
<u>Merluccius merluccius</u> (European hake)	fish								H	H			H
<u>Mugil auratus</u> (grey mullet)	fish								H	H			
<u>Mugil cephalus</u> (grey mullet)	fish								H	H			
<u>Penaeus kerathurus</u> (caramote prawn)	crus.								H	H			
<u>Boops salpa</u> (salema)	fish									H			
<u>Upeneus moluccensis</u>										H	H		
<u>Boops boops</u> (bogue)	fish									H			
<u>Dentex dentex</u> (common dentex)	fish									H			
<u>Dentex gibbosus</u> (dentex)	fish									H			
<u>Donax trunculus</u>	biv.									H			
<u>Epinephelus aeneus</u> (white grouper)	fish									H			
<u>Pagellus acarne</u> (axillary seabream)	fish									H			
<u>Pagellus erythrinus</u> (common pandora)	fish									H			H
<u>Surida undosquamis</u>											H		
<u>Sphyrna sphyraena</u>	fish										H		
<u>Parapenaeus longirostris</u> (shrimp)	crus.		D						PD	PD	PD		H
<u>Diplodus sargus</u> (white seabream)	fish										H?		
<u>Lithognathus mormyrus</u> (striped seabream)	fish										H?		
<u>Mactra corallina corallina</u>	biv.										H?		
<u>Mactra corallina stultorum</u>	biv.										H?		
<u>Arcularia gibbosula</u>	gas.										H?		
<u>Macropipus depurator</u>	crus.										H?		
<u>Sardina sp.</u> (pilchard)	fish										H?		

The North Sea Task Force - Quality Status Report (NSTF - QSR) has been suggested as a good way to assess a particular region. The principle of a concentrated short-term effort has an appealing tone to

policy makers and it tends to induce extra effort by the participants. The goals of the NSTF required the knowledge of many different sciences and hence, was bound to be more holistic touching on processes that steer the ecosystem. This approach however, does require a fairly good infrastructure and positive international atmosphere. These problems may be partly circumvented by incorporating fewer laboratories/institutions covering larger regions and devoting more effort to ensure that these have been intercalibrated and use GLP.

5. THE FUTURE OF MONITORING IN BIOTA

Even with stricter controls on the emissions of pollutants it is evident that some degree of monitoring will be necessary in order to control regulatory action and accommodate public pressure. However, it is unlikely that monitoring alone will be the only basis for regulatory action. The following observations can be made:

- a) Continued monitoring will provide better estimates of "background" levels from which a system of quality criteria may be improved.
- b) There is definitely a need for better data on emissions; both on the amount and composition and how these vary in time and geographically. Without this information it is nearly impossible to convince anyone of dose-response relationships.
- c) There is also a need to know what form these pollutants are in when they come into contact with the target organism. The water phase of contaminants is important for uptake in seaweeds, whereas also the particle phase is important for mussels and concentrations in prey species may be the determining factor for most fish species.
- d) In this respect there is a need to develop/improve analytical methods for other compounds such as: Toxaphene, PCN, PCP, PBDE and metabolized products of PAH or compounds that we know are associated with, for example PAH and make it harmful.
- e) There is further need to know the fate of the emissions with respect to areas of deposition such as sediment or deep water masses.
- f) We need to know more about the biochemistry of contaminants in the organisms we monitor; accumulation rates, storage/release, mobility under different life-stages or conditions.
- g) There is a pressing need to know what effects these changes have on the organism (behavioural studies, LC₅₀, Maximum Permissible Risk Level etc.). What are the damaging affects on the organisms themselves such as reduced reproduction or genetic "drift"?
- h) On a community level it is important to know how the contaminant functions at different trophic levels in the food chain.
- i) Because many people are interested in the health aspect of monitoring there is a need for improved risk assessments for example through toxicological feeding experiments. The problem might be formulated otherwise: at what contaminant level is monitoring irrelevant such as for PAH?

- j) We should be aware that remedial or regulatory action may also have positive side effects like reducing the particle load, reducing sedimentation or improving light conditions.
- k) Because it is often difficult to observe effects on a community level the chemical/behavioural study of selected smaller "key monitoring species may be a far better approach.
- l) Finally, the quality of our environment is not the sole responsibility of politicians, scientists or activists. What environmental standards are we, as a society, willing to accept?

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