

# **ICES COOPERATIVE RESEARCH REPORT**

**RAPPORT DES RECHERCHES COLLECTIVES**

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## **REPORT OF THE ICES ADVISORY COMMITTEE ON THE MARINE ENVIRONMENT 1995**

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# MEMBERS OF THE ADVISORY COMMITTEE ON THE MARINE ENVIRONMENT

1994/1995

| Member                      | Alternate Member    | Affiliation                                      |
|-----------------------------|---------------------|--|
| Dr (Ms) K. Richardson       |                     | Chairman   |
| Mr S. Carlberg              |                     | Chairman, Marine Environmental Quality Committee |
| Dr M. Reeve                 |                     | Chairman, Biological Oceanography Committee      |
| Dr H. Loeng                 |                     | Chairman, Hydrography Committee                  |
| Dr R.H. Cook                |                     | Chairman, Mariculture Committee                  |
| Dr M. Héral                 |                     | Chairman, Shellfish Committee                    |
| Dr H. Benke*                |                     | Chairman, Marine Mammals Committee               |
| Dr R.M. Cook*               |                     | Chairman, Statistics Committee                   |
| Dr K. Cooreman              | Mr P. Roose         | Belgium  |
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| Mr J. Ólafsson              |                     | Iceland  |
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| Dr (Ms) J. McDowell Capuzzo | Dr H. Windom        | United States of America                         |
| Dr (Ms) J. Pawlak           |                     | ICES Environment Secretary                       |
| Dr H. Dooley**              |                     | ICES Oceanography Secretary                      |
| Dr R.C.A. Bannister**       |                     | Chairman, Consultative Committee                 |

\*Invited Committee Chairman.

\*\*Participated part-time.

All countries were represented by *Members* except Denmark (represented by *Alternate Member*) and the United States (*not represented*).

## Also participating in the meeting or portions thereof:

|                       |                                   |
|-----------------------|-----------------------------------|
| Ms E.-L. Poutanen     | HELCOM Environment Secretary      |
| Dr J.-P. Rebert       | Director, IOC GOOS Support Office |
| Mr B. van de Wetering | OSPAR Executive Secretary         |
| Ms M. Karlson         | ICES Environment Assistant        |
| Mr J.-R. Larsen       | ICES Environment Data Scientist   |
| Ms M. Sørensen        | ICES Environment Assistant        |

## EXECUTIVE SUMMARY

The ICES Advisory Committee on the Marine Environment (ACME) met from 26–31 May 1995 at ICES Headquarters in Copenhagen. As part of its work during this period, the ACME prepared responses to the requests made to ICES by the Oslo and Paris Commissions and the Helsinki Commission. This report contains these responses. In addition to responses to direct requests, some sections of this report summarize the deliberations of ACME on topics for which advice was not directly requested but for which the ACME felt that there was information that would be of potential interest to the Commissions, ICES Member Countries, and other readers of this report.

### Information in direct response to requests from, or which is relevant to, the work of both the Oslo and Paris Commissions and the Helsinki Commission

#### Monitoring

##### *General comments on the design and implementation of international monitoring programmes*

During its 1995 meeting, the ACME reviewed plans for the new OSPARCOM Joint Assessment and Monitoring Programme (JAMP) and the further development of the HELCOM Baltic Monitoring Programme (BMP) and Coastal Monitoring Programme (CMP). On the basis of this review, the ACME agreed that the following general comments should be transmitted to the two Commissions.

International monitoring programmes and baseline studies need to be carefully designed and streamlined in order to address the environmental issues in question. Consequently, there is no need for such programmes to be identical in all regions or subareas, but there is a clear need for a firm lead in the planning and implementation of the activities.

It is essential that countries that have agreed to cooperate in such programmes provide sufficient resources and also make other relevant administrative arrangements.

In this particular context, a successful cooperation requires that the international agreement is given priority over other plans of a purely national character. Consequently, the establishment or revision of national monitoring programmes must never disregard the requirements identified or agreements achieved in the international cooperation.

##### *Specific topics covered by ACME*

A major topic of the 1995 ACME meeting was the review of a strategy for the incorporation of biological effects monitoring into an overall marine monitoring programme, with emphasis on the coordination of measurements of biological effects and contaminant concentrations in the same organism or at least in organisms from the same area and population. A document was considered and approved which describes an integrated strategy for biological monitoring in relation to the more traditional chemical monitoring, including strategies for determining the causes of biological effects observed. This document also contains a table of techniques presently or soon to be available for monitoring purposes. This strategy document appears as Annex 1 in this report and will serve as a basic document for the OSPARCOM/ICES Workshop on Biological Effects Monitoring in October 1995.

This report also contains further information on biological effects monitoring techniques to determine the toxicity of sediments and sediment pore water (Section 5.2). These techniques are particularly relevant to determining sediment quality and the potential development of sediment quality objectives. In addition, further information is provided on the use of statistics in planning monitoring programmes (Section 4.3) and examples are given of the statistical power of detecting temporal changes in concentrations of various contaminants in several species of organisms. Some information is also provided on monitoring anthropogenic nutrient inputs ("cultural eutrophication") and their possible effects on changing nitrogen/phosphorus (N/P) ratios (Section 5.8).

Given that both OSPARCOM and HELCOM are in the process of reviewing and revising their monitoring programmes, the ACME conducted a review of existing ICES monitoring guidelines; the results are contained in Section 5.4 of this report.

#### Quality Assurance and Intercomparison Exercises

The ACME reviewed the results of quality assurance related activities conducted during the past year and provided brief summaries of this work in Section 6.

## **Overviews of Contaminants in the Marine Environment**

The ACME considered information on low molecular weight chlorinated alkanes and benzene and alkylated benzenes in terms of their roles as contaminants in the marine environment. These overviews appear as Annexes 4 and 5, respectively, in this report.

### **Report sections responding to requests specific to the Oslo and Paris Commissions**

#### **Assessment Tools**

The ACME reviewed, as requested, the document “Background Concentrations of Natural Compounds”, which was prepared by a North Sea Task Force Workshop. This review appears in Section 12.1. In addition, the ACME reviewed the work on ecotoxicological reference values published by OSPARCOM in 1994 and provided advice on the problems encountered with the use of these values for retrospective evaluation of contaminants data (Section 12.2).

#### **Data Handling**

The annual review of data handling activities relevant to OSPARCOM requirements by the ICES Environmental Data Bank, including the development of a quality assurance (QA) database, is contained in Section 17 of this report.

### **Report sections responding to requests specific to the Helsinki Commission**

#### **Fish Diseases**

Section 8.3 contains a summary of knowledge pertaining to fish diseases and their prevalences in the Baltic Sea. In addition, Section 8.2 identifies major issues related to studies of fish diseases and parasites in the Baltic Sea that should be addressed by future research programmes. Further information on the M-74 syndrome in Baltic salmon is contained in Section 7.4 of the report.

#### **Information on concentrations of contaminants that are “not harmful to man or nature”**

This problem is briefly dealt with in Section 12.3 of this report. The ACME suggests, however, that the practice of dealing with individual contaminants and their concentrations in, and/or effects on, the environment is not consistent with our current understanding of the marine ecosystem and processes occurring within it. Therefore, the ACME recommends that HELCOM address the problem of “acceptable” levels of contaminants from an ecosystem perspective rather than attempting to assign concentration levels of individual contaminants as not harmful.

### **Information on topics of general interest**

#### **Dredging of Marine Aggregates**

To follow up the Guidelines for the Preparation of Environmental Impact Assessments of Marine Aggregates Dredging approved by ACME last year, the 1995 ACME report provides advice on environmental effects monitoring programmes that should be designed to confirm limitations on anticipated, significant negative physical and biological effects as predicted by the Environmental Impact Assessment prepared for a given extraction project (Section 15).

#### **Environmental Interactions of Mariculture**

In anticipation that there will be considerable interest in issues related to the environmental impacts of mariculture in coming years, the ACME has provided a summary of ten years of work within ICES on this topic. This is contained in Section 14, which gives general information on the types of issues that have been handled and new directions for this work in the relevant ICES Working Group.

#### **Code of Practice on the Introductions and Transfers of Marine Organisms**

The ACME made some small amendments to the Code as accepted and published by the ACME in 1994. The main amendment had to do with the definition of “genetically modified organism (GMO)” (see Section 13.1). The ACME once

again emphasizes the importance of following this Code of Practice when introductions or transfers of marine organisms are carried out (i.e., for aquaculture or stock enhancement purposes).

### **Major Environmental Issues**

The ACME prepared an annotated list of major environmental issues that should serve as a basis for scientific work coordinated by ICES over the next decade. This list appears in Section 16.

### **Sources of information considered by the ACME at its 1995 Meeting**

At its 1995 meeting, the ACME considered, *inter alia*, the most recent report of the following ICES groups:

|         |   |
|---------|---|
| BEWG    | Benthos Ecology Working Group   |
| MCWG*   | Marine Chemistry Working Group  |
| SGBSC   | Steering Group for the Coordination of the Baseline Study of Contaminants in Baltic Sea Sediments |
| SGM74   | Study Group on the Occurrence of M-74 in Fish Stocks  |
| SGQAB   | ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea      |
| SGQAC   | ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea        |
| WGBAST  | Baltic Salmon and Trout Assessment Working Group  |
| WGBEC*  | Working Group on Biological Effects of Contaminants   |
| WGBME   | Working Group on the Baltic Marine Environment  |
| WGEAMS* | Working Group on Environmental Assessment and Monitoring Strategies                               |
| WGEXT   | Working Group on the Effects of Extraction of Marine Sediments on the Marine Ecosystem            |
| WGEIM   | Working Group on Environmental Interactions of Mariculture  |
| WGITMO* | Working Group on Introductions and Transfers of Marine Organisms                                  |
| WGMS*   | Working Group on Marine Sediments in Relation to Pollution  |
| WGPDMO  | Working Group on Pathology and Diseases of Marine Organisms                                       |
| WGPE    | Working Group on Phytoplankton Ecology  |
| WGSDEM  | Working Group on Statistical Aspects of Environmental Monitoring                                  |

\*These groups report directly to ACME

Reports of the following other activities were also considered:

Joint Meeting of the Working Group on Biological Effects of Contaminants and the Working Group on Marine Sediments in Relation to Pollution

Joint Meeting of the Working Group on Environmental Assessment and Monitoring Strategies and the Working Group on Statistical Aspects of Environmental Monitoring

ICES/HELCOM Workshop on Temporal Trend Assessment of Data on Contaminants in Biota from the Baltic Sea



## **1 INTRODUCTION**

The Advisory Committee on the Marine Environment (ACME) is the Council's official body for the provision of scientific advice and information on the marine environment, including marine pollution, as may be requested by ICES Member Countries, other bodies within ICES, and relevant regulatory Commissions. In handling these requests, the ACME draws on the expertise of its own members and on the work of various expert ICES Working Groups and Study Groups. The ACME considers the reports of these groups and requests them to carry out specific activities or to provide information on specific topics.

The ACME report is structured in terms of the topics covered at the ACME meeting on which it has prepared scientific information and advice; the topics include both those for which information has been requested by the Commissions or other bodies and those identified by the ACME to enhance the understanding of the marine environment. Information relevant to the Commissions' requests and specific issues highlighted by the ACME for their attention are summarized in Sections 2 and 3, where the individual work items from each Commission are listed and related to relevant sections of the main text.

## 2 PROGRESS ON TASKS FOR THE OSLO AND PARIS COMMISSIONS, INCLUDING AUTOMATIC DATA PROCESSING OF JMP DATA

### 2.1 Progress on Tasks on the 1995 Work Programme

A summary of the progress on the 1995 programme of work requested by the Oslo and Paris Commissions is given below, along with reference to the relevant sections and annexes of the report where more detailed information may be found. This summary is provided according to the format of the Work Programme, with the headings and questions on the Work Programme shown in *italics* and a summary of the ACME advice below in normal print.

#### SCIENTIFIC ADVICE

##### 1 *Monitoring Techniques*

- 1.1 *to draw up a list of organic contaminants which can be monitored in biota and sediments on a routine basis and to advise on quality assurance measures for these contaminants;*

Section 6.6 of this report contains a list of organic contaminants that can be monitored on a routine basis in biota and sediments at least by specialist laboratories and, for several groups of contaminants, by a broader range of laboratories. This updates preliminary information that was provided in Section 6.8 of the 1994 ACME report.

Advice on relevant quality assurance procedures for some of the groups of contaminants covered in Section 6.6 is provided in Section 6.7. This covers mainly chlorobiphenyls and polycyclic aromatic hydrocarbons.

- 1.2 *to identify suitable organisms for spatial monitoring of contaminants in biota;*

In Section 5.3 of this report, the ACME has provided information on the use of seabird eggs for monitoring the spatial distribution of contaminants in biota. This follows the criteria, and supplements the information, contained in Section 5.1 of the 1994 ACME report.

- 1.3 *to elaborate guidelines for the use of recommended techniques for biological effects monitoring and to identify information on possible new techniques;*

A major strategy for the incorporation of biological effects measurements in an integrated monitoring programme for marine contaminants is presented in Section 4.1 and Annex 1 of this report. This strategy integrates biological and chemical components to obtain

an overall awareness of environmental quality in relation to issues of concern. The use of a selection of biological techniques directed at issues of concern is advocated, and the suite of techniques chosen should represent a range of levels of biological organization and representative species of natural communities.

In Section 5.2, guidelines are provided on the use of recommended techniques for biological effects monitoring, primarily with regard to measurements of EROD induction and acetylcholinesterase inhibition. This section also provides information on possible new techniques for biological effects monitoring, particularly some new molecular techniques that appear to be promising. The information in Section 4.2 is also relevant to the application of the overall biological effects strategy document.

- 1.4 *to update existing monitoring guidelines;*

Information relevant to the update of existing monitoring guidelines is contained in Section 5.4. This includes a revised table of spawning periods of finfish and shellfish species used in the OSPAR monitoring programme and information relevant to determining temporal trends in the main contaminants of interest to the Commissions in biota.

- 1.5 *to summarize new information on the relationship between inputs, concentrations and effects and to provide information on monitoring the effects of anthropogenic nutrients inputs as well as on possible effects of changing N/P ratios;*

Some information on monitoring the effects of anthropogenic nutrient inputs and the possible effects of changing nitrogen:phosphorus ratios is provided in Section 5.8 of this report. Feedback from relevant OSPAR bodies on this section would be useful to assist ACME in knowing what additional information is required on this topic.

## 2 QUALITY ASSURANCE

- 2.1 *to consider the need for an intercomparison exercise for measurements of lipids in marine samples;*

A summary of information on this topic is contained in Section 6.4 of this report. An intercomparison programme on lipid determinations is being conducted under the QUASIMEME project, but the most useful method employs chloroform for lipid extractions. As the production of chloroform may be banned under the

Montreal Protocol, work has begun on the development of alternative methods that do not require the use of chlorinated solvents.

### 3 ASSESSMENT TOOLS

- 3.1 *to review the Report on Background Concentrations of Natural Compounds and to supplement it with additional information, if available;*

Detailed comments on the Report on Background Concentrations of Natural Compounds are contained in Section 12.1 of this report.

- 3.2 *to identify further information relevant to the further development of ecotoxicological reference values;*

A discussion of the use of ecotoxicological reference values in retrospective evaluations of marine chemical monitoring data is contained in Section 12.2 of this report.

### 4 METHODOLOGIES

- 4.1 *to advise on the most appropriate means of monitoring to identify temporal trends under different hydrographic conditions, taking into account statistical requirements.*

Information on this topic, primarily based on statistical requirements, is presented in Section 4.3. Further work will need to be conducted to account for the influence of different hydrographic conditions. It would be useful for ACME, however, to receive some feedback from the relevant OSPAR bodies on the further development of this work.

### DATA HANDLING IN 1995

- 1 *To carry out data handling activities related to:*

- 1.1 *trend data for biota and sediments;*

- 1.2 *data on sea water;*

- 1.3 *data on biological effects;*

- 1.4 *the assessment by the AHWGM of temporal trend data for biota up to and including 1994;*

- 1.5 *to complement the database with information regarding, for example, the composition of relevant reference materials, consensus values in intercomparison exercises, results of such exercises and other appropriate data in order to facilitate an evaluation of the monitoring data.*

### 2.2 Handling of Data for the Oslo and Paris Commissions

The ICES Secretariat Environmental Data Bank has handled all data submitted in 1994, covering monitoring activities in 1993. However, possibly owing to a lack of assessment activities, the number of countries who submitted data has been very small. Only four OSPAR Contracting Parties submitted data in 1994: three submitted data on contaminants in biota, two submitted data on contaminants in sea water, and no data were submitted concerning sediments.

As a result of a decision by the Oslo and Paris Commissions in 1994, the 1994 AHWGM meeting was not held. The 1995 meeting of the OSPAR Environmental Assessment and Monitoring Committee (ASMO) decided that the AHWGM meeting in 1995 should consider monitoring guidelines, so the temporal trend assessment of contaminant concentrations in biota was postponed until 1997.

Further information on data handling activities, including the quality assurance (QA) database, is contained in Section 17 of this report.

### 3 PROGRESS ON TASKS FOR THE HELSINKI COMMISSION

The present status of work on 1995 requests by the Baltic Marine Environment Protection Commission (Helsinki Commission) is given below. The requests are shown in *italics* and a summary of the ACME advice is then given in normal print.

#### *Continuing responsibilities*

1. *To continue the work on evaluating the size of seal populations in the Baltic Sea and to assess their condition in relation to contamination;*

No information on this topic has been provided this year. The ICES Study Group on Seals and Small Cetaceans in European Seas will meet in December 1995, and it is anticipated that the 1996 ACME report will contain an update on the status of seal populations in the Baltic Sea.

2. *To provide information on "new contaminants", particularly those of special concern to the Baltic marine environment;*

Although they are not "new contaminants", this report provides overviews of two classes of contaminants in terms of their presence and significance in the marine environment: (1) chlorinated alkanes ( $C_1-C_3$ ), with a summary in Section 10.1 and details in Annex 4; and (2) benzene and alkylated benzenes, summarized in Section 10.2 with further details in Annex 5.

3. *To coordinate quality assurance activities on biological and chemical measurements in the Baltic Sea and report routinely on planned and ongoing ICES intercomparison exercises, and to provide a full report on the results;*

Summaries of the work conducted by ICES during the past year to coordinate quality assurance activities for biological and chemical measurements in the Baltic Sea are contained in Sections 6.1 and 6.3, respectively.

4. *To provide advice on further improvement of the BMP, particularly better sampling strategy and further improvement of the quality of the BMP data base;*

The ACME has reviewed the BMP on the basis of detailed reviews prepared by relevant working groups. Because much of the information and advice that could be provided overlapped other, somewhat more general advice, the ACME decided to draw attention to those more general sections of the ACME report that should be of use when revising the BMP. Particular attention should be given to the comments in Section 5.1.

A key piece of advice concerns a strategy for incorporating biological effects measurements in an integrated marine monitoring programme (see Section 4.1 and Annex 1). This strategy integrates biological and chemical components to obtain an overall awareness of environmental quality in relation to issues of concern. In Section 5.2, guidelines are provided on the use of several recommended techniques for biological effects monitoring. Section 4.2 is also relevant to the application of the biological effects strategy document, specifically in the context of sediment contamination.

This report also contains information on the incorporation of statistical considerations in a monitoring programme from the early planning stages (Section 4.3), organisms that can be used for monitoring spatial distributions of contaminants in biota (Section 5.3), and information relevant to the updating of monitoring guidelines (Section 5.4).

#### *Special studies*

5. *To coordinate the Baseline Study of Contaminants in Sediments 1993 and the compilation and review of results;*

A brief progress report on the Baseline Study of Contaminants in Baltic Sea Sediments is provided in Section 7.1 of this report.

6. *In cooperation with the Baltic Marine Biologists, to prepare a preliminary report on fish diseases in the Baltic Sea and to provide plans for future studies of fish diseases in the Baltic Sea;*

A brief overall report on fish diseases in the Baltic Sea is contained in Section 8.3 of this report; full information is contained in the chapter on fisheries described under item 7, below. In addition, information on diseases of Baltic fish is contained in Sections 8.1 and 8.2; the latter section also identifies major issues related to studies of fish diseases and parasites in the Baltic Sea that should be addressed by future research programmes. Flounder has been identified as the most useful species for fish disease/parasite monitoring purposes in the Baltic Sea and, taking account of the increasing effort to implement an integrated monitoring strategy combining both chemical and biological effects measurements on identical target species, the ACME has recommended that HELCOM reconsider the inclusion of flounder in the list of mandatory fish species for the BMP.

7. *To prepare a chapter on fisheries and fish stocks, including coastal species of fish, in the Baltic Sea, as well as a chapter on contaminants in marine sediments as a contribution to the Third Periodic Assessment;*

The chapter on fisheries and fish stocks comprises three sub-chapters: (1) commercial fish species, (2) coastal fish species, and (3) fish diseases and parasites. A draft sub-chapter on commercial fish stocks, prepared under the direction of the Chairman of the Baltic Fish Committee, was reviewed by the Advisory Committee on Fishery Management (ACFM) in May 1995; a draft sub-chapter on coastal fish stocks, prepared by the Baltic Marine Biologists, was received by ACFM during that meeting but not reviewed. The ACME reviewed the sub-chapter on fish diseases and parasites and accepted it for inclusion in the full chapter. The three sections will be compiled and edited, and thereafter reviewed by ACFM at its meeting in late October 1995 before being transmitted to HELCOM (see Section 7.2).

As also noted in Section 7.2, the ACME reviewed a draft version of a chapter on contaminants in Baltic sediments, based on results available from the Baseline Study of Contaminants in Baltic Sea Sediments. Additional data will be added and ACME will review the final draft in association with its Consultations Meeting in September 1995 before transmitting it to HELCOM.

8. *To provide advice on analytical methods and choice of matrices for the measurement of the presence of organotin compounds in the marine environment;*

Preliminary information on this topic is contained in Section 5.5 of this report.

9. *To provide advice on a strategy for incorporating biological effects monitoring in an integrated monitoring programme, and information on methods to determine the biological effects of contaminants, primarily on reproduction, immunology and metabolism of marine organisms, mainly fish;*

An integrated strategy for incorporating biological effects measurements in an overall marine monitoring programme is presented in Section 4.1 and Annex 1. Guidance on methods that can be recommended at the present time is included in Annex 1, Section 4.2 and Annex 2, and Section 5.2.

10. *To provide advice on whether the annual samples of fish for monitoring temporal trends of contaminants at individual sites can be reduced from the present 20–25 specimens, including an indication of the reduction in the power of the*

*programme associated with varying decreases in the number of specimens analysed;*

Information on calculating the power of a temporal trend monitoring programme is given in Section 4.3. An application of this method to a set of monitoring data is summarized in Section 5.4.4. Based on the fact that calculations have been conducted on only a very limited data set and that there is a need for better estimates of the variance components associated with time series data, no definitive advice on optimal sample size for temporal trend monitoring programmes can be provided at the present time.

The results of an assessment of temporal trends in contaminant concentrations in Baltic biota is contained in Section 7.3, along with a table indicating the power of the programme to detect changes of 5% and 10% per year over a ten-year period for a number of contaminants in the species monitored under the BMP.

11. *To evaluate the impact of different fishing practices (e.g., drift nets, gill nets, bottom trawling) in the Baltic Sea on target and non-target species, including, in addition to fish, invertebrates, marine mammals, and birds;*

This request, received in October 1994, has been transmitted to the Advisory Committee on Fishery Management for further handling.

12. *To compile available evidence on causes of the M-74 syndrome in Baltic salmon and to provide a summary of the progress in understanding the relevant environmental factors influencing the occurrence of M-74, along with an account of the geographical extent in the distribution of this syndrome;*

Information on the M-74 syndrome in Baltic salmon is contained in Section 7.4 of this report. This supplements the information provided in Section 9.1 of the 1994 ACME report.

13. *To provide information concerning the transfer of halogenated organic compounds through the food chains;*

Information on this topic is presented in Section 11 of this report. Considerable additional material is contained in the literature and could be provided later on the basis of a more focused request, particularly in terms of the type of food chain and the type of contaminants to be studied.

14. *To provide, to the extent possible, information on the concentrations that are not harmful to man or nature of the contaminants specified in the*

*HELCOM list of priority heavy metals and persistent organic pollutants on the basis of existing scientific knowledge.*

Some general information relevant to this request is provided in Section 12.3. It should be noted that, as the characteristics of the ecosystem vary strongly in different

parts of the Baltic Sea, the environmental response can also be expected to vary in these different regions. The ACME recommended that HELCOM address this problem from an ecosystem perspective rather than attempting to assign concentration levels of contaminants as not being harmful.



## 4 MONITORING STRATEGIES

### 4.1 Strategy for Incorporating Biological Effects in an Integrated Monitoring Programme

#### *Request*

Item 1.3 of the 1995 Work Programme of the Oslo and Paris Commissions and Item 9 of the 1995 requests from the Helsinki Commission.

#### *Source of the information presented*

The 1995 reports of the Working Group on Biological Effects of Contaminants (WGBEC) and the Working Group on Environmental Assessment and Monitoring Strategies (WGEAMS).

#### *Status/background information*

The ACME noted that the WGBEC had worked for several years on the development of a strategy for incorporating biological effects measurements in an integrated monitoring programme. A strategy document was accepted by the WGBEC at its 1995 meeting based on the rationale that:

- 1) the underlying criteria for marine environmental quality are principally biological although they are commonly expressed in chemical terms;
- 2) the health of the marine environment should be monitored in terms that relate to those criteria, using both biological effects techniques and chemical analyses as integrated diagnostic tools;
- 3) detailed chemical fingerprinting should then be focused on analyses of environmental samples taken mainly from areas where there are demonstrable biological problems, and where criteria for environmental health are, therefore, not being met.

The proposed strategy fully integrates biological and chemical components to obtain an overall awareness of environmental quality in relation to issues of concern. The use of a selection of biological techniques directed at issues of concern is advocated, and the suite of techniques employed should represent a range of levels of biological organization and representative species of natural communities.

For preliminary screening in areas where problems are not suspected, the use of diagnostic chemical and biological methods for the health status of individual

sentinel or bioassay organisms should be the first line of approach. The detection of significant adverse biological effects would then trigger detailed biological and chemical investigations whose purpose would be to establish the severity of any impacts in the ecosystem, and the chemical causes of those impacts.

This strategy does not preclude the need to use chemical monitoring techniques for assessing temporal trends in certain areas in relation to input controls, and for safeguarding the human food chain.

Finally, an evaluation of the effectiveness of the monitoring strategy should be made at all levels of measurement and any necessary adjustments made in order to redefine the objectives or modify the methods used.

This strategy document was then reviewed by the WGEAMS, who agreed that the principle of more effective links between chemistry and biology would be beneficial to monitoring programmes and would provide more information at similar or lower cost. Accordingly, the WGEAMS supported the conclusions of this document. The WGEAMS emphasized, however, that the document is likely to evolve in the future in response to comments from other expert groups and to scientific developments. In particular, the inclusion of measurements of physical factors in integrated monitoring programmes will be needed as new techniques are developed and refined.

It was recognized that the application of the strategy paper had yet to be worked out in detail in particular programmes. An opportunity will arise at the OSPARCOM/ICES Workshop on Biological Effects Monitoring to be held in Aberdeen in October 1995.

The WGBEC strategy document, as amended by WGEAMS and ultimately ACME, was approved by ACME and is attached as Annex 1 to this report.

In accepting this strategy document, the ACME noted that the implementation of integrated biological and chemical monitoring does not automatically imply the identification of effects and contaminants in the same organism. There will be circumstances in which clear dose-response relationships are not to be expected and causal links may often be more readily explained by the mechanism of the action of contaminants or by correlations between effects and chemicals in other matrices.

### *Need for further research*

Although the principles in the strategy document are ready for immediate adoption on the basis of a large suite of sensitive biochemical and cellular biomarkers now available, the need for the development of additional chronic bioassays and techniques measuring long-term effects of contaminants was recognized.

### *Recommendations*

The ACME recommended that, when new environmental monitoring programmes are designed, they should fully take account of this new integrated strategy (contained in Annex 1), with the aim of directing biological, chemical, and physical measurements at significant problems in a coordinated and effective manner.

The ACME further recommended to OSPARCOM that the new Joint Assessment and Monitoring Programme (JAMP) adopt a coordinated, concurrent, multi-disciplinary approach to monitoring, clearly targeted at the processes leading to biological causes for concern.

## **4.2 Integration of Biological and Chemical Measurements of Contaminants in Sediments**

### *Request*

There is no direct request, but this information will be of use to the monitoring groups within OSPARCOM and HELCOM. This section is particularly directed towards how the biological and chemical measurements of contaminants in sediments can be integrated in relation to the monitoring objectives of OSPARCOM.

### *Source of the information presented*

The report of the 1995 Joint Meeting of the Working Group on Biological Effects of Contaminants (WGBEC) and the Working Group on Marine Sediments in Relation to Pollution (WGMS).

### *Status/background information*

The starting point taken for the consideration of this topic was the objectives of the OSPARCOM Joint Assessment and Monitoring Programme (JAMP), which contained a list of issues to be addressed and questions to be answered, and the interpretation of these questions for the work programme of the OSPARCOM Working Group on Concentrations, Trends and Effects of Substances in the Marine Environment (SIME) under the Environmental Assessment and Monitoring Committee (ASMO). The Joint Meeting of WGBEC and WGMS noted ASMO's expressions of concern for some groups

of environmental contaminants, and interpreted these in terms of the underlying biological implications.

The Joint Meeting focused on those issues raised by JAMP which related to sediment monitoring in the biological and chemical fields. It was agreed that effective monitoring in sediments (and elsewhere) could only be achieved by a closer integration of biological and chemical measurements, activities which traditionally have been pursued almost independently. In many cases, this implies the need to conduct chemical and biological measurements on the same sample in order to provide the information necessary for proper interpretation. The whole approach must be targeted at the processes leading to *biological* causes for concern.

The ACME accepted the views of the Joint Meeting and concluded that the proposed retrospective use of Ecotoxicological Reference Values for sediments in the SIME programme was flawed because it relied solely on individual contaminant measurements and ignored the complexity of jointly acting materials, and of their relationship with the sediment substrate. Only an integrated chemical and biological monitoring strategy can provide reliable answers to the fundamental questions concerning impacts of contaminants on biota.

The ACME then considered two sediment contamination issues relevant to JAMP which can now be addressed by such an integrated approach. Full details are given in Annex 2.

- 1) **Monitoring related to PCBs, PAHs, dioxins, and dibenzofurans.** These contaminants have, *inter alia*, three types of effects on benthic organisms which can be measured in monitoring programmes: liver tumour formation in flatfish, damaged reproductive processes in benthic fish, and changes in growth in molluscs. Reproductive effects in marine mammals (that consume benthic organisms and demersal fish) were also briefly considered but this issue will be covered more comprehensively in a future report. In each case, a core set of monitoring measurements (both chemical and biological) is recommended which should be applied in a coordinated fashion in areas where these substances are suspected to be a problem (see Table 4.2.1).
- 2) **Monitoring related to the general health of benthic fauna.** The use of benthic community analysis on its own as a means of detecting sediment toxicity is a poor strategy for monitoring the general health of benthic fauna because of its high cost and difficulties of interpretation. However, it should be recognized that there will be some situations (e.g., dredged material disposal sites) where benthic com-



**Table 4.2.1.** Core elements of monitoring programmes for PCBs, PAHs, dioxins, and dibenzofurans.

← More specific response

Less specific response →

| Tumour Formation in Flatfish  | Reproductive Processes in Benthic Fish   | Growth in Molluscs                          |
|---|--|---|
| Prevalence of liver tumours   | Reproductive indices: fecundity, gonadosomatic index (GSI), sex ratio, larval survival | Scope-for-growth in filter feeding molluscs |
| Prevalence of pre-neoplastic change                                     | Blood chemistry: vitellogenin and vitamin A  | CBs, PAHs, and dioxins in mollusc tissue    |
| DNA damage  | Hepatic MFO/EROD   | Residues in suspended particulates          |
| Hepatic EROD activity   | CBs, PAHs,* and dioxin concentrations in liver and/or bile                             |   |
| CBs, PAHs,* and dioxin concentrations in liver and/or bile              | Residue concentrations in surficial sediments and benthic invertebrates                |   |
| Residue concentrations in surficial sediments and benthic invertebrates |  |   |

\*PAHs are rapidly metabolized in fish liver, so concentrations will be low. Measurement of PAH metabolites in bile may be the most appropriate technique.

munity analysis alone may be appropriate. The ACME recommended the adoption of a tiered and integrated sediment monitoring strategy which begins with bioassays conducted on whole sediment samples (and, to a lesser extent, pore water and/or elutriates) collected in areas of interest or concern. If these bioassays indicate that significant toxicity exists in the sediment, then more detailed fieldwork should be carried out which combines benthic community analysis followed, if necessary, by investigative analytical chemistry in order to establish cause and effect. The initial chemistry might involve analyses of the bulk sediment for the "routine" contaminant groups, but more sophisticated approaches could include selective sequential fractionation and tests with sensitive bioassays and biomarkers

#### *Need for further research*

Improved general understanding is required of the ways in which sedimentary contaminants can affect benthic communities. The Joint Meeting developed detailed proposals, that were endorsed by ACME, for a research programme which would:

- 1) determine the release of contaminants from sediments, prior to their uptake into sediment dwellers, by studying *in situ* partitioning;
- 2) determine the transfer of sedimentary contaminants into benthic organisms, via all pathways of uptake (oral, dermal, and branchial);

- 3) measure aqueous- and sediment-phase toxicity to benthic organisms for a wide range of organics and metals; and
- 4) using the above information, develop an appropriate and accurate partitioning model for predicting the hazards associated with sedimentary contaminants.

These proposals are now being developed into bids for research funding.

In support of the programmes outlined in (3), above, the ACME encouraged more research to be undertaken:

- a) to understand the causes and processes of hepatocellular carcinogenesis in fish;
- b) to develop improved methods of monitoring fish egg quality (e.g., measurement of chromosomal abnormalities) which are able to distinguish contaminant exposure from natural causes of abnormality;
- c) to study whether environmental oestrogens have an influence on marine fish;
- d) to investigate the effects which PAHs and PCBs may have on sedentary crustacea, in order to develop monitoring techniques which respond more accurately to local contamination;

- e) to develop sensitive marine whole-sediment bioassays based on chronic endpoints.

#### *Recommendations*

ACME recommends to OSPARCOM the adoption in JAMP of a coordinated approach to sediment monitoring that combines the use of chemical and biological measures to address issues of biological concern. Two proposals for integrated monitoring of this type are given in the discussion above.

### **4.3 Monitoring to Identify Temporal Trends: Statistical Requirements**

#### *Request*

Item 4.1 of the 1995 Work Programme from the Oslo and Paris Commissions, and an ACME request to identify the sequential stages in the design of a monitoring programme with the aim of detecting temporal trends.

#### *Source of the information presented*

The 1995 reports of the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM), and the Joint Meeting of the WGSAEM and the Working Group on Environment Assessment and Monitoring Strategies.

#### *Status/background information*

The WGSAEM provided a clear and detailed document describing a rational way of designing a monitoring programme with the aim of detecting temporal trends. This document was accepted by ACME and is included here *in toto*. ACME noted, however, that this document covered only the statistical aspects of the request with a demonstration using data for a single contaminant and that further work would need to be conducted to consider the influence of different hydrographic conditions on the ability to identify temporal trends. Designing a monitoring programme may be theoretically straight-forward if the objectives are explicit and there are estimates of the variance components. If the information is available, the design may also be optimized with respect to costs and other constraints. However, in practice it may be necessary to compromise on some sub-optimal design. The discussion below considers the phrasing of objectives for temporal monitoring programmes and how statisticians can interact with other persons involved in the development of a monitoring programme to prepare an effective sampling design.

## **Objectives for Temporal Trend Monitoring**

### **Coordination between statisticians and planners**

At the start of the design stage, the reasons for monitoring are typically rather vague. For example, monitoring might be required to determine whether levels of contaminants or other parameters are changing, but with no explicit idea about what those changes might be. There is also generally some intuitive idea about what would constitute a “successful” programme, and how much money the organization is willing to spend.

A dialogue between statisticians and planners, i.e., all others involved in setting up the programme, should then begin, to clarify the reasons for monitoring, quantify the costs, and place the intuitive ideas about “success” in an objective, measurable statistical framework. Assuming that there are estimates of all the relevant variance components, it is then possible to find a statistical design (i.e., number of samples, sampling frequency, etc.) that gives a satisfactory balance between cost and benefit.

There are many ways to find this balance. For example, consider designing a ten-year monitoring programme to detect any change in level. Further, consider using the percent yearly change detectable with 90% power (the “detectable trend”) to measure the effectiveness of a design. One approach is then to:

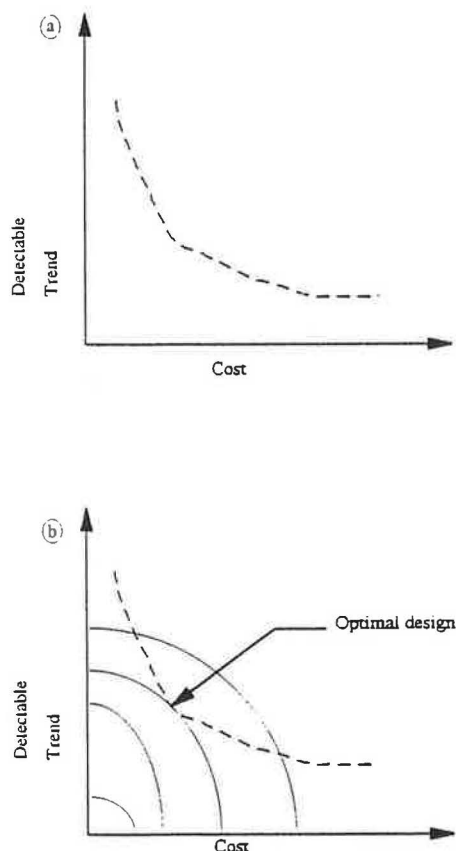
- specify the maximum allowable cost;
- find the minimum detectable trend given this cost;
- if the minimum detectable trend is unsatisfactory, reconsider the programme.

An alternative approach is to:

- specify the desired detectable trend;
- find the minimum cost of a programme that will achieve this detectable trend;
- if this cost is too much, reconsider the programme.

It may be useful to plot the minimum detectable trend against the corresponding cost of achieving it (Figure 4.3.1a). This is called the pareto optimal curve, and shows the best that can be obtained for a given sum of money. If the current monitoring programme lies above this line (nothing can lie below it), it should be possible, by re-allocating resources, to make monitoring more efficient without spending more money.

If the relative importance of cost and minimum detectable trend can be established, the plots can be made more informative by joining up combinations of minimum detectable trend and cost which are equally acceptable to the planners of the programme. For example, they may be equally happy to spend 1000 units and detect a 10% change or to spend 2000 units and detect a 1% change. The lines joining up equally acceptable combinations are called management indifference curves (Figure 4.3.1b). The optimal programme for a particular level of indifference is where the corresponding curve touches the Pareto optimal curve.



**Figure 4.3.1.** Pareto optimal curve without (a) and with (b) management indifference curves.

In principle, design is a matter of judging statistical (and environmental) benefits relative to monetary (and environmental) costs. However, in practice, it is often hard to specify the costs, the indifference curves, and the measure of statistical benefit. The problem is greater in large inter-national monitoring programmes, such as JAMP. Dialogue between statisticians and planners may be very indirect, and each national institute may have its own budgets and ideas about what is important. It is then imperative that the dialogue process be given a clear start by

- (a) employing a statistician to be responsible for designing the programme,

and/or

- (b) ensuring that the broad objectives of the programme are supplemented by a series of very detailed, quantified objectives that make explicit, for each part of the programme, what the programme is designed to detect and any cost constraints.

It should be noted that contact with other persons, particularly physical oceanographers, should also be established at an early stage in the planning process.

#### **A broad categorization of temporal monitoring objectives**

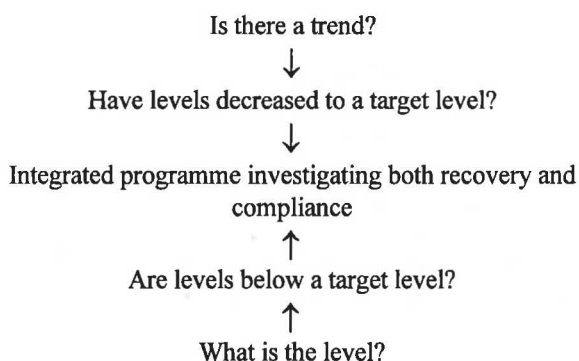
Many objectives fall within the framework of temporal monitoring, for example, determining whether levels are changing, estimating rates of change, or assessing whether levels have achieved target values. This section presents a range of the possible objectives that might be implied by the OSPARCOM broad statement of intent.

At one extreme is exploratory monitoring for **trends**: for example, are levels changing, or are levels decreasing? At the other extreme is exploratory monitoring for **level**: for example, what is the level, or what is the natural variation in level?

As soon as a target level is specified, monitoring becomes more focused. Monitoring can still be thought of in terms of trends. However, now there is particular interest in whether levels have decreased to, or below, the target level or are on course to reach the target level. Monitoring can also still be thought of in terms of level, but now the interest is in comparing the current level to the target level.

Finally, the approaches of monitoring for trends and for level converge to some integrated monitoring framework, in which tests of either recovery or compliance are linked to specific decisions defined in terms of environmental risk.

These five categories are summarized in the following flow diagram:



## Quantified Objectives for Trend Monitoring

Some ways of phrasing specified objectives for trend monitoring are now described. It is important to note that, although specific numbers have been used in the examples below, these numbers are simply given as examples and will not be suitable for all monitoring programmes; appropriate values must be chosen for the problem in hand. Further, there are many other ways of quantifying trend monitoring objectives than those described here.

First, in terms of notation, let  $y_t$  be the mean log-concentration in year  $t$ . Assume that

$$y_t = f(t) + \text{error}_t$$

where  $f(t)$  is some function of time that represents the underlying trend in log-concentration. The simplest parametric trend is linear in which  $f(t) = a + bt$ ; since this work is on a log-scale,  $b = -0.1$  approximately corresponds to a 10% yearly decrease in concentration,  $b = -0.05$  to a 5% yearly decrease in concentration, etc.

*Is there a trend?*

Probably the simplest question that can be asked is whether levels are increasing or decreasing, without actually specifying the form of increase or decrease. This can be phrased statistically, by saying that we want to design a programme to test the null hypothesis

$$H_0: f(t) = \text{constant}$$

against the alternative hypothesis

$$H_1: f(t) \text{ monotonically increasing or decreasing.}$$

To specify the objective fully, the significance level, or size, of the test must be indicated. This is the probability of rejecting  $H_0$  given that it is true, and should reflect the level of 'concern' about incorrectly inferring that levels are going up or down, when they are constant. A common choice is 5%, but depending on the circumstances, other values may be more appropriate.

The power of the test against some specified alternative hypothesis also needs to be indicated. This is the probability of correctly rejecting  $H_0$  when some specified monotonic trend has occurred. The specified monotonic trend should be one that it is 'important' to detect (should it occur); for example, here it might be important to detect a trend of 10% per year over 5 years. The specified power is somewhat arbitrary, but a common choice is 90%.

The objectives of the programme could then be phrased to test:

$$H_0: f(t) = \text{constant}$$

*versus*

$$H_1: f(t) \text{ monotonically increasing or decreasing}$$

at the 5% significance level, and with 90% power to detect  $b > 0.1$  or  $b < -0.1$  after 5 years.

This objective is depicted in Figure 4.3.2a, in which the bold line shows the null hypothesis and the dashed lines show the monotonic trends that must be detected with 90% power.

*Have levels decreased to a target level?*

Suppose that  $\mu_{\text{target}}$  is the target level, and that to reduce concentrations to the target level from the current level requires the concentration to decrease at 5% per year over 10 years. Further, suppose that we want to know if levels have decreased by only 2.5% per year over 10 years. Then this objective could be phrased to test:

$$H_0: b = -0.05$$

*versus*

$$H_1: b > -0.05$$

at the 40% significance level, and with 99% power to detect  $b > -0.025$  after 10 years.

This objective is depicted in Figure 4.3.2b.

Note that:

- accepting  $H_0$  does not ensure that levels have reached  $\mu_{\text{target}}$ , only that they are likely to be better than those achieved with a decrease of 2.5% per year;
- the significance level and power, although unusual, may better reflect the view that it is more dangerous environmentally to infer that levels have reached  $\mu_{\text{target}}$  when in fact they are much higher, than to infer that levels are too high, when in fact they have reached  $\mu_{\text{target}}$ .

This objective could also be phrased more directly in terms of tests about  $f(10)$ , the underlying mean log-concentration in ten years' time. For example (see Figure 4.3.2c), test

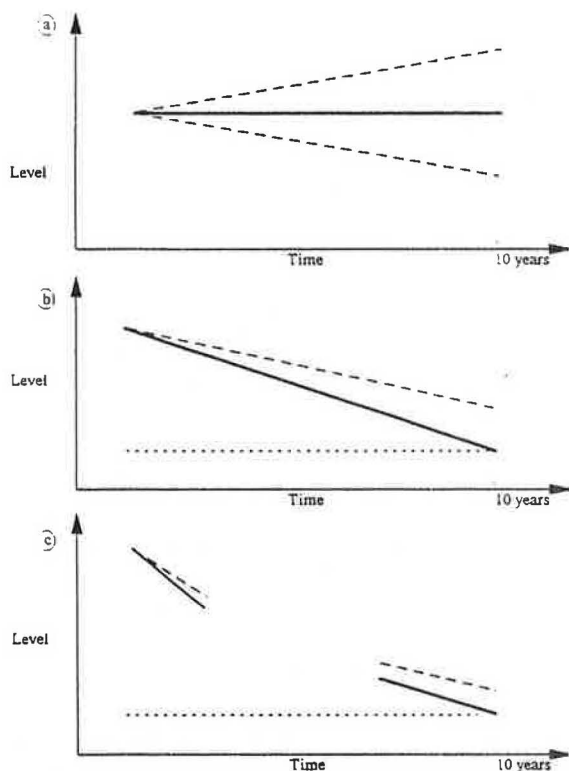
$$H_0: f(10) = \mu_{\text{target}}$$

*versus*

$$H_1: f(10) > \mu_{\text{target}}$$

at the 40% significance level, and with 99% power to detect  $f(10) > \mu_{\text{target}} + 0.125$ .

Note that phrasing the objective and corresponding test in terms of the level in ten-years' time allows any pattern of temporal change between the current level and  $\mu_{\text{target}}$ , which simplifies the analysis and lends itself to the case where concern is focused on the current level in the environment.



**Figure 4.3.2.** Three different possible objectives (a, b, and c). The solid, dashed, and dotted lines correspond respectively to the null hypothesis ( $H_0$ ), the alternative hypothesis ( $H_1$ ) that must be reached with specified power, and the target level ( $\mu_{\text{target}}$ ) to be reached; the gap means that there is no particular assumption about the way in which levels decrease.

Both of the above objectives can be reviewed during the ten-year programme. It might be clear after five years that levels have already decreased to  $\mu_{\text{target}}$  and that a different type of monitoring objective is required. Alternatively, it may be clear that a ten-year horizon is unrealistic given the variability observed, leading to a modification of the programme.

#### *Is there a change in the trend?*

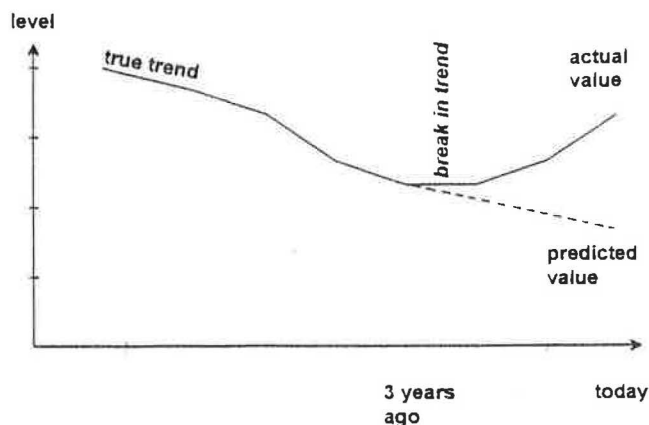
There are other plausible, sensible trend objectives that do not fall naturally into either of the above categories. For example, the current level could be tested against its predicted value from three years before to see whether the trend observed at, e.g., the previous assessment has been sustained (see Figure 4.3.3). The programme could be designed to test

$$H_0: f(t) = \text{predicted value}$$

versus

$$H_1: f(t) \neq \text{predicted value}$$

at the 5% significance level, and with 90% power to detect a 50% increase on the predicted value or a 30% decrease on the predicted value. An example of this is given in Fryer and Nicholson (1993).



**Figure 4.3.3.** Detecting changes in the trend.

### **Compliance Monitoring**

#### *Introduction*

The emphasis so far has been on defining objectives and statistical tests for temporal *changes* in the average level, e.g., to see whether the average level at the end of some time period is significantly lower than it was at the beginning. This has been labelled 'Recovery Monitoring'.

If average levels are believed to be satisfactorily low, it may be more appropriate to phrase objectives in terms of seeking evidence that the average level has remained low. This has been termed 'Compliance Monitoring'; in this context, the term 'compliance' is not intended to imply regulatory measures, but simply maintenance below a target level.

The difference between Recovery Monitoring and Compliance Monitoring relative to a specified target value is shown in Figure 4.3.4.

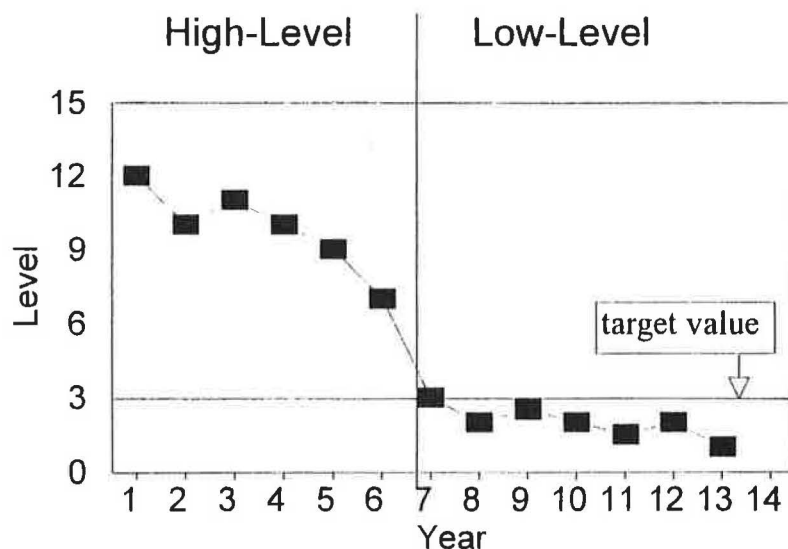
The objectives could be phrased statistically as

$$H_0: f(t) = \mu_{\text{target}}$$

versus

$$H_1: f(t) < \mu_{\text{target}}$$

at the 5% level with 99% power to detect  $f(t) < \mu_{\text{target}} - \Delta$  after T years.



**Figure 4.3.4.** 'Recovery monitoring' compared to 'compliance monitoring'. The left-hand side of the figure (labelled 'High-Level') shows the situation where the average level is decreasing. The objective of the monitoring programme could be to detect if the average level will reach the target level at the end of some time period. The right-hand side of the figure (labelled 'Low-Level') shows the situation where the target level has been reached. The objective of the monitoring programme will be to demonstrate that the average level continues to be at the target level.

Phrased in this way, the alternative hypothesis would be accepted if there was evidence that average levels are generally better than  $\mu_{\text{target}}$ . This may prompt a review of the need to continue monitoring, or of the intensity of monitoring required. Recovery and Compliance Monitoring may then be set into some sort of formal decision-making table, such as

|              | Recovery Monitoring         | Compliance Monitoring      |
|--------------|-----------------------------|----------------------------|
| Accept $H_0$ | Continue monitoring         | Continue monitoring        |
| Reject $H_0$ | Begin compliance monitoring | Review or cease monitoring |

If levels rise above the target during Compliance Monitoring, Recovery Monitoring should be reconsidered. The test could be extended to formally test this.

#### *Testing Hypotheses and Designing the Programme*

There are various statistical methods for testing the hypotheses given above. One way is simply to compare the average over the monitoring period with  $\mu_{\text{target}}$ . Figure 4.3.5 shows the distributions of the average when the average is based on few years/few observations labelled 'imprecise monitoring', and many years/many fish labelled 'precise monitoring'. This demonstrates the relationship between the target value, the critical value, and  $\Delta$ , the change that will be detected with 99% power. When monitoring is imprecise, the decrease in the underlying average has to be greater before it is likely to be detected.

As in the discussion above on interactions between statisticians and planners, it may be useful to plot the detectable change against the cost of achieving it. A line showing the minimum detectable change at a given cost (pareto optimal curve) may be added. If the relative value of a detectable change can be related to its cost, management indifference curves can also be added.

#### **OSPARCOM and HELCOM Requests for Advice on Setting Targets for Trend Detection and Measuring Power**

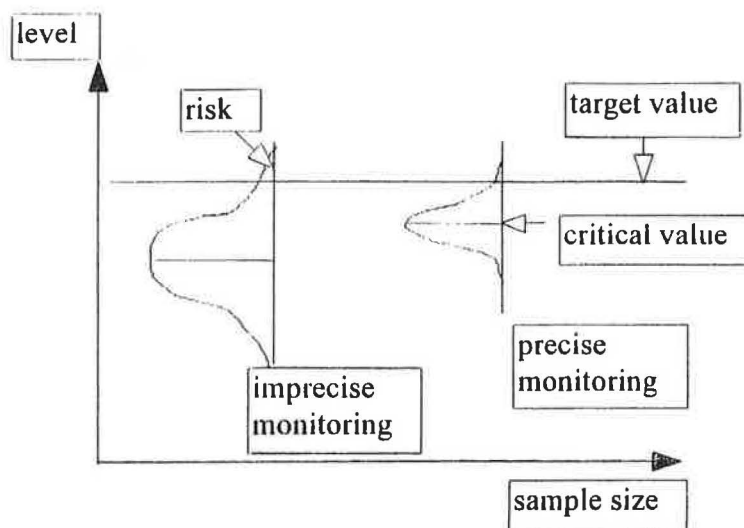
Both OSPARCOM and HELCOM have expressed a desire to assess the power of their temporal monitoring programmes, and to devise new programmes so that quantified objectives, such as those discussed above in this section, will have an adequate power of being achieved.

The basic theory for calculating power for the simple objective of wishing to be, e.g., 90% certain that a given linear trend will be found to be statistically significantly different from zero when  $R$  animals are collected and separately analysed in each of  $T$  years is described in Fryer and Nicholson (1993). They consider the simple case which assumes that a linear trend is present and is tested from a regression analysis of the annual mean log-concentration on year.

The power is a function of

$$\delta = b^2 \frac{(T-1)T(T+1)}{12\psi^2}$$





**Figure 4.3.5.** The relationship between the target value, the critical value, and  $\Delta$ . The results of 'compliance monitoring' could be compared to the target value by taking the average of the level over the monitoring period. If the average is based on few years/few observations, the distribution is labelled 'imprecise monitoring'. Many years/many observations is labelled 'precise monitoring'. The figure shows that  $\Delta$  (which is the difference between the critical value and the target value that it is likely to detect) is greater for 'imprecise monitoring' than for 'precise monitoring'.

where  $b$  is the change per year on a log scale,  $T$  is the number of years and  $\psi$  is the total standard deviation of an estimated yearly mean log concentration, given by

$$\psi^2 = \sigma_y^2 + \frac{\sigma_w^2}{R} + \epsilon_y^2 + \frac{\epsilon_w^2}{R}$$

where the components of variance correspond to between- and within-year sampling variability and between- and within-year analytical variability, respectively. If good estimates of these are available, the power can then be calculated for given values of  $R$ ,  $T$ , and  $b$ . If costs of analysis, sample preparation and collection are available, then costs may also be calculated.

In practice, it may be more appropriate to explore the effect on power of different values of the variance components. For example, the explanation of a request from OSPARCOM is phrased as:

*ICES is requested to advise on realistic (in terms of cost benefit relations) statistical requirements for establishing temporal trends for nutrients, inorganic and organic contaminants. What, for example, are the monitoring requirements in terms of sampling frequency, accuracy of measurements and minimum duration of the programme for establishing, with a 90% probability, a temporal trend of 5% per year for hydrographic regions with either low, medium or high natural variability?*

Published data for mercury concentrations in fish and shellfish will be used to demonstrate how appropriate values of the variance components may be obtained, and how these may be used to find appropriate combinations of sampling frequency, accuracy of measurements, and

minimum duration of the programme to meet the stated objectives.

As no tables of sampling and analytical costs are available, the ACME considers that it would be appropriate for at least relative costs of these procedures to be compiled and made generally available by the regulatory commissions.

Estimates of the components of sampling variability are available from ICES (1989, 1991) and from OSPARCOM assessment reports. From these, the distribution of relative standard deviations was divided into three approximately equal groups corresponding to High, Medium, and Low levels of variability, and the median value from each group was calculated.

Estimates of the analytical components of variability were taken from the report of the ICES Seventh Intercomparison on Trace Metals in Biological Tissue (Berman and Boyko, 1992), and again the medians from each of three groups corresponding to levels of High, Medium and Low levels of variability were computed.

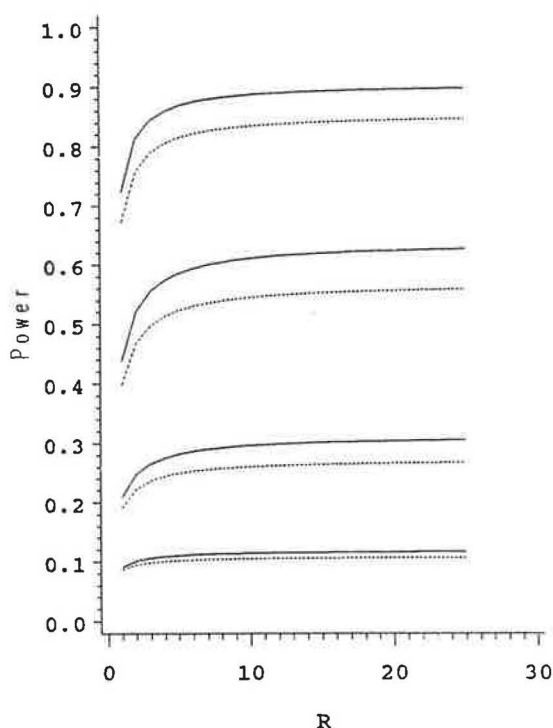
The median values of the standard deviations on a log scale are given in the following table:

|        | $\sigma_y$ | $\sigma_w$ | $\epsilon_y$ | $\epsilon_w$ |
|--------|------------|------------|--------------|--------------|
| Low    | 0.08       | 0.22       | 0.09         | 0.04         |
| Medium | 0.26       | 0.28       | 0.13         | 0.05         |
| High   | 0.52       | 0.42       | 0.24         | 0.10         |

Taking these values and  $b = 0.05$  it is now possible to explore the interaction between  $R$ ,  $T$ , and the

corresponding power (from  $\sigma$  as described in Fryer and Nicholson, 1993). The graphical aids described in Nicholson and Fryer (1994) may be useful for doing this. The ACME considers that dialogue between statisticians and planners can be very beneficial at this stage.

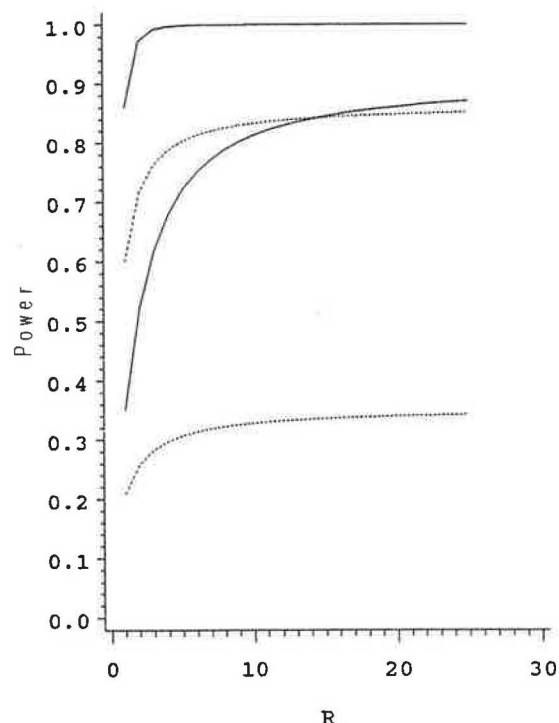
To demonstrate the types of display that may be useful, the change in power can be investigated as  $R$  varies for different values of  $T$  combining the variances from the High, Medium, or Low groups. For example, Figure 4.3.6 shows how the power in areas of High sampling variance is affected by incorporating either High or Low levels of analytical variance. From the top down, the solid lines show how the power varies with  $R$  for  $T = 25, 20, 15,$  and  $10$ , respectively, when there is Low analytical variability. The dotted lines show the corresponding powers when analytical variance is High. It can be seen that analytical variance and changes in  $R$  greater than 5 have only a small effect, and in areas of High sampling variability, monitoring should continue for at least 25 years to ensure a power of 90%.



**Figure 4.3.6.** The relationship between power and sample size ( $R$ ) for various values of  $T$  (sampling period), when the sampling variability is High. From the top, the sampling period is 25, 20, 15, and 10 years, respectively. Solid lines indicate Low analytical variability; dashed lines indicate High analytical variability.

Correspondingly, Figure 4.3.7 shows how the power in areas of Low sampling variance is affected by incorporating either High or Low levels of analytical variance. For clarity, only lines for  $T = 15$  and 10 have

been shown. It can clearly be seen that in areas of Low sampling variability, analytical quality can have a large impact on the achieved power, particularly with  $T = 10$  years.



**Figure 4.3.7.** The relationship between power and sample size ( $R$ ) for various values of  $T$  (sampling period), when the sampling variability is Low. From the top, the sampling period is 15 and 10 years, respectively. Solid lines indicate Low analytical variability; dashed lines indicate High analytical variability.

It should be noted that:

- 1) A specific and rather simple objective has been used for demonstration her.
- 2) Only one type of statistical design has been considered, and others might lead to improved power. For example, sampling on more than one occasion each year might be beneficial. The consequences of sampling twice a year or every second year could also be investigated. Another example might be splitting analyses among a number of laboratories to reduce between-year analytical noise.
- 3) The analytical variances are only loosely connected with the environmental variances in that they were estimated using data from a small number of laboratories over a short time period.
- 4) The analytical variances are poorly estimated on few data.



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## 5 MONITORING GUIDELINES AND TECHNIQUES

### 5.1 General Comments on the Design and Implementation of International Monitoring Programmes

During its 1995 meeting, the ACME reviewed plans for the new OSPAR Joint Assessment and Monitoring Programme (JAMP) and the further development of the HELCOM Baltic Monitoring Programme (BMP) and Coastal Monitoring Programme (CMP). On the basis of this review, the ACME agreed that the following general comments should be transmitted to the two Commissions.

International monitoring programmes and baseline studies need to be carefully designed and streamlined in order to address the environmental issues in question. Consequently, there is no need for such programmes to be identical in all regions or subareas, but there is a clear need for a firm lead in the planning and implementation of the activities.

It is essential that countries that have agreed to cooperate in such programmes provide sufficient resources and also make other relevant administrative arrangements.

In this particular context, a successful cooperation requires that the international agreement is given priority to other plans of a purely national character. Consequently, the establishment or revision of national monitoring programmes must never disregard the requirements identified or agreements achieved in the international cooperation.

### 5.2 Biological Effects Monitoring

#### 5.2.1 Guidelines on the use of recommended techniques for biological effects monitoring

##### *Request*

Item 1.3 of the 1995 Work Programme from the Oslo and Paris Commissions and Item 9 of the 1995 requests from the Helsinki Commission.

##### *Source of the information presented*

The 1995 reports of the Working Group on Biological Effects of Contaminants (WGBEC) and the Joint Meeting of the WGBEC and the Working Group on Marine Sediments in Relation to Pollution (WGMS).

##### *Status/background information*

Guidelines on several biomarker techniques, such as measurement of enzyme metabolism (EROD induction) and fish diseases including liver tumours, on bioassays (whole sediment bioassays, sediment porewater bioassays, sediment seawater elutriates, and water bioassays) and on benthic community analysis, to be followed in monitoring programmes, have been reviewed by ICES and some have been published in the *ICES Cooperative Research Report* series or the *ICES Techniques in Marine Environmental Sciences (TIMES)* series. The guidelines include recommendations on methodology (standardization of techniques, advice on sample sizes, suitable fish species, etc.) and reporting of data. The relevant documents are listed at the end of this sub-section.

In terms of the interpretation of EROD data in benthic fish, field data have shown that while EROD induction in livers of dab (*Limanda limanda*) caught on transects away from oil platforms is strongly correlated with concentrations of 5- and 6-ring PAHs in the liver, there is no correlation with PAH concentrations in the sediment at each station. The relationship between PAH contamination in sediment and the EROD response in benthic fish is clearly a complex one (probably affected by lipid metabolism, sex, season, maturity, temperature, etc.), and it is not even clear whether the sediment or the dissolved phase is the most important source of PAH contaminants to fish.

Other work with dab in the southern North Sea has also shown that variables such as sex and season are important in influencing the EROD response of these fish to PCBs, probably because of their hepatic lipid content. Natural factors, such as low temperature and starvation, usually lead to reduced EROD activities in uncontaminated fish; however, virtually uncontaminated fish would be expected to show very low levels of EROD activity throughout the year. The state of maturation of females has a major effect on their EROD response.

When reporting EROD data, it is therefore vital that seasonal factors such as those described above are reported and taken into account at the interpretation stage, and that EROD measurements are made several times during the year at any given site. It is also vital to identify the sex of the fish (use of males or immature females is preferred), to report the bottom water temperature at the time of trawling, and to measure the hepatic fat content.

With regard to the interpretation of acetylcholinesterase (AChE) inhibition data from fish and shellfish, it is not yet possible directly to compare concentrations in sediment of AChE-inhibitors with levels of AChE inhibition in benthic fish or shellfish, although studies with the dragonet (*Callionymus lyra*) have shown gradients of AChE inhibition along certain estuaries. Work with mussels (*Mytilus edulis*) has also failed to link contaminant levels in deposited sediment with AChE inhibition.

The WGBEC will continue its work to elucidate relationships between biomarker responses and specific contaminants, or classes of contaminants, in relevant marine media, and factors that influence these responses.

At the present time, no guidelines for techniques on monitoring effects of contaminants on reproduction and immunology have been recommended by the WGBEC.

### Quality assurance of biological effects techniques

The WGBEC felt that the development of quality assurance procedures should occur in parallel with the implementation of biological effects measurements in monitoring programmes. It was noted that the IOC Group of Experts on Effects of Pollutants (GEEP) was also considering this issue in relation to biological effects monitoring. The ACME noted that a review of the state-of-the-art of quality assurance procedures for biological effects techniques currently in use will be considered by the WGBEC in 1996.

Information about an intercomparison exercise on scope for growth measurements is contained in Section 6.2, below.

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Thain, J.E. 1991. Biological effects of contaminants: Oyster (*Crassostrea gigas*) embryo bioassay. Techniques in Marine Environmental Sciences, No. 11. 12 pp.

### 5.2.2 Information on possible new techniques for biological effects monitoring

#### *Request*

Item 1.3 of the 1995 Work Programme from the Oslo and Paris Commissions and Item 9 of the 1995 requests from the Helsinki Commission.

#### *Source of the information presented*

The 1995 report of the Working Group on Biological Effects of Contaminants (WGBEC).

#### *Status/background information*

### Use of molecular techniques in marine monitoring

The WGBEC reviewed and evaluated the molecular techniques used in biochemical monitoring programmes. The WGBEC decided that the measurement of bulky DNA adducts in invertebrates was of comparable status to the use of this method in fish and included the measurement of DNA adducts in invertebrates in Table 5.2.2 as a technique that is available for use at the present time. The inclusion of MUTATOX has been delayed because it was felt that there were insufficient data at present.

The WGBEC discussed the use of vitellogenin (yolk protein) as an indicator of exposure of oviparous vertebrates to oestrogenic substances in the environment. The level of vitellogenin in the plasma is very responsive to oestrogenic substances and is a good marker of exposure of males to environmental oestrogens. The method has shown to be very effective in freshwater systems, but the data set in marine systems is rather small at present. Nevertheless, the WGBEC thought that the measurement of vitellogenin should be included as a biological effects monitoring technique.

Two other promising methods, glutathione S-transferase (GST) and on-line monitoring by remote biosensors, are being developed and/or evaluated at the moment. GST has been used extensively in the field but results are still equivocal. It was decided that both techniques require further research effort before they can be recommended.

The currently used molecular techniques available for monitoring applications are summarized in Table 5.2.2. It was decided to include the most reliable of these methods also in Table A1.1 of the strategy paper for integrated environmental monitoring (Annex 1).

### Development of chronic and sublethal whole-sediment bioassays

Progress has been made with the development of sublethal sediment bioassays using a number of marine species (e.g., the polychaete *Arenicola marina*), and research is in progress to develop true chronic bioassays which measure endpoints such as growth or reproduction. The development of such tests is vital for marine monitoring because many sedimentary contaminants are very persistent, and benthic organisms are only expected to experience their primary effects after exposure for a significant proportion of their life cycle.

### Use of dragonet (*Callionymus lyra*) in marine monitoring

This species is not very mobile, and it lives largely submerged in soft sediments where it comes into close contact with sedimentary contaminants. Information collected along the French coast suggests that the dragonet is a suitable alternative to dab as a monitoring species for sediments, particularly in areas where dab are sparse. For example, in the Bay of Seine, dragonet show similar EROD activity to dab, and their cholinesterase is ten times more sensitive to organophosphorus compounds than the equivalent enzyme in sole.

### Chemical extraction of water

The use of chemical extraction techniques for improving the sensitivity of water bioassays was questioned. The WGBEC felt that methods based on concentrating the contaminants resulted in only acute and not chronic responses, and that the ecological relevance of such a method was unclear in that it would not reflect the bioavailability of contaminants in the environment.

### Mechanism and guidelines for the adoption of new biological effects techniques

The WGBEC reaffirmed the criteria decided in 1994 for the inclusion of new techniques in Table A1.1 of the strategy paper (Annex 1). The criteria are:

- methods should have been adequately tested in both the laboratory and the field;
- satisfactory dose-response or concentration-response relationships should be known for a reasonable number of contaminants, if appropriate. There will be some circumstances in which clear dose-response relationships are not to be expected (e.g., some enzymological responses);

- the methods should be practical ones that have been approved by the WGBEC. It is desirable that descriptions of as many methods as possible should be published in the *ICES Techniques in Marine Environmental Sciences* series;
- their sensitivity compared with existing equivalent monitoring techniques should be known, if appropriate.

### Need for further research

Research is required to continue the development of sublethal and chronic endpoints in whole-sediment bioassays, and to establish links between AChE inhibitors in sediment and enzyme inhibition in sediment dwellers.

### Recommendations

- 1) The ACME recommends to OSPAR and HELCOM that attention be paid to the possibility that AChE inhibitors such as organophosphate and carbamate pesticides may be contaminants of concern in some highly contaminated areas of the marine environment. At present, however, the importance of these pesticides as marine pollutants is not known.
- 2) The ACME recommends to OSPAR that consideration be given to using the dragonet (*Callionymus lyra*) as a suitable sediment monitoring species for biological effects studies, especially in areas where dab (*Limanda limanda*) are scarce.
- 3) The ACME recommends that the development of chronic sediment and water bioassays be encouraged.

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**Table 5.2.2.** Molecular biomarker techniques used in monitoring marine environmental quality.

| Biomarker<br>(type of tool)  | Use<br>(animal)   | Status  | References |
|--|---|---|------------|
| CYP1A1 (cDNA, antibody)  | Cytochrome P-450 1A1.<br>Hepatic indicator of exposure to organic contaminants (fish)   | Available for research studies                                      | 1–3        |
| Metallothionein (cDNA, antibody)   | Metal-binding protein.<br>Hepatic indicator of exposure to heavy metals (fish, mussels) | Available for research studies                                      | 4–8        |
| Vitellogenin (cDNA, antibody)  | Hepatic yolk protein.<br>Indicator of exposure to environmental oestrogens in male fish | Available for research studies                                      | 9–11       |
| Multi-drug/xenobiotic resistance (antibody, exclusion of fluorescent bioprobe) | Membrane transport protein. Indicator of exposure to xenobiotics (fish, invertebrates)  | Research tool, but could be included in monitoring with reservation | 12–23      |
| Oncogenes<br>• ras (cDNA, antibody)<br>• myc (cDNA, antibody)                  | Predictive markers of cancer (fish)   | Available for research studies                                      | 24–27      |
| Bulky DNA adducts  | Indicator of exposure to PAHs, PCBs and PCDDs (fish)                                    | Available for research studies                                      | 28–31      |

**Abbreviations**

cDNA = complementary DNA gene probe  
PCR = polymerase chain reaction  
PCBs = polychlorinated biphenyls

mRNA = messenger ribonucleic acid  
PAHs = polycyclic aromatic hydrocarbons  
PCDDs = polychlorinated dibenzo-*p*-dioxins

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### 5.3 Organisms for Spatial Monitoring of Contaminants in Biota

#### Request

Item 1.2 of the 1995 Work Programme from the Oslo and Paris Commissions and, more generally, Item 4 of the 1995 requests from the Helsinki Commission, concerning advice on further improvement of the BMP.

#### Source of the information presented

The 1995 report of the Working Group on Environmental Assessment and Monitoring Strategies (WGEAMS).

#### Status/background information

In its 1994 report (*ICES Cooperative Research Report*, No. 204, Section 5.1), the ACME stated basic prerequisites which should be considered when selecting species to be monitored for contaminants and biological effects. On this basis, the ACME had recommended that the eelpout or

viviparous blenny (*Zoarces viviparus*) as well as benthic macroalgae (the latter in localized areas or small regions if specific precautions are taken) be included as supplementary monitoring organisms. The ACME also pointed out that the use of seabird eggs should be further explored. This was done intersessionally and the WGEAMS provided information on the use of seabird eggs in its 1995 report.

### Seabird eggs

The ACME noted that the main advantages of using seabird eggs in contaminant monitoring are that the eggs offer a stable, well-defined matrix with a high fat content, where many contaminants accumulate, especially organic substances. Thus, they can be used for detecting spatial, as well as temporal, variations. Also, as birds are top predators, with a high rate of bioaccumulation, the monitoring of contaminants in birds can be combined with studies of biological effects on populations, such as egg-shell thinning or hatching failure. Among the drawbacks in using some seabirds are their migratory habits, the non-uniform distribution of nests or colonies, the very short period available for sampling, the varied feeding pattern of some species, both spatially and temporally (often leading to an exposure which cannot be circumscribed precisely), the protected status of many species (e.g., birds of prey), and the lower efficiency of eggs in accumulating trace metals.

Concerning the question of migration, it was felt that eggs would probably reflect uptake from the foraging area at the time of nesting, although this may depend on the mechanism for transferring lipids into the eggs. Since seabirds can forage over a fairly large area, it was expected that their eggs would act as good integrators to represent the contamination over such large areas rather than local ones. The question of clutch size was also raised and, although variability between eggs is not thought to be a problem if the sample size is sufficient, it was felt that the use of species laying only one or two eggs, such as the guillemot, would minimize this problem.

The situation with regard to the possible species for contaminant monitoring in the eggs is as follows:

#### Oystercatcher (*Haematopus ostralegus*)

A shorebird widely distributed along the coasts of the OSPAR and HELCOM areas. It could be chosen for monitoring contaminants in the coastal areas of Europe, but it is not strictly marine as it also nests and feeds inland.

#### Herring Gull (*Larus argentatus*)

A wide-ranging species over the entire ICES area, both inland and on coasts, but it is an opportunistic feeder whose diet is not representative of the marine areas only.

#### Kittiwake (*Rissa tridactyla*)

A truly pelagic bird, nesting on the northern European and Canadian Atlantic coasts. It does not breed in the Baltic Sea, in Spain or Portugal, nor in the Atlantic off the USA. It will feed on fish offal offshore.

#### Common Tern (*Sterna hirundo*)

Wide distribution over the European and North American Atlantic coasts as well as in the Baltic Sea, but not in Iceland. It feeds in marine, brackish, and fresh water.

#### Guillemot (*Uria aalge*)

A pelagic species, nesting on the Atlantic coasts of Europe, in the Baltic Sea, and on the Atlantic coast of Canada. It lays a small number of eggs (1–2). In the Baltic, it feeds on a couple of fish species, namely herring and sprat.

#### Black Guillemot (*Cepphus grylle*)

A more coastal and more Nordic species than the guillemot.

Given the distribution as well as the migration and feeding patterns of the above species, it was felt that the guillemot seemed the best choice to monitor wide marine areas. For coastal areas, the black guillemot could be a good choice, but it is not present in the southern European countries. All other species examined present the problem that their feeding is not entirely marine, although in many situations the common tern may only be feeding in coastal marine waters.

Hence, seabird eggs can be useful in marine monitoring programmes on the condition that the species be chosen carefully, taking into account regional particularities. They could also be used to study a number of biological effects on bird populations. As for the use of other bird tissues, this may be quite limited because of the difficulty of obtaining permission to collect specimens, and because the use of dead birds would not be acceptable for contaminant analysis.

#### *Need for further research*

There is a need to pursue research in many areas concerning the factors likely to affect contaminant concentrations in seabird eggs in relation to monitoring activities.

#### *Recommendations*

The ACME recommended that the analysis of seabird eggs could be used, on a voluntary basis and where sampling does not conflict with conservation interests, in the monitoring of organic contaminants, with guillemots and common terns from selected colonies as the most

appropriate species. It should be noted that the interpretation of the data must take account of feeding patterns, migrations, and lipid utilization and metabolism.

#### 5.4 Update of Existing Monitoring Guidelines

##### *Request*

Item 1.4 of the 1995 Work Programme from the Oslo and Paris Commissions.

##### *Source of the information presented*

The 1995 reports of the WGEAMS, MCWG, WGSAM, and the Joint Meeting between WGSAM and WGEAMS.

##### *Status/background information*

At its first meeting in February 1995, the OSPAR Working Group on Concentrations, Trends and Effects of Substances in the Marine Environment (SIME) pointed out areas in which it felt that the current guidelines on fish and shellfish monitoring required reconsideration and review for use in the new Joint Assessment and Monitoring Programme (JAMP). In this context, the ACME noted that Sections 4 and 5 and Annex 1 of its 1994 report (*ICES Cooperative Research Report*, No. 204) contain detailed information on monitoring strategies, guidelines and techniques, as well as on the design of monitoring programmes; Annex 1 of the 1993 ACME report (*ICES Cooperative Research Report*, No. 198) contain detailed guidelines for the use of sediments in monitoring. Further relevant information is presented here.

##### **5.4.1 Spawning periods of finfish and shellfish used in monitoring programmes**

Current ICES and OSPAR guidelines on the sampling of biota for contaminant analysis recommend that spawning periods be avoided. OSPAR has requested an update of the ICES table on spawning periods of finfish and shellfish sampled in European programmes for the monitoring of contaminants in the ICES area. This table was contained in the 1992 ACMP report (*ICES Cooperative Research Report*, No. 190).

This table has now been reviewed and updated, and is presented here as Table 5.4.1, with an accompanying map to show the locations of the ICES Fishing Areas listed in the table. It should be noted that this information should be used with care in the context of contaminant monitoring programmes.

In the case of finfish and bivalve molluscs, the figures quoted are the months when finfish are on the spawning grounds or when bivalve molluscs are producing gametes, and at this time the proportion of non-reproductive tissue to the total body weight will be more or less at a minimum.

The implication is that, outside this period, body condition and composition will be more stable and more suitable for sampling for the measurement of biological effects and chemical contaminants. Other changes in body condition and composition will occur during the remaining parts of the year, however, and it may well be that the best sampling window needs to be redefined to take this more fully into account, and with specific reference to the particular tests and analyses being conducted. Resolution of this issue may demand more precise questions, and a more subtle appreciation of the seasonal trends in biochemical composition, storage, and gametogenesis for each species.

For *Nephrops* and *Palaemon*, the tabulated information is further confounded by the realities of the crustacean cycle, wherein the "spawning period" is probably more analogous to a period prior to the extrusion of the egg mass rather than to either the extended period of egg carrying or the subsequent period of larval release. For these species, therefore, the data supplied also need to be validated against a more precise question.

#### **5.4.2 Monitoring major contaminants of interest**

##### **1) Metals**

###### *a) Statistical power*

The OSPAR Working Group on Concentrations, Trends and Effects of Substances in the Marine Environment (SIME) has noted that it is necessary to prepare detailed objectives for each contaminant in each matrix at each location in accordance with ICES advice, which also includes the assessment of the statistical power of each item within national monitoring programmes. It is very likely that the statistical power of temporal trend programmes previously undertaken under Joint Monitoring Programme (JMP) guidelines would differ between locations, laboratories, etc. The variance factors limiting the power of programmes include natural field variability, sampling variability, analytical variability, etc., which will not be constant between temporal trend studies. The variability of the inherent power of temporal trend programmes has not previously been taken into account in the assessment of temporal trend data, or in the design of OSPAR programmes.

The current ICES advice on statistical power assessment contains sufficient information for chemists and statisticians working together to make the necessary estimates of variance factors and power. There would be scientific logic in having an overall programme in which all temporal trend studies had at least some specified minimum statistical power. The interpretation of the presence or absence of apparent trends at different locations would then be simplified. However, this would tend to make the achievement of the agreed level of statistical power the dominant factor in planning sampling



and analytical strategies. This would imply that there could well be an apparent relaxation of the sampling guidelines to allow different approaches to be taken, provided that the statistical power of each study was adequate.

#### b) *Metal concentrations and lipid contents*

The choice of liver as a matrix for monitoring metals has to some extent been based on historic ease of measurement since higher metal concentrations in liver made the analyses more feasible for many laboratories a decade ago. It is apparent from recent studies that the relationship between trace metal concentrations and lipid contents in biological tissues is not resolved. However, it is suggested that fish species showing smaller variations in liver fat content might be more suitable for monitoring purposes. The ACME noted, based on the examination of the issue by the Marine Chemistry Working Group (MCWG), that analysis of individual livers is still recommended and that the use of pooling based on liver size should be explored. It was agreed that in any revision of monitoring guidelines, account should be taken of knowledge gathered over recent years. Furthermore, a need exists for a better understanding of the chemical associations between various metals and liver lipid types, and also of the chemical associations between metals and the lean tissue components.

### 2) Tributyltin (TBT)

The sampling of Neogastropods (particularly *Nucella lapillus*) and their examination for imposex should be the subject of a new guideline. The guideline should also cover the chemical analysis of these samples for TBT compounds, and the necessary quality assurance (QA) procedures to accompany both the chemical and biological effects measurements. It is expected that a guideline for at least the biological effects measurement of TBT will be prepared at the OSPAR/ICES Workshop on Biological Effects Monitoring in October 1995.

### 3) Chlorobiphenyls (CBs)

#### a) *Statistical power*

SIME has raised a number of concerns and issues regarding the occurrence and effects of CBs in the sea. These include the need for guidelines on temporal trend assessment, which would include the concepts of statistical power; therefore, the comments above regarding statistical aspects in relation to metals in biota also apply to CBs in biota.

#### b) *Determination of lipid concentrations*

SIME has called for the revision of monitoring guidelines to take into account ICES advice on the determination of lipid concentrations. This area has been under active

examination through combined efforts by both the ICES MCWG and QUASIMEME. Lipid determination has been the subject of a QUASIMEME workshop, and a comparison of methods of lipid extraction was included in a recent QUASIMEME exercise. There is a problem, particularly in lean fish muscle, in which different extraction procedures extract substantially different amounts of lipid, the phospholipids being rather more difficult to extract. The problem is much less significant in fatty fish muscle, and negligible in lipid-rich liver tissue. There is an additional problem that the most complete extraction methods employ chlorinated solvents, the use of which could be prohibited in the near future. Thus, there is a need for ICES to prepare a recommendation on the most appropriate method to determine the lipid content of biota samples. However, it is premature to undertake this work until the results of current investigations have been assessed.

#### c) *Size stratification of samples*

The need stated by SIME for new guidelines concerning the requirement for data on size, sex, and reproductive state of the organisms sampled to be included with CB data is partially met by the existing ICES Guidelines which stipulate size stratification of fish samples, and the time of year at which samples should be collected. (It was noted that recommendations from HELCOM did not follow the ICES Guidelines, but indicated that small fish of a single size, rather than a length-stratified sample, should be used in HELCOM trend monitoring programmes, owing to the fact that young fish (less than two years old) in the Baltic Sea lack mobility and are thus representative of their area of collection.

#### d) *Sampling and analysis*

SIME requested guidelines on sampling of marine organisms and their analysis for non-*ortho* and mono-*ortho* CBs. ICES has recently undertaken an informal pilot intercomparison exercise on the analysis of these compounds in a fish oil but additional work needs to be done. The following points should be noted:

- Analysis of planar CBs should primarily be carried out in association with measurements of biological effects of these contaminants.
- Analysis of planar CBs is also relevant in connection with risk assessment to human health.
- At this stage, analysis of planar CBs on a routine basis in spatial distribution and temporal trend studies is not recommended, due to the difficulties associated with the analysis of these compounds by other than a few specialist laboratories.

**Table 5.4.1.** Spawning periods (given as numbers for the months of the year) for finfish and shellfish sampled in Northeastern Atlantic ICES fishing areas in relation to international programmes for the monitoring of contaminants.

| FINFISH SPECIES                |                | ICES FISHING AREA |     |      |             |      |      |      |     |     |                          |     |      |        |       |        |         |        |       |       |                  |        |                   |
|--------------------------------|----------------|-------------------|-----|------|-------------|------|------|------|-----|-----|--------------------------|-----|------|--------|-------|--------|---------|--------|-------|-------|------------------|--------|-------------------|
| Latin name                     | English name   | I                 | II  | IIIa | IIIc        | IVa  | IVb  | IVc  | Va  | Vb  | VIa                      | VIb | VIIa | VIIb,c | VIIId | VIIe,h | VIIIf,g | VIIJ,k | VIIIa | VIIIb | VIIIc            | IIIIId | IXa               |
| <b>1st Choice Species</b>      |                |                   |     |      |             |      |      |      |     |     |                          |     |      |        |       |        |         |        |       |       |                  |        |                   |
| <i>Limanda limanda</i>         | Dab            | 5-8               | NI  | 4-6  |             | 2-5  | 2-5  | 2-5  | 3-5 | 4-6 | 3-5                      | NA  | 2-5  | 2-5    | (2-5) | (2-5)  | 2-5     | 2-6    |       |       | NA               |        | NA                |
| <i>Gadus morhua</i> *          | Cod            | 2-5               | 2-5 | 1-4  | 3-8         | 1-4  | 1-3  | 12-3 | 3-5 | 2-5 | 1-3                      | 2-4 | 2-4  |        | 12-2  | 2-4    | 2-4     |        | NA    | NA    | NA               | NA     | NA                |
| <b>2nd Choice Species</b>      |                |                   |     |      |             |      |      |      |     |     |                          |     |      |        |       |        |         |        |       |       |                  |        |                   |
| <i>Nephrops norvegicus</i>     | Norway lobster | NA                | NI  | 9-11 |             | 9-11 | 7-11 |      | 5   | 6-8 | 6-11                     | NA  | 9-10 | 9-10   |       |        | 8-10    | 8-10   | 5-8   | 5-8   | 6-8              |        | 5-10              |
| <i>Platichthys flesus</i> *    | Flounder       | 4-7               | NI  | 1-4  | 3-5         | 1-6  | 1-8  | 1-4  | NA  | 1-5 | NI                       | NA  | NI   | NI     | 2-4   | 2-4    | NI      | NI     | 1-3   | 1-3   | NA               |        | 1-6               |
| <i>Merlangius merlangus</i>    | Whiting        | NA                | NA  | 2-7  |             | 3-7  | 2-8  | 1-8  | 5-6 | 5-6 | 3-7                      | NA  | 3-5  | 3-5    |       |        | 3-5     | 3-5    | 2-6   | 2-6   | NA               |        | NA                |
| <i>Merluccius merluccius</i>   | Hake           | NA                | NA  | 4-8  |             | 5-7  | NA   | NA   | NA  | 4-6 | 5-8                      | NA  | NA   | 5-7    |       |        | 5-7     | 5-7    | 1-4   | 1-4   | 1-4              |        | 12-4              |
| <b>Other Species</b>           |                |                   |     |      |             |      |      |      |     |     |                          |     |      |        |       |        |         |        |       |       |                  |        |                   |
| <i>Pleuronectes platessa</i> * | Plaice         | 2-6               | 3-4 | 1-4  |             | 1-3  | 1-4  | 12-3 | 3-4 | 2-7 | 1-3                      | NA  | 1-3  | 2-4    | 12-3  | 12-3   | 1-4     | 2-4    | NA    | NA    | NA               |        | NA                |
| <i>Microstomus kitt</i>        | Lemon sole     | NI                | NI  | 4-8  |             | 5-10 | 5-10 | 4-6  | 5-8 | 5-8 | 4-7                      | NA  | NI   | NI     | 4-6   | 3-6    | NI      | NI     | NA    | NA    | NA               |        | NA                |
| <i>Solea vulgaris</i>          | Common sole    | NA                | NA  | 4-7  |             | NA   | 3-6  | 3-6  | NA  | NA  | NA                       | NA  | 4-6  | 3-5    | 3-5   | 2-5    | 2-5     | 2-5    | 2-4   | 2-4   | 1-4 <sup>3</sup> |        | 12-4              |
| <i>Sardina pilchardus</i>      | Pilchard       | NA                | NA  | NA   |             | NA   | NA   | NA   | NA  | NA  | NA                       | NA  | NA   | NI     |       |        | 2-3     | 1-3    | 9-6   | 9-6   | 10-6             |        | 10-4 <sup>1</sup> |
| <i>Clupea harengus</i>         | Herring        | NA                | 2-4 | 2-4  | 3-6<br>9-10 | 8-9  | 8-10 | 9-1  | 6-7 | 2-4 | 3-4<br>8-10 <sup>2</sup> | NA  | 9-3  | 10-12  | 11-12 |        | 10-3    | 10-11  | 11-1  | NA    | NA               |        | NA                |

\*Species recommended by the former Joint Monitoring Group of the Oslo and Paris Commissions.

NI = No information.

NA = Not applicable.

<sup>1</sup>Spawning period with two peaks, the largest one in Nov.-Dec. and another between Mar. and Apr./May.

<sup>2</sup>North Minch 3-4, remainder VIa 8-10.

<sup>3</sup>Dec.-Feb. or Jan.-Apr., depending on subarea.

Table 5.4.1. (continued)

| COASTAL SHELLFISH SPECIES  |                | COUNTRY |                   |                     |         |         |                     |             |            |          |           |        |                                    |
|----------------------------|----------------|---------|-------------------|---------------------|---------|---------|---------------------|-------------|------------|----------|-----------|--------|------------------------------------|
| Latin name                 | English name   | Belgium | Denmark           | France              | Germany | Iceland | Ireland             | Netherlands | Norway     | Portugal | Spain     | Sweden | UK                                 |
| <b>1st Choice Species</b>  |                |         |                   |                     |         |         |                     |             |            |          |           |        |                                    |
| <i>Mytilus</i> sp.*        | Mussel         | 4-5     | 5-6, 9            | 2-6                 | 4-9     | 6-7     | 2-5 (main)          | 4-5         | 5-7 (main) | 4-6      | 3-5, 9-10 | 5-6    | 4-5 (Eng.)<br>4-10 (Sco.)          |
| <b>2nd Choice Species</b>  |                |         |                   |                     |         |         |                     |             |            |          |           |        |                                    |
| <i>Crassostrea gigas</i>   | Pacific oyster | NA      | Variable          | 6-9                 | 6-9     | NA      | NA                  | 7-8         | NA         |          | NI        | NA     | 7-10 (Eng.)<br>(occasionally only) |
| <b>Other Species</b>       |                |         |                   |                     |         |         |                     |             |            |          |           |        |                                    |
| <i>Palaemon serratus</i> * | Prawn          | NI      | 5-7<br>(sp. rare) | 11-6 (egg carrying) |         | NI      | 11-2 (egg carrying) |             | NI         | 12-1     | 12-1, 3-5 | NI     | NI                                 |

\*Species recommended by the former Joint Monitoring Group of the Oslo and Paris Commissions.

NI = No information.

NA = Not applicable.

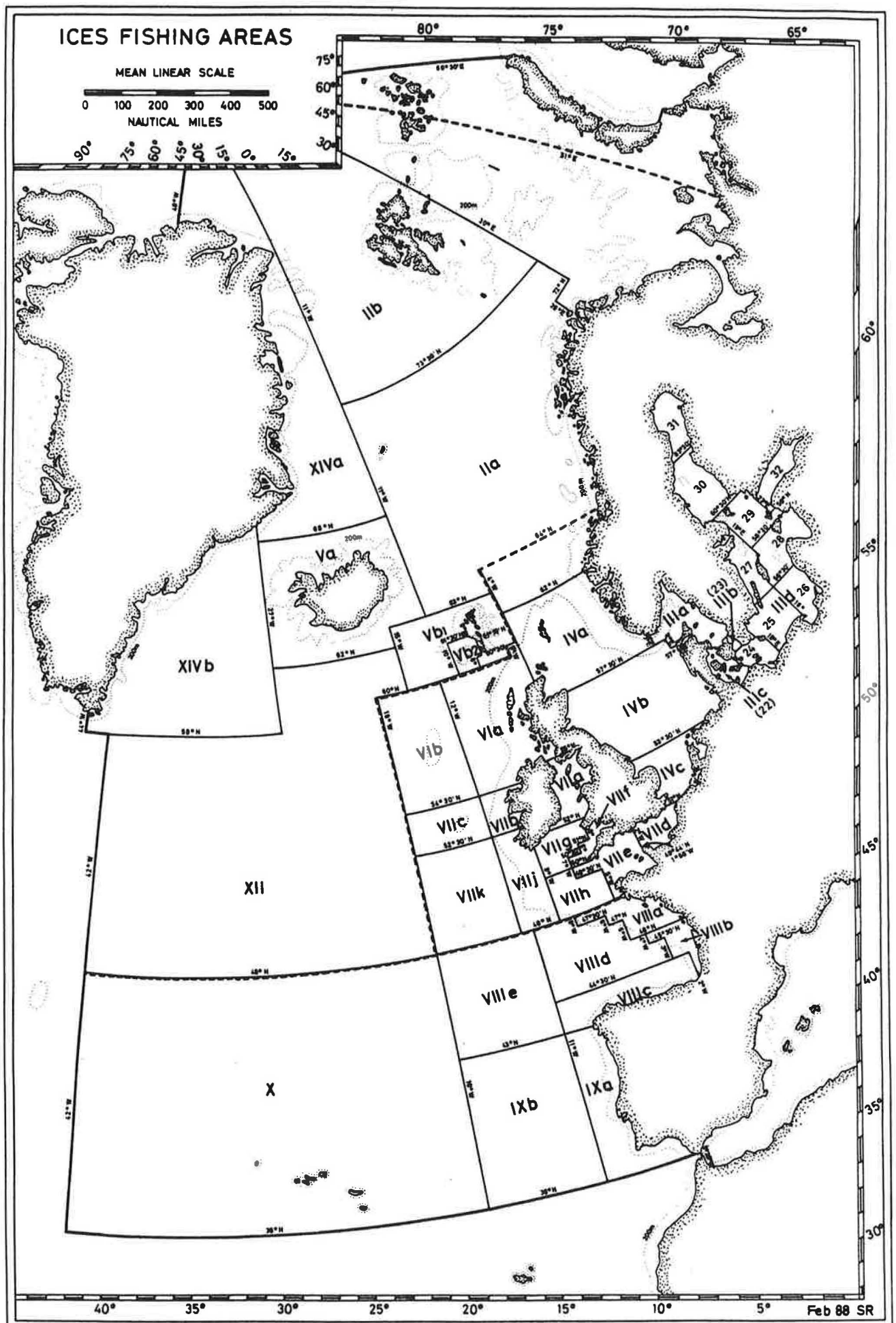


Figure 5.4.1. Map depicting ICES Fishing Areas in the Northeast Atlantic.

- In spatial/temporal trend studies, the more dominant CBs, e.g., CB 153, can be used to represent the burden of CBs since these can be analysed much more easily.

#### e) *Marine mammals*

Concerning marine mammals, a distinction must be made between the different species because of their varying behaviour and biology. Some species are unsuitable for spatial or temporal trend programmes because of their mobility and longevity, however, other species seem to be suitable. In several countries, research is being conducted to investigate the possibility of using marine mammals for contaminant monitoring. Countries are encouraged to continue their national programmes, and to submit data for the planned OSPAR Regional Assessments. They should also submit data to ICES for the new database on contaminants in marine mammals.

### 4) Polycyclic aromatic hydrocarbons (PAHs)

#### a) *Statistical power*

SIME comments on PAHs also implied a need for an assessment of the necessary power of monitoring programmes, as discussed for metals and CBs, above.

#### b) *Choice of species*

In fish tissues, PAH concentrations are likely to be low because of their high metabolic capacity towards these compounds, and analysis of fish muscle should generally be considered only if it is necessary to confirm a low human dietary intake from this source (Law and Biscaya, 1994). Exposure of fish can be assessed by measurement of polar metabolites in bile. In shellfish, the metabolic capacity is lower, and bioaccumulation can yield higher concentrations in their tissues. Shellfish are, therefore, considered more suitable for studies of the spatial distribution of PAHs in the environment, although care must still be taken in choosing sampling locations, as relatively small local sources can be important in determining PAH burdens.

#### Reference

Law, R.J., and Biscaya, J. 1994. Polycyclic aromatic hydrocarbons (PAH): Problems and progress in sampling, analysis and interpretation. *Marine Pollution Bulletin*, 29: 235–241.

### 5) Other compounds of concern

The 1992 report of the Advisory Committee on Marine Pollution (ICES, 1992) includes a review of the hazard classification schemes in use at that time for the selection

of priority contaminants; this advice could be of use in designing the JAMP.

#### Reference

ICES. 1992. Report of the ICES Advisory Committee on Marine Pollution, 1992. ICES Cooperative Research Report, No. 190, pp. 62–67.

### 5.4.3 Spatial distribution of contaminants

The ACME considered that while the statistical advice already available should enable informed decisions to be made on how to design temporal trend studies, there is clearly a need to further develop comparable guidance on objectives and statistical methodology for spatial distribution programmes. This is particularly the case for some of the objectives of the SIME programme concerning the spatial distribution of TBT, non-*ortho* and mono-*ortho* CBs, and PAHs in sediment (with bivalves as an alternative).

A spatial survey may have different objectives, such as mapping, obtaining estimates of a parameter distribution, or localization of “hot spots.”

#### a) *Concentration mapping*

Mapping aims at visualizing spatial structures. Various methods of interpolation are available by which iso-concentration curves may be drawn. It must be emphasized, however, that methods of interpolation such as kriging should be done by skilled analysts. The estimates will be better if they are made from a regular grid sampling scheme with estimations of spatial correlation at a small scale.

#### b) *Estimation of distribution population parameters (mean, range, quantiles) in a given area*

For the estimation of these quantities, random sampling is the simplest technique with the additional advantage of wide applicability. It should be noted, however, that methods optimal for the estimation of means over an area, etc., may not be optimal for the purposes of mapping and spatial interpolation.

#### c) *Identification of localized areas with elevated levels*

Detecting “hot spots” could become a very costly exercise if nothing is known about the various means of locating these hot spots. Concentration gradients in the region around hot spots can be explored by sampling along a transect leading away from the identified hot spot with, perhaps, logarithmically spaced stations.

It is to be noted that power does not apply to mapping because there is no hypothesis to be tested unless some specific objectives have been defined. However, power is relevant to some of the objectives. For example, the power of a programme to detect an 'area of special concern' of a certain size can be considered.

The ACME emphasized that spatial data require a clear statement about the area sampled and the method by which sampling sites are selected.

#### **5.4.4 Sample sizes for monitoring temporal trends of contaminants in fish**

##### *Request*

Item 10 of the 1995 requests from the Helsinki Commission.

##### *Source of the information presented*

The report of the ICES/HELCOM Workshop on Temporal Trend Assessment of Data on Contaminants in Biota from the Baltic Sea, the 1995 report of the Working Group on Statistical Aspects of Environmental Monitoring (WGSAM), and the report of the 1995 Joint Meeting of WGSAM and the Working Group on Environmental Assessment and Monitoring Strategies (WGEAMS).

##### *Status/background information*

The Joint Meeting of WGSAM and WGEAMS investigated available data from time series on concentrations of mercury in fish and shellfish within the OSPAR area and the results of relevant analytical intercomparison exercises. It considered a model of a linear change in log-median concentrations, and then divided the overall variance into several components. Finally, it studied how the individual components were affected by changes in the length of the time series (T) and the sample size (R). It was concluded that the power is generally low and only slightly affected for  $R > 10$ . It was emphasized that the material behind this study is weak, and that a more thorough study, covering all combinations of matrix, contaminant, and location should be performed.

This conclusion was subsequently reviewed and adopted by the Workshop on Temporal Trend Assessment of Data on Contaminants in Biota from the Baltic Sea, which added that this conclusion stems from the fact that within-sample variation seems to be relatively small compared to other sources of variation. When these other sources of variation (mainly variations in laboratory performance and variations between cruises) are reduced, the question of sample size should be readdressed.

The ACME noted that these conclusions on sample size were based on a very limited data set, and did not find that it was in a position to provide definitive advice on optimal sample size for temporal trend monitoring programmes at the present time. Moreover, ACME recognized the need for better estimates of the various variance components associated with time series studies. Accordingly, the ACME recommended that WGSAM produce a detailed overview of the information needed and/or design a pilot project that can provide this information.

#### **5.5 Analytical Methods and Choice of Matrices for the Measurement of Organotin in the Marine Environment**

##### *Request*

Item 8 of the 1995 requests from the Helsinki Commission.

##### *Source of the information presented*

The 1995 report of the Marine Chemistry Working Group (MCWG).

##### *Status/background information*

On the basis of its consideration of the topic of analytical methods and choice of matrices for the measurement of organotin in the marine environment, the Marine Chemistry Working Group recommended that a preliminary survey of existing concentrations of organotin be made before a new monitoring programme is started. For this purpose, sediment samples should be analysed, given that the highest concentrations in the marine environment are expected to be found in the sediments because organotin compounds are accumulated there and are only very slowly degraded. In anaerobic sediments, for example, TBT has a half life of several years. Sediment samples from coastal areas, including areas close to and in different types of marinas and also from an important shipping lane (e.g., the major shipping lane between Sweden and Finland), should be analysed. In addition, samples from the recent Baseline Study of Contaminants in Baltic Sediments should be analysed for organotin, if possible. Also where possible, mussel samples from the same areas could form a supplement to the sediment samples.

The MCWG further recommended that from the geographical survey, suitable sites for trend monitoring should be chosen. It was recommended that a biological tissue sample (possibly *Macoma balthica*) should be chosen as a matrix, as models have shown that the concentrations in bivalve tissues reflect a recent exposure. Thus, it will be possible to follow a change in the organotin load by measuring the concentrations in a



biological tissue. The sediment concentrations represent an integrated exposure.

It was recommended that only a few specialized laboratories be used for the analysis of all samples, due to the rather difficult procedure.

Finally, it was noted that it is important to find a good biological indicator for less saline areas for biological effects monitoring. Here more research is needed.

## **5.6 Techniques for Monitoring Contaminants in Sediments**

### **5.6.1 Variance factors in sediment analysis**

#### *Request*

There is no specific request; this is part of the continuing work of ICES on issues related to monitoring contaminants in marine sediments.

#### *Source of the information presented*

The 1995 reports of the Working Group on Marine Sediments in Relation to Pollution (WGMS), and the Joint Meeting of the Working Group on Environmental Assessment and Monitoring Strategies (WGEAMS) and the Working Group on Statistical Aspects of Environmental Monitoring (WGSAM).

#### *Status/background information*

Noting the importance of identifying and quantifying sources of variance in monitoring programmes for contaminants in marine media, the WGMS developed a list of the sources of variance and reviewed available information on the magnitudes of each type of variance identified, including variance in normalizing or compensating variables. The sources of variance include:

- 1) Analytical variance (measurement error) in the determination of metal concentrations in sediments;
- 2) Analytical variance in the determination of organic contaminant concentrations in sediments;
- 3) Analytical variance in organic carbon determinations in sediments;
- 4) Precision of determinations of carbon and nitrogen concentrations in marine sediments;
- 5) Analytical variance in particle size analysis;

- 6) Interannual variation in metal concentrations in fine-grained surface sediment, e.g., at a sludge disposal site.

For some of these variables, information was available from the QUASIMEME programme on within- and between-laboratory components of variance of chemical analyses. The analytical variance in the determination of concentrations of metals in sandy sediments is shown in Table 5.6.1 and in silty sediments in Table 5.6.2. Table 5.6.3 gives between-laboratory coefficients of variation for single determinations of a number of organic contaminants in sediments. This information has been compiled from reports on the results of QUASIMEME Laboratory Performance Studies for 1993 and 1994.

In addition, the results of a UK study (Kelly *et al.*, 1994) examining the short- and long-term analytical variance and field variance of organic contaminants in sediments from the Garroch Head sludge disposal site in Scotland were reviewed. Knowing both analytical variances and field distribution variances and the relative costs of field sampling, sample processing, and chemical analysis allowed estimation of the relative cost-effectiveness of different sampling and sample pooling strategies. The results of a German study on spatial variance of trace metals at a tidal mudflat in the Weser estuary were also reviewed. Total metal analyses of the < 20 µm fraction revealed that inhomogeneous distribution maps were produced upon kriging the data. Spatial variance was attributed to inhomogeneity in post-depositional diagenetic processes rather than grain size distribution or mineralogy at the site.

The joint meeting of WGSAM and WGEAMS discussed methods for assessing the statistical power of monitoring programmes in mapping spatial distributions of contaminants in sediments and biota, using data sets from the ICES/HELCOM Baseline Study of Contaminants in Baltic Sea Sediments and the OSPAR/NSTF Baseline Study of Contaminants in North Sea Sediments. Five objectives for sediment monitoring programmes were defined, along with an indication of the information that the statistician would need from the geochemist to design the programme.

These objectives are:

- 1) To estimate the concentration at all points in an area with a certain precision. The procedure will involve sampling followed by interpolation. The geochemist will tell the statistician the area, the financial and logistical resources available, and the desired precision. If possible, the geochemist will also provide information leading to a better estimate of the variogram: analytical variability, ideas of micro-scale distributions or spatial extent of the observed phenomenon. Defining the precision is another way of defining the resolution of the map.



**Table 5.6.1.** Assigned values (robust means in 1993) and coefficients of variation (CV) of analyses of metals in sandy sediment.

| Element   |      | Assigned value<br>(mg kg <sup>-1</sup> ) | Mean within-lab<br>CV%<br>1993 | Between-lab CV% of<br>means<br>1993 | Between-lab CV% of<br>means<br>1994 |
|-----------|------|--|--------------------------------|-------------------------------------|-------------------------------------|
| Aluminium | 1993 | 19810                                    | 4.9                            | 13.2                                |                                     |
|           | 1994 | 29300                                    |                                |                                     | 36.5                                |
| Cadmium   | 1993 | 0.031                                    | 14.9                           | 53.0                                |                                     |
|           | 1994 | 0.03                                     |                                |                                     | 69.1                                |
| Copper    | 1993 | 3.02                                     | 9.83                           | 26.5                                |                                     |
|           | 1994 | 4.59                                     |                                |                                     | 20.4                                |
| Lead      | 1993 | 4.2                                      | 5.68                           | 14.5                                |                                     |
|           | 1994 | 17.1                                     |                                |                                     | 17.7                                |
| Mercury   | 1993 | 0.023                                    | 18.6                           | 38.8                                |                                     |
|           | 1994 | 0.024                                    |                                |                                     | 52.8                                |
| Zinc      | 1993 | 30.5                                     | 6.14                           | 11.4                                |                                     |
|           | 1994 | 30.5                                     |                                |                                     | 8.4                                 |
| Arsenic   | 1994 | 6.1                                      |                                |                                     | 19.1                                |
| Chromium  | 1994 | 35.0                                     |                                |                                     | 23.5                                |
| Nickel    | 1994 | 12.0                                     |                                |                                     | 11.2                                |

**Table 5.6.2.** Assigned values (robust means in 1993) and coefficients of variation (CV) of analyses of metals in silty sediment.

| Element   |      | Assigned value<br>(mg kg <sup>-1</sup> ) | Mean within-lab<br>CV%<br>1993 | Between-lab CV% of<br>means<br>1993 | Between-lab CV% of<br>means<br>1994 |
|-----------|------|--|--------------------------------|-------------------------------------|-------------------------------------|
| Aluminium | 1993 | 30110                                    | 4.26                           | 13.2                                |                                     |
|           | 1994 | 36400                                    |                                |                                     | 24.2                                |
| Cadmium   | 1993 | 0.33                                     | 9.25                           | 20.1                                |                                     |
|           | 1994 | 1.46                                     |                                |                                     | 21.6                                |
| Copper    | 1993 | 9.11                                     | 6.88                           | 19.4                                |                                     |
|           | 1994 | 24.60                                    |                                |                                     | 10.1                                |
| Lead      | 1993 | 29.2                                     | 6.55                           | 16.7                                |                                     |
|           | 1994 | 49.8                                     |                                |                                     | 16.0                                |
| Mercury   | 1993 | 0.15                                     | 5.33                           | 14.2                                |                                     |
|           | 1994 | 0.38                                     |                                |                                     | 19.6                                |
| Zinc      | 1993 | 77.13                                    | 3.90                           | 8.49                                |                                     |
|           | 1994 | 170                                      |                                |                                     | 7.7                                 |
| Arsenic   | 1994 | 16.6                                     |                                |                                     | 11.3                                |
| Chromium  | 1994 | 79.3                                     |                                |                                     | 28.6                                |
| Nickel    | 1994 | 22.3                                     |                                |                                     | 17.2                                |

**Table 5.6.3.** Assigned values and between-laboratory coefficients of variation (%) of analyses of organic contaminants in a marine sediment sample, QUASIMEME 1994 report.

| Determinand     | Assigned value<br>$\mu\text{g kg}^{-1}$ | Between-lab<br>CV% |
|-----------------|---|--------------------|
| CB28            | 0.80                                    | 42.2               |
| CB52            | 1.4                                     | 38.3               |
| CB101           | 3.4                                     | 26.3               |
| CB105           | 1.1                                     | 44.6               |
| CB118           | 2.7                                     | 30.1               |
| CB138           | 5.2                                     | 33.4               |
| CB153           | 6.2                                     | 26.5               |
| CB156           | 0.58                                    | 54.1               |
| CB180           | 3.8                                     | 31.9               |
| HCB             | 0.54                                    | 36.1               |
| p,p'-DDE        | 0.90                                    | 42.3               |
| $\alpha$ -HCH   | 0.08                                    | 83.5               |
| $\gamma$ -HCH   | 0.13                                    | 77.3               |
| p,p'-DDD        | 1.1                                     | 49.9               |
| p,p'-DDT        | 0.54                                    | 100.6              |
| dieldrin        | 0.42                                    | 63.4               |
| trans-nonachlor | 0.06                                    | 91.0               |

- 2) To estimate a parameter or parameters (e.g., mean, median, 95th percentile) to describe a population within an area with a specified precision. The geochemist will tell the statistician the available resources and desired precision, and, if possible, provide an estimate of the variance in the data.
- 3) To locate all areas of special concern of a certain size in a geographical area, with a specified probability of success (i.e., with a specified precision). The geochemist will tell the statistician the size and shape of the area of special concern and the desired probability of success. (Normal mapping as described in (1), above, may not show areas of special concern.)
- 4) To determine a specified change in a parameter (as in (2), above) with a specified precision over a specified time period. The geochemist will tell the statistician the size of the change, the precision, and the time period.
- 5) To determine a specified change in the spatial extent of an area with a specified precision over a specified time period. For example, in the case of a sewage disposal site, the boundary could be where the sediment has more than 2% carbon. The geochemist will tell the statistician what constitutes the area, the precision, and the time period.

The theory for assessing temporal changes in maps is not yet well developed, although work is continuing in this field. Geochemists should enhance their understanding of precision in terms of geochemical variation.

## Reference

Kelly, A.G., Wells, D.E., and Fryer, R.J. 1994. Sampling strategy to detect a change in concentration of trace organic contaminants in marine sediment. *Science of the Total Environment*, 144: 217–230.

## 5.6.2 Influence of sieving techniques and organic carbon on concentrations of contaminants in sediments

### Request

There is no specific request; this is part of the continuing work of ICES on issues related to the monitoring of contaminants in marine sediments.

### Source of the information presented

The 1995 report of the Working Group on Marine Sediments in Relation to Pollution (WGMS).

### Status/background information

A number of questions have been raised concerning the influence of sieving techniques on concentrations of contaminants in sediments, both in terms of the potential loss of contaminants from the sample and the potential con-tamination of the sample during sieving. In order to study these potential problems, an investigation was carried out on the influence of wet sieving techniques on concentrations of organic contaminants in sediments. The sieving process included simultaneous ultrasonic treatment and the addition of agate balls. Sieving of the fraction  $< 20 \mu\text{m}$  was conducted on samples with considerably different grain size compositions (ranging from 28% to 99%  $< 20 \mu\text{m}$ ) and contamination levels. All samples were analysed for total organic carbon, a number of organochlorine compounds, and PAHs. Based on the results presented, it was concluded by WGMS that the sieving technique used did not affect the concentrations of organic contaminants and that it seems to be an appropriate approach for compensating for grain size effects, except possibly for lindane and PAHs. For these compounds, further studies are needed and will be performed.

Various procedures for determining organic carbon concentrations in sediments were reviewed. The procedures included wet oxidation methods and dry combustion methods. Different approaches even among the dry combustion methods may lead to considerable variability in between-laboratory comparisons. In view

of the importance of organic carbon determinations in the interpretation of the observed distributions of organic and inorganic contaminants, it is recommended that further attention be given to the intercomparison of organic carbon determinations; this may best be achieved through the QUASIMEME programme.

### **5.7 Determination of Dissolved Organic Carbon in Sea Water**

#### *Request*

There is no specific request; this is part of the continuing work of ICES on issues relevant to measurements of marine parameters.

#### *Source of the information presented*

The 1995 report of the Marine Chemistry Working Group (MCWG).

#### *Status/background information*

It was noted that information presented at the 1994 MCWG meeting, indicating that wet oxidation methods for the determination of dissolved organic carbon (DOC) in sea water gave comparable results to methods involving high-temperature combustion, has now been confirmed by independent investigations. An intercomparison exercise within the Joint Global Ocean Flux Study (JGOFS) showed that there was no significant difference in the results from several different methods, using both high-temperature combustion and wet oxidation (Marine Chemistry, 48: 91–108 (1995)).

In addition, MCWG members presented further evidence from their own laboratories that the wet oxidation/UV technique can give results that show excellent comparability with results obtained by high-temperature combustion.

Concern was expressed, however, over the way that DOC data are gathered and treated. As the nature of DOC is not yet well established, and since the DOC composition undoubtedly varies both seasonally and geographically, there are potential dangers in treating a non-specific determinand like DOC as a single component with known behaviour. Some persons tend to overestimate the usefulness of DOC in linking variations in the DOC content in sea water to the variations of other substances. Unless the DOC fraction is more specifically characterized, it is unlikely to supply useful information for monitoring. There is a need for more background work on how DOC should be used before it can be generally recommended for inclusion in monitoring programmes.

### **5.8 Monitoring the Effects of Anthropogenic Nutrient Inputs and Possible Effects on Changing N/P Ratios**

#### *Request*

Item 1.5 of the 1995 Work Programme from the Oslo and Paris Commissions.

The Oslo and Paris Commissions asked ICES to provide a synthesis of new information on the relationship between inputs of contaminants (including nutrients), concentrations in water, sediment, and biota and possible effects thereof. The request arose from the view previously iterated by ACME that increased fluxes of nutrients, rather than elevated nutrient levels, cause an increased algal biomass. Based on this summary, OSPAR requested further advice on how to monitor the effects of changing nutrient inputs from diffuse sources and point sources.

#### *Source of the information presented*

The 1995 report of the Working Group on Phytoplankton Ecology (WGPE).

#### *Status/background information*

Connections between increased total nutrient levels and phytoplankton and associated ecosystem responses have become evident from long-term data sets available from coastal areas. Evaluation of site-specific events often indicates seemingly paradoxical responses, however. Very high production rates may occur during periods of non-detectable inorganic nutrient levels, or relatively low biomass concentrations. This discrepancy reveals that fluxes of nutrients or effects thereof, instead of residual concentrations, would be more meaningful objects for monitoring.

Plant biomass in the marine environment is, at least during some periods, limited by nutrient availability and increasing nutrient input via eutrophication will, when nutrient limitation is in effect, increase plant growth and/or change the species composition of the plant community. In addition to inorganic nutrients, organic nutrients might also support a considerable primary production.

Nutrients enter into and cycle in the coastal ecosystem in a variety of processes in scales ranging from atmospheric inputs and major river inflows to nutrient uptake by single algal cells. The WGPE drew attention to these different flux scales with examples of the time required to replace the initial nutrient supply in different situations and sources from where the resupply might originate. However, the 'nutrient flux' concept was not fully qualified in the WGPE report.

The path *nutrient input* → *nutrient uptake* → *growth* → *biomass accumulation* in planktonic organisms is a complex one and the relevant time scales are short, within the range of hours to days. Measurements of the fixation of nutrient molecules by plankton, e.g.,  $^{14}\text{CO}_2$  uptake (the traditional method for measuring primary production) cannot, for several reasons, be converted to an overall estimate of nutrient flux in the ecosystem. Firstly, the nutrient fixation value consists of two components: 'new production' and 'regenerated production'. The proportions of these components vary depending upon factors affecting nutrient concentrations in the proximate environment of the plankton, i.e., season, loading from land, turbulence, upwelling, etc. Regenerated nutrient uptake is operative without external input of nutrients into the system, and the same nutrient molecules are repeatedly used for biomass production. 'New' production is based on external input of nutrients from loading or through nutriclines. 'New' production would be a suitable estimate for the nutrient flux into the pelagic community. However, the direct methods using, e.g., isotope tracers are not suitable for monitoring work and are very expensive. Secondly, instantaneous nutrient concentrations are subject to variability due to changing hydrographic conditions (currents, mixing, pycnocline processes) and tidal flush. The main driving forces for these are weather conditions and the variations are, therefore, highly stochastic.

Although measured fixation rates of nutrients by plankton may be considerable, they may not result in increased biomass due to several loss factors. Biomass accumulation in plankton results, in fact, from a balance/imbalance between growth-supporting factors (nutrients, 'bottom-up control') and loss factors due to trophic relationships (grazing, 'top-down control'), sedimentation or advection.

The effects of changing N/P ratios on the pelagic community have been actively investigated in cultures and 'mesocosm' experiments. In these investigations it has been possible to define theoretical levels of N/P ratios where changes in species composition, mean population cell size, food-web structure, toxin production, etc., start to appear. However, due to the complexity of the regulating factors of pelagic primary production described above, these theoretical levels have not been verified in nature.

#### *Need for further research or additional data*

A substantial part of the nutrient flux is cycled and retained in the littoral ecosystem, which obviously alters the quantity and the ratio of nutrients in the flux reaching offshore waters. There are regions where a large anthropogenic input may be trapped in the littoral ecosystem and regions where the same level of input is mainly directed to planktonic organisms. Basic information is required on the retention of nutrients in littoral/onshore ecosystems, a question which will be highlighted in projects within the framework of the

programme Land-Ocean Interactions in the Coastal Zone (LOICZ).

#### *Recommendations*

In summary, it appears that the relationships between nutrient inputs, concentrations, and effects are highly site-specific and modified by local conditions. It is possible to prepare a scientifically acceptable synthesis of causal relationships between the three components on a regional basis, when the different boundary conditions, coastal current dispersions, hydrographic characteristics, anthropogenic activities, etc., can be taken into account. The ACME recommended that in future the question be considered on a regional basis; otherwise, the advice given by ACME remains at too general a level and does not help OSPAR in its regulatory decisions.

The ACME supported the view of WGPE that the sampling strategies and devices to detect the effects of anthropogenic nutrient inputs should be designed in correspondence with the spatial and temporal scales of the phenomena under consideration. If plankton, especially algal blooms, are monitored, there is a requirement for high resolution measurements, which cannot be done without some degree of automation. The ACME supported the recommendation of the WGPE concerning the installation of automated, even unattended, systems on ships and buoys with high spatial and temporal coverage to determine plankton biomass and composition, especially blooms. These systems will provide an efficient tool for 'early warning' of plankton blooms as well as a statistically satisfactory data set about the levels of algal biomass over large areas.

The ACME also supported the recommendation of the WGPE concerning the use of a gradient approach by selecting monitoring stations along an onshore-offshore line of decreasing nutrient levels, decreased benthic-pelagic coupling, and decreased coastal current dispersion. Nutrient concentration measurements probably cannot be totally omitted, because this information is important for *a posteriori* examination of, e.g., exceptional harmful blooms. However, the locations of sampling stations for measurements of nutrient concentrations, ratios, and bioavailability should be chosen to give information about the retention and transformation of nutrients along the transect *end of the pipe discharge* → *littoral ecosystem* → *offshore*.

However, the ACME noted that some of the proposals presented by the WGPE will be expensive in manpower and resources to implement. Integrating methods may in some cases provide a satisfactory, cost-effective solution to the problem. In some situations, inventories of the increase in biomass of macroalgae and rooted plants may give a satisfactory estimate of the effects of changing nutrient fluxes. As suggested by the WGPE, measurement

of sedimentation rate as an estimate of 'new' production is another possible, integrative method. The ACME also recalled that the results of Norwegian research concerning the monitoring of oxygen consumption rates in Norwegian fjords had been drawn to its attention during its 1993 meeting. The Working Group on Shelf Seas Oceanography had reviewed this method and noted certain caveats related to fluctuations in the coastal zone. However, it is clear that this technique offers potentially a very cost-effective and statistically reliable means to monitor the effects of changing nutrient fluxes in the North Sea. This work is now being prepared for peer review publication.

The monitoring programme needs to be complemented by nutrient flux measurements between different food-web and ecosystem components, aiming at compilation of a complete nutrient budget at different times of the annual cycle. This cannot be included in a monitoring programme, but is a subject of research programmes. The ACME emphasized the importance of basic research programmes to support a proper understanding and interpretation of nutrient/plankton interactions.

## 6 QUALITY ASSURANCE PROCEDURES AND INTERCOMPARISON EXERCISES

### 6.1 Quality Assurance of Biological Measurements in the Baltic Sea

#### *Request*

Item 3 of the 1995 requests from the Helsinki Commission.

#### *Source of the information presented*

The 1995 report of the ICES/HELCOM Steering Group on Quality Assurance of Biological Measurements in the Baltic Sea (SGQAB).

#### *Status/background information*

The ACME noted that the development of national Quality Assurance (QA) procedures for biological determinands is well under way in several countries, but recognized with concern that it had not yet started in some of the countries and that no information was available from two countries.

The ACME recognized that the SGQAB had prepared recommendations to produce "In-House QA Manuals" for microbiology, phytoplankton, and chlorophyll *a* measurements, to be completed by September 1995, and for measurements of macrozoobenthos and zooplankton before the end of this year. Furthermore, shipboard working practices in relation to macrozoobenthos monitoring were recommended to be documented by videotape. These materials will serve as a good basis for the standardization of methods.

The ACME also reviewed the plans of the SGQAB to organize a Second Workshop on Quality Assurance of Pelagic Measurements in the Baltic Sea in Warnemünde, Germany, on 16–20 September 1995 and noted that plans for this workshop are well under way for phytoplankton and microbiological parameters. Regional intercalibrations of macrozoobenthos methods are in different stages of preparation in different regions, but all of them should be completed during 1995. Intercomparisons/intercalibrations of zooplankton and primary productivity measurements are planned to be made in 1996.

It was agreed that, from the quality assurance point of view, some means should be found to continue the series of species identification workshops for phytoplankton that were begun several years ago; in addition, the initiation of such workshops for other parameters including taxonomical information is desirable.

#### *Recommendations*

The ACME recommended that the SGQAB continue its work with the aim of completing the intercomparison/intercalibration exercises according to the planned schedule by the end of 1996. The SGQAB was advised to take a coordinating role when the laboratories prepare their "In-House QA Manuals" for the various parameters.

### 6.2 Intercomparison Exercise on Scope for Growth Measurements

#### *Request*

This is part of the continuing ICES work of coordinating quality assurance activities and reporting on the results and their implications for monitoring programmes.

#### *Source of the information presented*

The 1995 report of the Working Group on Biological Effects of Contaminants (WGBEC).

#### *Status/background information*

The ACME noted that progress on the Scope for Growth (SFG) intercomparison exercise has been slow mainly due to a lack of funding for the exercise of the coordinating institute, the Plymouth Marine Laboratory. The preliminary work that has been carried out includes the identification and establishment of contact with laboratories capable of measuring SFG in bivalves. Agreement has been reached to adopt a standard set of procedures, based on the manual produced by the Plymouth Marine Laboratory (UK) for FAO and UNEP training workshops in the Mediterranean and Thailand. Appropriate and reliable procedures have been developed for dosing mussels with toxicants prior to sending them to various laboratories in Europe for subsequent measurement of SFG.

In addition, a preliminary run has been conducted with control mussels (sending them out for measurement) to identify any potential problems and differences among laboratories before sending the exposed and unexposed mussels for measurement as part of the laboratory intercomparison exercise proper. The exercise is being carried out in a manner similar to that of inter-laboratory comparisons of chemical analytical procedures.



When the exercise has been completed (at the end of 1995), an overall analysis and interpretation of the results will be prepared and this information will be supplied to participating laboratories.

It was noted that the WGBEC has requested the organizer to consider whether the measurement of clearance rate alone could be used as the initial screening method. Clearance rate is a simpler method but it is unclear at present how serious the loss of information would be if only clearance rate was determined in monitoring programmes. Nonetheless, it was agreed that laboratories should be allowed to participate in the intercomparison exercise on the basis of measurements of clearance rate alone.

### **6.3 Quality Assurance of Chemical Measurements in the Baltic Sea**

#### *Request*

Item 3 of the 1995 requests from the Helsinki Commission.

#### *Source of the information presented*

The 1995 report of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea.

#### *Status/background information*

The ACME reviewed the report of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea and noted that progress has been made in the development and implementation of quality assurance (QA) activities in the laboratories contributing to the HELCOM Baltic Monitoring Programme (BMP).

A major activity of the Steering Group has been to prepare analytical quality assurance guidelines for chemical components to be measured in the next phase of the BMP. A draft of the quality assurance guidelines document was presented for review. This document covers appropriate procedures for the mandatory determinands to be measured in the open Baltic Sea under the BMP. These include nutrients (nitrate, nitrite, ammonium, total nitrogen, phosphate, total phosphorus, and silicate), organic contaminants (DDTs, chlorobiphenyls (CBs), hexachlorobenzene (HCB), and  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane ( $\alpha$ - and  $\gamma$ -HCH)), and inorganic contaminants (mercury, lead, cadmium, and copper). It was noted, however, that in principle these guidelines could also be applied to these and other determinands and matrices to be measured under the HELCOM Coastal Monitoring Programme.

For nutrient measurements, the QA guidelines describe appropriate procedures for the collection, storage, and pre-treatment of samples, and the analysis of the sample, including calibration procedures and blank measurements. For contaminants, the guidelines describe appropriate procedures for the dissection of fish and mussel samples, the storage of samples, and sample pre-treatment. Key issues concerning the analytical procedures for organic and inorganic contaminants are then covered, including calibration and blank measurements. Finally, descriptions are given of the main types of internal quality control methods used, such as control charts and Cusum charts.

The ACME noted that these guidelines will be given further review over the next few months. The final document will be completed in late 1995 or early 1996, and will be submitted to the Helsinki Commission after final review.

### **6.4 Intercomparison Exercise on Measurements of Lipids in Marine Samples**

#### *Request*

Item 2.1 of the 1995 Work Programme from the Oslo and Paris Commissions.

#### *Source of the information presented*

The 1995 report of the Marine Chemistry Working Group (MCWG).

#### *Status/background information*

The Marine Chemistry Working Group reviewed the work concerning the determination of lipids that has been undertaken within the QUASIMEME project, including an on-going lipid intercomparison exercise. A workshop has also been held, the report of which contains the results of the first step of the lipid intercomparison exercise, the outcome of the various workshop discussions, copies of the posters presented, and a summary of a questionnaire that was circulated to the participants beforehand. The results obtained in the intercomparison exercise compared well, especially for those laboratories using the Bligh and Dyer total lipid extraction method, considering that most laboratories were applying this method for the first time. This method was, as a result, recommended for the determination of total lipids and participants were requested, during the next step of the intercomparison exercise, to determine total lipids using the Bligh and Dyer method along with the determination of extractable lipids using their routine laboratory method. This intercomparison exercise will continue for the duration of the project, and should provide both an indication of the overall laboratory performance, and an assessment of the Bligh and Dyer

total lipid method and the extractable lipid methods. However, the fact that the Bligh and Dyer method is considered to be the best available creates an additional problem, as it involves the use of chloroform, production of which could cease in the near future under the Montreal Protocol. A number of laboratories are, therefore, working on alternative methods that do not require the use of chlorinated solvents. It was suggested that this work should be coordinated, so that effort is not duplicated. Another suggestion was that the applicability of using lipid proportion as a normalizing factor for organic contaminant data should be reconsidered. The lipid content of an organism is dependent, for example, on the physiological state of the organism, and this may therefore influence the validity of lipids as a cofactor, for instance during fish spawning.

#### *Need for further research*

The ACME noted that research is required to consider the value of using lipids as a normalizing factor in the evaluation of data on organic contaminants in biota. This should include an investigation of the function of lipids as a normalizing factor, and the advantages and disadvantages of using total lipids or extractable lipids as a normalizing factor. Alternatives or additional cofactors to lipids for use as normalizing factors should also be investigated.

### **6.5 Sixth Intercomparison Exercise on Analysis of Trace Metals in Sea Water**

#### *Request*

This is part of the continuing ICES work of coordinating quality assurance activities and reporting on the results and their implications for monitoring programmes.

#### *Source of the information presented*

The 1995 report of the Marine Chemistry Working Group (MCWG).

#### *Status/background information*

The ACME noted that forty laboratories out of 48 indicated through a questionnaire a desire to participate in the Sixth Intercomparison Exercise on the Analysis of Trace Metals in Sea Water. This was considered a sufficient degree of interest to warrant the further planning of the exercise.

It was further noted that the original coordinator of this exercise was no longer able to take on this work, however, there were other experienced ICES laboratories available and willing to cooperate in carrying out an exercise if operational funding could be obtained through participant subscription or funding from ICES.

A possible scenario for the collection and processing of samples in 1996 for this exercise was noted as well as a tentative timetable which could result in a report being available for the MCWG meeting in 1997.

### **6.6 Organic Contaminants that can be Monitored in Biota and Sediments on a Routine Basis**

#### *Request*

Item 1.1 of the 1995 Work Programme from the Oslo and Paris Commissions.

#### *Source of the information presented*

The 1995 report of the Marine Chemistry Working Group (MCWG).

#### *Status/background information*

The ACME noted that the exact request was to draw up a list of organic contaminants which can be monitored in biota and sediments on a routine basis and to advise on quality assurance measures for these contaminants.

A preliminary list of organic contaminants that can be monitored in biota and sediments on a routine basis was presented in the 1994 ACME report in Section 6.8. This list has been updated, using the most recent information from several intercomparison exercises and is presented here in Table 6.6.1. Where information was available from intercomparison exercises, standard deviations and reproducibilities are given under the heading "Laboratory capability" in Table 6.6.1. Only a few specialist laboratories are able to produce reliable data for a number of compounds at present. Where the between-laboratory coefficient of variation (R) exceeds 50%, it is reasonable to conclude that there is insufficient agreement for the group of laboratories, **as a whole**, to undertake these measurements. A selection of more experienced laboratories would be recommended. As the table shows, R is at or above 50% for most of the compounds listed.

Apart from the CBs mentioned in the list, several laboratories are also able to analyse a number of other CBs, for which in some cases CRMs are available. There is, however, no information on the comparability of data on these additional CBs from the different laboratories. In addition to the compounds mentioned in the table, polychlorinated naphthalenes, chlorinated paraffins, polybrominated diphenylethers, polybrominated biphenyls, polychlorinated terphenyls, tris(4-chlorophenyl) methanol, chlorophenols, tris(4-chlorophenyl) methane and volatile short-chain (C<sub>1</sub>-C<sub>3</sub>) alkanes can also be determined by some specialist laboratories. However, for these compounds there are no intercomparison exercise

**Table 6.6.1.** Organic contaminants that can be monitored in biota and sediments on a routine basis.

| Organic Contaminant   | Recent I/C data available <sup>1)</sup>                            | QC material available               | Laboratory capability <sup>8)</sup>  |
|---|--|-------------------------------------|--|
| 1. Chlorobiphenyls<br>CBs 101, 118, 138, 153, 180   | Yes (sediment, lean and fatty fish tissue, seal oil) <sup>2)</sup> | CRMs (SRMs) and certified standards | sediment CBs 118, 138, 153 $S_R$ <sup>3)</sup> 15%, R 50%<br>seal oil CBs 138, 153, 180 $S_R$ 15%, R 50%<br>fish oil CBs 101, 118, 138, 153, 180 $S_R$ 15%, R 50%<br>lean fish CBs 118, 138, 153, 180 $S_R$ 50–70%, R 200–330% |
| 2. Non-ortho CBs 77, 126, 169   | Yes (fish oil) <sup>4)</sup>                                       | No                                  | Some specialist laboratories (fish oil) $S_R$ 20–50%, R 65–200%  |
| 3. Organochlorine pesticides<br>HCHs, DDT, DDD,<br>DDE, HCB, dieldrin,<br><i>trans</i> -nonachlor | Yes (sediment, fish oil) <sup>5)</sup>                             | CRMs and certified standards        | fish oil $S_R$ 15–30%, R 50–100%<br>sediment $S_R$ 35–100%, R 130–800%   |
| 4. PAHs   | No   | CRMs and certified standards        | Unknown  |
| 5. Chlorinated dioxins and furans   | No   | CRMs and certified standards        | Some specialist laboratories   |
| 6. CHBs (toxaphene)   | Yes <sup>6)</sup>  | No                                  | Some specialist laboratories $S_R$ ca. 50%, R 200%<br>(fish oil)   |
| 7. Organotin (TBT, TPT)   | No   | CRM (TBT)                           | Some specialist laboratories   |
| 8. Methyl mercury   | No <sup>7)</sup>   | No                                  | Some specialist laboratories   |

**Abbreviations**

CHBs = chlorinated bornanes  
HCB = hexachlorobenzene  
OCP = organochlorine pesticides  
TBT = tributyltin

CRM = certified reference material  
HCHs = hexachlorocyclohexanes  
PAHs = polycyclic aromatic hydrocarbons  
TPT = triphenyltin

SRMs = standard reference materials  
QC = quality control

<sup>1)</sup> This column refers to intercomparison exercises (I/C) carried out with regard to marine environmental samples.

<sup>2)</sup> References: ICES reports on the results of the ICES/IOC/OSPARCOM Intercomparison Programme on the Analysis of Chlorobiphenyls in Marine Media; QUASIMEME reports on CB intercomparison exercises (1993–1995).

<sup>3)</sup>  $S_R$ : standard error; R: reproducibility

<sup>4)</sup> References: Voogt, P. de, *et al.* 1994. Analytical Chemistry, 66: 1012–1016; Wells, D.E. 1994. Report on ICES intercomparison exercise on non-ortho CBs. Working Paper at the 1994 MCWG meeting.

<sup>5)</sup> Reference: QUASIMEME reports on CB and OCP intercomparison exercises (1994–1995).

<sup>6)</sup> Reference: Andrews, P.A. 1994. Interlaboratory study on the analysis of toxaphene. Proceedings of the 24th International Symposium on Environmental Chemistry. Ottawa, Canada. A second study is under way.

<sup>7)</sup> Recently information from an intercomparison exercise on sediment became available from the European Commission. A CRM for sediment is in preparation.

<sup>8)</sup> Where the between-laboratory coefficient of variation (R) exceeds 50%, it is reasonable to conclude that there is insufficient agreement for the group of laboratories, **as a whole**, to undertake these measurements. A selection of more experienced laboratories would be recommended.

data, nor are there certified reference materials (CRMs) or certified standards available. Laboratories should be encouraged to measure such compounds since there is a lack of information on them, and also considering their relatively high production figures and bioaccumulative properties. The production of CRMs for such compounds is also recommended. The ACME emphasized that the Commissions should be aware that the production of CRMs, establishing acceptable quality assurance/quality control procedures, and conducting intercomparison exercises for these compounds can take at least three years.

It is intended that this table will be updated on an annual basis.

## **6.7 Quality Assurance Procedures for Organic Contaminants to be Measured in Monitoring Programmes**

### *Request*

Item 1.1 of the 1995 Work Programme from the Oslo and Paris Commissions. Under this item, OSPARCOM requested ICES to draw up a list of organic contaminants that can be monitored in biota and sediments on a routine basis and to advise on quality assurance measures for these contaminants. The list itself is contained in Section 6.6, above. The present section deals with the plans for and results of intercomparison exercises for some of these contaminants.

As this material deals with chemical analyses for monitoring, the advice given below would be equally interesting to HELCOM and fits well with the ICES continuing task to advise HELCOM on improvements in the BMP.

### *Source of the information presented*

The 1995 report of the Marine Chemistry Working Group (MCWG).

### *Status/background information*

#### **Overall Results of the ICES/IOC/OSPARCOM Intercomparison Programme on the Analysis of CBs in Marine Media**

An overall report evaluating the results of the ICES/IOC/OSPARCOM Intercomparison Programme on the Analysis of Chlorobiphenyls in Marine Media showed that a measurable improvement had been obtained over the four steps of the study in the participants' ability to analyse chlorobiphenyls (CBs). Much better results were obtained in comparison with other interlaboratory studies on CBs occurring at similar concentrations. On the other hand, the demanding

requirements of international monitoring programmes still necessitate further improvements if the whole group of laboratories is to be included. Standard errors of around 15% were obtained in seal oil and sediment for three CBs, corresponding to reproducibilities of around 50%. The determination of CBs in lean fish tissue resulted in standard errors of around 100%. The results obtained by the laboratories in the last three steps of the study (Steps 2, 3b and 4) were assessed and the improvement in each laboratory's performance was demonstrated. Laboratories with deviating results were identified for each matrix. These results should not serve as a selection mechanism for laboratories for possible future monitoring programmes or baseline studies since the performance of a laboratory may differ from time to time. Also, there is additional information which should be considered in the reports on the individual steps of the exercise, such as chromatographic conditions and information from principal component analyses. During the conduct of baseline studies or monitoring programmes, blind samples should be distributed for analysis alongside the environmental samples, and laboratories should demonstrate their ability to measure CBs by delivering quality control (QC) charts.

The results emphasized the need for quality assurance (QA) as an integral part of baseline studies and monitoring programmes. In this regard, it was stressed that prior to the organization of such programmes it is necessary to establish whether there is any disparity between what should be measured and what can actually be measured by laboratories in terms of precision and accuracy. For example, even when only six or seven selected laboratories with good performance are considered, their best performance would still give standard errors of around 10%, corresponding to reproducibilities of 25–30%.

#### **Plans for an intercomparison exercise on the determination of non-ortho CBs in marine media**

This item was considered on the basis of a request from OSPARCOM to ICES to develop a QA programme for non-ortho and mono-ortho CBs, including guidelines for sampling and analysis, and to organize an intercomparison exercise for these CBs.

Over the last 18 months, several laboratories have been engaged in the development and validation of methods for the determination of mono-ortho and non-ortho CBs in environmental samples under an EU programme.

From these studies, the following conclusions can be drawn:

- 1) The methodology to reliably measure mono-ortho and di-ortho CBs is currently available and a description has been published. Further specific details will be available later during 1995.

- 2) The determination of mono-*ortho* and non-*ortho* CBs should be developed as part of an overall strategy of CB measurements and not as a separate analysis. The value of obtaining data on as many CBs as possible, i.e., extending the number of congeners monitored, is a preferred approach, rather than focusing on the non-*ortho* CBs in isolation. The methods of analysis should reflect this approach.
- 3) There should be a systematic, step-wise approach to developing the capability to employ these methods in as many marine laboratories as possible using the valuable information obtained from previous exercises, e.g., the ICES intercomparison programme and the QUASIMEME project.
- 4) The step-wise intercomparison exercise should be developed into a continuous laboratory testing scheme to extend the existing CBs which are currently being determined, e.g., in QUASIMEME, to include the non-*ortho* CBs.

#### Current

di/tri-*ortho* CBs: 28, 52, 101, 138, 180  
mono-*ortho* CBs: 118, 105, 156, (157)

#### New

non-*ortho* CBs: 77, 126, 169

- 5) In view of the current interest in and requirements to provide a QA system for these additional compounds, the programme should include from one to four intercomparison stages carried out over a two-year period.

The step-wise learning programme required for mono-*ortho* CBs is already being undertaken by QUASIMEME. Following an initial assessment of laboratories, a step-wise improvement programme will be carried out which should develop into a continuous testing scheme.

#### PAHs-Intercomparison exercise

The determination of PAHs was introduced into the laboratory testing and learning programme of QUASIMEME during the second half of 1994. The first part included analysis of two sets of standard solutions to assess the present capabilities of the laboratories involved. The aim is to develop the determination of PAHs into a regular proficiency testing scheme.

#### PAHs-Limits of detection

A limit of determination of  $1 \mu\text{g kg}^{-1}$  wet weight for single PAH compounds in biological tissues could be attained using both high-performance liquid chroma-

tography/UV fluorescence (HPLC/UVF) and gas chromatography/mass spectrometry (GC/MS) methodologies, while utilizing modest sample masses. No collaborative studies have been conducted to date which indicate the degree of interlaboratory comparability that can be achieved at this concentration, however. Indeed, earlier studies conducted within ICES (Farrington *et al.*, 1986; Uthe *et al.*, 1986) have shown poor comparability at higher concentrations. Further studies involving the determination of PAHs are under way within QUASIMEME.

#### References

- Farrington, J. W., David, A. C., Livramento, J. B., Clifford, C. H., Frew, N. M., and Knap, A. 1986. ICES/IOC Intercomparison Exercise on the Determination of Petroleum Hydrocarbons in Biological Tissues (mussel homogenate) - ICES/2/HC/BT. ICES Cooperative Research Report, No. 141, pp. 1-75.
- Uthe, J.F., Musial, C.J., and Sirota, G.R. 1986. Report on the intercomparative study 03/HC/BT on the determination of polycyclic aromatic hydrocarbons in biological tissue. ICES Cooperative Research Report, No. 141, pp. 76-85.

#### Intercomparison exercises for other organic contaminants

Proficiency testing concerning determinations of chlorobiphenyls (CBs) and organochlorine pesticides (OCPs) has been conducted in the QUASIMEME programme twice during 1994 (and once so far during 1995). The reports on the results are available through the QUASIMEME Secretariat in Aberdeen, UK.

#### Recommendation

The ACME recommended that the Helsinki Commission and the Oslo and Paris Commissions use the above information for planning and implementing their monitoring and assessment work. Particular attention should be drawn to the need for quality assurance (QA) as an integral part of all baseline studies and monitoring programmes. In this context, it is essential that prior to the organization of such programmes it be established whether there is any disparity between what the requirements are and what can be measured, in terms of precision and accuracy, by the laboratories that are expected to participate.



## 7 ENVIRONMENTAL STUDIES IN THE BALTIC SEA

### 7.1 Baseline Study of Contaminants in Baltic Sea Sediments

#### *Request*

Item 5 of the 1995 requests from the Helsinki Commission.

#### *Source of the information presented*

The 1995 report of the Steering Group for the Coordination of the Baseline Study of Contaminants in Baltic Sea Sediments (SGBSC).

#### *Status/background information*

The ACME reviewed the 1995 report of the Steering Group for the Coordination of the Baseline Study of Contaminants in Baltic Sea Sediments and noted that progress has been made in this Baseline Study.

The field work and sampling for the Baseline Study was carried out in 1993 on board the Finnish R/V "Aranda". Samples for mineralogical characterization were delivered to relevant laboratories directly after the cruise, while samples for chemical analysis were freeze-dried and distributed to participants in February and March 1994. As of mid-1995, the grain size determinations and mineralogical descriptions of the samples had been completed, as well as the radiological dating measurements using Cs-137 and Pb-210. Approximately half of the analytical work on the determination of trace elements, nutrients, and extractable and adsorbable organohalogens (EOX/AOX) had also been completed. Initial work had begun on the determination of individual organic contaminants. In the case of trace elements and nutrients, two laboratories were sharing the analysis of the samples; for all other determinands, only one laboratory was involved in the analysis of all samples.

All analytical data are expected to be available by the end of 1995, as scheduled. Quality control has been applied at every step of the process. This comprises the following: (1) work diaries have been maintained during the field work and in all laboratories participating in the chemical analyses; (2) the chemical methods have been documented; (3) certified reference materials (or other well-documented materials) have been used whenever available; and (4) laboratories conducting analyses of trace elements are presently participating in the EU quality assurance programme QUASIMEME.

Available results will be used in the preparation of a chapter on contaminants in Baltic sediments for the

Third Periodic Assessment of the State of the Baltic Marine Environment under HELCOM (see Section 7.2).

### 7.2 Chapters on Contaminants in Marine Sediments and Fish Diseases for the HELCOM Assessment

#### *Request*

Item 7 of the 1995 requests from the Helsinki Commission.

#### *Source of the information presented*

The 1995 report of the Steering Group for the Coordination of the Baseline Study of Contaminants in Baltic Sea Sediments and the draft chapter on contaminants in Baltic Sea sediments. The 1995 report of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO) and the draft sub-chapter on diseases and parasites of Baltic fish.

#### *Status/background information*

The ACME noted that the Helsinki Commission is in the process of preparing the Third Periodic Assessment of the State of the Baltic Marine Environment and had requested ICES to prepare two chapters for this report: (1) a chapter on contaminants in Baltic sediments and (2) a chapter on Baltic fish and fish diseases.

The ACME reviewed the draft Chapter on Contaminants in Baltic Sea Sediments that had been prepared on the basis of results available from the Baseline Study of Contaminants in Baltic Sea Sediments. However, as not all anticipated data were yet available, it was agreed that the chapter would be finalized for review in autumn 1995, before transmitting it to the Helsinki Commission.

Thereafter, the ACME reviewed the draft sub-chapter on diseases and parasites of Baltic fish, that had been prepared on the basis of the results of the BMB/ICES Symposium on Diseases and Parasites of Flounder (*Platichthys flesus*) in the Baltic Sea and the BMB/ICES Sea-going Workshop on Fish Diseases and Parasites in the Baltic Sea (see Sections 8.1 and 8.2, below), as well as other relevant information. After review by the Working Group on Pathology and Diseases of Marine Organisms, the sub-chapter had been transmitted to ACME for approval.

The ACME agreed that this sub-chapter provided an interesting and useful summary of the information available on parasites and diseases of Baltic fish. The ACME approved this sub-chapter for inclusion in the



overall chapter on Baltic fish, the other parts of which comprise a sub-chapter on commercial fish stocks, prepared under the ICES Baltic Fish Committee, and a sub-chapter on coastal fish, prepared under the Baltic Marine Biologists (BMB). These sub-chapters will receive final review by the Advisory Committee on Fishery Management (ACFM) in October 1995 before transmission of the entire chapter to the Helsinki Commission.

### 7.3 Results of Temporal Trend Analyses of Data on Contaminants in Biota in the Baltic Sea

#### *Request*

ICES offered to coordinate an assessment of data on contaminants in biota from the Baltic Sea for temporal trend evaluation, for use in preparing the HELCOM Third Periodic Assessment of the State of the Baltic Marine Environment. As part of this work, the Helsinki Commission requested ICES to calculate the power of the component of the Baltic Monitoring Programme concerned with temporal trends of contaminant concentrations in biota.

#### *Source of the information presented*

The report of the ICES/HELCOM Workshop on Temporal Trend Assessment of Data on Contaminants in Biota from the Baltic Sea and an associated report providing a quality assurance evaluation of the data submitted.

#### *Status/background information*

It was noted that data submitted to the HELCOM Environmental Data Centre as well as to the ICES Environmental Data Bank are to be supported by quality assurance (QA) information, including the results of participation in intercomparison exercises, the results of analyses of certified reference materials (CRMs), and written documentation on the analytical procedures used.

However, the data submitted to the ICES Environmental Data Bank for these temporal trend analyses were in most cases not supported by QA information. Most laboratories had participated in at most one intercomparison exercise in the entire period 1978–1993. When the laboratories had participated, their results were usually fully acceptable.

Some laboratories have either not analysed samples of CRMs or have analysed only a few CRMs. The laboratories that have analysed CRMs on a regular basis have in general obtained very good results.

Written documentation of the analytical procedures applied was only available from a few laboratories.

### Temporal trend assessment

Data were received from Denmark, Finland, Poland, and Sweden for the assessment, covering the period from 1978 to 1993. Data comprised concentrations of the trace metals Cd, Cu, Hg, Pb, and Zn and the organic contaminants PCBs, DDTs, HCB and HCHs in herring (*Clupea harengus*), cod (*Gadus morhua*), dab (*Limanda limanda*), flounder (*Platichthys flesus*), mussel (*Mytilus edulis*), *Macoma balthica*, and *Saduria entomon*. These data were subjected to the standard ICES procedure for the evaluation of temporal trends in contaminant concentrations in biota. This procedure is described in Nicholson *et al.* (in press).

Although the geographical coverage was limited, some were apparent trends in certain regions. This included increasing concentrations of cadmium in the Baltic Proper and the Bothnian Bay, and upward trends in concentrations of copper and zinc in the Bothnian Bay. In some parts of the Baltic Sea, there appears to be a decreasing trend in concentrations of hexachloro-cyclohexanes (HCHs) in biota and also perhaps of hexachlorobenzene (HCB).

In a number of situations, however, no trends were detected. It was not possible to decide whether this was due to a low statistical power of the time series or the absence of trends. In general, the time series are often still too short to reveal anything but relatively large changes.

The full report on the results of this assessment is being finalized for ultimate publication in the *ICES Co-operative Research Report* series.

### Power assessment

The power of a statistical test can be defined as the probability of detecting a difference, when present. The Workshop calculated the power of the BMP to detect temporal log-linear changes. The probability to detect such changes depends on the magnitude of the change, the number of years under consideration, and the overall variation.

Calculations were carried out separately for each combination of species, tissue, and contaminant. The probabilities of detecting changes of 5% and 10% per year over a ten-year period (equal to a total decrease of 40% and 65%, respectively, or a total increase of 63% and 159%, respectively) were calculated (see Table 7.3).

The general conclusions are that a 10% per year change in zinc and copper concentrations will always be detected, while there is a chance of roughly 50% for the other contaminants. A 5% per year change in concentration will be detected with more than 50%

chance for zinc, but with equal to or less than 50% chance for the other contaminants.

It should be emphasized that the calculations are based on the national implementation of the BMP, which sometimes differs from what is recommended in the BMP guidelines. Moreover, the calculations are based on data obtained over a number of years, and do not take into account potential improvements in analytical performance achieved over the most recent years.

#### Recommendations

It is recommended that the following QA measures be incorporated in the future Baltic Monitoring Programme:

- 1) A description of the sampling strategy, which must be clearly oriented towards the objectives of the monitoring programme;
- 2) A description of the sample collection procedures, which assure that representative and uncontaminated samples are obtained;

- 3) A description of storage and pre-treatment procedures, which maintain the integrity of samples prior to their analysis;
- 4) A description of the validated analytical method applied;
- 5) A list of interlaboratory reference materials and appropriate certified reference materials regularly in use;
- 6) A description of the design and implementation of an intralaboratory quality control programme to ensure that daily measurements fall within acceptable limits of accuracy and precision;
- 7) A documentation of participation in intercomparison exercises.

#### Reference

Nicholson, M.D., Fryer, R.J., Larsen, J.R. In press. Contaminants in marine organisms: A robust method for analysing temporal trends. ICES Techniques in Marine Environmental Sciences, No. 20.

**Table 7.3.** Percent power to detect 5 or 10% annual change over 10 years, i.e., a total decrease of 40% and 65%, respectively, or a total increase of 63% and 159%, respectively, according to substance, tissue, and species.

| Substance | Tissue         | Species        | 5% Change | 10% Change |
|-----------|----------------|----------------|-----------|------------|
| Cd        | Liver          | Herring        | 50        | 97         |
|           |                | Cod            | 14        | 41         |
|           |                | Dab            | 15        | 44         |
|           |                | Flounder       | 31        | 80         |
|           |                | Herring        | 14        | 39         |
|           | Muscle         | <i>Macoma</i>  | 84        | 100        |
|           |                | <i>Mytilus</i> | 38        | 89         |
|           | Soft body      | <i>Saduria</i> | 11        | 30         |
|           | Whole organism |                |           |            |
| Cu        | Liver          | Herring        | 64        | 99         |
|           |                | Cod            | 25        | 71         |
|           |                | Dab            | 69        | 100        |
|           |                | Flounder       | 28        | 77         |
|           |                | Herring        | 67        | 100        |
|           | Muscle         | <i>Macoma</i>  | 34        | 85         |
|           |                | <i>Mytilus</i> | 77        | 100        |
|           | Soft body      | <i>Saduria</i> | 23        | 67         |
|           | Whole organism |                |           |            |
| Hg        | Muscle         | Herring        | 13        | 36         |
|           |                | Cod            | 10        | 23         |
|           |                | Dab            | 16        | 45         |
|           |                | Flounder       | 26        | 70         |
|           |                | <i>Macoma</i>  | 20        | 58         |
|           | Soft body      | <i>Mytilus</i> | 45        | 94         |
|           |                | <i>Saduria</i> | 38        | 90         |
|           | Whole organism |                |           |            |
|           |                |                |           |            |
| Pb        | Liver          | Herring        | 23        | 65         |
|           |                | Cod            | 14        | 39         |
|           |                | Dab            | 29        | 77         |
|           |                | Flounder       | 13        | 35         |
|           |                | Herring        | 11        | 29         |
|           | Muscle         | <i>Macoma</i>  | 15        | 43         |
|           |                | <i>Mytilus</i> | 9         | 19         |
|           | Soft body      | <i>Saduria</i> | 27        | 75         |
|           | Whole organism |                |           |            |
| Zn        | Liver          | Herring        | 94        | 100        |
|           |                | Cod            | 48        | 96         |
|           |                | Dab            | 57        | 99         |
|           |                | Flounder       | 70        | 100        |
|           |                | Herring        | 94        | 100        |
|           | Muscle         |                |           |            |

Table 7.3. (continued)

| Substance     | Tissue         | Species        | 5% Change | 10% Change |
|---------------|----------------|----------------|-----------|------------|
| Zn (cont.)    | Soft body      | <i>Macoma</i>  | 47        | 95         |
|               |                | <i>Mytilus</i> | 39        | 90         |
|               | Whole organism | <i>Saduria</i> | 99        | 100        |
| $\gamma$ -HCH | Liver          | Cod            | 29        | 77         |
|               |                | Herring        | 18        | 52         |
|               |                | Dab            | 15        | 43         |
|               |                | Flounder       | 11        | 28         |
|               | Soft body      | <i>Mytilus</i> | 14        | 41         |
| $\alpha$ -HCH | Liver          | Cod            | 29        | 77         |
|               | Muscle         | Herring        | 19        | 54         |
|               |                | Dab            | 9         | 20         |
|               |                | Flounder       | 10        | 25         |
|               | Soft body      | <i>Mytilus</i> | 24        | 68         |
| $\beta$ -HCH  | Liver          | Cod            | 10        | 24         |
|               | Muscle         | Herring        | 9         | 20         |
|               |                | Dab            | 100       | 100        |
|               |                | Flounder       | 46        | 95         |
|               | Soft body      | <i>Mytilus</i> | 8         | 16         |
| HCB           | Liver          | Cod            | 19        | 55         |
|               | Muscle         | Herring        | 14        | 39         |
|               |                | Dab            | 77        | 100        |
|               |                | Flounder       | 7         | 12         |
|               | Soft body      | <i>Mytilus</i> | 7         | 14         |
| CB 118        | Liver          | Cod            | 28        | 75         |
|               | Muscle         | Herring        | 41        | 92         |
|               |                | Dab            | 17        | 51         |
|               |                | Flounder       | 17        | 51         |
|               | Soft body      | <i>Macoma</i>  | 94        | 100        |
|               |                | <i>Mytilus</i> | 10        | 26         |
|               | Whole organism | <i>Saduria</i> | 46        | 95         |
| CB 138        | Liver          | Cod            | 21        | 60         |
|               | Muscle         | Herring        | 44        | 94         |
|               |                | Dab            | 13        | 16         |
|               |                | Flounder       | 12        | 32         |
|               | Soft body      | <i>Macoma</i>  | 100       | 100        |
|               |                | <i>Mytilus</i> | 15        | 43         |
|               | Whole organism | <i>Saduria</i> | 21        | 60         |
| CB 153        | Liver          | Cod            | 24        | 69         |
|               | Muscle         | Herring        | 72        | 100        |
|               |                | Dab            | 16        | 48         |
|               |                | Flounder       | 13        | 36         |
|               | Soft body      | <i>Macoma</i>  | 100       | 100        |
|               |                | <i>Mytilus</i> | 15        | 43         |
|               | Whole organism | <i>Saduria</i> | 45        | 94         |
| p,p'-DDT      | Liver          | Cod            | 9         | 20         |
|               | Muscle         | Herring        | 14        | 41         |
|               |                | Dab            | 7         | 12         |
|               |                | Flounder       | 14        | 38         |
|               | Soft body      | <i>Macoma</i>  | 12        | 33         |
|               |                | <i>Mytilus</i> | 7         | 12         |
|               | Whole organism | <i>Saduria</i> | 54        | 98         |
| p,p'-DDE      | Liver          | Cod            | 21        | 59         |
|               | Muscle         | Herring        | 27        | 75         |
|               |                | Dab            | 12        | 31         |
|               |                | Flounder       | 9         | 21         |
|               | Soft body      | <i>Macoma</i>  | 55        | 98         |
|               |                | <i>Mytilus</i> | 10        | 23         |
|               | Whole organism | <i>Saduria</i> | 15        | 44         |
| p,p'-DDD      | Liver          | Cod            | 11        | 29         |
|               | Muscle         | Herring        | 15        | 43         |
|               |                | Dab            | 7         | 14         |
|               |                | Flounder       | 7         | 15         |
|               | Soft body      | <i>Macoma</i>  | 96        | 100        |
|               |                | <i>Mytilus</i> | 10        | 24         |
|               | Whole organism | <i>Saduria</i> | 12        | 32         |

#### 7.4 Causes of the M-74 Syndrome in Baltic Salmon and Progress in Understanding Relevant Environmental Factors

##### Request

Item 12 of the 1995 requests from the Helsinki Commission.

##### Source of the information presented

The 1995 reports of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO) and the Baltic Salmon and Trout Assessment Working Group, both of which contain an overview of new information on the M-74 syndrome; additional information from the 1994 report of the Study Group on the Occurrence of M-74 in Fish Stocks.

##### Status/background information

The ACME reviewed the relevant sections of the above-mentioned reports and noted that the M-74 syndrome continued to cause high mortalities in the offspring of Atlantic salmon (*Salmo salar*) from the Baltic Sea in 1994. Both in Finland and Sweden, the mortality in yolk-sac fry originating from wild-caught spawners was again in the range of 50–90%. A minor decrease was recorded at some Swedish hatchery sites, which was probably due to a much stricter selection of the brood stocks as compared to previous years.

##### Recent findings on causes of the M-74 syndrome

The latest information indicates that a dietary condition related to a vitamin component is probably one of the key factors involved in the occurrence of the M-74 syndrome. In parts of Canada and the USA bordering the Great Lakes, an M-74-like syndrome described under several names (early mortality syndrome (EMS), Cayuga syndrome, Swim-up syndrome) has been noted to occur in salmonids (Atlantic salmon, lake trout *Salvelinus namaycush*, coho salmon *Oncorhynchus kisutch*). After having excluded PCBs, DDTs, and other xenobiotics as main causative factors, American scientists started to focus on the role of vitamins, particularly thiamine (vitamin B<sub>1</sub>). The uptake of thiamine with the food is essential, since its activated form (thiamine pyrophosphate) is needed as a coenzyme in carbohydrate metabolism.

The main reason for starting these investigations was that studies on the food composition of the affected fish species in the Great Lakes revealed that their main food item has changed to alewife (*Alosa pseudoharengus*), a

clupeid fish species which is new to that area and which probably has been introduced via ballast water. Since this species is characterized by high levels of thiaminase activity, a possible thiamine deficiency in the predator species, the salmonids, was suspected to occur and to be involved in the occurrence of the M-74-like syndrome in their offspring.

This possible link has been supported by the results of chemical analyses of yolk-sac fry from the Great Lakes, which provided evidence that fry suffering from the M-74-like syndrome have much lower thiamine contents as compared to healthy fry. Moreover, the behavioural symptoms in affected fry are very similar to the symptoms reported for other animal species suffering from thiamine deficiency.

In healthy and M-74-affected yolk-sac fry from the Baltic salmon stock these findings were confirmed in 1994. Again, diseased fry were found to have much lower thiamine levels than healthy fry. Since the main food items of Baltic salmon are herring (*Clupea harengus*) and sprat (*Sprattus sprattus*), both being clupeid species with high thiaminase activities, a resulting thiamine deficiency is also suspected to be the cause of the M-74 syndrome in Baltic salmon.

Similar to results derived from North American experiments, Swedish and Finnish experiments conducted in 1994 succeeded in significantly reducing mortality in M-74-affected salmon fry by adding thiamine at different concentrations to the water (in Finnish experiments, mortality was reduced from 60% in the untreated control group to 1.5% in the thiamine-treated group).

Although this treatment technique may be regarded as a very promising symptomatic treatment for the salmon stock enhancement programme in the Baltic Sea using artificially reared salmon, the wild Baltic salmon stocks will still continue to suffer seriously from the M-74 syndrome and will probably continue to decline significantly in stock size.

The ACME noted that the induction of disease symptoms and mortality related to a thiamine deficiency has been known previously from cultured salmonids fed extensively with herring and related species with high thiaminase levels.

The WGPDMO reported that there is some indication that an M-74-like problem also occurs in the Baltic cod (*Gadus morhua*) stock; this, however, requires further research.

### **Geographical distribution of the M-74 syndrome of Baltic salmon**

No new information on the geographical distribution of the M-74 syndrome of Baltic salmon is presently available. From the 1994 report of the Study Group on the Occurrence of M-74 in Fish Stocks and the 1995 report of the Baltic Salmon and Trout Assessment Working Group there is evidence that mainly Swedish and Finnish salmon spawning rivers are affected. However, an increased yolk-sac fry mortality (10.2% in 1992) possibly linked with M-74 has also been reported from Latvia, but to a much lesser extent. In addition, an Estonian study carried out in 1993 in one of the main salmon rivers revealed the total absence of a salmon year class 1993. However, it is not clear whether this was due to the M-74 syndrome since a total lack of year classes has been observed on other occasions during the past ten years. In the other Baltic Sea countries, no occurrences of the M-74 syndrome have been reported so far.

When evaluating the information on geographical characteristics of the M-74 syndrome, it has to be considered that Baltic salmon comprises several stocks with different migratory behaviour. The salmon spawning in the Swedish and Finnish rivers where the highest prevalences of M-74 have been recorded seem to belong to a stock which, in its marine period, stays in the southern part of the Baltic Main Basin (ICES Sub-division 25). Therefore, it has been discussed whether the origin of the syndrome is mainly related to environmental changes (including changes in the abundance of important prey species) in that particular area. That could explain why other, more localized Baltic salmon stocks (e.g., in the northeastern Baltic Sea) seem to be less affected. However, from information provided by the Baltic Salmon and Trout Assessment Working Group there is also evidence that other, more local salmon stocks are affected, such as the stock inhabiting the Gulf of Bothnia and the Gulf of Finland which spawns in the River Neva.

With regard to changes in food composition for Baltic salmon, there is some indication that the ratio between

clupeids and non-clupeid prey species has changed towards clupeids during past years. However, further studies are needed before final conclusions on the role of dietary composition can be drawn.

#### *Need for further research or additional data*

The ACME appreciated the progress that has been made in understanding the factors involved in the aetiology of the M-74 syndrome of Baltic salmon. However, it endorsed the view of the WGPDMO that there still are open questions related to the causes of the M-74 syndrome to be solved.

Future work should address the following aspects:

- 1) Since herring and sprat have been the major food items of Baltic salmon for decades, why has the M-74 syndrome not occurred at an earlier time?
- 2) Is there any evidence for changes in the food composition of Baltic salmon which may account for the drastic increase in fry mortalities due to the M-74 syndrome recorded over the past few years?
- 3) Can other dietary problems be involved in the occurrence of M-74 (changes in the contents of vitamin C and/or thyroxide)?
- 4) Is there any indication that vitamin deficiencies possibly involved in the M-74 syndrome may be caused by other environmental factors, including exposure to pollutants?
- 5) Are there key factors other than vitamin deficiency involved in the aetiology of the M-74 syndrome (including the role of pathogens/parasites)?
- 6) Are other Baltic Sea fish species affected by the M-74 syndrome or similar conditions?

### 8.1 Results of the BMB/ICES Symposium on Diseases and Parasites of Flounder (*Platichthys flesus*) in the Baltic Sea

#### Request

Item 6 of the 1995 requests from the Helsinki Commission.

#### Source of the information presented

The 1995 report of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO).

#### Status/background information

The BMB/ICES Symposium on Diseases and Parasites of Flounder (*Platichthys flesus*) in the Baltic Sea was held on 27–29 October 1994 in Åbo (Espoo), Finland, under the convenership of Dr G. Bylund. In addition to twenty participants from countries around the Baltic Sea, several invited specialists from other countries participated.

The aims of the Symposium were:

- 1) to bring together specialists actively engaged with work on flounder diseases to give presentations on the present state of knowledge concerning these diseases;
- 2) to discuss and evaluate the significance of recent advances and new research methods;
- 3) to discuss the direction for further investigations;
- 4) to evaluate the use of certain target diseases and health parameters of flounder as biomarkers in biological effects monitoring programmes and for hazard assessment.

The presentations and discussions mainly addressed the following topics: *lymphocystis disease*, *skin ulcer disease*, *liver neoplasia*, and *new biomarkers*. The participants in the Symposium agreed on a number of summary statements with regard to these topics, an extract of which is given below.

#### Lymphocystis disease

Lymphocystis is the most prevalent externally visible disease of Baltic flounder occurring in the entire Baltic Sea. In the southwestern Baltic Sea, a clear increase in the prevalence has been recorded since 1986. In contrast

to other prevalent diseases, its aetiology is well understood (*Iridovirus* infection). However, the existence of different virus strains/species possibly being responsible for variations in the prevalence and spatial distribution of the disease cannot be excluded. The prevalence is linked with sex and length of flounder (males and intermediate size groups are more frequently affected in comparison with females and small/large size groups). The participants in the Symposium considered that increased prevalences of lymphocystis might be an unspecific biological indicator of environmental changes (including pollution) leading to physiological stress and associated effects on the immune defense mechanisms of fish.

#### Skin ulcer disease

Flounder from the Baltic Sea and the North Sea show differences in the epidemiology of skin ulcer disease which may reflect differences in the biology of the flounder in these areas and/or the disease aetiology. The aetiology of the disease is clearly multifactorial involving bacterial infection. Studies of Baltic flounder suggest that one particular pathogen (atypical *Aeromonas salmonicida*) is involved, whereas studies carried out in the North Sea indicate that the disease may be due to secondary infections by a variety of opportunistic bacteria. As with lymphocystis, skin ulcer disease is likely to be a non-specific disease which may be considered a general indicator of environmental stress.

#### Liver neoplasia

In the southern Baltic Sea, liver neoplasia in flounder has been recorded at low prevalences. In contrast, flounder from the northern Baltic Sea (particularly the largest size groups) show high prevalences of pre-neoplastic and neoplastic liver lesions. The aetiology of these lesions has not yet been resolved. However, from North American field and laboratory studies as well as from Dutch mesocosm studies, there is evidence that organic contaminants (especially certain aromatic hydrocarbons) are involved in the aetiology of neoplastic liver lesions.

#### New biomarkers

With regard to field studies on the link between exposure to organic contaminants and the occurrence of neoplastic liver lesions, the participants advocated investigation of a number of additional biomarkers that can quantify actual exposure to xenobiotics as well as measure more specific biochemical and molecular responses to contaminant exposure. These include:



- a) measures of levels of particular metabolites of aromatic hydrocarbons present in bile (fluorescent aromatic compounds (FACs));
- b) measures of induction of xenobiotic metabolism in the cytochrome P-450 mixed-function oxidase system as induction of the CYP1A isoenzyme (activity of aryl hydrocarbon hydroxylase (AHH), or 7-ethoxyresorufin-O-deethylase (EROD); expression of the mRNA transcript (Western blotting), or the mature enzyme (ELISA));
- c) measures of genotoxic damage as xenobiotic-DNA-adducts ( $^{32}\text{P}$ -postlabelling).

The outcome of the BMB/ICES Symposium, including the papers presented and an account of the discussions, has been published in a proceedings volume (The Baltic Marine Biologists, Publication No. 15, 1994 (ISSN 0282-8839)).

#### *Need for further research*

The ACME noted with appreciation that the BMB/ICES Symposium provided valuable information on diseases of flounder which can be used as a basis for fish disease/parasite monitoring programmes in the Baltic Sea. However, it also noted from the conclusions of the Symposium that there is still a lack of information on the role of contaminants in the aetiology of diseases. The ACME, therefore, proposed that, in general, more effort should be dedicated to elucidating the causal links between contaminant exposure and the occurrence of diseases.

## **8.2 Results of the BMB/ICES Sea-going Workshop on Fish Diseases and Parasites in the Baltic Sea and Plans for Future Studies of Fish Diseases**

### *Request*

Item 6 of the 1995 requests from the Helsinki Commission.

### *Source of the information presented*

The 1995 report of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO) and a report from one of the co-conveners of the Workshop.

### *Status/background information*

The BMB/ICES Sea-going Workshop on Fish Diseases and Parasites in the Baltic Sea was held from 25 November to 8 December 1994 on board the German R/V "Walther Herwig III" under the convenership of Dr T. Lang and S. Møllergaard. The Workshop was attended

by eleven scientists representing eight of the nine countries bordering the Baltic Sea. Only Sweden was not represented.

The objectives of the Workshop were:

- 1) to enhance international cooperation and methodological standardization among Baltic Sea countries with regard to research and monitoring of fish diseases and parasites in the Baltic Sea;
- 2) to provide scientific data on the prevalence and spatial distribution of fish diseases and parasites in the Baltic Sea to be used as baseline information for further research and monitoring programmes;
- 3) to assess the applicability of the ICES standard methodologies recommended for fish disease surveys which have mainly been developed based on experience from the North Sea and, if necessary, to recommend modifications to adapt these for Baltic Sea conditions.

Practical work was carried out at eleven stations (in a total of 36 fishery hauls) on a transect from the western (German waters) to the eastern (Gulf of Finland, Estonian waters) Baltic Sea (see Figure 8.2). The region covered represents the largest area in the Baltic Sea ever studied for the occurrence of fish diseases and parasites using identical methodologies during a narrow time window.

The following parameters were studied:

- 1) gross (mainly external) visible diseases and parasites of flounder, cod, herring, and sprat;
- 2) liver nodules of flounder;
- 3) mixed-function oxygenase (EROD, AHH) activity;
- 4) external/internal parasites of flounder;
- 5) bacteriology of the ulcer disease in flounder and other species.

In addition, flounder otoliths were taken to include age as a factor in the statistical analysis of the prevalence data, and selected hydrographical parameters ( $\text{O}_2$  concentration, water temperature, salinity) were measured in bottom-water samples.

Although the full analysis of Workshop data is not yet complete, the results available so far reveal some marked spatial patterns for diseases and parasites of flounder and cod. For example, the prevalence of lymphocystis in

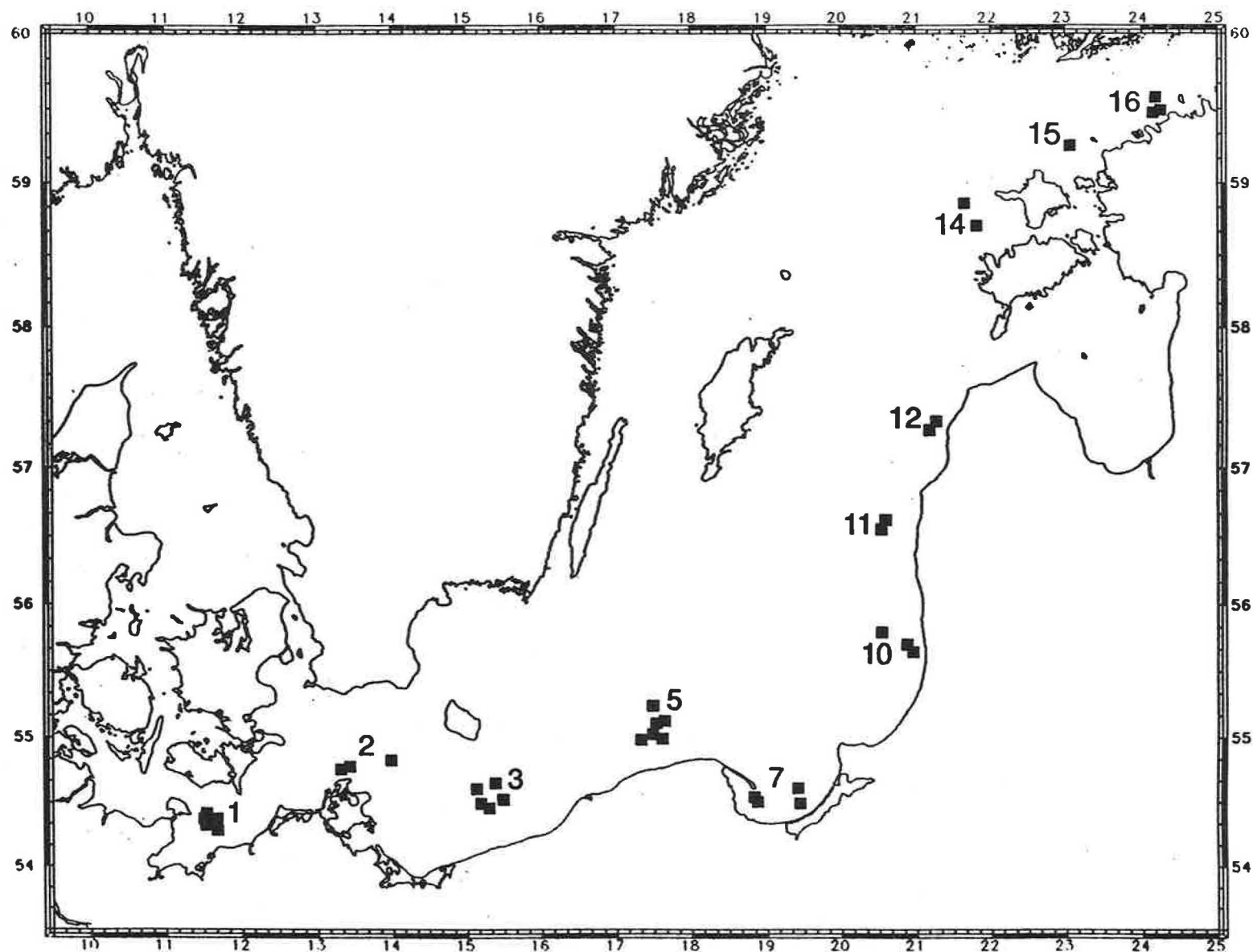


Figure 8.2. Location of sampling stations for the BMB ICES Sea-going Workshop on Fish Diseases and Parasites in the Baltic Sea.

flounder decreased from the western to the eastern stations, whereas for skin ulcerations and liver nodules an opposite trend was recorded. In cod, externally visible parasites (*Lernaeocera* sp., *Cryptocotyle* sp.) used for monitoring purposes in the North Sea occurred only at the western-most stations.

From the experience gained in this work, the Workshop participants considered Baltic flounder, due to its wide distribution and abundance and the occurrence of conspicuous disease signs and parasites, to be the most promising target species for fish disease and parasite monitoring programmes in the Baltic Sea. Furthermore, they considered it necessary to recommend some new standard methodologies to be followed in disease monitoring programmes in the Baltic Sea, consisting of both new methodologies and modifications to the ICES standard methodologies. These will include guidelines for sampling strategies, disease diagnosis and grading (including parasitological and bacteriological methodologies suitable for monitoring purposes), statistical analysis, and measurements of additional risk factors involved in the aetiology/pathogenesis of diseases.

The Workshop participants agreed that the recommendations, together with the results of the practical work, should be submitted as a series of separate papers for publication in a special volume of the *ICES Journal of Marine Science*.

#### *Need for further research*

The ACME noted with appreciation the progress that has been made in fish disease and parasite studies in the Baltic Sea and in the intercalibration and standardization of the methodologies used in this context. It emphasized the need to further strengthen the cooperation among Baltic Sea countries already established, mainly due to the activities of the BMB WG 25 on Fish Diseases and Parasites in the Baltic Sea and the WGPDMO. On-going and future fish disease and parasite research and monitoring programmes should be coordinated among all Baltic Sea countries.

The ACME identified two major issues related to studies of fish diseases and parasites in the Baltic Sea that future research should address:

- 1) to elucidate the role of environmental factors (xenobiotics, hydrography) in the aetiology of fish diseases and parasitoses (in this context, joint studies on the aetiology of neoplastic and non-neoplastic liver lesions of Baltic flounder seem to be most promising);
- 2) to assess the impact of diseases and parasites on fish stock performance (mortality, recruitment, reproduction) in collaboration with stock assessment working groups.

#### *Recommendations*

The ACME noted that the participants in the BMB/ICES Sea-going Workshop considered flounder to be the most useful species for fish disease/parasite monitoring purposes in the Baltic Sea and noted also that there is information in the literature on the suitability of flounder with regard to other biological effects techniques. However, flounder is not considered a mandatory fish species for the chemical part of the revised HELCOM Baltic Monitoring Programme (BMP). Taking into account the increasing effort to implement an integrated monitoring strategy (as detailed in Annex 1 of this report) comprising a combination of both chemical and biological effects monitoring techniques, a prerequisite of which would be the use of identical target species, the ACME recommended that HELCOM reconsider the inclusion of flounder in the list of mandatory fish species for the BMP.

### **8.3 Overall Report on Fish Diseases in the Baltic Sea**

#### *Request*

Item 6 of the 1995 requests from the Helsinki Commission.

#### *Source of the information presented*

The 1995 report of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO).

#### *Status/background information*

#### **Fish disease and parasite studies in the Baltic Sea**

The ACME noted with satisfaction that, due to political changes in the eastern Baltic Sea countries as well as to the activities of the Baltic Marine Biologists (BMB) Working Group 25 on Fish Diseases and Parasites in the Baltic Sea and the ICES Working Group on Pathology and Diseases of Marine Organisms (WGPDMO), considerable progress has been made during recent years in research and monitoring activities concerning fish diseases and parasites in the Baltic Sea.

The majority of the nine countries bordering the Baltic Sea are presently carrying out more or less regular monitoring of fish diseases and parasites. Some of the countries started their programmes a considerable time ago (e.g., Denmark, Germany, Sweden, Poland) and others only recently (Estonia, Latvia), while still others are intending to do so in the near future (Lithuania). However, the ACME noted with concern that countries such as Denmark and Sweden have recently reduced or even discontinued their efforts.

Most of the on-going programmes are carried out in restricted areas, mainly national waters (an exception is the German programme which includes annual monitoring at stations in the entire southwestern Baltic Sea, from the Kiel Bight to the Gdansk Bay), and focus on defined target species (flounder; cod, *Gadus morhua*; herring, *Clupea harengus*) and selected grossly visible diseases and parasites, such as those recommended by ICES for fish disease surveys (ICES, 1989). The main aim of these programmes is to monitor the quality of the marine environment, mostly in relation to biological effects of contaminants, rather than investigating the effects of diseases on fish stocks (mortality, reproduction).

In contrast to the North Sea, there is still a lack of information on fish diseases in the Baltic Sea, particularly on temporal trends in disease and parasite prevalences (an exception is the results from the German monitoring programme in the southwestern Baltic Sea). This is due to the fact that many disease and parasite monitoring programmes have only been carried out in small areas and not continuously and that, seemingly, the results of a number of programmes have not been published in the open literature. Moreover, the differences between the Baltic Sea and the North Sea in the state of available data might also be partly due to the permanent under-representation of the eastern ICES Member Countries on the WGPDMO, which has been coordinating most of the fish disease and parasite monitoring activities in the North Sea since the start of these programmes.

However, there is good reason to believe that this situation will improve in the future because, owing to the efforts of the BMB WG 25 in the past years and two joint activities of BMB and ICES in 1994 (the BMB/ICES Symposium on Diseases of Flounder (*Platichthys flesus*) in the Baltic Sea, and the BMB/ICES Sea-going Workshop on Fish Diseases and Parasites in the Baltic Sea, see Sections 8.1 and 8.2, above), good contacts between scientists and organizations engaged in fish disease and parasite studies in the Baltic Sea have been established and there is general consensus that future activities will be better coordinated.

The BMB/ICES Sea-going Workshop, which was attended by key scientists from eight of the nine Baltic Sea countries, in addition to providing baseline information on prevalences and spatial distributions of the major grossly visible diseases and parasites of the most abundant fish species, constituted the first major attempt to intercalibrate and standardize methodologies for fish disease and parasite surveys in the Baltic Sea on the basis of practical field experience. Both the scientific results obtained from the practical work and the recommendation of standard methodologies adapted to the particular conditions in the Baltic Sea are envisaged

to constitute a basis for future monitoring of fish diseases and parasites in the Baltic Sea.

### Impact of fish diseases and parasites on Baltic Sea fish stocks

The ACME noted that there is little conclusive information regarding the impact of fish diseases or parasites on mortalities in Baltic Sea fish stocks. In only a few cases have mortalities induced by specific diseases or environmental factors been so obvious that the assumption seems justified that these conditions might have had a significant effect on stock size in the affected fish species. Examples are mortalities in garfish (*Belone belone*) at the south coast of Sweden due to gas supersaturation associated with thermal discharge effluents from a nuclear power plant, mortalities in perch (*Perca fluviatilis*) attributed to effects of pulp mill effluents, and mortalities in western spring spawning herring due to the *Ichthyophonus* sp. epidemic. The most recent case is the heavy mortalities in yolk-sac fry of the Baltic stock of Atlantic salmon (*Salmo salar*) due to the M-74 syndrome (see Section 7.4, above).

The *Ichthyophonus* sp. epidemic in herring has so far been the only disease affecting parts of the Baltic Sea for which attempts have been made to estimate mortality due to the infestation and the resultant impact on the stock. However, attempts to quantify disease-induced mortalities in general suffer from a number of confounding factors, some of which are listed below:

- 1) large fluctuations in fish stock sizes due to natural and anthropogenic causes other than diseases may mask and/or exceed disease-induced changes;
- 2) methods employed in fish stock assessments do not permit a distinction to be made between mortality due to specific diseases, natural factors, or fishing effort;
- 3) the prevalence of a disease, on which mortality estimates are based, only gives information at the time of sampling and does not provide important information from the past (e.g., number of fish that have already died) or the future (number of fish that will become infected);
- 4) the prevalence estimated from a sample may not reflect the true prevalence in a fish population or stock since diseased fish may be over- or under-represented due to differences in the spatial distribution of infected and uninfected fish and/or because the gear used selects for infected or uninfected fish;
- 5) the prevalence may not be an appropriate measure of mortality, at least as long as there is no clear evidence

of how lethal a disease is under natural conditions and the length of the survival time of infected fish.

Probably due to these problems, it has thus far not been possible to provide conclusive evidence for an *Ichthyophonus*-induced herring stock decline nor to develop realistic models for mortality rates due to the infestation.

From this experience with a disease condition which has been very prevalent in the affected herring stocks and which is considered to be highly lethal for infected individuals, it seems questionable whether disease-induced mortalities and associated effects on the population can be estimated by applying current methods of epidemiology and stock assessment.

#### *Need for further research*

Future research and monitoring programmes on fish diseases and parasites in the Baltic Sea should be internationally coordinated to the greatest extent possible and should be based on standardized methodologies such as those already recommended by ICES (ICES, 1989) and those derived from the BMB/ICES Sea-going Workshop (see Section 8.2, above).

#### **Reference**

ICES. 1989. Methodology of fish disease surveys. ICES Cooperative Research Report, No. 166. 43 pp.

#### **8.4 Externally Visible Fish Diseases as a Tool in Monitoring Biological Effects of Contaminants**

##### *Request*

There has been no specific request; the ACME considered this topic to be of importance in the light of the on-going discussion of suitable techniques to be incorporated in monitoring programmes on biological effects of contaminants.

##### *Source of the information presented*

The 1995 reports of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO) and the Working Group on Biological Effects of Contaminants (WGBEC).

##### *Status/background information*

In its 1994 report, the Working Group on Biological Effects of Contaminants (WGBEC) presented a list of already established and promising techniques that the WGBEC recommended to be used for the monitoring of biological effects of contaminants in the marine

environment. In this list, externally visible fish diseases were not included because the WGBEC considered them to be too non-specific an indicator in comparison with the other recommended techniques. However, externally visible fish diseases and parasites constitute a major component of national monitoring programmes in many ICES Member Countries and, therefore, their exclusion from the list of recommended techniques caused some debate.

In order to provide some clarification with regard to this subject, the ACME requested the WGPDMO, which has long-term experience in standardizing and coordinating disease/parasite studies in wild fish stocks, to evaluate the usefulness of externally visible fish diseases as a tool in the monitoring of biological effects of contaminants.

At its 1995 meeting, the ACME reviewed the relevant sections of the WGPDMO report on this issue and noted that the WGPDMO considered externally visible fish diseases to be a useful tool that should be incorporated into programmes for monitoring biological effects of contaminants, especially as a component of long-term monitoring. Advantages of this approach are:

- a) it is a cost-effective means of biological effects monitoring not requiring expensive laboratory analyses;
- b) externally visible fish diseases represent an integrative endpoint in a chain of biochemical and physiological changes affecting the homeostasis of the fish;
- c) the measurement of significant changes in the prevalence of externally visible diseases can be used as an ecologically relevant warning signal of environmental change.

However, from field studies there is indication that most diseases have a complex multifactorial aetiology. Thus, attempting to establish a clear cause-effect relationship between environmental contamination and the occurrence of fish diseases is difficult. Variation in the relative frequency of fish diseases may, then, be a non-specific indicator of environmental changes causing stress rather than a specific indicator of contaminant exposure. Therefore, the WGPDMO recommended that the monitoring of externally visible fish diseases should be supplemented by the application of other, more contaminant-specific biological effects techniques in order to establish in a clearer manner possible links between exposure and the onset of pathological changes.

##### *Need for further research*

The ACME considered externally visible fish diseases and parasites to be an important component in the

monitoring of biological effects of environmental changes. However, it endorsed the view of the WGPDMO that they are likely to be a non-specific indicator reflecting environmental stress imposed by any type of natural or anthropogenic factor (one of which could be contaminant exposure) with serious impacts on the physiological balance of the fish and that, therefore, fish disease studies in the framework of biological effects monitoring should be supplemented by other, more specific techniques, such as some of those recommended by the WGBEC and accepted by the ACME (see Section 4.1 and Annex 1).

#### *Recommendations*

The ACME recommended that, in order to establish in a clearer manner possible cause-effect relationships between contaminants and fish diseases, additional experimental and field studies are needed to elucidate the role of contaminants in the complex aetiology and pathogenesis of externally visible diseases. Increased efforts should be dedicated to studies on the *in situ* dynamics of diseases, including investigations of immunological and behavioural aspects. In addition, effects at the population level should be investigated.



*Request*

There is no specific request; this is part of the on-going ICES work on studies of benthos in marine ecosystems.

*Source of the information presented*

The 1995 report of the Benthos Ecology Working Group (BEWG).

*Status/background information*

**Indicator species sensitive to physical disturbance of the seabed**

In 1994, the ACME requested further consideration of indicator species that are sensitive to physical disturbance of the seabed, particularly in relation to the effects of heavy trawling gear used in demersal fisheries. The BEWG responded by providing an extensive list of kinds of damage that may be caused to individual benthos by physical disturbance, population characteristics of sensitive species as well as characteristics of species that are not vulnerable or that are able to take advantage of disturbed bottoms. They noted that sensitivity is related to the characteristics of the disturbance such as frequency, magnitude, and proportion of individuals of a population disturbed, as well as the biological characteristics of the biota that are disturbed. Annex 3 provides more detailed information on this topic.

**North Sea Benthos Survey**

In 1986, the Benthos Ecology Working Group performed a synoptic mapping of benthos in the North Sea Benthos Survey. The outcome of this survey showed clear patterns in biomass, diversity, and species distributions within the North Sea. These patterns seemed to be closely linked to grain size distribution in combination with depth.

In order to have a more complete picture of North Sea benthos, however, more detailed knowledge needs to be gathered about the epifauna and larger infauna. Accordingly, the BEWG has planned a new survey in the North Sea to investigate these types of benthos. It was noted that, as epifauna and large infauna are highly sensitive to physical disturbance of the seabed, for example by bottom trawl fisheries, the results can form the basis for evaluating the effects of fisheries. The epifauna, because of their relatively large size and their life style (generally motile and living on or near the surface of the sediment) make up a large proportion of the food for demersal fish. Finally, the results of this new survey, combined with the results of the 1986 survey, can be expected to form the basis for a classification and mapping of benthic habitats in the North Sea, giving a picture of the benthic species and assemblages and the benthic biodiversity in the North Sea.

The ACME noted that this new North Sea Benthos Survey has been authorized by the Council in C.Res. 1994/4:6.

### *Request*

Item 2 of the 1995 requests from the Helsinki Commission; this has also previously been on work programmes for the Oslo and Paris Commissions.

### *Source of the information presented*

The Marine Chemistry Working Group (MCWG) coordinates the preparation of overviews on contaminants that may be of interest in a marine environmental context. Papers that have passed their review are transmitted to ACME for further consideration.

### *Status/background information*

At its 1995 meeting the ACME considered two review papers on groups of potential marine contaminants, "Chlorinated Alkanes in the Marine Environment" and "Benzene and its C<sub>1</sub>-C<sub>2</sub> Alkylderivatives in the Marine Environment", provided by the MCWG. The ACME agreed to the summary material presented in the following sections and included the two papers in this report as Annexes 4 and 5, respectively.

#### **10.1 Chlorinated Alkanes in the Marine Environment**

This review note, prepared by P. Roose (Belgium), is attached as Annex 4. A summary is provided below.

Chlorinated alkanes are a large group of compounds and for this review a selection was made of compounds to be considered based on toxicity, persistence, production, and use. The resulting list of potentially harmful substances contained mainly low molecular weight (one to three carbon atoms) chlorinated alkanes, such as chlorinated methanes, chlorinated ethanes, and chlorinated ethenes. These compounds exhibit similar physico-chemical properties; they are produced in large quantities and have a widespread use. Due to their persistence and volatility, they may be transported via the atmosphere over considerable distances, resulting in a widespread distribution in the environment.

Although most of these compounds have been intensively studied in ground water and fresh water, much less is known about their presence and behaviour in the marine environment. Concentrations of chlorinated alkanes in sea water are generally in the nanogram per litre range, with evaporation apparently the principal removal process. The data available for sediments show that concentrations are in the low nanogram per gram ( $\equiv \mu\text{g kg}^{-1}$ ) range, indicating that sediments have the potential to accumulate chlorinated

alkanes at levels higher than those normally found in the water column.

Very few data are available on chlorinated alkanes in biota. Concentrations in marine fish and invertebrates have generally been reported in the range 0.5 to 1100 ng g<sup>-1</sup>, indicating a certain degree of bioaccumulation in comparison with sediments and water. Although the potential for bioaccumulation appears to be low, the toxicity data suggest that these compounds should be considered important environmental contaminants. Nonetheless, on the basis of the information presented, it is not possible to assess their importance in a marine environmental context. Clearly, more information is needed which, given the difficulties associated with analysing these compounds in marine compartments, will need to be based on research programmes.

#### **10.2 Benzene and Alkylated Benzenes in the Marine Environment**

This review note was prepared by P. Roose (Belgium). The full note is attached as Annex 5, and a summary is given below.

Benzene and C<sub>1</sub> and C<sub>2</sub> alkylated benzenes are important industrial products with large quantities produced annually. They have similar physico-chemical properties and behave in a similar way in the marine environment. Owing to their relatively high vapour pressure, in combination with their production in the combustion of fossil fuels, they are important atmospheric contaminants. The main routes of entry to the marine environment are via atmospheric deposition and industrial wastewater discharges.

There are few data on concentrations of benzene and alkylated benzenes in the marine environment. Concentrations in sea water generally do not exceed the ng l<sup>-1</sup> level, while the maximum concentration in an estuarine sediment was reported to be 480 ng g<sup>-1</sup>. The few data available for marine organisms indicate maximum concentrations in bivalve molluscs of around 260 ng g<sup>-1</sup>, although considerably higher levels may be observed in fish from heavily contaminated harbours.

These compounds have a low potential for bioaccumulation and generally a short half-life in the marine environment (mainly from days to weeks). Thus, although benzene is a confirmed carcinogen and alkylated benzenes are suspected to be carcinogenic, it would appear that exposure of marine organisms to these compounds is low. Thus, these compounds do not appear to be important contaminants in a marine environmental context.

## 11 TRANSFER OF HALOGENATED ORGANIC COMPOUNDS THROUGH THE FOOD CHAIN

### *Request*

Item 13 of the 1995 requests from the Helsinki Commission.

### *Source of the information presented*

The 1995 report of the Marine Chemistry Working Group (MCWG).

### *Status/background information*

In response to the request to provide information concerning the transfer of halogenated organic compounds through the food chain, the ACME accepted the following information from the Marine Chemistry Working Group.

In phytoplankton and zooplankton, adsorption and desorption processes probably control the transfer of halogenated compounds from water to the plankton, although they may subsequently be absorbed. In some species of zooplankton, as well as in invertebrates and fish, the uptake of halogenated compounds can occur from water via the gills, and also from food and particulate material. Within their bodies, exchange equilibria between body lipids, blood, and water control these concentrations. Due to the lipophilic nature of these contaminants, lipid physiology plays an important role and leads to redistribution, for instance, during spawning. Also, in fish the equilibria established are dependent on the size of the organism (the larger the fish, the greater the bioaccumulation that occurs). In the transfer from fish to birds and mammals, biomagnification occurs and the highest concentrations are found in these top predators. In these animals there is also often a greater potential for enzymatic biotransformation to compounds that can be excreted, but which may also be either more or less harmful than the original compounds.

Some of the properties of chemicals which are important for bioaccumulation are:

- 1) *Hydrophobicity* (or, inversely, the solubility in water): Molecules having an octanol:water partition

coefficient ( $K_{ow}$ ) in the range  $10^3$ – $10^6$  are bioaccumulated. These molecules do not have polar functional groups that increase their solubility, and also facilitate their degradation. Chloroaromatic (halogenated) and chloroaliphatic compounds meet these requirements.

- 2) *Persistence*: The compounds are not easily degraded, either chemically or photochemically, nor biodegraded or biotransformed. A suitable cutoff level of the half-life value in water, sediment, and biota could be selected for this parameter.
- 3) *The size of the molecule and the spatial configuration* should also be considered because of limitations on the transport through gills and/or membranes that constitute the biological tissues. Molecular size around 10 Angstroms may represent the upper limit in this case.

Furthermore, the subject also needs to be addressed in terms of ecology. For example, a clear distinction has to be made between pelagic and benthic food webs. Bioaccumulation depends not only on properties of the contaminants, but also on environmental factors that determine bioavailability, and on properties of the organisms.

### *Need for further research or additional data*

The literature concerning food chain transfer and bioaccumulation is extensive and to summarize all the information available would represent a considerable task. For specific aspects, however, more detailed information could be provided at a later date in response to a more focused request, particularly in terms of the type of food chain (benthic, pelagic) and the type of contaminants (PCBs, pesticides) to be studied.

## 12 ASSESSMENT TOOLS

### 12.1 Background Concentrations of Natural Compounds

#### *Request*

Item 3.1 on the 1995 Work Programme from the Oslo and Paris Commissions.

#### *Source of the information presented*

The 1995 reports of the Marine Chemistry Working Group (MCWG) and the Working Group on Environmental Assessment and Monitoring Strategies (WGEAMS).

#### *Status/background information*

As part of the work carried out under the framework of the North Sea Task Force, an International Workshop on Background Concentrations of Natural Compounds was held in The Netherlands in April 1992. On the basis of this Workshop, a report was prepared, entitled "Background Concentrations of Natural Compounds". This document has, however, never been formally scientifically reviewed and it has been unclear for those organizations or groups wishing to use this report as to whether or not the conclusions expressed in the report are generally accepted. Accordingly, OSPARCOM requested ICES to review the report "Background Concentrations of Natural Compounds" and supplement it with additional information, if available.

#### *Review*

#### **Objectives of the document**

The underlying purpose and aims of the document were to compile data on background concentrations of nutrients, metals, natural radionuclides, and organic compounds in river water, sea water, the atmosphere, and mussels. However, the document seems to derive a single value for each contaminant/matrix combination, and this is inconsistent with an appreciation of natural geographical variability arising, for example, from geochemical factors. The task can only be approached on a location-by-location basis.

#### **Background concentrations**

The definition of background values developed early in the report was helpful, but it then appeared that the definition was not followed rigorously throughout the document, such that the conclusions were not consistent with the report contents. There were considerable problems in attempting to determine background values

for matrices such as sea water and the atmosphere, which change with time and which leave little or no record of their previous composition. By seeking to represent background conditions as those which existed before 1950, direct analyses of sea water and the atmosphere cannot be available. The alternative, but rather different, approach of seeking to determine typical values in pristine areas also has inherent problems. Firstly, the natural geographical variability mentioned above remains largely unaccounted for and, secondly, it is debatable whether it is possible to find any truly pristine environment at the present time. The transport of a range of contaminants over long distances in the atmosphere results in the contamination of remote areas, although not to the same extent as areas closer to primary sources.

The information presented in the report as background concentrations is a mixture of:

- a) *present-day concentrations* from areas that can be used for reference purposes (reference concentrations);
- b) *historical concentrations*, that may be used for some kind of reference although they do not meet the requirements for background; and
- c) *background concentrations*.

This inconsistent use of the concept may cause confusion and lead to incorrect use of the information in, e.g., assessment work.

The report sets one background value for each respective parameter. Background values are in general highly dependent on natural processes in the area, e.g., different geological, chemical, and biochemical processes including natural variations in rock compositions. Therefore, in all tables in that report, a background value should not be given as an average value, but as a range.

It should also be stated more clearly from which locations the different values have been derived, e.g., for metals, from which rivers, or whether values were based on surface water or deep sea water as, due to natural biological processes, the deep sea is enriched with dissolved constituents compared with the surface waters.

This would make it possible to apply the values given in the report in a more appropriate manner.

It is important that the report be updated taking new literature into account, as newer data are generally more reliable.

## Specific Comments

Some specific comments are contained in the following paragraphs.

### Use of available data

The lack of a structured way of compiling the data sets from which “historical” concentrations have been deduced is a shortcoming. This particularly applies to the sections of the report concerning nutrients data. The data compilation appears to rely on what the Workshop participants knew personally. However, consultation of national and international data sets and documents may well have filled some of the gaps, especially in areas where no “historical” (pre-1950) data could be located by the participants. The Workshop should also have ensured that all data on which the current document is based are available in the international databases to facilitate future studies of this nature.

Some effort to compile these types of data is now being employed in a number of European Union (EU) projects including the North-West European Shelf Project (NOWESP), and the results of this may well help future attempts to obtain a list of “historical” values.

### Nutrients

Of the methods described in the methods section, some are more obviously intended to be applicable for work on nutrients than others. These methods can be accepted with the exception of method 6 (extrapolation based on salinity *versus* nutrient concentration plots), since this method incorrectly assumes that concentrations of nutrients are necessarily low in unpolluted natural sea water.

The sub-chapter on sea water makes a very important statement that intensive agriculture involving large-scale use of industrially manufactured fertilizers started in the early 1950s. The operational consequence of this statement is that, in the absence of data on concentrations of nutrients in a pristine North Sea, reliable analytical data from the period before 1950 could be used as the best approximation of historical reference data (not background data). The sub-chapter is acceptable with the exception that the legend to Table 4 should state that the concentrations are “historical reference values” and data obtained after 1950 should be omitted.

It is not clear in the sub-chapter on rivers whether the authors have made any distinction between data before and after the early 1950s in the same way. The legends to Tables 1–3 make reference to a number of publications from the years 1920–1992. It is possible, but not obvious, that these publications deal only with

“historical” data. The report would have gained in credibility if the presentation had included clear reference to the years that these data and estimations refer to, in the same way as was done for Table 4.

This criticism should not detract from the fact that the chapter on nutrients contains useful information both in the text and the tables.

### Metals

The statement on page 32, line 3, “Furthermore and unlike for nutrients, advection of Atlantic water across the shelf break cannot be considered as a source of trace metals to the North Sea” might need to be modified. An on-going EU project, Ocean-Margin Exchange (OMEX), dealing with the exchange of deep-sea water and shelf water, will presumably give valuable information as to whether Atlantic waters also can act as a source of metals.

In Chapter 5, paragraph 3, it is not correct to use results of metal concentrations from “old” deep sea water as background concentrations, e.g., for the North Sea. Even if the deep sea water were “old”, the metals and/or contaminants could have been transported to the area more recently. In addition, natural processes could have taken place which also might have an influence on the present concentrations in the deep sea areas.

Regarding Chapter 5, paragraphs 7–8, it should be noted that models should always be tested through field investigations.

Some of the values in the table on page 32 were questioned: the Pb concentration in Atlantic waters was too high, as well as the Zn value given as  $0.13 \pm 0.40$ . The river values according to Zuurdeeg were also surprisingly high as background values.

As for the other matrices, it would not be possible to set one background value per contaminant for blue mussels, as this would depend both on the area where they live as well as on the different conditions of the mussel during the different seasons.

### Organic contaminants

The report considers three groups of organic compounds: those with no natural sources (e.g., DDT, toxaphene); those for which there may be minor natural sources (e.g., chlorophenols, dioxins, and furans); and those for which natural sources could provide a significant quantity of material (e.g., PAHs). For PAHs processes of incomplete combustion have represented a source throughout history. The Workshop investigated the use of sediment core data to infer background concentrations. Few such data were available from the North Sea, however. Some



tentative data were also explored for water, mussels, and the atmosphere.

In the discussion, it was reported that some additional data concerning PCBs, dioxins, and furans in sediment cores were now available in Canada. Degradation of PAHs in deep sediments could lead to an underestimate of the natural background concentrations. Sediment case studies are now underway in the Skagerrak/Norwegian Trench area, and a report including additional data for PAHs should be available by the end of 1995. There could still be problems in defining historic background concentrations adequately if they are below current limits of detection.

Assuming that the Workshop had succeeded in gathering together all the relevant data on organic contaminants, the report heightened the awareness of the scientific community to the scarcity of such data. It may take some years before sufficient new data are available to make a full reassessment either feasible or necessary; until then, the sub-chapter on organics can stand.

#### Overall conclusions

The analysis and interpretation of "background" concentrations lack scientific credibility, and an inadequate database has been employed from which to derive statistically sound conclusions. There are also a significant number of inaccuracies, technical errors, and poor proof-reading evident in the document.

It was noted that to some extent the document was already being superseded. Workshops under the auspices of OSPARCOM are planned for autumn 1995 and 1996, at which both background concentrations and ecotoxicological reference values will be discussed as possible assessment tools.

Because of the significant number of serious flaws and inconsistencies in the report, the declared intention of OSPARCOM to undertake new work on the subject was considered appropriate.

#### **Reference**

Laane, R.W.P.M. (Ed.) 1992. Background concentrations of natural compounds in rivers, sea water, atmosphere, and mussels. Directorate-General of Public Works and Water Management, The Hague. DGW-92.033.

#### **12.2 Ecotoxicological Reference Values**

##### *Request*

Item 3.2 on the 1995 Work Programme of the Oslo and Paris Commissions.

##### *Source of the information presented*

The 1995 report of the Joint Meeting of the Working Group on Biological Effects of Contaminants (WGBEC) and the Working Group on Marine Sediments in Relation to Pollution (WGMS), and the 1995 and 1994 reports of WGBEC.

##### *Status/background information*

This request asks for the provision of information relevant to the further development of ecotoxicological reference values or assessment criteria, which are intended to be of assistance to the monitoring groups in OSPARCOM that may wish to use such criteria for both the retrospective and prospective assessment of chemical monitoring data.

The request is based on a document entitled "Ecotoxicological Assessment Criteria for Trace Metals and Organic Microcontaminants in the North-East Atlantic" published by OSPARCOM in 1994, which develops a set of so-called assessment criteria for up to 17 contaminants in sea water, marine sediments, and biota. The proposed values (given in each case as a range, rather than a single number) are based largely on extrapolation from laboratory toxicity data, although field information was also used. Many of the criteria are indicated to be 'provisional' due to deficiencies in the database, and several of the values for non-synthetic organic compounds lie very close to, or below, the natural background level for the contaminant in question.

This approach to the evaluation of marine chemical monitoring data has received strong criticism from both the WGBEC and the Joint Meeting between WGBEC and WGMS. Apart from the shortcomings of the database and the anomalies concerning background concentrations, the essence of the criticism is that one should not use chemical data alone to evaluate the pollution status of the marine ecosystem. By definition, 'damage' or 'pollution' has ultimately to be assessed in biological terms, because organisms make an integrated response to all the contaminants to which they are exposed. Mixtures may act synergistically, additively or antagonistically, so the presence of a particular contaminant at concentrations below a notional 'safe' level does not necessarily imply that it is not contributing to any overall toxic effect. In other words, a mixture of contaminants, each at individually negligible concentrations, may act together to produce a damaging effect. Furthermore, many chemical monitoring data do not distinguish between the bioavailable and non-bioavailable fractions of contaminants, thus many xenobiotic substances may be present in a given matrix, and yet not all will necessarily be in a form that can affect the organisms in that matrix. Finally, chemical monitoring does not take into account any environmental modulations of toxicity, such as seasonal changes in



sensitivity. For example, some species may be much more sensitive to fat-soluble contaminants during periods when their fat reserves are being mobilized.

Thus, at the most, ecotoxicological assessment criteria (assuming that they were to be founded on an adequate database) might be applied to give some orientation to the assessment of marine monitoring data, but should not serve as firm standards or triggers for action. To be fair, the OSPARCOM report referred to above itself urges the use of caution, common sense, and expert judgement when applying ecotoxicological assessment criteria in specific situations, but there is a danger that the monitoring organizations may ignore this good advice.

#### *Need for further research*

If the concept of ecotoxicological assessment criteria was a valid one, the values that have been published by OSPARCOM would still need revisiting in the light of an improved ecotoxicological database. This especially applies to data on the toxicity of sedimentary contaminants and on toxic levels in biota, both of which are currently very sparse. There would also be a need to develop chemical analytical methods which clearly identified the bioavailable fraction of a contaminant in a given matrix, although there are fundamental difficulties with this approach. In addition, greater understanding would be required about the influence on toxicity of environmental factors such as seasonal change. Last, but not least, a way would have to be agreed on concerning how to evaluate the expected joint action of the mixture of contaminants which would inevitably be present at a given sampling location. This presupposes that assessment criteria were available on the majority of environmental contaminants, and that monitoring data on all of them were also at hand—a daunting task.

However, given the criticisms which have been made concerning the validity of the whole approach, it is arguable whether the research outlined above is justified in the present context.

#### *Recommendations*

The ACME advises the OSPARCOM monitoring groups that the concept of ecotoxicological assessment criteria is fraught with major scientific and practical difficulties, and does not form a valid basis for the retrospective evaluation of the biological significance of existing chemical monitoring data. Any future development and use of such criteria for evaluating the capacity of the marine environment to support a healthy ecosystem should be treated with the greatest caution, and should be combined with the simultaneous deployment of biological measures of environmental quality. In other words, the prospective use of assessment criteria must be restricted to the context of a monitoring strategy which

fully integrates chemical and biological measurements (see Section 4.1 and Annex 1).

### **12.3 Assessment of Concentrations of Contaminants not Harmful to Humans or Nature**

#### *Request*

Item 14 of the 1995 requests from the Helsinki Commission. In this request, HELCOM asks for information on concentrations of the contaminants specified in the HELCOM list of priority heavy metals and persistent organic pollutants “that are not harmful to man or nature”, on the basis of existing scientific knowledge. This was interpreted by ACME to mean that HELCOM wants to know how far they have to go in proposing regulations concerning discharges of these priority pollutants. For this purpose, they need to know some kind of maximum allowable concentration (MAC) in nature for each pollutant, i.e., the level at which no measurable harm is detected in humans or in nature.

#### *Source of the information presented*

The 1995 report of the Marine Chemistry Working Group (MCWG). Information on the closely related issue of ecotoxicological assessment criteria is also relevant (see Section 12.2, above).

#### *Status/background information*

In 1991, the Helsinki Commission adopted a “Baltic Sea list of priority harmful substances other than nutrients for immediate action in order to reach the 50% reduction goal by 1995.” In 1994, the Commission, meeting at ministerial level, decided to make further efforts “to ensure a reduction of pollution to levels that are not harmful to man or nature”. This goal is primarily aimed at the list of priority harmful substances, which comprises eight metals and their compounds, 21 biocides, and seventeen other organic substances.

These substances have been identified as harmful on the basis of certain criteria. These criteria are founded on either intrinsic properties of the substances, i.e., persistence, toxicity, or other noxious properties, and potential to bioaccumulate, or other characteristics such as:

- the ratio between observed concentrations and concentrations having no observed effect;
- transboundary or long-range significance;
- risk of undesirable changes in the marine ecosystem and irreversibility or durability of effects;

- serious interference with harvesting of seafoods or with other legitimate uses of the sea.

The harmful substances listed all have at least one of the three intrinsic properties. Concerning the other characteristics, the key words clearly are "concentrations having no observed effect", "undesirable changes in the marine ecosystem", and "irreversibility or durability of effects."

No doubt the classification of these harmful substances was based, *inter alia*, on a number of laboratory studies of their effects. There are a number of publications describing such results and at least some of the material would be relevant for a brackish sea area such as the Baltic Sea.

It is not clear from the request whether the effects in nature should be considered at the community level or on the individual organism level to satisfy the requirements of HELCOM. It is also not known what HELCOM would regard as an acceptable change in the ecosystem. Therefore, the ACME cannot in a strict sense describe the borders for what is undesirable.

Furthermore, the answer to the question from HELCOM has both a political and a scientific dimension and, therefore, science alone cannot and will not provide the

answer. The obvious political dimension is to define what is an acceptable change in the ecosystem and, possibly, what risk level is acceptable concerning the threat to man.

The scientific dimension is that the risk to man or nature caused by the discharge and presence in nature of the priority pollutants cannot be handled on a substance-by-substance basis in a generalized way. Depending on speciation, only a certain fraction of an amount of a substance may be bioavailable. Synergistic as well as antagonistic or additive effects caused by several pollutants (as well as other, natural substances) acting on the same organism, under various conditions, must be taken into consideration. Furthermore, the characteristics of the ecosystem vary strongly between different subregions of the Baltic Sea. Consequently, the environmental response can be expected to be different in different parts of the Baltic Sea. ICES can assist in describing these ecosystem aspects.

#### *Recommendations*

The ACME recommended that HELCOM address the problem from an ecosystem perspective, applying the precautionary principle, rather than using an oversimplified approach of assigning concentration levels of contaminants as not being harmful.

## 13 INTRODUCTIONS AND TRANSFERS OF MARINE ORGANISMS

### *Request*

ICES Member Countries may request ICES to review proposed introductions and transfers of marine organisms for mariculture purposes. These proposals receive in-depth review by the Working Group on Introductions and Transfers of Marine Organisms, with ultimate review by ACME. The Working Group also keeps under review the progress of such introductions and reports on the outcome to ACME.

No new requests for introductions were received in 1995, but the status of on-going and proposed introductions and transfers was reviewed.

### *Source of the information presented*

The 1995 report of the Working Group on Introductions and Transfers of Marine Organisms (WGITMO).

### *Status/background information*

The ACME reviewed the WGITMO report and agreed to present the information and advice contained in the following sections.

#### **13.1 The 1994 Code of Practice on the Introductions and Transfers of Marine Organisms**

This Code of Practice was adopted by ACME in 1994 and has been published in its 1994 report (ICES, 1994).

However, taking into account the reports of and discussions with the respective chairmen of the WGITMO and the Working Group on Applications of Genetics in Fisheries and Mariculture, the ACME agreed to adopt the following revised definition of genetically modified organism (GMO) for inclusion in the Code of Practice:

“An organism in which the genetic material has been altered anthropogenically by means of gene or cell technologies.<sup>1</sup>

<sup>1</sup>Such technologies include the isolation, characterization, and modification of genes and their introduction into living cells, as well as techniques for the production of living cells with new combinations of genetic material by the fusion of two or more cells.”

The Code is to be published as a leaflet in two languages, English and French, and circulated to a wide audience, since it applies to both public (commercial and

government) and private (including scientific) interests. It should also be translated into other ICES languages at the national level. The ACME endorsed this suggestion.

The ACME also took note that the WGITMO had decided not to use the term “non-indigenous” in the Code of Practice. This had been decided as a result of problems in the definition and interpretation of the term; for example, new species had been identified in the 1986 benthos survey of the North Sea, but it was not clear whether these were new recordings of existing species or introduced “non-indigenous” species.

#### **13.2 ICES/EC Dialogue on Species Movements**

In response to Council Resolution 1994/3:2, the WGITMO will collect case studies with appropriate documentation of incidents in which shipments of live fish or shellfish from one European Union (EU) country to another, as permitted by EC Council Directive 91/67/EEC, have been ‘contaminated’ by other organisms such as parasitic copepods, molluscs, worms, and/or dinoflagellates that would then be released ‘accidentally’ as non-indigenous species in the waters of the recipient country.

The ACME endorsed the view that there is a need for historical case studies to be carried out on intentional introductions of the Pacific oyster (*Crassostrea gigas*) and other selected species in order to understand the ecological and economic impacts that may result from such introductions. The case studies will provide a basis on which to make risk assessments for future introductions of marine organisms into ICES Member Countries.

In addition, the ACME considered it important to stress that authorities should continue to be aware of the *potential* for contamination of shellfish and fish shipments, by associated non-target species including pathogens, from one country to another, and that alerting agencies to be so aware could serve as the basis for discussion between ICES and the EU.

#### **13.3 Trade in Aquarium Species and Epizootic Ulcerative Syndrome (EUS)**

The ACME noted that trade in aquarium species was a subject of common interest to many ICES Member Countries. It has been well recognized that the species used in the aquarium trade from different biological provinces can, and do, become released into new areas. Such species introductions or their associated biota may have negative consequences for native species and their communities.

Recent statistics indicate that EU countries import large quantities of exotic fishes annually. Both marine and freshwater species are derived from fish farms or from wild collections in the Indo-Pacific, South and North America, and Africa.

The recent expansion of Epizootic Ulcerative Syndrome (EUS), associated with many fish species in the Indo-Pacific region, is of some concern. The continued flow of aquarium introductions may provide a vector for the inoculation of such a disease elsewhere. Practical measures to reduce the risk of releases, and procedures for the correct disposal of dead fish need to be considered further.

#### **13.4 Status of On-going and Proposed Introductions and Transfers**

##### **Introduction of hybrid bass *Morone saxatilis* x *M. chrysops* to Ireland**

The ACME noted that this introduction has not yet proceeded.

##### **Transfer of halibut from Norway to Ireland (fish culture trials)**

A proposal to introduce halibut fingerlings from Norway into onshore concrete ponds in Ireland was noted. The purpose of this transfer was to assess whether the halibut fingerlings could be reared to market size when given a diet of fish food. Since the halibut has been reported from waters even further south, this should be considered as a transfer rather than an introduction. The transfer of fingerlings would proceed only if the pathologist's report confirms that the area in Norway from which the fingerlings would be obtained is free of a viral disease that is present in some Norwegian waters.

##### **Japanese seaweed (Nori) *Porphyra yezoensis* in the USA**

A report on the culture of this species was noted. Changes in the production systems have recently been made which shortened the production cycle. The seeding of the nets has been improved so that most nets treated during 1994 had very few contaminating macroalgae. There has also been a change in the cultivation sites, and a new, more effective technology for lifting nets from the water for drying the alga is being used.

On inspection of growing sites, plants were found attached to header ropes, but the ACME concluded that there is no evidence to suggest that the full life cycle has been or can be completed. Monitoring of sites will continue.

#### **13.5 Status of On-going Accidental Invasions in European Waters**

##### **Invasion of the green alga *Caulerpa taxifolia* in the Mediterranean**

The ACME took note of a report on the further spread of the green alga *Caulerpa taxifolia* in the Mediterranean Sea. As yet, there has been no report of observations of *Caulerpa* in the Atlantic. A document signed by several scientists attending a meeting in Barcelona in December 1994 (Annex 6) had been drawn up to alert other experts in the Mediterranean area, and was subsequently also distributed by the ICES Secretariat. The main mechanism of transport of the alga is via attachment to anchor systems on boats.

In the scientific literature, there is evidence to suggest that: the alga can withstand temperatures of 10°C for at least three months and it can grow in temperatures ranging from 10 to 30°C; light intensities that occur during the winter can support growth of *Caulerpa* in certain areas; *Caulerpa* may be a threat to seagrass *Posidonia oceanica* beds; some new toxins have been isolated; and *Caulerpa* may threaten biodiversity.

##### **Invasion of the American Comb Jellyfish *Mnemiopsis***

The ACME reviewed an update of information on this ctenophore, native to American waters (from Cape Cod in the north to Brazil in the south) and introduced via ballast water into the Black Sea in 1982. By 1987–1989 its abundance had increased dramatically, accompanied by an observed decline in the anchovy fishery. By 1994 the anchovy fishery, particularly in the Sea of Azov, had almost disappeared. In its native habitat, *Mnemiopsis* is a voracious consumer of zooplankton and the abundance of copepods is at times negatively correlated with increasing concentrations of the ctenophore.

*Mnemiopsis* has also spread to the eastern Mediterranean, from where it is spreading westwards by the vectors of currents and shipping. Potentially it could be transported through the Suez Canal and the Red Sea into the Indian Ocean.

There has been a proposal for biological control of this invasive species. This would involve the introduction of a predatory fish species from North America or the Baltic Sea that would eat the ctenophores. No mechanical or chemical removal is practical. If the plan to introduce a fish as a biological control were to proceed, this effort would be the first example of biocontrol in the marine environment.

The United Nations Environment Programme (UNEP) has formed a special working group to consider this proposal. This working group has now finished its study and will present its report through GESAMP. It is likely that a proposal will be made for research to be carried out on the potential for and concepts of biological control.

### **13.6 Baltic Marine Biologists (BMB) Working Group on Non-indigenous Marine and Estuarine Organisms in the Baltic Sea**

The ACME noted that the Baltic Marine Biologists (BMB), dealing with the marine biology and environment of the Baltic Sea, has established a Working Group on Non-indigenous Marine and Estuarine Organisms (NEMO) in the Baltic Sea (BMB WG 30).

The preliminary objectives for this group were formulated as follows:

- 1) to promote a closer cooperation between biologists dealing with NEMOs within the Baltic Sea and between the Baltic and other marine areas, e.g., the Black Sea, since both seas are affected by NEMOs;
- 2) to collect and summarize information on NEMOs in the Baltic Sea in order to make a cooperative report (or monograph) covering their role in the ecosystem they invaded;
- 3) to seek cooperation with the ICES Working Group on Introductions and Transfers of Marine Organisms (in addition to the national reports prepared every year by Germany, Denmark, Finland, and Sweden, among others);
- 4) to elaborate a recommendation for HELCOM to include NEMOs in the revised Guidelines for the Baltic Monitoring Programme;
- 5) to report to national agencies responsible for International Maritime Organization (IMO) activities in each country.

The Baltic Sea is a sea of few species of plants and animals; its water is too fresh for marine species, and too saline for freshwater species. More than 30 species of anthropochorous immigrants, mainly unintentionally introduced plants and animals, have been reported from the Baltic marine, estuarine or coastal ecosystems. Most of these species have become important, and some have even become key components in the ecosystems they invaded. The introduced species may bring with them their diseases and parasites causing severe damage to natural, autochthonous communities. In particular, the ACME noted the introduction and rapid spread of the

American polychaete *Marenzelleria viridis*, as reported by several countries.

The ACME endorsed the view that there would be several advantages for both the WGITMO and the BMB WG 30 if a close cooperation could be arranged and they could establish valuable contacts with eastern European scientists to provide better knowledge on introductions in their countries. The Baltic Sea has a very special morphology and hydrography and is, being a brackish water system, a simplified ecosystem. Thus, it could be very suitable as a kind of "experimental aquarium" for studying the effects of introduced species.

The WGITMO, on the other hand, could provide information on work with the Code of Practice, including technical and methodological aspects when implementing the Code.

The ACME endorsed this outline of cooperation and agreed that a joint meeting between the two groups should be held in the near future, preferably in a Baltic country.

### **13.7 Ballast Water Activities: Research and Management in ICES Member Countries and Globally**

Shipping has always been a means of spreading and dispersing aquatic organisms to new habitats. Over several decades, sea transportation has undergone rapid changes towards larger and faster ships and this trend has had technical implications such as larger ballast water capacities. As a consequence, the frequency of releases and the water volumes transferred over long distances has dramatically increased. This has increased the probability of successful introductions of organisms of all taxa, many of which have proven to be harmful to ecosystems and also detrimental to other users of aquatic resources.

The ACME agreed to the advice by WGITMO that the following issues need to be addressed in studies of ballast water impacts on the receiving environment:

- 1) the extent of introduction needs to be documented;
- 2) the survival capacity of introduced species in the new habitat needs to be evaluated;
- 3) the fate of introduced species in the new surroundings needs examination;
- 4) the consequences for other species needs to be estimated; and
- 5) the consequences arising from such introductions to other resource users (e.g., shellfish farming, fish



farming, tourism (bathing beaches), fisheries, wildlife, and industry (e.g., cooling water supplies)) need to be evaluated.

The studies should include sampling at start- and end-points of national and intercontinental shipping routes through networking among interested laboratories of ICES Member Countries. Such networking is considered to be a cost-effective means of studying the various taxa, while experts for identification of various taxonomic groups could be involved in a larger network, if necessary. In order to realize a sampling strategy involving multi-laboratory participation, an intercalibration exercise on sampling techniques and sampling profiles in relation to type and size of ship and ballast water tanks is required. Such an intercalibration may be achieved through a "concerted action" programme under the EU umbrella.

The ballast water studies would help in:

- 1) understanding the conditions under which successful transfers via different routes and vectors are realized (e.g., seasonal differences, operational differences, and differences between types of ships: bulk carriers, container ships, petroleum tankers, etc.);
- 2) assisting in developing strategies on ballast water management;
- 3) suggesting the development of techniques and strategies in ballast water treatment and initiating studies on the effectiveness of such techniques;
- 4) developing appropriate protocols and monitoring programmes to minimize environmental risks arising from ballast water discharges.

The importance which ICES attaches to the risk of unwanted introductions posed by ballast water is reflected in the programme for the 1995 Annual Science Conference, where a Theme Session will focus on "Ballast Water: Ecological and Fisheries Implications". The Chairman of WGITMO, Dr J. Carlton, will also give the Open Lecture on this topic at the Conference.

#### Reference

ICES. 1994. Report of the ICES Advisory Committee on the Marine Environment, 1994, pp. 95–98. ICES Cooperative Research Report, No. 204.



## 14 ENVIRONMENTAL INTERACTIONS OF MARICULTURE

### *Request*

There is no direct request, however, the ACME is aware that there is a growing interest in mariculture operations in terms of their effluents and in the context of coastal zone management.

### *Source of the information presented*

Reports of the Working Group on Environmental Interactions of Mariculture (WGEIM) and the ICES paper presented at the Bordomer-Coastal Change 95 meeting entitled "Some Activities in the Coastal Zone: Environmental Impact Assessments".

### *Status/background information*

#### **Introduction**

The coastal zone is being increasingly utilized by ICES Member Countries for economic purposes including fisheries, mariculture, tourism (including eco-tourism), navigation, sport fishing, shoreline development, dredging, ocean dumping, gravel extraction, and effluent discharge. Often, one type of use is not compatible with another, nor with the scientific standards for the sustainability and maintenance of an acceptable level of environmental quality.

The pressures of urbanization, shoreline development, and economic development will not lessen as demands for marine renewable fisheries resources, and their value, continue to increase. Mariculture shows considerable promise to enhance the production of marine resources, yet these developments not only compete with space used by existing fishing activity but, in turn, are adversely affected by other coastal activities and are particularly sensitive to sources of pollution. Mariculture itself interacts with fisheries resources and contributes waste products which can lead to adverse environmental conditions.

The mariculture industry, therefore, finds itself in the dual role of being a source of chemicals and wastes with an impact on the ecosystem and, at the same time, requiring clean, unpolluted waters for successful production.

#### **History of the work**

The issue of environmental impacts of mariculture was initially addressed in the ICES community by the establishment of an *Ad Hoc* Study Group (later a Working Group) on the Environmental Impacts of Mariculture in 1985. In its first report in 1987, the group identified a number of environmental issues of

international importance related to mariculture, which included:

- a) the effects of mariculture on microbial communities and on the possible spread of pathogens;
- b) possible changes in the populations of marine algae (phytoplankton and macroalgae) related to mariculture;
- c) the influence of mariculture and its physical structures on sedimentation to the benthos;
- d) the use and environmental effects of chemicals (including therapeutants and medicaments) in mariculture;
- e) the importance of site selection criteria in minimizing environmental effects of mariculture operations; and
- f) the development of predictive models of mariculture impacts.

This group was also charged with producing guidelines which could be used in resource management and with compiling a directory of chemicals, and their properties, currently used in mariculture, with a view to providing advice to Member Countries. This review of chemicals used in mariculture culminated in the publication of the report *Chemicals Used in Mariculture* (ICES, 1994) in August 1994.

The Working Group also became involved in a survey of monitoring and modelling programmes related to the assessment of the impact of mariculture, and in its 1991 report the concept of coastal zone management was introduced and defined as a "means of anticipating and thereby minimizing potential ecological change associated with mariculture development".

As its work developed, new activities were added to the remit of the Working Group, including:

- developing criteria for and a standard system of monitoring and reporting;
- delineating the scope and nature of environmental interactions between mariculture and other uses of coastal marine resources;
- providing advice on approaches to improved site selection;
- reviewing and evaluating national monitoring programmes and preparing regular status reports on

the impact of mariculture within ICES Member Countries;

- assembling evidence for interactions of complexed and/or particle-bound contaminants (e.g., antibiotics, antifoulants, biocides) from fish farms with marine flora and fauna and the significance of these interactions within marine ecosystems; and
- preparing guidelines on the ecotoxicological information necessary to permit assessment of the relative environmental impacts of therapeutants.

A special Topic Session on "Mariculture and Coastal Zone Management (CZM)" was held at the 1994 ICES Annual Science Conference. This session included a number of international contributions:

- 1) A case study of the Seto Inland Sea, Japan, showed how that country is addressing the relationship between mariculture and environmental change by monitoring and regulating nutrient concentrations that influence the appearance of toxic algal blooms.
- 2) A review of the coastal zone research in different Asian countries showed how a lack of communication among different government departments with responsibilities for aquaculture can cause developmental problems, particularly when specific mariculture-related legislation does not exist.
- 3) The Swedish model used for CZM showed that an integrated multilevel governmental approach was very efficient in resolving and preventing user group conflicts while defining future mariculture development.
- 4) The planning process for CZM encourages the approach of integrating all levels of government and users of renewable resources; moving from a management policy based on a single coastal activity to a multiple user-functioning ecosystem approach was advocated.
- 5) Norway is using modelling methods for CZM and is incorporating carrying capacity and environmental impact models to determine mariculture loading and the appropriate environmental monitoring required.

- 6) An example from Nova Scotia, Canada, showed how both direct community involvement and their perceptions must be included in a pro-active manner to resolve CZM problems.

The main discussion in the Theme Session revolved around the point that coastal zone management is based on understanding the ecosystem carrying capacity of the mariculture site and the interrelationships among all coastal activities, including the regulatory framework of the different governmental management bodies. Coastal zone management is a basic cornerstone for the continued development of mariculture in response to the need for organized sustainable development.

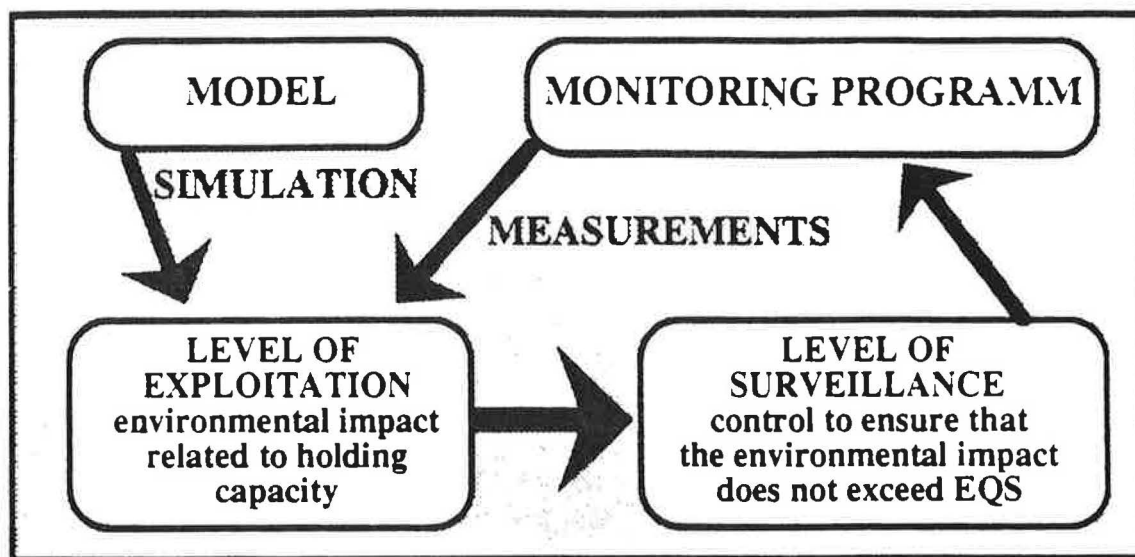
### Current Issues

A number of relevant issues that have recently been highlighted by the WGEIM are:

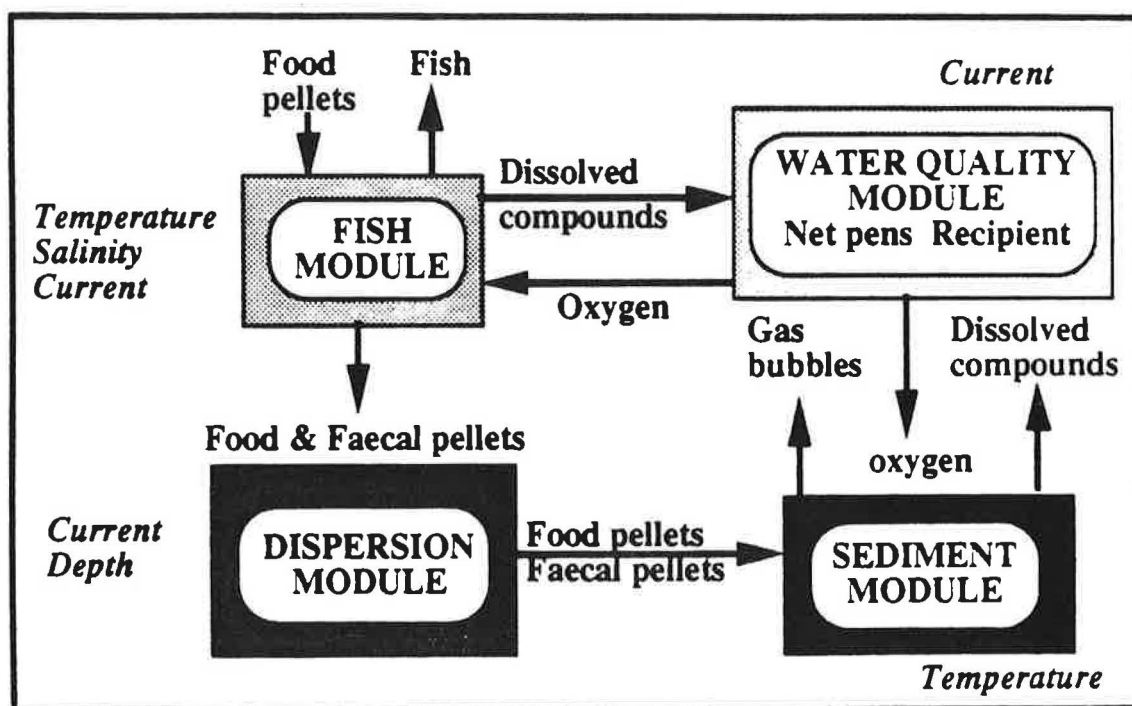
- *Potential environmental effects of new culture systems in ICES Member Countries.* At its 1994 meeting, the Working Group discussed alternative scenarios for salmon cultivation in Norway. Cage farming is the most cost-effective grow-out system for salmon at present, but alternative strategies (e.g., utilizing various combinations of land-based and water-based systems) are receiving increasing consideration by the industry to overcome environmental problems and to conform to regulatory measures.
- *New approaches to environmental assessment and monitoring of mariculture development.* A new approach to environmental assessment and monitoring termed MOM (the acronym is based on the Norwegian words for monitoring and modelling of fish farms; the system was developed by A. Stigebrandt, Sweden) will be tried out in Norway in 1995. The relationships among the four components of this approach (the model, the monitoring programme, the level of exploitation, and the level of surveillance) are illustrated in Figure 14.1.

The interactions among the four components of MOM (the fish module which simulates the actual effluent, the water quality module which simulates dissolved compounds and oxygen, the dispersion module which simulates the farm area, depth and current conditions, and the sediment module which simulates the accumulation and decay of the waste) are shown in Figure 14.2

**Figure 14.1.** Principal components of the Norwegian MOM (for monitoring and modelling of fish farms) programme (EQS = environmental quality standard).



**Figure 14.2.** Schematic representation of the essential sub-models of the Norwegian MOM programme for monitoring and modelling environmental impacts of mariculture for regulatory purposes.



- *The role of models in mariculture and recent relevant developments in modelling.* The WGEIM identified the main goals of modelling in the context of mariculture as follows:

- 1) providing information on environmental issues to regulatory agencies (this is essential for effective planning of development in the coastal zone where defining the holding capacity and/or carrying capacity are of great importance);
- 2) providing a basis for improving husbandry and optimizing productivity; providing advice on site selection and management practices;
- 3) aiding in the design of practical and appropriate monitoring strategies which allow assessment of regulatory thresholds and acceptable risk;
- 4) serving as a basis for coastal zone management advice, including socio-economic factors such as value of production, costs of input, employment implications, and other macroeconomic issues related to the contribution of mariculture to regional-scale economy and employment.

These goals raise more specific requirements for model development:

- a) the modelling approach and design should include an appropriate and flexible interface to be accessible to persons making regulatory, monitoring and socio-economic decisions;
  - b) model output should include ecologically significant consequences as well as more easily quantifiable loading values;
  - c) thresholds of environmental degradation need to be defined;
  - d) different types of models are required.
- *Integration of Mariculture into Coastal Zone Plans and Management Strategies*
    - a) *The role of mariculture in integrated coastal zone management.* The mariculture industry is relatively new and its development has coincided with a substantial increase in environmental awareness. Unlike many other industries located in the coastal zone, mariculture relies heavily on natural aquatic resources for its existence, and is characterized by the demand for a high quality environment. Mariculture development, because of its specific site selection requirements, is frequently forced into remote and disadvantaged regions with limited opportunities for

development. However, a parallel increase has occurred in a number of other interests competing for coastal space. The mariculture industry operates in all environments (e.g., physical, social, economic), and requires many inputs to be successful; it also has multiple impacts on these environments, some positive and some negative. On the one hand, in the physical and biological environment, mariculture has been accused of causing visual, organic, chemical, and genetic pollution, and disease and parasite transfer to the native fish populations, as well as being the cause of navigational hazards. On the other hand, mariculture offers employment and economic benefits from harvesting living marine resources, and the presence of mariculture facilities will help to discourage pollution from less environmentally friendly industries. The future role of mariculture in integrated coastal area management (ICAM) is to develop the industry with a full appreciation of ecosystem/industry interdependencies and become a legitimate component of the overall ecosystem. Mariculture techniques and planning and management must be developed with natural ecosystems and other coastal users in mind so that negative impacts can be reduced.

- b) *Pro-active coastal zone planning and management for sustainable mariculture.* There is an urgent need to promote pro-active approaches for planning and managing mariculture as an integral part of the coastal zone management plans and investment strategies. Plans and management strategies must be based on sound scientific management principles for the protection of environmental processes which maintain the functional integrity of coastal ecosystems and sustain mariculture and other renewable resource dependent activities. Although the process of integrating mariculture in planning activities has started in a significant number of ICES Member Countries, full implementation of coastal zone management practices can only be realized by incremental steps as part of an overall strategic approach where different scenarios between communal management and private property rights and obligations may occur depending on local and regional development priorities. Among other objectives, it is important (a) to promote institutional arrangements that foster integrated multi-sectoral planning of coastal resource utilization and facilitate the transfer of information between scientists, industry, and regulatory bodies; (b) to improve evaluation of the capacity of coastal living resource systems to sustain mariculture within a multiple-use management framework; and (c) to initiate interdisciplinary research into the planning and management of mariculture by the development

of criteria to help evaluate the benefits and costs of mariculture, including the socio-economic impact and corresponding cultural implications. The WGEIM will study the interactions of mariculture with other users of coastal resources and analyse the outcome of relevant workshops and other activities in order to prepare guidelines for the management of mariculture within the larger context of a Coastal Zone Management Programme (CZMP).

c) *Preparation of guidelines.* Guidelines for policy makers, planners, and managers responsible for formulating and implementing coastal zone management programmes will, *inter alia*, address the following issues:

- inventory, mapping, and development of Geographical Information Systems (GIS) for land and water resources in the coastal zone;
- different users associated with coastal zone conflicts;
- institutional infrastructures and legal systems;
- integration and coordination of mariculture activities within the regulatory system adopted by the authorities responsible for the coastal zone;
- planning of mariculture and other activities at the community level;

- public education in mariculture at the community, regional, national, and international levels;
- international cooperation for solving various issues;
- international conventions and bodies.

#### ICES Activities in 1995

Some relevant ICES events taking place in 1995 include: (1) a Workshop on Principles and Practical Measures for Interaction of Mariculture and Fisheries in Coastal Area Planning and Management (19–22 July in Kiel, Germany); (2) a Workshop on Modelling Environmental Interactions in Mariculture (6–8 September in Dartmouth, N.S., Canada); and (3) a Theme Session on “Mariculture: Understanding Environmental Interactions”, at the 1995 ICES Annual Science Conference (21–29 September in Aalborg, Denmark). Reports from these activities will be available during the course of 1996.

#### Reference

ICES. 1994. Chemicals used in mariculture. ICES Cooperative Research Report, No. 202. 100 pp.

## 15 ENVIRONMENTAL EFFECTS MONITORING OF EXTRACTION OF MARINE AGGREGATES

### *Request*

There is no specific request; this is part of continuing ICES work concerning the effects of marine aggregate extraction on the marine ecosystem and means of reducing this impact.

### *Source of the information presented*

The 1995 report of the Working Group on the Effects of Extraction of Marine Sediments on the Marine Ecosystem (WGEXT).

### *Status/background information*

In 1994, the ACME accepted and published guidelines for preparing environmental impact assessments of proposed marine aggregate extraction operations (ICES, 1994) based on the 1994 WGEXT report.

The ACME reviewed the 1995 report of the WGEXT and agreed to present the information and advice contained in the following sections concerning the design and implementation of environmental effects monitoring programmes in relation to marine aggregate extraction projects.

### **Introduction**

The purpose of environmental effects monitoring (EEM) needs to be clearly defined for each project. In general, the EEM should be designed to confirm limitations on anticipated, significant negative physical and biological effects as predicted by the Environmental Impact Assessment (EIA) prepared for that project.

### **Preliminary Design Requirements**

The following points were considered with regard to preliminary design requirements:

- 1) Existing information from the Environmental Impact Assessment and other sources should be used to identify physical and biological factors that may be impacted. To ensure that the EEM is designed to allow scientifically acceptable analyses and produce statistically significant results, it may be necessary to undertake additional exploratory sampling and/or studies, especially if spatial or temporal boundaries are shown to be greater than those covered in the EIA.
- 2) Spatial boundaries for the EEM must be clearly defined. This will be achieved by using physical models to determine the expected zone of impact and

then designing the sampling to cover not only this zone but also reference areas.

- 3) Temporal boundaries must also be clearly defined. Baseline information and environmental sensitivities may be influenced by daily, seasonal, annual, or inter-annual variations. It should not be assumed that impacts cease when the extraction terminates since there may be long-term subtle or cumulative effects. This may require post-extraction EEM.
- 4) Monitoring needs to be scaled to the nature and magnitude of the risk. Not all projects necessarily require monitoring.
- 5) The EEM must be flexible in order that it can be adjusted to include unforeseen circumstances and also to economize measurements where warranted. Independent peer review is essential to this.
- 6) At the outset of the EEM, quality control and quality assurance procedures need to be established for sampling. Reporting needs to be standardized and a firm review schedule should be established and rigorously enforced. Results of the review may require feedback into item 5, above.
- 7) There should be a feedback mechanism to permit modification and/or termination of the operation and, in extreme cases, there may be a requirement to develop compensation plans.

### **Modelling of Physical Processes**

Modelling activities should take into account the following issues:

- 1) During dredging, the substrate will be removed and altered, and spill from the dredging process will create a plume in the water column which later will settle out. Inside the dredging area the surface of the seabed will be partly or totally removed, and sediments from the overflow will be spread in the area.
- 2) The primary impact outside the actual dredging area will depend on the turbidity and sedimentation of fines from the dredging operation.
- 3) Different hydrodynamic models and sediment dispersion modules are available for the evaluation of turbidity and sedimentation of fines spilled during the dredging operation. The complexity of the model needed will depend on the size of the dredging operation and the environmental interests in the area.



- 4) In many dredging projects, a worst-case assessment based on a relatively simple model will be sufficient to identify the likely impact area and the magnitude of turbidity and sedimentation.
- 5) Detailed information on the grain-size composition of the resource is needed, allowing an estimate of the maximum potential release of fines during a dredging operation. If more accurate data are needed, spill measurements during production performance tests (i.e., before the issuance of a full production license) should be carried out.
- 6) The likely physical impact can be evaluated through the modelling of a number of dredging scenarios illustrating typical dredging activities and quantities.
- 7) The results from modelling the turbidity and sedimentation should be compared to natural background levels of turbidity and sedimentation rates in order to delimit the area and magnitude of potential impact. This information can act as a basis for setting up a realistic monitoring programme.

#### **Design and Implementation of a Monitoring Programme**

There are sound practical reasons why the benthic fauna are an appropriate target for seabed monitoring of the biological effects of many types of man-made disturbances (Rees *et al.*, 1991) and their use in the monitoring of dredging impacts can be recommended. Additionally, in establishing a rationale for the design of such a monitoring programme, an analogy may be drawn with a programme developed for point-source discharges. This is because the area within which dredging occurs may, in general, be assumed to be heavily impacted and hence for management purposes may be equated with a "mixing zone" immediately surrounding an effluent discharge. The main focus of concern will, therefore, be on events beyond the licensed area, notably in association with the dispersion of "plumes" of fine particulate material released during dredging. Thus, similar considerations to those outlined in Rees *et al.* (1991) apply to the design of sampling programmes for dredging effects.

Some qualifications must nevertheless be attached to the analogy with discharge monitoring. For example, one management strategy that may be considered at certain dredging locations is the zoning of a licensed extraction area in such a way that sub-areas remain "fallow" for a specified period. In other cases, seasonal restrictions on dredging may be considered in relation to the migratory habits of commercially important species, and related fishing practices. Clearly, in such circumstances there may be an interest in the biological processes within the licensed area as well as beyond it.

It should also be emphasized that any effects resulting from a discontinuous 'effluent' plume arising from aggregate dredging will invariably be manifestations solely of the physical rather than chemical consequence of settling particulates (that is, chemical contamination will rarely be an issue).

Routine monitoring programmes will, therefore, involve measurement of a combination of biological and physical variables (notably the structure of seabed sediments and concentrations of suspended solids). The amount of monitoring effort required, as well as the apportioning of that effort between biological and physical studies, will vary from site to site and according to the magnitude of the dredging operation.

In general, commonly used methods for fish stock assessment are unlikely to yield useful information in the assessment of effects of single dredging operations (unless conducted on a very large scale or at a location of known sensitivity, e.g., near to spawning grounds or migratory routes of valued species). This is because it can be anticipated that such dredging operations will have highly localized effects relative to the distribution of most fish stocks. There may, however, be legitimate concerns about the effects of localized dredging on fishing practices, even though such concerns are beyond the scope of biological monitoring programmes.

An important consideration which may influence the design of any monitoring programme concerned with a single point-source "discharge" is the possibility of effects from other man-made impacts in the area, which may, of course, include nearby port and harbour dredging operations. In these circumstances, a point may be reached where the emphasis in monitoring must shift from an assessment of the effects of individual activities to those arising cumulatively from several operations. Depending on the anticipated magnitude and spatial extent of impacts arising from multiple activities, it may be necessary to expand the scope of biological monitoring, for example, to address regional-scale fishery or nature conservation interests which would not otherwise be considered to be threatened by dredging operations when each is assessed in isolation.

For the monitoring of a typical dredging operation, stations will be located along predicted gradients of effect beyond the licensed area, as will be determined by hydrographic conditions and available dispersion models. The initial monitoring strategy should incorporate a contingency for modification in the light of evidence of any significant changes in dispersion patterns that may not conform with original predictions, e.g., as may arise from changes in dredging practices.

Post-dredging conditions at and beyond the licensed area will be of interest, notably with respect to biological recovery, and the possibility of continuing to monitor for

a period of time after dredging operations cease should be considered. In such cases, it is clearly essential to be able to refer to a baseline survey of the licensed area prior to the commencement of commercial dredging.

In addition to established methods for the quantitative assessment of benthic fauna, provision should also be made for the conduct of surveys of the epifauna including the status of commercial fish and shellfish populations in the general vicinity of dredging operations, where they have been identified as matters of particular concern. Clearly, the necessity for such assessments, and the target species, will vary from site to site. This may necessitate the development of new assessment methodologies for local-scale studies, for which adequate resources must be allocated.

### Monitoring of the Industrial Process

The following parameters can be considered for monitoring, subject to the findings of the Environmental Impact Assessment (EIA) and consultative processes.

They should only be considered when relevant, necessary and feasible. Reference should also be made to ICES (1992).

Any of the suggested monitoring methods listed below or combinations of these methods can be undertaken for both environmental and resource management purposes.

The ACME noted that further development of the environmental effects monitoring scheme related to marine extraction operations should include work on:

- sampling strategies related to impact assessments and monitoring of dredging operations in order to develop reliable and cost-effective methods;
- requirements for and developments in habitat mapping, with particular reference to demersal spawning grounds, and consideration of research investigations and strategies that will lead to an increased understanding of the effects of aggregate extraction activities on sensitive or critical habitat

| Monitoring parameter   | Possible methods of monitoring  |
|--|---|
| Spatial position   | Electronic Monitoring (EM)<br>Ships log<br>Aerial/boat/satellite surveillance   |
| Quantity of material   | Audit returns<br>Periodic bathymetric survey  |
| Time and duration  | Electronic monitoring   |
| Seabed material  | Sampling of dredged material<br>Vibrocores<br>Grab sampling   |
| Monitoring of dredged material for biological and archaeological content | Periodic sampling and visual observation during shore processing  |
| Measurement of overboard discharge (Plume)                               | Sampling of reject chutes and spillways<br>Monitoring of plume in water column<br>Remote sensing<br>Bottle sampling<br>Acoustic Doppler Current Profiler (ACDP)<br>Video camera |
| Draghead plume   | Sampling of suspended material by draghead<br>Video camera  |
| Measurements of contaminants   | Sampling of material from water column  |
| Direction of dredge track  | Electronic monitoring   |

areas of importance to the early life histories of demersal spawning fish and shellfish stocks.

The ACME also noted that the WGEXT had considered a number of systems for the classification of aggregate material based on particle size limits. The ACME accepted the WGEXT recommendation that marine geologists involved in marine aggregate resource mapping should follow the sediment size classification systems specified in European (or equivalent) standards that have been adopted by local industry. The ACME also endorsed the WGEXT recommendation that the method used for the determination of particle size should be stated in all cases due to variations in the degree of accuracy of present laboratory techniques.

The ACME further recommended that in all cases the terminology used to describe the morphology and origin of bedforms should be based on a defined and accepted

system of classification; all maps and reports should strive to explain fully any terminology used that could be a source of confusion.

## References

- ICES. 1992. Effects of Extraction of Marine Sediments on Fisheries. ICES Cooperative Research Report, No. 182. 78 pp.
- ICES. 1994. Report of the ICES Advisory Committee on the Marine Environment, 1994, pp. 67–69. ICES Cooperative Research Report, No. 204.
- Rees, H.L., Heip, C., Vincx, M., and Parker, M.M. 1991. Benthic communities: Use in monitoring point source discharges. ICES Techniques in Marine Environmental Sciences, No. 16. 70 pp.

## 16 MAJOR ENVIRONMENTAL ISSUES

### *Request*

There is no specific request. At its 1994 meeting, the ACME had identified a need to assess the most important marine environmental issues within the ICES area over the next decade, so as to be able to assess how best ICES strengths can be used in the cooperative design of an overall monitoring strategy.

### *Source of the information presented*

The 1995 report of the Working Group on Environmental Assessment and Monitoring Strategies (WGEAMS).

### *Status/background information*

On the basis of the work conducted on this topic by the Working Group on Environmental Assessment and Monitoring Strategies, the ACME decided to propose the following as a list of major environmental issues which will need to be addressed by ICES scientists over the next decade. These issues are not ranked in order of importance.

#### 1) Large-scale changes in the oceans and their biological productivity

Changes on a large scale, such as global warming, can arise from both natural and anthropogenic processes. Recent research has indicated that changes in Atlantic oceanic circulation and in exchanges with shelf sea areas can be correlated with changes in fisheries, for example, through affecting the transport of fish larvae and their subsequent recruitment to the fisheries. There is a need to improve the monitoring activities which address variability in the physical environment (temperature, salinity, etc.) and also the primary and secondary production processes. This should lead to the development of techniques to incorporate ocean climate forecasts into the fish and shellfish stock assessment process, for instance. There is also a need to develop models and predictive methods.

Remote sensing techniques can be applied to some physical parameters and to primary production, but other, more traditional, approaches need to be taken for zooplankton populations. The aims of the combination of physical and biological measurements must include the forecasting of the development of algal blooms, and of the more localized processes of eutrophication which are of particular concern in parts of the Baltic Sea and the southern North Sea. Furthermore, modelling of the impact of physical parameters on production processes needs to be supported by monitoring in key locations, and the scope of the modelling needs to be extended.

#### 2) Habitat changes and coastal zone stress

Many forms of exploitation of the sea and the coastal margin are known to lead to alteration and degradation of marine habitats and loss of species diversity. The impacts of trawling using heavy gears, dredging, and aggregate extraction on the seabed have been recognized for some years. The harvesting of macroalgae for alginate extraction also leads to loss of habitat and increased erosion of adjacent coastal areas. Drainage and construction activities can damage intertidal and immediately sub-tidal areas which may be important spawning and nursery grounds for marine species. Litter can cause problems for marine species and lead to increased costs of fishing activities; it is also aesthetically unsatisfactory on beaches.

Furthermore, the on-going use of coastal areas also for other activities such as recreation, marine transportation, and dredge spoil dumping, among others, means that organisms are exposed to a variety of stress factors, some of which have received little attention so far. The combination of these stress factors with other more commonly recognized factors, such as chemical pollution, threatens the quality of the marine environment.

#### 3) Effects of contaminants on the reproduction of fish, shellfish and marine mammals, and on human health

So far as fish populations are concerned, the most damaging environmental processes are those which affect the reproductive capacity, or rather the capacity to produce young which subsequently recruit to the spawning, or exploitable, stocks. These processes can adversely affect the fecundity, sexual maturation, larval growth, development and survival, and subsequent stock recruitment. A range of chemical compounds (e.g., alkyl phenols) have been found to mimic steroids (sex hormones) in freshwater fish species with potentially serious impacts on their breeding capacity. Tributyltin (TBT) has been found to have an effect on the reproduction of some species of shellfish in the sea. Other groups of environmental contaminants are known to have the potential to affect reproductive processes in marine mammals, fish and shellfish, but the scale and significance of the effects are unknown. Additionally, an important challenge is to understand the effects of contaminant mixtures to which all organisms are exposed.

Furthermore, the importance of contaminants in relation to the quality of seafoods, and to the quality of the environment in general is well known, but must continue to be regarded as a priority issue. There is an increasing understanding of these matters; however, concern remains over contaminants such as mercury, polycyclic aromatic

hydrocarbons (PAHs), chlorinated biphenyls (CBs), TBT, and other synthetic organic chemicals.

#### 4) Introduction and transfer of organisms

There is increasing concern over the actual and potential impact of species and accompanying diseases introduced from other parts of the globe to waters where they have not previously been found. There are many examples of both accidental and intentional introductions of non-indigenous species which have had impacts far greater and less desirable than might have been expected or intended. Transfer can take place through tanker ballast water, transport of animals for aquaculture, and other processes which can move live organisms from one area to another. A related issue concerns the importance of viruses in the sea. The impact of the phocine distemper virus has been well recorded, but the importance of viruses as disease vectors in other marine populations is little studied.

#### 5) Mariculture and sea ranching

The growth of mariculture has been extremely rapid over the last ten years, and is likely to continue. For example, harvests of cultured Atlantic salmon in certain areas are now much larger than those of wild caught animals. This development not only competes with space used by existing fishing activity but, in turn, is adversely affected by other coastal activities and is particularly sensitive to sources of pollution. Furthermore, mariculture itself interacts with the fisheries resource and contributes waste products that can lead to adverse environmental conditions.

The mariculture industry, therefore, finds itself in the dual role of being a source of chemicals and wastes with an

impact on the ecosystem and, at the same time, requiring clean, protected, and unpolluted waters for successful production. Mariculture development involves such issues as chemical and therapeutic use, nutrient loading and benthic effects from fish wastes and unused feeds, and the requirements for monitoring programmes. Other questions include the role of escaped cultured salmon on the genetic integrity of wild stocks, the transfer and interchange of fish diseases and parasite infestations between wild and cultured stocks, the interference caused by sea cage mooring systems and shellfish culture floats and buoys with recreational and commercial navigation, and the increasing demands from shoreline property owners for aesthetic views and mariculture exclusion zones. However, mariculture itself is increasingly being threatened by industrial and land-based pollution, wastes discharged from boats, phytoplankton blooms, and the expanded presence of phycotoxins.

#### 6) Implications of land-based processes

There are a small number of large-scale or widely distributed land-based processes that can affect the quality of the marine environment. Agricultural run-off and forestry operations can greatly influence the quantities of pesticides, nutrients or silt reaching the coastal seas. Acid precipitation, in addition to affecting stocks of anadromous fish species, can lead to increased riverine discharge of contaminants through alteration of weathering processes in soils. Also, the impoundment of water in lakes for subsequent use in the generation of hydroelectric power has altered the freshwater flow to marine areas such as the St Lawrence Estuary and the northern Baltic Sea areas. This can affect ice cover, primary production, and fish and marine mammal reproduction, in addition to other processes.



### 17.1 Handling of Data for the Oslo and Paris Commissions

The ACME took note of information presented by the ICES Secretariat on the handling of data from the Joint Monitoring Programme (JMP) on contaminants in biota, sediments, and sea water and on biological effects of contaminants. Only four countries had submitted data in 1994 covering monitoring activities conducted in 1993. Of these, three data sets were submitted for contaminants in biota and two for sea water; no data were submitted for sediments or biological effects.

As part of the data handling service to OSPARCOM, ICES has established a quality assurance (QA) database. The QA database has three components:

- 1) a list of available reference materials, with their composition and consensus concentration values;
- 2) results of intercomparison exercises; and
- 3) written documentation of storage and analytical procedures.

At present, an extensive list of reference materials is available in computerized form. Results of intercomparison exercises are being entered into the database. However, the problem here is that most of the relevant information is available as printed reports only. The organization of written documentation will start in autumn 1995.

The OSPARCOM *Ad Hoc* Working Group on Monitoring (AHWGM) did not hold a meeting to assess JMP monitoring data in 1994; however, work was carried out to finalize the previous AHWGM report. That report, prepared by the 1993 meeting of the AHWGM, "Assessment of Temporal Trend Monitoring Data for 1983–1991: Trace Metals and Organic Contaminants in Biota", gave rise to a number of discussions, especially in terms of which data sets and contaminants should be included in the assessment. The Netherlands delegation offered to revise the report, and undertook this task in cooperation with the ICES Secretariat/Environmental Data Bank. This has involved re-doing the statistical analysis, tables and maps. This work has been completed and the report will be published by OSPARCOM.

### 17.2 Revised ICES Environmental Data Reporting Format

On the basis of a major review, Version 2.2 of the ICES Environmental Data Reporting Format was released in November 1994 to replace Version 2.1, which had

originally been released in January 1992. All laboratories reporting data to the ICES Environmental Data Bank have received a copy of this revised reporting format along with a diskette containing the associated revised screening program.

In addition to a general update of the text and code tables, Version 2.2 incorporates changes and additions requested for use in reporting JMP data. It also contains a number of new features including an extension of geographical coverage to the entire northern hemisphere, mainly for Arctic Monitoring and Assessment Programme (AMAP) purposes, and an extension of the reporting format to cover the submission of data on contaminants in marine mammals and seabirds (adults as well as eggs).

Provision has also been made for the submission of quality assurance results from the QUASIMEME programme. In addition, a complete revision has also been made of the fish disease reporting format.

### 17.3 Other Relevant Activities

#### 17.3.1 World Wide Web

The ICES Secretariat has established a home page on the World Wide Web server of Internet. The URL of the ICES home page is: <http://www.ices.inst.dk>. The ICES home page also provides links to similar pages of marine institutes in ICES Member Countries.

#### 17.3.2 Fish disease data entry program

Following discussions in the ICES Working Group on Pathology and Diseases of Marine Organisms (WGPDMO), it was recommended that the reporting format for fish disease prevalence data should be revised and a data entry program should be developed to facilitate the reporting of these data. This was accepted by Council and a test version of the program was prepared and presented to the 1995 meeting of WGPDMO. The WGPDMO accepted the program, which is now being finalized. Diskettes containing this program will be distributed to relevant laboratories by the ICES Secretariat.

The ACME noted this information with satisfaction and recommended that ICES Member Countries utilize this new data entry program to submit their fish disease data to ICES. The ACME noted that, as the new reporting format provides for the submission of data on an individual-fish basis, the data submissions should cover all past years for which data are available. Previously, only aggregated data have been submitted.



#### **17.4 Analysis of temporal trends in contaminants in biota from the Baltic Sea**

In association with the HELCOM Third Periodic Assessment of the State of the Baltic Marine Environment, ICES coordinated an assessment of temporal trends of contaminant concentrations in biota. The assessment was conducted by the ICES/HELCOM Workshop on Temporal Trend Assessment of Data on Contaminants in Biota from the Baltic Sea, held in late April 1995 (see Section 7.3).

The preparations for the workshop involved the transfer of Baltic Monitoring Programme (BMP) data on contaminants in biota held at the HELCOM data centre. It had been anticipated that the data were organized according to the protocol for storage and transfer of environmental data using electromagnetic media, as defined by the Environmental Data Bank. Since this was not the case, the preparations included an additional effort to convert, check, and validate the data.

In support of the assessment, the ICES Secretariat Environment Department coordinated a preliminary

quality control evaluation, based on a review of available quality assurance information. The outcome of this evaluation was presented to and revised by the Workshop.

The Environment Department supported the Workshop by conducting statistical analyses and power studies of the data.

##### **17.4.1 Baseline Study of Contaminants in Baltic Sea Sediments**

The ICES Secretariat Environment Department has organized the data handling for the Baseline Study of Contaminants in Baltic Sea Sediments (see Section 7.1). This has included the development of a data entry program tailored for this purpose. A final version of the program has been presented to and accepted by the Steering Group for the Coordination of the Baseline Study of Contaminants in Baltic Sea Sediments. Data will be submitted in late 1995 and early 1996 for this project data set.

## 18 RESEARCH REPORTS

### 18.1 Influence of Diagenetic Processes on the Assessment of Contamination in Marine Sediments

#### *Request*

There is no specific request. ICES working groups initiate work on topics that they identify as requiring investigation. The ACME chose the results of two such investigations for reporting here.

#### *Source of the information presented*

The 1995 report of the Working Group on Marine Sediments in Relation to Pollution (WGMS).

#### *Status/background information*

Chemical and microbial processes at the sediment-water interface may influence the trace metal composition of marine sediments. Post-depositional mobility of trace metals during diagenesis also affects the down-core profiles of a number of metals. As these processes may affect the assessment of metal contamination of marine sediments, a review of several relevant investigations was conducted by WGMS. In terms of diagenetic processes that may influence cadmium concentrations in marine sediments, a review was made of Canadian data showing sedimentary profiles of cadmium in different marine sediments. The results of these sediment profiles illustrate that cadmium concentrations may vary strongly with depth in marine sediments. For example, in many cores from the Beaufort and East Siberian Seas, cadmium values range from  $0.15 \mu\text{g g}^{-1}$  to  $0.80 \mu\text{g g}^{-1}$  at the sediment surface, decrease progressively with depth, and then increase to values higher than those found at the sediment surface. This sub-surface increase observed in many cores always appears below the sediment surface enriched in manganese oxides. It appears that the considerable variations in cadmium concentrations with depth are not due to changes in grain size distribution or mineralogical composition, nor can they be associated with any carbonate- or organic-rich layer in the sedimentary column. The strong sub-surface profiles are also not related to modern anthropogenic influences because they consistently appear below the manganese-rich surface layer, despite great variations in the thickness of this layer. Such a consistent relationship between cadmium and manganese rather suggests control by diagenetic processes, most probably the diffusion of dissolved cadmium into the sediment and its subsequent precipitation as cadmium sulphide. It was suggested that sedimentation rate, sulphate reduction rate, and cadmium concentrations in bottom waters are key factors controlling both the cadmium concentration and cadmium distribution in marine sediments. As a

result, it appears that current normalization techniques cannot be used solely to compensate for the influence of the natural variability of cadmium concentrations in marine sediments.

German data on cadmium mobility in intertidal mudflat sediments were also reviewed. Repeated sampling on the same site over a four-year period showed evidence of a 100% increase in cadmium concentrations below the redox boundary due to post-depositional migration of cadmium down the sediment column. Post-depositional diagenetic reactions may also significantly influence the sediment record of other trace metals such as Cu, Ni, Pb, As, Zn, Co, Mo, and U. Both the diagenetic remobilization and accumulation processes depend on the establishment of an oxidized sediment surface associated with the establishment of a redox zonation at depth. Special caution should be exercised in productive areas with manganese and iron diagenesis in sub-oxic sediment layers; Mn and Fe should always be analysed in trace metal assessment studies. The influence of diagenesis on the assessment of anthropogenic signals is less significant in sediments which are entirely anoxic to the topmost layers.

#### *Recommendation*

The ACME recommended that cadmium data obtained in monitoring programmes of contaminants in sediments be interpreted with great caution. Site-specific diagenetic processes can cause substantial variations in the cadmium concentrations in marine sediments and, thus, comparison of contamination levels over broad geographical regions will be very difficult to achieve.

### 18.2 PCB Patterns in Different Species of Fish-Eating Mammals in Relation to Food and Biotransformation Capacity

#### *Source of the information presented*

The 1995 report of the Marine Chemistry Working Group (MCWG).

#### *Status/background information*

This research project involves the interpretation of data on concentrations of PCBs in fish-eating mammals obtained by a number of laboratories participating in the work of the MCWG.

The data made available to this project by the different laboratories had involved a number of years of analytical effort. The results from the different laboratories were merged to a common database without any problems. The intercalibration exercises carried out within the

framework of the MCWG have been supportive in obtaining reliable data for the project. For logistic reasons, this amount of data could not have been gathered by a single laboratory. Last, but not least, the team involved developed a high level of mutual cooperation and stimulating discussions which have greatly contributed to the success of the work and which have also directed new research within the individual laboratories.

The hypothesis of the project is that differences in CB patterns between marine mammals and fish can be explained in terms of the availability of CBs in food and their biotransformation by the cytochrome P-450 system.

The great majority of samples used for the calculations were blubber samples of which the data on the concentrations of PCBs were already available at the different laboratories. Some previously published comparisons of PCB patterns in different tissues of marine mammals have shown that the PCB pattern in blubber is a good representation for the pattern in the majority of other tissues. For the discussion of the results of the calculations, all PCB congeners have been divided into different structural groups with regard to metabolism by the cytochrome P-450 system, as derived from previously published experimental and field studies on seals and cetaceans. In the description below, the term 'vicinal H atoms' means hydrogen atoms linked to adjacent carbon atoms. The structural groups are:

- I. Congeners without any vicinal H atoms (e.g., CBs 153, 180, 183, 187, 194).
- II. Congeners with vicinal H atoms only in the *ortho*- and *meta*-positions in combination with  $\geq 2$  *ortho*-Cl substituents (e.g., CBs 99, 128, 138, 158, 163, 170).
- III. Congeners with vicinal H atoms in the *ortho*- and *meta*-positions in combination with  $\leq 1$  *ortho*-Cl (e.g., CBs 28, 105, 118, 156, 157).
- IV. Congeners with vicinal H atoms in the *meta*- and *para*-positions in combination with  $\leq 2$  *ortho*-Cl (e.g., CBs 44, 49, 52, 101).
- V. Congeners with vicinal H atoms in the *meta*- and *para*-positions in combination with  $\geq 3$  *ortho*-Cl (e.g., CB149).
- VI. Congeners with vicinal H atoms both in the *ortho*- and *meta*-positions and *meta*- and *para*-positions in combination with  $\leq 1$  *ortho*-Cl (e.g., CB31).

The calculations carried out using Principal Component Analyses were based on absolute concentrations and on PCB patterns which were made independently of

absolute concentrations by normalizing the data to the concentration of CB153, which is the CB congener present in the highest concentrations and belonging to structural group I, and thus highly resistant to enzymatic attack:

$$Ratio_{153} = \frac{[CBX](in \mu g g^{-1} lipid)}{[CB153](in \mu g g^{-1} lipid)}$$

Subsequently, the CB patterns in tissues of the fish-eating mammals were compared with cod liver oil (CRM349), as a general model for the CB pattern in fish from the North Sea, by calculation of  $R_{rel}$ . Thus, the relative ratio of a given congener (CBX) in a tissue of a marine mammal in comparison to its diet, i.e., fish is given as:

$$R_{rel}(CBX) = \frac{Ratio_{153}(CBX \text{ in mammals})}{Ratio_{153}(CBX \text{ in CRM349})}$$

For individual congeners, some plots combining data on absolute concentrations and pattern analyses were also made.

Although the project is still going on, the preliminary conclusions can be summarized as follows:

- 1) For the PCB congeners expected to be persistent, i.e., those belonging to the structural groups I and II, the cod liver oil CRM349 provides a very reasonable source pattern from which the PCB pattern in predators can be derived.
- 2) The majority of the PCB patterns show a strong covariance. Such congeners show mostly, but not always,  $R_{rel}$  values around unity.
- 3) Congeners with  $R_{rel}$  values  $< 1$  often vary in a different manner from the persistent congeners, resulting in a decreasing correlation.
- 4) The  $R_{rel}$  values of metabolizable congeners often relate in a concentration-dependent manner to the absolute concentration of CB153.
- 5) The metabolic capacity especially for congeners with *m,p* vicinal H atoms increases in the order whale, delphinidae, *Phoca groenlandica* < harbour porpoise < grey seal, harbour seal < otter. Thus, the more strongly a species is associated with the terrestrial environment, the greater its metabolic capacity for this type of congener seems to be. In rat, this type of congener is metabolized by the cytochrome P-450B family. A possible exception is *Phoca groenlandica*.

6) There is a considerable difference in patterns in the population of grey seals from Arctic waters as compared to the population from waters around Scotland.

7) The resistance to biotransformation of congeners belonging to the same structural group differs as follows:

Group III ( $o, m \leq 1$ ):

CB28(3) < CB118(5), CB105(5) < CB156(6).

The latter sometimes behaves as a completely persistent compound.

Group IV ( $m, p \leq 2$ ):

CB44, CB49(4) < CB101(5) < CB52(4).

Group V ( $m, p \geq 3$ ):

CB149(6) is persistent in cetaceans but appears to be degradable by grey seal, otter, and cormorant.

Group VI ( $o, m + m, p \leq 1$ ):

CB31(3) is degradable in all species investigated.

The ACME expressed its appreciation for this information and thanked the participants in this project for their work. The participants are: J.P. Boon, J. van der Meer, P.E.G. Leonards (The Netherlands), R.J. Law, C.R. Allchin, D.E. Wells, C. McKenzie (UK), J. Klungsøyr, J. Utne-Skaare (Norway), E. Storr-Hansen, H. Spliid (Denmark).

## AN INTEGRATED MARINE ENVIRONMENTAL MONITORING STRATEGY BASED ON THE NEED FOR CLOSER INTEGRATION OF CHEMICAL AND BIOLOGICAL MONITORING TECHNIQUES

### *Executive Summary*

This annex addresses the problem of how to monitor man's impact on the marine environment in the most cost-effective way. The underlying assumption is that the objective of monitoring is to evaluate the "health" of the marine ecosystem, in much the same way that a doctor assesses the health of a patient. Medical procedures make use of an integrated suite of chemical and biological tests which aim to give a holistic picture of the patient's status, and a similar philosophy is required for diagnosing the ills of the environment. Without a holistic diagnosis which clearly identifies both the effects and their causes, environmental managers will not be in a position to make appropriate decisions affecting the control of anthropogenic inputs to the marine ecosystem.

For historical, legal, and technical reasons, the marine monitoring activities of the Oslo and Paris Commissions (OSPARCOM) have until recently been based essentially on the detection and quantification of chemical contaminants in the various environmental compartments, with the primary aim of charting spatial and temporal changes in environmental loadings in relation to inputs. Monitoring the biological effects of contaminants has until now been seen as a secondary activity, although not, of course, an unimportant one. The basic philosophy has been to conduct broad spatial surveys of chemical contamination for the identification of "hot spots", and then to follow up with detailed investigations of possible ecological changes at the "hot" locations. The present strategy has also produced a large database of chemical information which is valuable for determining the significance of contamination in biota for human consumers of seafood.

More recently, a few biological effects procedures have been included in monitoring programmes such as the North Sea Task Force (NSTF) Monitoring Master Plan (MMP), but they have not been properly integrated with chemical measurements, so the results are difficult to interpret. Part of the problem has also been that the acceptance and implementation of sensitive biomonitoring techniques has, until now, lagged behind that of chemical analytical procedures.

Chemical data alone are of limited value for the retrospective evaluation of possible environmental impacts, and this is illustrated by current attempts to develop so-called "Ecotoxicological Assessment Criteria". On the other hand, the use of diagnostic tests (comprising both biological effects techniques and chemical analyses)

will alert environmental managers to potentially serious problems that will then require more comprehensive investigation. Subsequent measurement of harmful biological effects in conjunction with detailed chemical fingerprinting will in many cases allow the identification of the causal agent(s).

In the past, a shortage of suitable biological effects techniques has hindered progress in monitoring, but this situation is being rapidly redressed. Table A1.1 lists biological monitoring techniques that are now ready for incorporation into international monitoring programmes, such as the OSPARCOM Joint Assessment and Monitoring Programme (JAMP), while Table A1.2 identifies some necessary and novel methods which are likely to be ready within a short time. Furthermore, these tables identify the main uses of these techniques, and the principal types of situations where they are applicable. Although the "toolbox" of sensitive diagnostic techniques is still not complete in all respects, it is now sufficiently sophisticated to allow biological effects monitoring to take a more important role. This does not imply that chemical monitoring has become redundant; on the contrary, it can now be used in a more targeted and cost-effective way.

The main reason biological techniques should now become fully integrated in strategic monitoring programmes is that they allow a more holistic evaluation of the potential impacts of **all** the contaminants present, irrespective of whether or not their identity is known. There is evidence that serious effects detected by bioassays, especially in the more industrialized areas, are not always the result of any individual pollutant, but represent the joint effect of many substances acting together. Biological effects techniques also provide a clear indication of whether the contaminants present in water or sediment are bioavailable and, hence, potentially harmful. *In situ* biological methods can, in addition, integrate the effects of temporally fluctuating contaminants. No chemical techniques can perform either of these functions with any degree of reliability. Finally, and crucially, biological techniques can be combined with chemical fractionation procedures to define the broad chemical properties of the causative agents and thus assist their definitive chemical identification. This final step is essential if the results of environmental monitoring are to be fed back into effective remedial action.

In essence, this document proposes that a suite of biological effects techniques at each organizational level should be fully integrated into monitoring programmes such as the JAMP in a tiered assessment strategy



(summarized in Figure A1.1). Furthermore, the techniques deployed should be targeted towards specific issues, and biological and chemical methods should be used concurrently in a fully integrated manner where appropriate. This strategy would also retain purely chemical-based monitoring for assessing temporal trends of inputs in chosen locations, and for detecting pollutants of concern for human health which may be present in seafood. A list of methods is contained in Table A1.1 together with the issues addressed by each technique. Methods regarded as promising but not yet ready for inclusion in monitoring programmes are indicated in Table A1.2.

A number of different integrated monitoring approaches could be adopted, depending on programme objectives. For example, in addition to the use of biological effects techniques for initial screening of areas where impacts are not expected and the employment of bioassays in programmes of identification of causative agents by means of fractionation and chemical analysis, integrated methods should also be used to address specific environmental problems such as the causes of elevated liver tumours in flatfish. Complex environmental problems are rarely solved solely by chemical or biological techniques operated independently.

This integrated strategy is both more cost-effective and more precautionary than the monitoring strategy followed by the OSPARCOM in the past. Furthermore, it is recognized that new technological breakthroughs, together with developments in both biological effects techniques and analytical chemistry, will inevitably lead to the construction of new and more effective diagnostic tools. Ultimately, a monitoring strategy of the type proposed here will target both biological and chemical expertise in an optimal and coordinated way, producing assessments of the harmful effects of marine pollution and its causes which can be used with precision to manage chemical inputs to the environment.

Accordingly, this proposed integrated monitoring strategy is deemed to be the most appropriate way forward given the current state of knowledge.

### ***Introduction and Background***

The underlying assumption of environmental assessment work is that it is possible to evaluate the "health" of the ecosystem in an analogous way to the medical diagnosis of patients. Both undertakings should involve the application of an integrated suite of chemical and biological tests to achieve a holistic diagnosis of the problem and its causes. Without this diagnosis, doctors cannot treat patients, and environmental managers cannot apply remedial measures to chemical inputs and the ecosystem which receives them.

The primary purpose of the ICES Working Group on Biological Effects of Contaminants (WGBEC) and the

Intergovernmental Oceanographic Commission (IOC) Group of Experts on the Effects of Pollutants (GEEP) since their inception has been to provide justification, appropriate techniques, and a strategy for the use of biological techniques in monitoring programmes. These groups have provided a clear rationale (ICES, 1989), a selection of approved techniques (ICES, 1993), and a strategy within which they could be embedded (ICES, 1985). Despite these activities and the practical workshop series in Oslo and Bermuda organized by the IOC GEEP (Bayne *et al.*, 1988; Addison and Clarke, 1990), and most recently in the North Sea in collaboration with the WGBEC (Stebbing *et al.*, 1992), biological monitoring methods have yet to be fully integrated with chemical approaches. Monitoring programmes are still dominated by chemical measurements despite the fact that biological effects monitoring has been recognized as important, and has already been used to some extent in the NSTF Monitoring Master Plan.

It is self-evident that contaminants in the environment are of ecological significance not because of their presence, but because of their effects; so the essential interdependence of biological and chemical techniques should be recognized in designing monitoring programmes. What seems to prevent their wider adoption is the failure to see the potential that biological techniques provide as a means of using chemical effort more effectively, directing it to where there are demonstrable biological problems.

There is now a wide range of reliable and sensitive biological effects techniques that have been tested in a series of practical workshops (Oslo, Bermuda, Bremerhaven), although it is recognized that some further methods development is still needed. Several methods have been fully intercalibrated and agreed protocols have been published in the *ICES Techniques in Marine Environmental Sciences* (TIMES) series. A list of techniques recommended by the WGBEC, and endorsed by ACME, for use in international monitoring programmes such as JAMP is contained in Table A1.1 of this report. Although this compilation is still incomplete, it nevertheless offers a practical way forward.

### ***The Limitations of Existing Monitoring***

The number of chemical contaminants in estuarine and plume waters is given in terms of thousands (an estimated 40,000 in the river Rhine plume) and the geographical scale is such that the analytical chemical load to provide adequate monitoring is massive. Also, the number of new compounds likely to become environmental contaminants grows significantly each year, and the toxicity of some may be such as to have deleterious effects at ng/l or ng/kg concentrations. In the context of monitoring ecosystem health, this results in a number of problems:



- a) the number of determinands which has to be analysed is enormous, and overwhelms the available analytical facilities;
- b) a risky assumption is made that chemical programmes monitor all the contaminants likely to occur at biologically significant concentrations;
- c) it is assumed that the parent compound (the one analysed) is responsible for the toxic effect observed, which is not the case in the frequent instances where metabolites and other breakdown products are the active agent;
- d) the large temporal variations in contaminant concentrations that occur, particularly in estuarine and coastal waters, cannot be fully characterized;
- e) the data on contaminant concentrations cannot be considered in a manner that takes into account their interactions with one another (synergism, addition, and antagonism) and with the major environmental factors that affect bioavailability such as salinity, complexing capacity, and particulate load.

None of these problems can be solved by chemical means alone, invalidating any strategy that relies exclusively on chemical monitoring. Although most programmes do include at least some biological aspects, nevertheless the chemical and biological components are rarely deployed in an integrated strategy in a way that reflects their interdependence.

### *The New Strategy*

Within the major national and international organizations concerned with the marine environment (e.g., ICES, UNEP, and IOC), there are separate biological and chemical groups, each confronting different halves of the same problem, which need to be better linked. Disciplinary boundaries do not serve the interests of the environment, where an ability to cross these boundaries is so often essential in solving environmental problems. Environmental toxicology sits at the interface between biology and chemistry, and the new monitoring strategy needs to incorporate knowledge and techniques from both disciplines in an integrated approach.

The rationale for the new strategy may be summarized briefly as follows:

- a) The underlying criteria for marine environmental quality are principally biological although commonly expressed in chemical terms.
- b) The health of the marine environment should therefore be monitored in terms that relate to those criteria, using

both biological effects techniques and chemical analyses as integrated diagnostic tools.

- c) Detailed chemical fingerprinting should then be focused on analyses of environmental samples taken mainly from areas where there are demonstrable biological problems, and where criteria for environmental health are therefore not being met. This does not preclude chemical monitoring of temporal trends or of foodstuffs.

There are cases when it may be appropriate to use biological systems as initial "filters" or screens in a monitoring strategy. Thus, strategic monitoring of areas not suspected to be suffering impacts would depend largely on the use of biological tests to provide a continuous means of measuring marine environmental quality, allowing chemical analytical effort to be reserved for those times and places where there are demonstrable problems. Apart from making biological sense, this approach is more cost-effective than the present strategy.

Of course, chemical monitoring would still be required to establish temporal trends in selected contaminants in defined areas, and to detect contamination which might be a threat to the human food chain. However, there is little point in directing comprehensive analytical resources to the repeated detection of trace or inconsequential concentrations of contaminants over large areas, particularly if it is only possible to monitor a small subset of those contaminants that could be important. It is much better to use a system that provides integrated indices of water and sediment quality, and that at the same time has the capability of detecting toxic concentrations of new and unsuspected contaminants not covered by chemical monitoring.

There are many different monitoring situations in which a fully integrated approach is likely to be much more effective than existing procedures. A move in the right direction was made by the North Sea Task Force Monitoring Master Plan (MMP) by its adoption of a range of techniques including biochemical (EROD in dab), embryonic (teratogenesis in oyster embryos), whole organism (gross pathology in dab), and community level (benthic community structure) effects. However, it should be noted that even the MMP did not properly integrate chemical measurements with the biology (e.g., levels of known EROD inducers were not determined in the same fish livers in which the EROD measurements themselves were made, and the most potent inducers were not measured at all).

### *Examples*

There are many ways in which an integrated approach using biological and chemical techniques can be applied. Three examples are given below.

- 1) A more fruitful integrated approach would be a problem-oriented programme to tackle a subject such as the localized incidence of liver cancer in flatfish. Such a programme would use a suite of techniques over a range of levels of biological organization. This could involve simultaneous measurements of the suspected causative agents (PAHs, PCBs and dioxins) in various environmental matrices including fish liver, measurements in flatfish of biomarkers of exposure and biochemical/cellular effects of these compounds (EROD, DNA adducts, oncogene activation), and surveys of the incidence of pre-neoplastic liver pathology and overt liver tumours.
- 2) A different form of integrated monitoring could involve a strategy to identify the chemical causes of toxicity as identified by a biological screening programme. This might include a system of chemical fractionation of the suspect medium, with the use of biological tests and chemical analytical procedures to narrow down the search for the causative chemical(s).
- 3) Yet another approach might involve the use of "sentinel" organisms (Holdgate, 1980) such as mussels held *in situ* to integrate chemical impacts over time and express the result as altered biomarker responses or impaired scope for growth. When combined with analyses of contaminants of known toxicity in the organisms, this technique can identify the main substances contributing towards the observed adverse effects.

It is important to note that the design of monitoring programmes must take into account the possibility of seasonality in the sensitivity and responsiveness of organisms/tissues/processes adopted as measurement systems.

There are many other possible ways in which chemical and biological techniques can now be integrated in a more effective monitoring strategy. Such integration is seen as the most logical approach to the full understanding of environmental problems, and it is recommended to be implemented as the central philosophy of JAMP.

### Causality

Implicit in any integrated use of chemical and biological techniques within a monitoring strategy is the need to establish causality with some degree of rigour, if the purpose is to achieve control of harmful chemical inputs. While a wide range of techniques has been considered, ranging from the manipulation of water samples linked to bioassays (Bening *et al.*, 1992) to specific indices (Gibbs *et al.*, 1989), it is clear that absolute specificity in the environment is not possible even in relatively straightforward examples such as that provided by TBT. It is not feasible to prove causality *sensu stricto*, so "operational criteria" for establishing causality are needed

(Stebbing, 1992). Criteria for establishing causality in an operational sense include the following:

- a) **Tissue burden analyses in relation to toxicity thresholds:** Causality would be assumed if tissue levels exceeded some threshold concentration known to be capable of inducing a deleterious biological effect. The use of such data circumvents the question of bioavailability, as toxic effects result from contaminants within the organism. Some organic contaminants may be so rapidly metabolized and excreted that tissue burdens are sometimes inadequate for this purpose.
- b) **Contaminant concentrations in relation to toxicity thresholds:** If the concentration of a contaminant in water or sediment exceeds that which is known to cause toxic effects, then it would be assumed that biological effects measured in the relevant medium were causally linked to the contaminant in question.
- c) **Biomarkers:** These are early-warning responses which to a greater or lesser extent identify, or are diagnostic of, their causes (e.g., cytochrome CYP 450 A1 induction is specifically triggered by planar molecules such as aromatic hydrocarbons and planar organohalogens), or else are predictors of pathology.
- d) **Chemical manipulation of environmental matrices in relation to toxicity:** The use of physico-chemical manipulations of water or sediments that selectively remove or destroy contaminant groups, associated with indices of toxicity, makes possible the identification of groups of causal agents in cases where one or a few contaminants are responsible for the observed impacts.

The need to define these criteria is an important and necessary prerequisite before adopting any integrated pollution monitoring and control strategy.

### The Economics of Marine Monitoring

The cost of any predominantly chemically based monitoring strategy is enormous and prone to increase, given the number of phases in which contaminants occur and the growing number of contaminants with potentially deleterious biological effects. While savings are being made with the help of automated systems of analysis, the pressure to improve spatial and temporal discrimination more than offsets any savings.

Participation in any such monitoring programme is intellectually unattractive for persons involved because a large proportion of the data indicate inconsequential levels close to detection limits. The work is technically demanding, but scientifically unsatisfying, as it does not involve hypothesis testing. Little further use is found for

the data sets created and incomplete coverage of the contaminants present is inevitable.

An integrated monitoring strategy is inevitably much more cost-effective, since the responses or effects measured provide an integration of all the contaminants present, known and unknown. The detection of significant biological effects would then trigger the conduct of chemical investigations whose objective would be to establish the identity of a chemical cause (or causes). In this way, it is proposed that detailed chemical effort be focused on sites where there are demonstrable biological effects, accepting the premise that contamination that has no biological effect is inconsequential. Such a focusing of chemical monitoring effort would make possible significant savings in costs, while providing more effective monitoring of our coastal seas.

It should be noted, however, that the simultaneous deployment of the new integrated chemical/biological approach as well as the traditional chemical monitoring approach will lead to increased chemical analytical costs.

### Conclusions and Recommendations

- 1) A marine monitoring strategy that fully integrates its chemical and biological components is proposed in order to allow an overall awareness of environmental quality in relation to issues of concern.
- 2) For preliminary screening in areas where problems are not suspected, the use of diagnostic chemical and biological methods for the health status of individual sentinel or bioassay organisms should be the first line of approach. The detection of significant adverse biological effects would then trigger detailed biological and chemical investigations whose purpose would be to establish the severity of any impacts in the ecosystem, and the chemical causes of those impacts.
- 3) This strategy does not preclude the need to use chemical monitoring techniques for assessing temporal trends in certain areas in relation to input controls, and for safeguarding the human food chain.
- 4) The use of a selection of biological techniques directed at issues of concern (Table A1.1) is advocated. These techniques were chosen from the wide range that have been tried and tested in the IOC and ICES series of workshops and elsewhere.
- 5) The suite of techniques should cover a range of levels of biological organization and representative species of natural communities.
- 6) There should be evaluation of the effectiveness of the monitoring strategy at all levels of measurement and

necessary adjustment in order either to redefine the objectives or else modify the methods used.

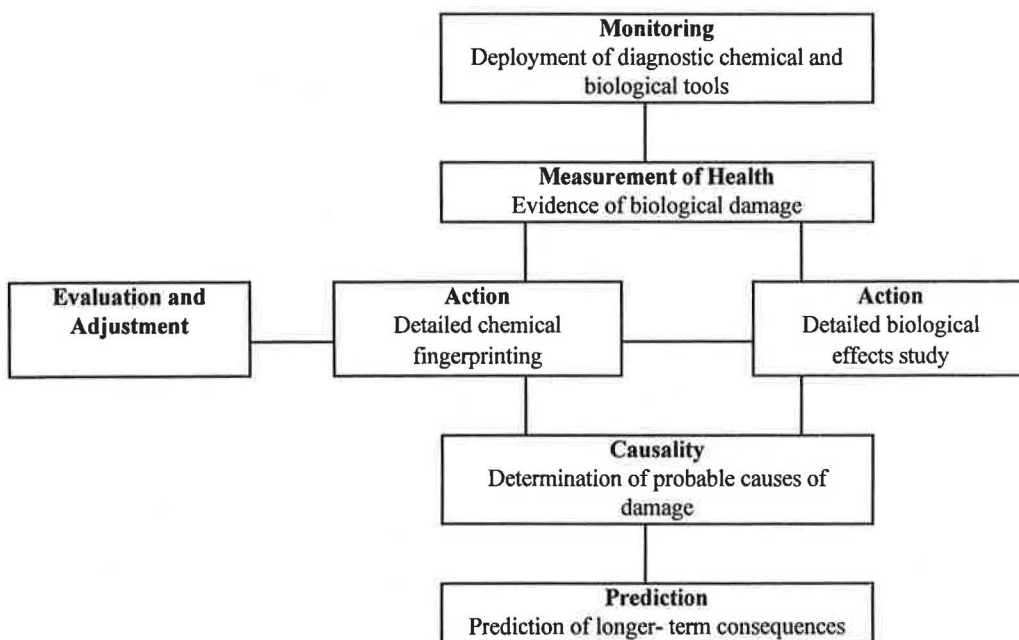
- 7) This proposed integrated environmental monitoring strategy is deemed to be the most appropriate way forward given the current state of knowledge.

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**Figure A1.1.** Flow chart of an integrated chemical and biological effects monitoring strategy for pollution impact on marine environmental health.



**Table A1.1.** Recommended techniques for monitoring programmes at the national or international level.

| Method   | Organism   | Ref.       | Issues addressed  | Biological significance   |
|--|--|------------|---|---|
| Bulky DNA adduct formation                         | Fish<br>Bivalve molluscs   | 1–6        | PAHs<br>Other synthetic organics, e.g., nitro organics, amino triazine<br>Pesticides (Triazines).                       | Measures genotoxic effects.   |
| Neoplastic and pre-neoplastic liver histopathology | Fish   | 7–11       | PAHs<br>Other synthetic organics, e.g., nitro organics, amino triazine<br>Pesticides (Triazines).                       | Measures pathological changes associated with exposure to genotoxic and non-genotoxic carcinogens.  |
| AChE inhibition                                    | Fish, crustacea, bivalve molluscs  | 12–16      | Organophosphates and carbamates or similar molecules. Possibly algal toxins.  | Measures exposure.  |
| Metallothionein induction                          | Fish   | 17–22      | Measures induction of metallothionein protein by certain metals (e.g., Zn, Cu, Cd, Hg).                                 | Measures exposure and disturbance of copper and zinc metabolism.  |
| Lysosomal stability                                | Fish<br><i>Mytilus</i> spp.  | 23–25      | Not contaminant specific but responds to a wide variety of xenobiotic contaminants and metals.                          | Measures cellular damage and is a good predictor of pathology. Provides a link between exposure and pathological endpoints. Possibly, a tool for immuno-suppression studies in white blood cells. |
| The detection of vitellogenin                      | Male fish  | 26–30      | Oestrogenic substances  | Measures feminization of male fish and reproductive impairment.   |
| Whole sediment bioassays*                          | • <i>Corophium</i><br>• <i>Echinocardium</i><br>• <i>Arenicola</i><br>• <i>Leptocheirus</i><br>• <i>Grandidierella</i><br>• <i>Rhepoxynius</i><br>• <i>Ampelisca</i> | 31–35      | Not contaminant specific, will respond to a wide range of environmental contaminants in sediments.                      | Acute/lethal and acute/sublethal toxicity only at present. May enable retrospective interpretation of community changes.  |
| Sediment pore water bioassays*                     | Any water column organism including:<br>• <i>Dinophilus</i><br>• sea urchin fertilization, etc.<br>• bivalve embryo<br>• <i>Microtox</i>                             | 36–41      | Will respond to a wide range of environmental contaminants.   | Acute and chronic toxicity, including genotoxicity, etc. Toxicity of hydrophobic contaminants might be under-estimated in pore water assays.  |
| Sediment sea water elutriates*                     | Any water column organism, as above  | 36–41      | Will respond to a wide range of environmental contaminants in<br>• dredge spoils<br>• sediments liable to resuspension. | Acute/lethal and acute/sublethal toxicity, including genotoxicity, etc.   |
| Water bioassays*                                   | As for pore water and elutriates (see above)   | 36–41      | Not contaminant specific, will respond to a wide range of environmental contaminants in inshore and estuarine waters.   | Acute/lethal and acute/sublethal toxicity, including genotoxicity, etc.   |
| Benthic community analysis*                        | Macro-, meio-, and epi-benthos   | 42–45, 100 | Responds to a wide variety of contaminants, particularly those resulting in organic enrichment.                         | Ecosystem level.<br>Retrospective.<br>Particularly useful for point sources. Most appropriate for deployment when other monitoring methods indicate a problem may exist.                          |
| EROD or P-450 1A1 induction*                       | Fish   | 46–51, 99  | Measures induction of enzymes which detoxify planar organic contaminants (e.g., PAHs, planar PCBs, dioxins).            | Possible predictor of pathology through mechanistic links. Sensitive indicator of exposure.   |
| Imposex  | Neogastropod molluscs, e.g., dogwhelk ( <i>Nucella lapillus</i> )  | 52–54      | Specific to organotins.   | Reproductive interference.<br>Estuarine and coastal littoral waters ( <i>Nucella</i> ) and offshore waters ( <i>Buccinum</i> ).   |
| Scope for growth                                   | Bivalve molluscs, e.g., <i>Mytilus</i>   | 55–58      | Responds to a wide variety of contaminants.   | Integrative response which is a sensitive and sublethal measure of energy available for growth.   |

\*Intercomparisons or quality control procedures complete for some methods (e.g., Refs. 31, 40, 99, 100).



**Table A1.2.** Promising methods which require further research before they can be recommended.

| Method  | Organism  | Ref.  | Issue addressed   | Biological significance  |
|---|---|-------|---|--|
| Degenerative liver, gill and kidney histopathology          | Fish (especially flatfish such as dab ( <i>Limanda limanda</i> )) | 59–66 | General toxicological response which will respond to a wide variety of contaminants.              | Measures degenerative change in tissues.   |
| Pollution-induced community tolerance (PICT) water bioassay | Microalgae  | 67–69 | Specific contaminants can be tested.  | Measure of degree of adaptation to specific pollutants. Not yet widely tested.   |
| Abnormalities in wild fish embryos and larvae               | Many fish, including demersal and pelagic species                 | 70–71 | Not yet linked unequivocally to contaminants.   | Measures frequency of probably lethal abnormalities in fish larvae. Mutagenic, teratogenic.  |
| Reproductive success in fish                                | <i>Zoarcetes viviparus</i>  | 72    | Not contaminant specific, will respond to a wide range of environmental contaminants.             | Measures reproductive output and survival of eggs and fry in relation to contaminants in a viviparous fish species. Restricted to period when young are carried by female. |
| DNA strand breaks   | Fish and mussels  | 1–6   | Not contaminant specific, will respond to a wide range of environmental contaminants.             | Measures genotoxic effects, but is also extremely sensitive to other environmental parameters.   |
| Various methods of measuring immuno-competence              | Fish and invertebrates  | 73    | Not contaminant specific, will respond to a wide range of environmental contaminants.             | Measures factors which influence susceptibility to disease.  |
| ALA-D inhibition  | Fish  | 74–75 | Lead  | Index of exposure.   |
| Antioxidant enzymes   | Fish  | 76–78 | Not contaminant specific, will respond to a wide range of environmental contaminants.             | Measures the presence of free radicals.  |
| Fluorescent bile metabolites                                | Fish  | 79–80 | PAHs  | Measure of exposure to and metabolism of PAHs.   |
| Allometric response in the benthic community                | Macro-, meio-, and epi-benthos                                    | 81–84 | Not contaminant specific, will respond to a wide range of environmental contaminants.             | Ecosystem level. Retrospective.  |
| Multidrug/xenobiotic resistance (MDR/MXR)                   | Fish, invertebrates   | 85–92 | Organic xenobiotics   | Measure of exposure.   |
| Oncogenes   | Fish  | 93–95 | PAHs<br>Other synthetic organics, e.g., nitro organics, amino triazine<br>Pesticides (Triazines). | Activation of oncogenes ( <i>ras</i> ) or damage to tumour suppressor genes ( <i>p53</i> ). Measures genotoxic effects leading to carcinogenesis.                          |
| Protein or enzyme altered foci                              | Fish  | 92    | PAHs<br>Other synthetic organics, e.g., nitro organics, amino triazine<br>Pesticides (Triazines). | Indicates exposure to carcinogen(s).   |
| P-450 induction   | Invertebrates   | 96    | Estuarine, coastal and offshore   | Measures induction of enzymes which detoxify certain organic contaminants (e.g., PAHs, planar PCBs, dioxins).  |
| Chronic whole sediment bioassays                            | Invertebrates   |       | Responds to a wide range of contaminants.   | Measurements such as growth and reproduction, coupled to biomarker responses, which will give a measure of the bioavailability and chronic toxicity in whole sediments.    |
| Glutathion-S-transferase(s) (GST)                           | Fish  | 97    | Predominantly organic xenobiotics.  | Measures exposure and the capacity of the major group of Phase II enzymes.   |
| On-line monitoring  | Mussels and crabs   | 98    | Responds to metals and xenobiotics.   | Measures the effects of chemicals on heart rate using a simple and inexpensive remote biosensor. Gives an integrated response.   |



# **References for Tables A1.1 and A1.2**

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## ANNEX 2

### INTEGRATION OF BIOLOGICAL AND CHEMICAL MEASUREMENTS IN SEDIMENTS

#### 1 Monitoring Related to Issues Concerning PCBs, PAHs, and Chlorinated Dioxins and Dibenzofurans

Two main underlying concerns related to PCBs, PAHs, and chlorinated dioxins and dibenzofurans are the potential of these substances to be accumulated or metabolized by organisms and give rise to tumours (e.g., in fish livers) or to adversely affect reproductive processes. The processes by which these compounds may give rise to tumours are indicated schematically in Figure A2.1.

##### a) Tumour formation

The target of concern in this case is the formation of liver tumours in flatfish (Stage 6 in Figure A2.1). It is known that flatfish (for example, dab) show varying degrees of prevalence of liver tumours and it appears that they are linked to pollution. The preceding stage, namely the appearance of abnormal liver histopathology, is shown as Stage 5. There is experimental evidence that

substances such as PCBs, PAHs, and dioxins which occur in the environment (Stage 1) can accumulate, with varying degrees of bioconcentration, in fish tissues (Stage 2). It is also known that these compounds can induce activity in the Mixed Function Oxidase (MFO) enzyme system (Stage 3), which is commonly assayed as EROD activity. Between Stages 3 and 5 is a complex of interacting processes which are not fully understood. They include DNA damage, the formation of DNA adducts, changes in the levels of antioxidants, the activation of oncogenes, and lipid peroxidation.

A comprehensive, but targeted, monitoring programme aimed at understanding the potential for pollutants to cause liver tumours in flatfish should, therefore, include components that provide information at each stage in the sequence of processes described in Figure A2.1. The programme would have chemical components (measuring concentrations in the environment and the fish tissues), biochemical components (measuring the MFO system), and histological and disease studies (measuring the changes in the liver associated with pre-

**Figure A2.1.** Effects on fish leading to liver tumours, caused by exposure to chemical contaminants.

| Stage | Sequence of Processes                                   | Monitoring Targets  |
|-------|---|---|
| 1     | Compounds in the environment<br>↓                       | PCBs, PAHs, dioxins in sediment, suspended particulate matter, mussels          |
| 2     | Compounds in the organism<br>↓                          | Same substances in fish liver   |
| 3     | Induction of MFO/EROD systems<br>↓                      | MFO/EROD in fish liver  |
| 4     | Molecular and cellular processes of carcinogenesis<br>↓ | DNA adducts, oncogene activation; oxidative modification of DNA and chromosomes |
| 5     | Pre-neoplastic changes in liver tissue<br>↓             | Fish liver histopathology   |
| 6     | Liver tumours   | Presence of liver cancers   |



cancerous and cancerous conditions). Such a programme would make the best use of efforts expended in each discipline, and lead to a greater understanding of the processes, and risks, involved. It would permit greater confidence in any subsequent management decisions.

On a practical level, such a comprehensive programme would be inappropriate for application in all areas of the Northeast Atlantic, but it could be applied initially in those areas where flatfish are already known to exhibit elevated prevalences of liver tumours or pre-neoplastic changes in liver tissue. The core elements of the monitoring programme would be measurement of:

- 1) prevalence of liver tumours;
- 2) prevalence of pre-neoplastic changes in liver tissue;
- 3) DNA damage;
- 4) EROD activity in liver;
- 5) concentrations of CBs, PAHs, and dioxins in liver tissue;
- 6) concentrations of these substances in the environment, primarily in surficial sediment and benthic invertebrates.

This scheme largely omits the complex Stage 4 of the tumour formation sequence. The ACME considered that the details of this stage should be the subject of supporting research activities.

The ACME recognized that such a programme would require a high degree of coordination at the international level in defining and controlling the programme, its methodology, and the interpretation of results, and also that there would be a need to ensure the necessary coordination among scientists from different disciplines within individual countries.

#### **b) Impacts on reproductive processes**

The second, but less well established, biological cause for concern about this group of organic contaminants is over their potential to affect reproductive systems of fish. This may occur via a number of mechanisms, such as interaction with hormonal and pheromonal systems, and genotoxic effects during early development; other compounds may also have direct effects, such as the possibility that environmental oestrogens may influence the reproductive success of marine (or at least estuarine) fish in the same way that they have been shown to have impacts in fresh water environments. Figure A2.2 presents the sequence of processes involved in relation to the impact of contaminants on hormonal systems.

Contaminants in the environment (Stage 1, Figure A2.2) accumulate in organisms (Stage 2), notably flatfish livers. This may lead to the induction of the MFO system (Stage 3), which subsequently affects the hormonal system of the fish (Stage 4). This, in turn, can affect the reproductive success of the fish. The monitoring targets for each of these stages is shown in Figure A2.2. The first three stages are identical to those in Figure A2.1, and so need not be discussed further here. The monitoring targets to assess the impact on the hormonal system are not commonly included in marine monitoring programmes. However, the assay techniques are readily available in other branches of marine science and in medicine, and should be relatively readily adapted to this application. The first three indices of reproductive success (gonado-somatic index (GSI), fecundity, and sex ratios) can be readily measured in marine fish. The assessment of egg quality (e.g., through measurement of chromosomal abnormalities) is not as well developed, and should be the subject of a scientific programme to develop methodologies appropriate to monitoring programmes. There have been a number of studies of the viviparous blenny (*Zoarces viviparous*) in estuaries which have demonstrated its value in the assessment of environmental quality.

The possible influence of environmental oestrogens is not shown in the above diagram. They are known to have effects directly at Stage 4, without necessarily affecting the MFO system. There have been no investigations so far of the influence of these substances on marine fish. It is therefore premature to include them in a monitoring scheme. However, environmental oestrogens should be the subject of a research programme to determine whether they have significant influence in the sea, and therefore whether they should be the subject of a monitoring programme.

As in the case of concern over the potential of contaminants to cause tumours in flatfish, a monitoring programme addressing concern that PCBs, PAHs, or dioxins may affect the reproductive success of flatfish (or other fish species) requires the coordination of effort from several disciplines, namely, chemistry (to measure concentrations of contaminants), biochemistry (to assay the MFO system and blood), and biology (to assess the impact on reproduction). At the current state of knowledge and expertise, a monitoring programme should initially be directed to areas where available information suggests that benthic fish reproduction may be impaired, or chemical or biological data indicate that gradients of contamination or effect may exist. It should include the following elements:

- 1) indices of reproductive success, probably fecundity, GSI, sex ratio and larval survival;

- 2) blood chemistry, covering vitellogenin and vitamin A. (This will require some development work to bring the assays into routine use for marine fish. Research is required to investigate further the effects on hormone levels.);
- 3) MFO system activity in fish liver;
- 4) concentrations of PCBs, PAHs, and dioxins in fish liver;
- 5) concentrations of these substances in the environment, primarily in surficial sediment and benthic invertebrates.

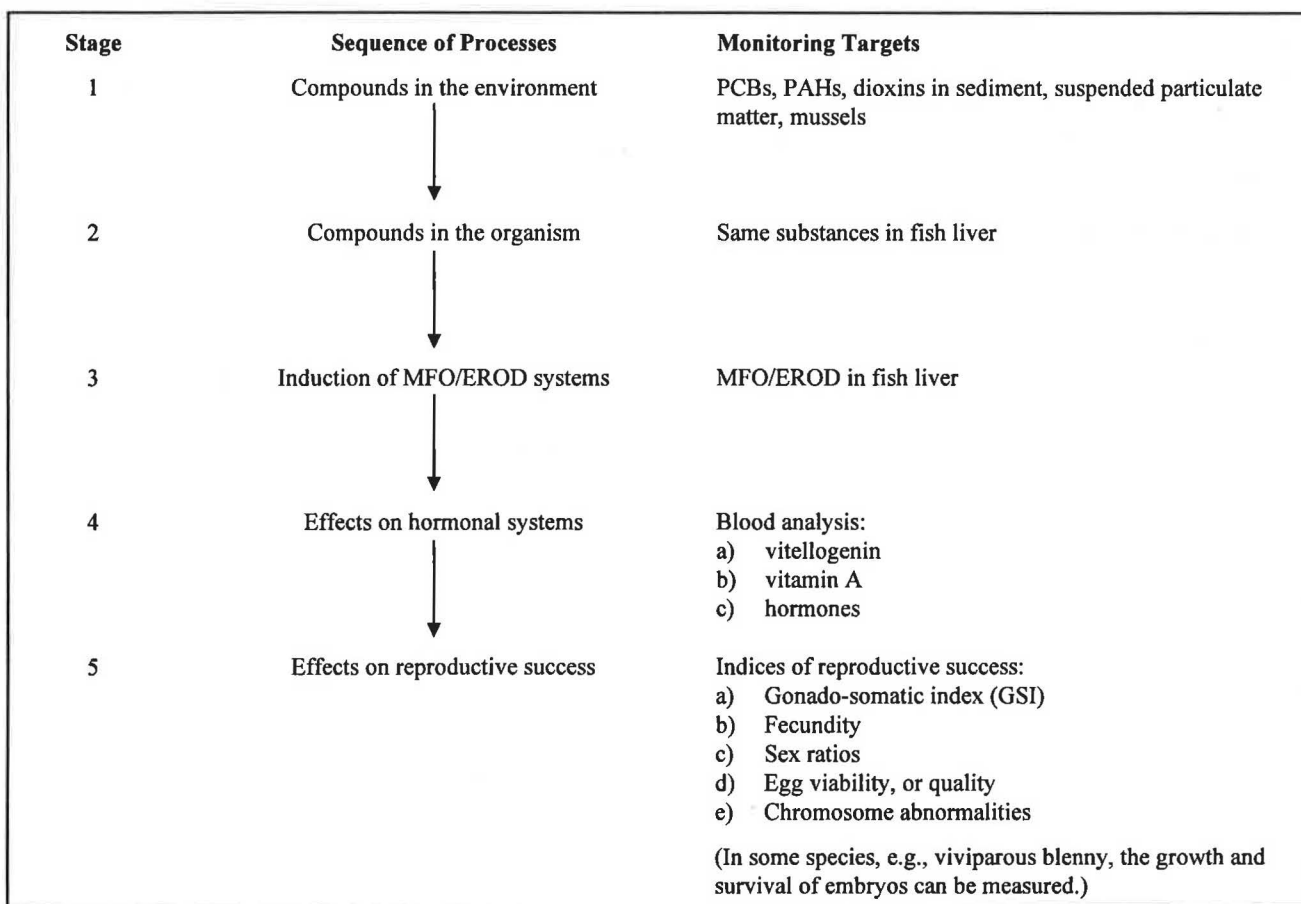
### c) Impacts on shellfish

In terms of a possible concern for shellfish with respect to PCBs and PAHs, the ACME noted that the likely biological basis for this concern was not related to the formation of liver tumours, as was the case for fish. Molluscs do not have MFO systems as well developed as those of fish. In many cases, the activity of the system cannot be measured, although there are some reports in

the literature of inducible activity at low levels in molluscs. Molluscs can accumulate planar CBs and the cannot be measured, although there are some reports in literature of inducible activity at low levels in PAHs to very high concentrations compared to fish, and it appears that molluscs are not able to metabolize PAHs to the same degree fish are able to metabolize them. There is evidence that exposure to these compounds can produce DNA adducts and affect antioxidants in molluscs. A biological effect of concern in molluscs, which may be linked with contaminant levels, is reduction in the scope for growth. There is good experimental evidence to show that exposure to PAH compounds will reduce the scope for growth of molluscs.

The current state of knowledge would, therefore, suggest that any monitoring of molluscs arising from exposure to PAHs should include measurement of scope for growth and of the concentrations of PCBs and PAHs in mollusc tissue. It is unlikely that measurements of the concentrations of these contaminants in sediment will be immediately relevant to the contaminant concentrations in filter-feeding molluscs; the ACME tentatively suggested that supporting chemical measurements should be made of these contaminants in the shellfish tissue and in suspended particulate matter.

**Figure A2.2.** Effects on reproductive success of fish caused by the impact of chemical contaminants on hormonal systems.



#### d) Impacts on marine mammals

The ACME noted that there may also be cause for concern over the possible effects of PCBs and PAHs on seals and other marine mammals. Further work will be conducted on this topic in the near future.

## 2 Monitoring Related to Issues Concerned with the General Well Being of Benthic Fauna

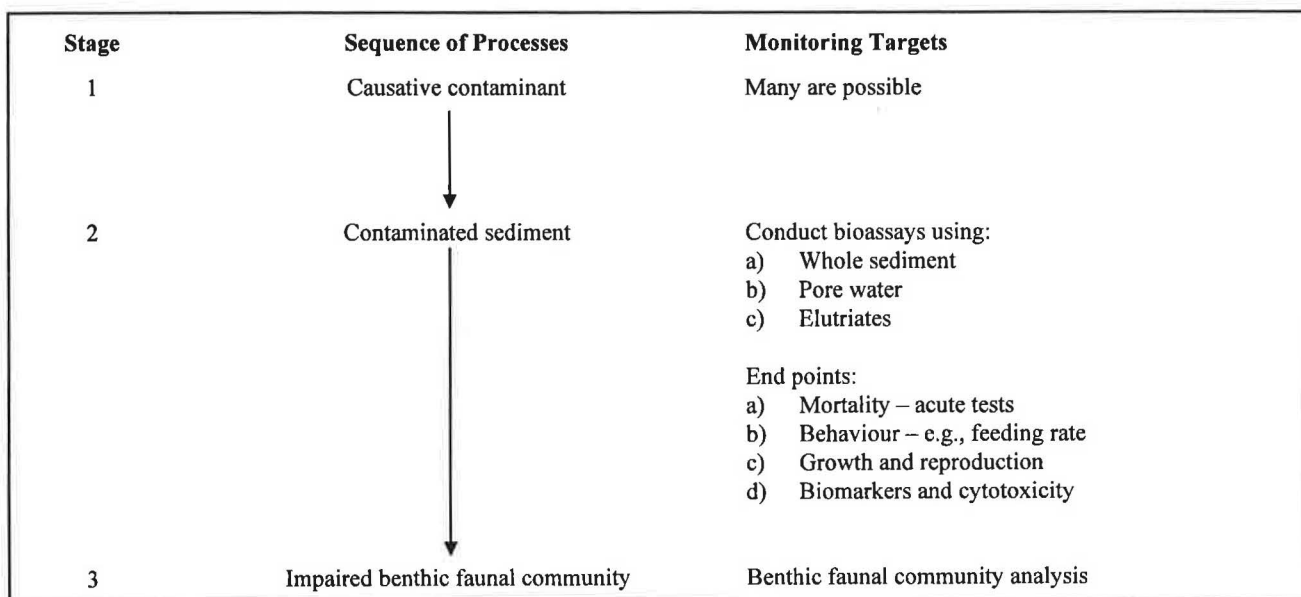
One expression of the quality of the marine environment which is frequently used in the contexts of both broad assessment programmes and localized programmes investigating particular point sources of contaminants is the “health” or “normality” of the benthic infaunal community. This may be considered as a component of the assessment of the health of the ecosystem. However, benthic faunal community analyses are notoriously difficult to interpret in terms of the possible effects of contaminants. In addition to marked temporal changes in the fauna which are known to occur in “uncontaminated control sites” (for example, following extreme weather conditions), the characteristics of the benthic fauna are very strongly influenced by season, and by particle size and organic carbon content of the sediment. Variations in these factors work to obscure any possible impacts from contaminants. The relatively high costs of benthic faunal analyses also present problems to many monitoring organizations. Figure A2.3 indicates the roles that toxicology, biology, and chemistry can play in monitoring programmes concerned with the health of the benthic community.

The structure of a monitoring programme to address the health of the benthic community based on the approach

described in Figure A2.3 differs from those in Figures A2.1 and A2.2, in that it is essentially a sequential scheme of monitoring and investigative activities, which do not necessarily involve the direct measurement of the biological cause for the concern, i.e., the actual benthic community. It is envisaged that sediment samples from geographical areas of interest should be investigated using whole sediment (and possibly additional pore water or elutriate) bioassays. The availability of chronic endpoints for these tests depends on the species being used and, in particular, there is a need for more sensitive chronic endpoints in whole sediment bioassays. If bioassays indicate that the sediments have significant toxicity, further ecological field work should be carried out to determine whether the benthic community is indeed impaired in some way. If it is, chemical and other toxicological studies should be undertaken to determine the chemical cause of the observed effects.

If the bioassays indicate that the sediment or its pore water/elutriates have toxic properties, and the subsequent benthic faunal analysis confirms that the community is in some way impaired, it would then be appropriate to initiate investigative analyses to determine the causative agent. Such investigations could include chemical analysis of the bulk sediment for the “routine” groups of contaminants. Other possible approaches include extraction of contaminants from the sediment by organic solvents or other means, and the fractionation of the extract, for example, by polarity, molecular weight, or partition coefficient. These fractions could then be used as the test substances in further bioassays, possibly using more specific biomarkers as end points (e.g., in tissue culture) in addition to mortality. Toxic fractions could then be subjected to more investigative chemical analysis.

**Figure A2.3.** An approach to investigating the effects of contaminants on the health of the benthic infaunal community.



## ANNEX 3

### INDICATOR SPECIES SENSITIVE TO PHYSICAL DISTURBANCE OF THE SEABED

#### 1 Introduction

In addressing the continuing request for a list of indicator species sensitive to physical disturbance of the seabed, the Benthos Ecology Working Group (BEWG) reviewed its previous reports as well as the 1994 report of the Working Group on Ecosystem Effects of Fishing Activities. The BEWG accepted the definitions and characteristics of vulnerable species established in these earlier reports, but organized some of the information in a slightly different manner so as to produce a set of criteria that might be broadly applicable within the ICES area. Further, the use of the term "sensitive" is preferred over "vulnerable" to describe species that may be affected in some way by physical disturbances. Of special note here, however, is that not only have the direct effects on individuals been considered (which is the central theme of the definition of vulnerability in the 1994 report), but the discussion has been extended to include characteristics that might lead to local extinction of a species given sufficiently intensive repetition of the physical disturbance.

No list of indicator species has been drawn up here; however, using the criteria outlined in this annex, it should be possible to make, for each habitat within each biogeographical province, a list of the most likely sensitive species. A complication that must be considered is that, for most regions of interest, the seabed has been trawled for so many years that it is difficult to know which species are absent because of their sensitivity to physical disturbance or because of some other habitat requirement that is not met in that region. It is likely that the species which are present in these heavily trawled areas are those which have survived and, therefore, are not very vulnerable to physical disturbances, at least not at the population level. It should also be noted that many of the most sensitive species, and consequently the species whose absence is most likely to be indicative of physical disturbance, are small invertebrates about which little is known. It must be noted that the single most important impediment to the preparation of such a list is the lack of natural history information for most species.

#### 2 Characteristics of Species that Make Them Vulnerable

Whether a species is sensitive to the effects of physical disturbance is dependent on several aspects of its life style and life history. These characteristics must be viewed in a hierarchical manner, however, as it is possible for individuals of a species to be damaged, killed, or removed locally, but the regional population can produce sufficient new recruits that the species will have the capability of recovering from the disturbance.

To assess this capability, effects of physical disturbance on benthic species are arranged into two main categories: direct effects on individuals and long-term effects on the population of a species. Obviously, if there are no direct effects on individuals, the long-term population effects are unimportant. On the other hand, if individuals are impacted in some way, then criteria at the population level must be invoked in order to determine ultimately whether a species is sensitive to physical disturbances.

To complete the assessment of sensitivity, information is also needed on the effect on a species of disturbance frequency, and the proportion of the area occupied by the species that is disturbed. For example, some species may suffer severe physical damage from a single disturbance event and have very limited recolonization ability. Other species may be able to repair physical damage after one disturbance event, but do not have the energetic capability to do so several times. Still other species may suffer severe physical damage from repeated disturbances, but the undisturbed part of the population is capable of producing sufficient propagules to recolonize the disturbed area following the cessation of disturbance.

##### *Direct Effects on Individuals*

*Damage to the body of the individual.* Species with very fragile bodies are most likely to be killed on contact with the agent of disturbance, or with sediment particles being moved by this agent. Examples include polychaetes such as cirratulids and terebellids as well as some echinoderms such as *Echinocardium*.

*Damage to burrow dwellings.* Species which maintain complex, shallow burrows, and expend considerable energy doing so, may consume energy by having to repeatedly excavate the burrow. A few species are also known to house their young in the burrow; these species will suffer losses of young as well as adults. Examples include various amphipods and polychaetes.

*Removal of individuals from their burrow or tube.* Species which continuously make small incremental changes to their burrow as they grow often lose their ability to burrow vigorously as they age. If individuals of these species are removed from their burrow by the agent of the physical disturbance, it is unlikely that they will be able to re-burrow. Examples include *Mya*.

*Damage to tubes.* Species which make a single tube over their life time will be unable to replace one destroyed by a physical disturbance. Animals whose tubes are damaged or destroyed are liable to increased predation. Examples include polychaetes such as *Pectinaria*.

*Removal of individuals from the substratum.* Species which are attached to the substratum by structures that are easily broken will be readily removed by most agents of physical disturbance. Examples include sponges, bryozoans, and hydroids.

*Damage to shells.* Breakage of shells increases the vulnerability of a species to predators. Examples include *Arctica*.

*Clogging of feeding structures.* Resuspension of bottom muds can coat or clog feeding structures of species living in water with low suspended particle concentrations, resulting in starvation and eventual death of individuals. Examples include bryozoans, *Glycymeris*.

*Burial of individuals by resuspended sediment.* Many small species may be unable to burrow upward through several centimetres of sediment deposited following a resuspension event or thrown up into mounds by fishing or dredging gear. Such species may die from increased exposure to hydrogen sulphide or lack of porewater oxygen. Examples might include small mud-dwelling polychaetes confined to tubes and requiring a connection to the surface to maintain oxygenated water flow.

#### **Population Characteristics of Sensitive Species**

Species whose individuals suffer direct impacts of physical disturbance may be capable of local recovery due to sufficiently rapid growth or recruitment potential. On a population level, however, a species may be vulnerable to local extinction if its life history includes one or more of the following features:

- *low growth rate;*
- *low regenerative capability;*
- *low fecundity or infrequent recruitment;*
- *low mobility of reproductive propagules;*
- *specialized housing of juveniles;*
- *loss of specialized habitat, e.g., commensal losing their host;*
- *narrow substrate tolerance.*

The direct effects on individuals and population characteristics of sensitive species can be combined to produce some examples of most likely sensitive species. Two examples are given below.

*Severe damage to the body of the individual and low fecundity:* such a species, after losing much or all of the body mass, would be unlikely to recover within a considerable period of time, e.g., *Paragorgia arborea*.

*Removal of individuals from the substratum and narrow substrate tolerance:* such species would only recolonize the type of habitat that is being repeatedly disturbed and, given frequent removals, the species would eventually be so reduced that a breeding population would not be large enough to maintain itself, e.g., *Neptunea antiqua*, *Aporrhais pes-pellicani*.

### **3 Characteristics of Species that are Not Vulnerable**

In contrast, many species may suffer some direct effects from physical disturbance, but long-term effects on the populations of these species are unlikely to occur because they exhibit some or all of the following characteristics:

- *highly mobile;*
- *freely burrowing, as in Capitella;*
- *rapid burrowing capability, as in some bivalves;*
- *wide tolerance to natural disturbance;*
- *high densities;*
- *rapid reproduction and high fecundity;*
- *species.*

Species that are characterized as “r” species (i.e., opportunistic) would not generally be considered to be vulnerable.

### **4 Species Taking Advantage of Disturbed Bottoms**

One additional category of possible indicator species are those that are capable of taking advantage of the results of physical disturbance. Most of these species are highly mobile, have strongly developed chemosensory capabilities, and are capable of rapidly consuming soft tissues. High densities of scavengers are representative of this category.

### **5 Recommendation**

There are very likely many species that are sensitive to the effects of physical disturbance of the benthic habitat. Before the degree of sensitivity can be assessed, some indication of the intensity and frequency of disturbance needs to be given. Further, it may be necessary to examine the recolonization of areas newly closed to fishing in order to know which species have historically been lost due to long-term effects of physical disturbance.



## ANNEX 4

### CHLORINATED ALKANES IN THE MARINE ENVIRONMENT

#### INTRODUCTION

Chlorinated alkanes are a large group of compounds and it can be assumed that not all members are relevant for the marine environment. GESAMP (1990) made a selection based on criteria such as log  $K_{ow}$ , toxicity, persistence, production, and use of the chemical. The resulting list of potentially harmful substances contained mainly low molecular weight ( $C_1$ – $C_3$ ) chlorinated alkanes such as chlorinated methanes (e.g., dichloromethane, chloroform, carbon tetrachloride), chlorinated ethanes (e.g., 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane), chlorinated ethenes (e.g., 1,1,2,2-tetrachloroethylene, 1,1,2-trichloroethylene) and epichlorohydrin (1-chloro-2,3-epoxypropane).

The compounds in question exhibit similar physico-chemical properties, have a widespread use, and are produced in large quantities. Due to their persistence and volatility, they may be transported over considerable

distances (Krysell, 1989). A number of these compounds therefore have been used as tracers for atmospheric mixing and ocean flux studies (Fogelqvist *et al.*, 1982; Krysell and Wallace, 1988; Krysell, 1992). It can therefore be expected that a certain amount will enter the oceans through equilibrium partitioning. Biodegradation (mostly aerobic) has been reported but the data are somewhat conflicting, varying from practically none to considerable degradation (Howard, 1991; Howard *et al.*, 1991). No significant adsorption to sediments is expected, especially not in sediments with a low organic carbon content, and no significant bioconcentration is expected (Howard, 1991). However, concentrations in biota (Dickson and Riley, 1976) and sediments (Bianchi *et al.*, 1991) are significantly higher than those in the surrounding environment.

Most of the above compounds have been intensively studied in groundwater and freshwater systems. However, much less is known about their presence and

**Table A4.1.** Relevant physico-chemical parameters for a number of chlorinated ( $C_1$ – $C_2$ ) hydrocarbons (after Howard, 1991; van Leeuwen *et al.*, 1992).

| Compound   | BP <sup>1</sup><br>(°C) | MP <sup>2</sup><br>(°C) | MW <sup>3</sup><br>(g) | log $K_{ow}$ <sup>4</sup> | S <sup>5</sup><br>(mg/l) | Vapour pressure<br>(mm Hg) | H <sup>6,7</sup><br>(atm·m <sup>3</sup> /mole) |
|--|-------------------------|-------------------------|------------------------|---------------------------|--------------------------|----------------------------|--|
| carbon tetrachloride<br>CCl <sub>4</sub>                         | 76.54                   | –23                     | 153.84                 | 2.83                      | 805                      | 113.8 at 20°C              | 3.04E–2 at 24.8°C                              |
| chloroform<br>CHCl <sub>3</sub>                                  | 61.7                    | –63.5                   | 119.39                 | 1.97                      | 7950                     | 246 at 25°C                | 4.35E–3 at 25°C                                |
| dichloromethane<br>CH <sub>2</sub> Cl <sub>2</sub>               | 39.75                   | –95.1                   | 84.94                  | 1.25                      | 13000                    | 434.9 at 25°C              | 2.68E–3  |
| 1,1-dichloroethane<br>CH <sub>3</sub> CHCl <sub>2</sub>          | 57.3                    | –96.98                  | 98.96                  | 1.79                      | 5060                     | 227 at 25°C                | 5.87E–3  |
| 1,2-dichloroethane<br>CH <sub>2</sub> ClCH <sub>2</sub> Cl       | 83.47                   | –35.36                  | 98.96                  | 1.48                      | 8524                     | 78.7 at 20°C               | 9.77E–4  |
| 1,1,2,2-tetrachloroethane<br>CHCl <sub>2</sub> CHCl <sub>2</sub> | 146.5                   | –36                     | 167.86                 | 2.3                       | 2962                     | 6.1 at 25°C                | 4.55E–4 at 25°C                                |
| tetrachloroethylene<br>C <sub>2</sub> Cl <sub>4</sub>            | 121                     | –19                     | 165.82                 | 3.4                       | 150.3                    | 18.49 at 25°C              | 1.49E–2  |
| 1,1,2-trichloroethane<br>CHCl <sub>2</sub> CH <sub>2</sub> Cl    | 113.8                   | –36.5                   | 133.42                 | 2.07                      | 4420                     | 30.3 at 20°C               | 1.2E–3 at 20°C                                 |
| 1,1,1-trichloroethane<br>CCl <sub>3</sub> CH <sub>3</sub>        | 74.1                    | –30.4                   | 133.42                 | 2.49                      | 1495                     | 123.7 at 25°C              | 8E–3   |
| trichloroethylene<br>CCl <sub>2</sub> CHCl                       | 87                      | –73                     | 131.40                 | 2.42                      | 1100                     | 69.0 at 25°C               | 1.03E–2  |
| pentachloroethane<br>CCl <sub>3</sub> CHCl <sub>2</sub>          | 161                     | –29                     | 202.29                 | 3.05                      | 480                      | 3.5 at 25°C                | 1.94E–3 at 25°C                                |

<sup>1</sup>Boiling point    <sup>2</sup>Melting point    <sup>3</sup>Molecular weight    <sup>4</sup>Log octanol/water partition coefficient    <sup>5</sup>Solubility in water  
<sup>6</sup>Henry's Law constant    <sup>7</sup>Values are given in exponential scientific notation, e.g., 3.04E–2 indicates 3.04 × 10<sup>–2</sup>



behaviour in the marine environment. This paper is deliberately limited to findings in the marine environment.

## CHEMICAL AND PHYSICAL PROPERTIES

An overview of the most important physico-chemical properties of a number of chlorinated alkanes can be found in Table A4.1. All compounds are liquids at room temperature, but will exist primarily in the vapour phase as a result of their relatively high vapour pressure. This property has led them to be important atmospheric contaminants. It can be expected that atmospheric transport followed by equilibrium partitioning will cause a widespread distribution in the environment, especially since residence times in the atmosphere are relatively high. It is believed (Howard, 1991) that as a result of their water solubility, Henry's Law constant and vapour pressure, no significant adsorption to soil will occur. The compounds are believed to be rapidly removed from soil by evaporation or leached out into ground water, where their fate remains unknown. The relatively low  $\log K_{ow}$  would also suggest that no significant bioconcentration will occur.

## SOURCES

### Natural sources

No natural sources are known for the members of this group of compounds with the exception of chloroform, which is a plant volatile (Graedel, 1978).

### Other sources

All members of the group are important industrial products or intermediates and are used in a variety of roles such as degreaser, fire extinguisher, grain fumigant, solvent, coupling agent in anti-knock gasoline, dilution agent for pesticides, floatation agent, paint remover, metal degreaser, and dry cleaning agent (IARC, 1979; Drury and Hammons, 1979; Khan and Hughes, 1979; U.S. EPA, 1979, 1980; Vershueren, 1983; Wallace *et al.*, 1987).

Contamination of the environment will take place as a result of fugitive emissions during production and use of the chemicals or through waste water and effluents of the following industries: paint and ink industries, metal industries, non-ferrous metal industries, organic chemical industries (petroleum refining, pesticide production, rubber industries, plastic industries), pharmaceutical industries, and cleaning industries (Drury and Hammons, 1979; Johns, 1976; Khan and Hughes, 1979; Singh *et al.*, 1979; U.S. EPA, 1980, 1981; Vershueren, 1983). Chloroform is also produced during

the chlorination of drinking water, cooling water, and municipal waste water (IARC, 1979; U.S. EPA, 1975, 1984). Annual production rates for a number of chlorinated hydrocarbons can be found in Table A4.2.

**Table A4.2.** Annual production of selected chlorinated hydrocarbons (Sittig, 1980).

| Compound              | Annual Production (tonnes) |
|-----------------------|----------------------------|
| monochloroethane      | 304 000 (1976)             |
| 1,1,1-trichloroethane | 286 000 (1976)             |
| 1,2-dichloroethane    | 3.6 million (1976)         |
| carbon tetrachloride  | 266 000                    |

## ANALYSIS

Volatile compounds are extracted from the matrices by liquid-liquid extraction or by volatilization. Eklund *et al.* (1978) used a batchwise liquid-liquid extraction in a funnel with pentane for the extraction of volatiles from sea water (see also Fogelqvist *et al.*, 1982; and Fogelqvist, 1985, in Krysell, 1989). Fogelqvist and Krysell (1986) used a liquid-liquid extraction in a segmented flow directly coupled to the on-column injector of the gas chromatograph for the analysis of sea water. This on-line extraction method requires minimum sample handling and thus guarantees a minimum of contamination.

Most other analytical methods are based on the volatilization of the compounds in question, using either static (equilibrium) (Helz and Hsu, 1978) or dynamic (non-equilibrium) headspace techniques (Bellar and Lichtenberg, 1974; Bianchi *et al.*, 1989, 1991; Borén *et al.*, 1982; Grob, 1973; Grob and Grob, 1974; Grob *et al.*, 1975; Grob and Zürcher, 1976). The contaminants in the sample are mobilized by vacuum extraction techniques, heating the sample, purging the sample with an inert gas such as He or N<sub>2</sub>, or a combination of both methods. The resulting gas phase is then immediately analysed (static headspace techniques) or an additional concentration step is performed (dynamic headspace techniques). To this purpose, off-line or on-line cold traps, solid traps (Tenax, activated carbon, silica gel or combinations) or a combination are used to concentrate the contaminants prior to analysis. A variant of the latter is the use of the gas chromatography (GC) column, cooled down to temperatures around -90°C, as the trap (P/WCC: Purging and Whole Column Cryotrapping) (Cohran, 1987; Pankow and Rosen, 1988; Pankow, 1990; Pankow and Rounds, 1991). Analysis is then performed through desorption of the traps and immediate injection in a gas chromatograph with an appropriate detector (electron capture detector, Hall detector, or mass spectrometer).

## DISTRIBUTION AND LEVELS IN THE MARINE ENVIRONMENT

Few data are available on the presence and distribution of these compounds in the marine environment, compared to other types of compounds such as polychlorinated biphenyls (PCBs). This is probably the result of problems that are associated with the analysis of the compounds and the assumption that the group in question should not be considered as a direct threat to the marine environment.

## Water

Concentrations in sea water are generally low, in the  $\text{ng l}^{-1}$  range or below, but exceptional concentrations up to  $200 \mu\text{g l}^{-1}$  have been reported (Table A4.3).

Evaporation appears to be the principal removal process for chlorinated alkanes, with half-lives ranging from several days to several years (Howard, 1991). The majority of data for removal processes is found in studies concerning ground water, fresh water, and drinking water (Wilson *et al.*, 1986). Biodegradation, hydrolysis,

**Table A4.3.** Concentrations of several chlorinated hydrocarbons in marine and estuarine water.

| Compound              | Location                | Concentration                  | References                             |
|-----------------------|-------------------------|--------------------------------|--|
| carbon tetrachloride  | Solent Estuary, UK      | <10–311 $\text{ng l}^{-1}$     | Bianchi <i>et al.</i> , 1991           |
|                       | Humber Estuary, UK      | 3.1–18 $\text{ng l}^{-1}$      | Krysell and Nightingale, 1994          |
|                       | Weddell Sea, Antarctica | 1.2–1.3 $\text{ng l}^{-1}$ *   | Krysell, 1992                          |
|                       | Rhine Estuary           | 0.96–8.1 $\text{ng l}^{-1}$    | Krysell and Nightingale, 1994          |
|                       | Tees Estuary, UK        | <25–29 $\text{ng l}^{-1}$      | Dawes and Waldock, 1994                |
|                       | Wear Estuary, UK        | <25–102 $\text{ng l}^{-1}$     | Dawes and Waldock, 1994                |
| 1,1,1-trichloroethane | Liverpool Bay, UK       | max. 3.3 $\mu\text{g l}^{-1}$  | Pearson and McConnell, 1975            |
|                       | Solent Estuary, UK      | 0.01–1.01 $\mu\text{g l}^{-1}$ | Bianchi <i>et al.</i> , 1991           |
|                       | Weddell Sea, Antarctica | 2 $\text{ng l}^{-1}$ *         | Krysell, 1992                          |
|                       | Humber Estuary, UK      | 5.1–53 $\text{ng l}^{-1}$      | Krysell and Nightingale, 1994          |
|                       | Tees Estuary, UK        | <10–602 $\text{ng l}^{-1}$     | Dawes and Waldock, 1994                |
|                       | Wear Estuary, UK        | <10–64 $\text{ng l}^{-1}$      | Dawes and Waldock, 1994                |
| 1,2-dichloroethane    | Gulf of Mexico          | 0–210 $\text{ng l}^{-1}$       | Sauer, 1981, in Howard, 1991           |
|                       | Solent Estuary, UK      | 0.04–0.53 $\mu\text{g l}^{-1}$ | Bianchi <i>et al.</i> , 1991           |
|                       | Tees Estuary, UK        | 720–4020 $\text{ng l}^{-1}$    | Dawes and Waldock, 1994                |
| trichloroethylene     | Sea water               | max. 3.6 $\mu\text{g l}^{-1}$  | Dyksen and Hess, 1982, in Howard, 1991 |
|                       | Rhine Estuary           | 1.3–74 $\text{ng l}^{-1}$      | Krysell and Nightingale, 1994          |
|                       | Wear Estuary, UK        | <10–132 $\text{ng l}^{-1}$     | Dawes and Waldock, 1994                |
| tetrachloroethylene   | Sea water               | 0.1–0.8 $\text{ng l}^{-1}$     | Murray and Riley, 1973                 |
|                       |                         |                                | Pearson and McConnell, 1975            |
|                       | Humber Estuary, UK      | 0.87–17 $\text{ng l}^{-1}$     | Krysell and Nightingale, 1994          |
|                       | Rhine Estuary           | 1.3–47 $\text{ng l}^{-1}$      | Krysell and Nightingale, 1994          |
| chloroform            | Tees Estuary, UK        | <10–175 $\text{ng l}^{-1}$     | Dawes and Waldock, 1994                |
|                       | NE Atlantic Ocean       | 4–13 $\text{ng l}^{-1}$        | Sauer, 1981, in Howard, 1991           |
|                       | Gulf of Mexico          | 4–200 $\mu\text{g l}^{-1}$     | Murray and Riley, 1973                 |
|                       |                         | 20–35 $\mu\text{g l}^{-1}$     | Bianchi <i>et al.</i> , 1991           |
|                       | Tees Estuary, UK        | <10–11,500 $\text{ng l}^{-1}$  | Dawes and Waldock, 1994                |
|                       | Rhine Estuary           | 4.8–91 $\text{ng l}^{-1}$      | Krysell and Nightingale, 1994          |

\*Values reported are calculated from Figure 4 in Krysell (1992) and are therefore approximations.

and photo-oxidation rates are considered to be insignificant in comparison with evaporation processes (Howard, 1991). Adsorption to sediments and bioconcentration in aquatic organisms are also not considered to be important removal processes (Howard, 1991). Table A4.4 gives an overview of both estimated and calculated half-lives for a number of chlorinated alkanes in aqueous systems. The half-lives reported in the table are the net result of the different processes mentioned above. Aerobic conditions will generally result in shorter half-lives, due to increased biodegradation.

**Table A4.4.** Aqueous half-lives for a number of volatile chlorinated hydrocarbons (Howard *et al.*, 1991).

| Compound              | Aqueous half-life          |                             |
|-----------------------|----------------------------|-----------------------------|
|                       | Aerobic                    | Anaerobic                   |
| chloroform            | H: 6 months<br>L: 4 weeks  | H: 4 weeks<br>L: 1 week     |
| 1,1-dichloroethane    | H: 22 weeks<br>L: 32 days  | H: 88 weeks<br>L: 128 days  |
| 1,2-dichloroethane    | H: 6 months<br>L: 100 days | H: 24 months<br>L: 400 days |
| 1,1,1-trichloroethane | H: 39 weeks<br>L: 20 weeks | H: 156 weeks<br>L: 80 weeks |
| trichloroethylene     | H: 1 year<br>L: 6 months   | H: 4.5 years<br>L: 98 days  |
| tetrachloroethylene   | H: 1 year<br>L: 6 months   | H: 4.5 years<br>L: 98 days  |

H = high value

L = low value

### Sediments

Little is known of the fate and concentrations of chlorinated alkanes in marine sediments. Howard (1991) expected that evaporation from water will be the principal pathway for removal of chlorinated alkanes. Based on their physico-chemical properties, he also stated that sorption to sediments should be insignificant in comparison. However, O'Connor and Connolly (1980) in Bianchi *et al.* (1991) stated that sorptive action by sediments was directly involved in the removal of volatile organic compounds from overlying water, regardless of the sediment type. Similarly, Bianchi *et al.* (1991) demonstrated, during a case study in the Solent Estuary, that volatile organic compounds are ubiquitous in the estuary. They concluded that sediments have the potential to accumulate and concentrate much higher levels than might normally be found in the water column. A distinctive seasonal variation was also observed, with the lowest concentrations in the period July–August and the highest concentrations in October–January. Apparently, higher temperatures during summer cause evaporation from the surface water to be dominant over deposition and sorption to sediments. Concentrations increase during autumn and winter as a

result of lower temperatures combined with increased organic loads. Table A4.5 gives an overview of concentrations of a number of compounds in marine sediments and water. The concentrations in the sediments are generally higher than those in the surrounding water, confirming a concentration gradient between water and sediment.

**Table A4.5.** Concentrations of a number of volatile chlorinated hydrocarbons in the Solent Estuary (Bianchi *et al.*, 1991).

| Compound              | Concentration in water<br>ng l <sup>-1</sup> | Concentration in sediment<br>ng g <sup>-1</sup> |
|-----------------------|--|---|
| carbon tetrachloride  | <10–311                                      | 0.075–1.9                                       |
| dichloromethane       | 15–1000                                      | 0.020–2.7                                       |
| 1,1,1-trichloroethane | <5–2790                                      | 0.070–31  |
| 1,2-dichloroethane    | 15–955                                       | 0.070–11  |
| trichloroethylene     | <10–603                                      | 0.070–4   |
| tetrachloroethylene   | <10–343                                      | 0.085–20  |
| chloroform            | 10–7500                                      | 0.097–23  |

### Biota

Very few data are available on the presence and distribution of these compounds in marine biota. A number of authors (Dickson and Riley, 1976; Pearson and McConnell, 1975) have analysed biological tissues for the presence of these short-chained chlorinated hydrocarbons. Concentrations in marine fish and invertebrates vary up to 1100 ng g<sup>-1</sup> and 1040 ng g<sup>-1</sup>, respectively. Their results (see Table A4.6) clearly demonstrate that the concentrations in biota are significantly higher than those in sediments or water (see above), indicating a certain degree of bioconcentration.

However, the potential for bioconcentration or biomagnification is considered to be very low (Howard, 1991; Dickson and Riley, 1976; Neely *et al.*, 1974; Pearson and McConnell, 1975; McConnell *et al.*, 1975; U.S. EPA, 1978) since calculated or estimated bioconcentration factors (BCFs) are generally low (between 0.3 and 226, see Table A4.7), especially compared to other well-known environmental contaminants such as PCBs (BCFs up to 50 000, Veith *et al.*, 1979). As a general rule, it can be stated that bioconcentration increases with the degree of chlorination. It should be noted that the data in Table A4.6 date back to the 1970s and may therefore not reflect current conditions.

Even though the potential for bioconcentration is thought to be low, toxicity data suggest that the selected compounds should be considered important environmental contaminants.

**Table A4.6.** Concentrations of a number of chlorinated hydrocarbons in marine biota.

| Compound              | Biota                                  | Concentration (ng g <sup>-1</sup> ) | References   |
|-----------------------|--|-------------------------------------|--|
| chloroform            | marine fish (various species)          | 5–851                               | Dickson and Riley, 1976<br>Pearson and McConnell, 1975 |
|                       | marine invertebrates (various species) | 2–1040                              | Dickson and Riley, 1976<br>Pearson and McConnell, 1975 |
| 1,1,1-trichloroethane | marine fish (various species)          | 2–26                                | Dickson and Riley, 1976<br>Pearson and McConnell, 1975 |
|                       | marine invertebrates (various species) | 0–34                                | Dickson and Riley, 1976<br>Pearson and McConnell, 1975 |
| trichloroethylene     | marine fish (various species)          | 0.66–1100                           | Pearson and McConnell, 1975                            |
|                       | marine invertebrates (various species) | 2–250                               | Pearson and McConnell, 1975                            |
| tetrachloroethylene   | marine fish (various species)          | 0.3–479                             | Pearson and McConnell, 1975                            |
|                       | marine invertebrates (various species) | 0.5–176                             | Pearson and McConnell, 1975                            |
| carbon tetrachloride  | marine fish (various species)          | 3–209                               | Dickson and Riley, 1976                                |
|                       | marine invertebrates (various species) | 2–114                               | Dickson and Riley, 1976                                |

**Table A4.7.** Calculated or estimated bioconcentration factors of some chlorinated C<sub>1</sub>–C<sub>2</sub> hydrocarbons.

| Compound              | Bioconcentration Factor | References   |
|-----------------------|-------------------------|--|
| carbon tetrachloride  | 10–100                  | Pearson and McConnell, 1975  |
| chloroform            | 1.6–10.35               | Anderson and Lusty, 1980<br>Barrows <i>et al.</i> , 1980                                 |
| trichloroethylene     | 2–25                    | Dickson and Riley, 1976<br>Pearson and McConnell, 1975                                   |
| 1,2-dichloroethane    | 0.3–8                   | Barrows, <i>et al.</i> , 1980<br>Howard and Evenson, 1976, in Howard, 1991               |
| 1,1,1-trichloroethane | 8.9                     | Davies and Robs, 1984, in Howard, 1991   |
| tetrachloroethylene   | 38.9–226                | Neely <i>et al.</i> , 1974<br>Barrows <i>et al.</i> , 1980<br>Lyman <i>et al.</i> , 1982 |

## TOXICOLOGY

A variety of toxic responses, mainly in the liver and kidney, have been described (Della Porta *et al.*, 1961; Klaassen and Plaa, 1967, 1969; National Cancer Institute, 1976; Nielsen and Larsen, 1965; Recknagel *et al.*, 1973; Reuber and Glover, 1967). Humans are exposed by inhalation, skin contact, and the intake of contaminated water and food. Moreover, most members of this group of chlorinated hydrocarbons are suspected or confirmed carcinogenic substances (Sittig, 1980). This also implies that even though the potential to bioconcentrate is low, the consequences may be important.

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## ANNEX 5

### BENZENE AND ITS C<sub>1</sub>-C<sub>2</sub> ALKYL DERIVATIVES IN THE MARINE ENVIRONMENT

#### INTRODUCTION

Benzene and C<sub>1</sub> and C<sub>2</sub> alkylated benzenes have similar physico-chemical properties, are important industrial products with high annual production rates, and behave in a similar way in the marine environment. They are well-known atmospheric pollutants mainly associated with the use and combustion of fossil fuels. Atmospheric deposition and industrial wastewater discharges are the principal routes of entry of these compounds into the marine environment. The compounds are readily degraded in the atmosphere through reactions with photochemically produced hydroxyl radicals and residence times in the atmosphere are therefore short. Biodegradation (mostly aerobic) is reported for all members of the group, with half-lives varying from several days to several weeks. No significant adsorption to sediments is expected, especially to sediments with a low organic carbon content, and no significant bioconcentration is expected to occur (Howard, 1990, 1991).

#### CHEMICAL AND PHYSICAL PROPERTIES

Table A5.1 gives an overview of the most important physico-chemical properties of these compounds. At room temperature they exist as liquids with a relatively high vapour pressure. This property, in combination with their production during the combustion of fossil fuels, has resulted in their being important atmospheric contaminants. Although the residence times of mono-aromatic hydrocarbons in the atmosphere are short, a proportion will reach the oceans and seas through equilibrium partitioning and wet deposition. Howard (1991) reported that little adsorption to soil will occur due to the high water solubility and vapour pressure of

these compounds. They are rapidly removed from soil by evaporation or leached out into ground water. Biodegradation in ground water has been demonstrated in the presence of oxygen (Barker *et al.*, 1987). The relatively low log K<sub>ow</sub> would also suggest that no significant bioconcentration will occur.

#### SOURCES

##### Natural sources

Benzene and its C<sub>1</sub> and C<sub>2</sub> alkyl derivatives are natural constituents of crude oil (Graedel, 1978; IARC, 1982; NAS, 1980; Vershueren, 1983) and are produced as plant volatiles or during volcanic eruptions and forest fires (Graedel, 1978).

##### Other sources

These chemicals are important industrial intermediates and are used in the production of paints, varnishes, glues, and styrene, and as solvents (Fishbein, 1985; Graedel, 1978; Hawley, 1977; IARC, 1982; NAS, 1980; Vershueren, 1983; Walker, 1976). Contamination of the environment results from emissions and spills during their production and use as a chemical intermediate and during processes of petroleum refining, coke processing, and ore mining (Graedel, 1978; IARC, 1982; NAS, 1980). Wastewaters from these industries are another source of contamination. A significant amount will also enter the environment during production, venting, transport, and combustion of gasoline and diesel oil or emissions from residential wood-burning stoves and fireplaces (NAS, 1980). Annual production amounts can be found in Table A5.2.

**Table A5.1.** Relevant physico-chemical parameters for benzene and alkylated benzenes (after Howard, 1990, 1991; van Leeuwen *et al.*, 1992).

| Compound         | BP <sup>1</sup><br>(°C) | MP <sup>2</sup><br>(°C) | MW <sup>3</sup><br>(g) | log K <sub>ow</sub> <sup>4</sup> | S <sup>5</sup><br>(mg l <sup>-1</sup> ) | Vapour pressure<br>(mm Hg at 25°C) | H <sup>6</sup><br>(atm-m <sup>3</sup> /mole) |
|------------------|-------------------------|-------------------------|------------------------|----------------------------------|---|------------------------------------|--|
| benzene          | 80.1                    | 5.5                     | 78.11                  | 2.13                             | 1791                                    | 95.19                              | 5.43 x 10 <sup>-3</sup>                      |
| toluene          | 110.6                   | -95                     | 92.13                  | 2.73                             | 534.8                                   | 24.8                               | 5.94 x 10 <sup>-3</sup>                      |
| <i>o</i> -xylene | 144.4                   | -25                     | 106.17                 | 3.12                             | 175                                     | 6.6                                | 5.1 x 10 <sup>-3</sup>                       |
| <i>m</i> -xylene | 139.3                   | -47.4                   | 106.17                 | 3.20                             | 146                                     | 8.3                                | 7.68 x 10 <sup>-3</sup>                      |
| <i>p</i> -xylene | 137                     | 13-14                   | 106.17                 | 3.15                             | 156                                     | 8.7                                | 7.68 x 10 <sup>-3</sup>                      |
| ethylbenzene     | 136.2                   | -94.97                  | 106.16                 | 3.15                             | 161                                     | 9.53                               | 8.44 x 10 <sup>-3</sup>                      |

<sup>1</sup>Boiling point    <sup>2</sup>Melting point    <sup>3</sup>Molecular weight    <sup>4</sup>Log octanol/water partition coefficient    <sup>5</sup>Solubility in water  
<sup>6</sup>Henry's Law constant

**Table A5.2.** Annual production of benzene, toluene, and ethylbenzene in the United States (Sittig, 1980).

| Compound     | Annual Production (tonnes) |
|--------------|----------------------------|
| benzene      | 4 million                  |
| toluene      | 2.5 million                |
| ethylbenzene | 3 000                      |

## ANALYSIS

Traditional liquid extraction techniques (Law *et al.*, 1991) or static (equilibrium) and dynamic (non-equilibrium) headspace techniques (Bellar and Lichtenberg, 1974; Bianchi *et al.*, 1989, 1991; Borén *et al.*, 1982; Grob, 1973; Grob and Grob, 1974; Grob *et al.*, 1975; Grob and Zürcher, 1976) are used to isolate these compounds. Dynamic headspace techniques (purge and trap) offer the advantage of an additional concentration step. This concentration step is, in many cases, necessary to obtain adequate sensitivity for environmental samples. Chemicals in the sample are mobilized by heating and/or purging the sample with inert gases such as He or N<sub>2</sub> or by using vacuum extraction techniques. The resulting gas phase is subsequently injected into a gas

chromatograph (static headspace techniques) equipped with a suitable detector (in most cases a mass spectrometer), or an additional concentration step is performed (dynamic headspace techniques). Components in the carrier gas are subsequently concentrated using off-line or on-line cold traps, solid traps (Tenax, activated carbon, silica gel or combinations) or a combination of these, prior to injection into a gas chromatograph.

## DISTRIBUTION AND LEVELS IN THE MARINE ENVIRONMENT

Data on the presence and distribution of these chemicals in the marine environment are generally sparse. This is probably due both to difficulties associated with analysis and the assumption that they are not considered to be a danger to the marine environment.

### Water

Concentrations in sea water are generally low, in the ng l<sup>-1</sup> range or below, but exceptional concentrations up to 400 µg l<sup>-1</sup> have been reported (Table A5.3). Evaporation is thought to be one of the principal processes of removal, but biodegradation can be equally

**Table A5.3.** Marine and estuarine water concentrations of benzene and alkylated benzenes.

| Compound                        | Location           | Concentration               | References                         |
|---------------------------------|--------------------|-----------------------------|------------------------------------|
| benzene                         | Gulf of Mexico     | 5–15 ng l <sup>-1</sup>     | Sauer, 1981, in Howard, 1991       |
|                                 | Solent Estuary, UK | 0.10–55 µg l <sup>-1</sup>  | Bianchi <i>et al.</i> , 1991       |
| toluene                         | Gulf of Mexico     | 3–376 ng l <sup>-1</sup>    | Sauer, 1978, 1981, in Howard, 1991 |
|                                 | Solent Estuary     | 0.01–490 µg l <sup>-1</sup> | Bianchi <i>et al.</i> , 1991       |
|                                 | Vineland Sound     | 10–54 ng l <sup>-1</sup>    | Sauer, 1978, 1981, in Howard, 1991 |
| <i>m</i> - and <i>p</i> -xylene | Gulf of Mexico     | 2.7–24.4 ng l <sup>-1</sup> | Sauer, 1978, 1981, in Howard, 1991 |
|                                 | Vineland Sound     | 4.5–66 ng l <sup>-1</sup>   | Sauer, 1978, 1981, in Howard, 1991 |
| <i>m</i> -xylene                | Solent Estuary     | 0.01–400 ng l <sup>-1</sup> | Bianchi <i>et al.</i> , 1991       |
| <i>o</i> -xylene                | Vineyard Sound     | 1.8–2.5 ng l <sup>-1</sup>  | Gschwend <i>et al.</i> , 1982      |
|                                 | Solent Estuary     | 0.01–400 µg l <sup>-1</sup> | Bianchi <i>et al.</i> , 1991       |
|                                 | Gulf of Mexico     | 1–30 ng l <sup>-1</sup>     | Sauer, 1978, 1981, in Howard, 1991 |
| ethylbenzene                    | Gulf of Mexico     | 0.50–5.0 µg l <sup>-1</sup> | Sauer, 1978, 1981, in Howard, 1990 |
|                                 | Solent Estuary     | 0.01–312 µg l <sup>-1</sup> | Bianchi <i>et al.</i> , 1991       |

important (Howard, 1990, 1991; Wakeham *et al.*, 1983). The predominant process will depend on water temperature, mixing conditions, the existence of acclimated micro-organisms, and the presence of oxygen. Degradation half-lives for benzene and the alkylated benzenes can be found in Table A5.4. Adsorption to sediments and bioconcentration in aquatic organisms are not considered to be important removal processes (Howard, 1991), although some adsorption to sediments may be expected. The half-lives are the net result of all the processes that lead to degradation in aquatic systems and are an estimate of the highest and lowest rates of removal (Table A5.4). The differences between the half-lives under aerobic and anaerobic conditions are mainly the result of different biodegradation processes. Aerobic conditions will generally enhance biodegradation.

**Table A5.4.** Aqueous half-lives for benzene and alkylated benzenes (Howard *et al.*, 1991).

| Compound         | Aqueous half-life        |                             |
|------------------|--------------------------|-----------------------------|
|                  | Aerobic                  | Anaerobic                   |
| benzene          | H: 16 days<br>L: 5 days  | H: 24 months<br>L: 16 weeks |
| toluene          | H: 22 days<br>L: 4 days  | H: 30 weeks<br>L: 8 weeks   |
| <i>o</i> -xylene | H: 4 weeks<br>L: 1 week  | H: 12 months<br>L: 6 months |
| <i>m</i> -xylene | H: 4 weeks<br>L: 1 weeks | H: 16 weeks<br>L: 1 week    |
| <i>p</i> -xylene | H: 4 weeks<br>L: 1 week  | H: 16 weeks<br>L: 4 weeks   |
| ethylbenzene     | H: 10 days<br>L: 3 days  | H: 228 days<br>L: 176 days  |

H = high value

L = low value

## Sediments

Concentrations reported in sediments are given in Table A5.5. Although adsorption to sediments is thought to be unimportant, some adsorption might occur (Howard, 1991). Bianchi *et al.* (1991) demonstrated that benzene, alkylated benzenes, and other volatile organic compounds were ubiquitous in the Solent Estuary. They concluded that sediments have the potential to accumulate and concentrate much higher levels than might normally be found in the water column. A distinctive seasonal variation was also observed, with the lowest concentrations in the period July–August and the highest concentrations in October–January. Higher temperatures during summer cause evaporation from the surface water to dominate over deposition and sorption to sediments. Concentrations increase during autumn and winter as a result of lower temperatures combined with increased organic loads. This was in agreement with the

statement of O'Connor and Connolly (1980) cited in Bianchi *et al.* (1991) which claimed that sorptive action by sediments was directly involved in the removal of volatile organic compounds from overlying water, regardless of the sediment type.

**Table A5.5.** Concentrations of benzene and alkylated benzenes in the Solent Estuary (Bianchi *et al.*, 1991).

| Compound         | Concentration<br>in water<br>$\mu\text{g l}^{-1}$ | Concentration<br>in sediment<br>$\text{ng g}^{-1}$ |
|------------------|---|--|
| benzene          | 0.10–55   | 0.3–97   |
| toluene          | 0.01–490  | 0.55–120   |
| <i>o</i> -xylene | 0.01–400  | 0.87–480   |
| <i>m</i> -xylene | 0.01–400  | 0.88–480   |
| ethylbenzene     | 0.01–312  | 0.51–201   |

## Biota

Few data are available on the concentrations and distribution of benzene and alkylated benzenes in marine biota. Table A5.6 gives an idea of concentrations that were determined in several marine species. Concentrations are low and in the same range as those in sediments. A conclusion might be that this group of chemicals shows little tendency to bioconcentrate. Similar results were expected from calculated and estimated bioconcentration factors (BCFs) (Howard, 1991).

It is very likely that the physico-chemical properties, such as  $\log K_{ow}$ , of the selected aromatics are not the only factors influencing bioconcentration. Rapid metabolism prevents bioaccumulation and can result in detoxification or toxic activity. In the case of benzene, metabolism is a prerequisite for toxicity (Kalf *et al.*, 1987). The environmental impact of benzene lies in its presence and widespread distribution rather than its potential to bioconcentrate.

## TOXICOLOGY

Of these chemicals, only benzene has been confirmed as a carcinogen (leukemic agent) in humans (Verschuere, 1983). Uptake by humans will occur primarily from inhalation of contaminated air and ingestion of contaminated water. Consumption of fish need not be considered as an important source, since the chemical has a low potential for bioconcentration. Carcinogenicity of the alkylated benzenes is suspected, but not proven. Benzene and toluene have been shown to adversely affect aquatic organisms (Verschuere, 1983). Exposure of marine organisms to these compounds via their food is likely to be low, but data are non-existent.



**Table A5.6.** Concentrations of benzene and alkylated benzenes in marine biota.

| Compound     | Species  | Concentration            | References  |
|--------------|--|--------------------------|---|
| benzene      | oyster ( <i>Crassostrea virginica</i> ): Lake Pontchartrain, Louisiana | 220 ng g <sup>-1</sup>   | Ferrario <i>et al.</i> , 1985                       |
|              | clam ( <i>Rangia cuneata</i> ): Lake Pontchartrain, Louisiana          | 260 ng g <sup>-1</sup>   | Ferrario <i>et al.</i> , 1985                       |
| toluene      | oyster ( <i>Crassostrea virginica</i> ): Lake Pontchartrain, Louisiana | 3.4 ng g <sup>-1</sup>   | Ferrario <i>et al.</i> , 1985                       |
|              | clam ( <i>Rangia cuneata</i> ): Lake Pontchartrain, Louisiana          | 11–18 ng g <sup>-1</sup> | Ferrario <i>et al.</i> , 1985                       |
|              | marine fish (in a petroleum contaminated harbour, Japan)               | 5 µg g <sup>-1</sup>     | Tsani-Bazaca, <i>et al.</i> , 1981, in Howard, 1991 |
| ethylbenzene | bottom fish  | 100 ng g <sup>-1</sup>   | Nicola, 1987, in Howard, 1990                       |

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## ANNEX 6

### BARCELONA APPEAL

#### Translation

#### ***Caulerpa taxifolia*: Confirmation of a major risk for the coastal ecosystems in the Mediterranean**

For the last ten years the tropical alga *Caulerpa taxifolia* has spread widely in the Mediterranean. In Monaco, the area where it was observed for the first time, and east of the Alpes Maritimes (southeastern part of France), the alga population has reached almost 1,350 hectares. In Italy, near Imperia, 150 hectares are now affected. Outside these areas nearly 15 minor surface stations were discovered (from some tens of m<sup>2</sup> to 1 hectare), but each of these colonies grows at the same rhythm as the ones observed in the first affected sites. These colonies spread along the northern coasts of the Mediterranean, from the Balearic Islands to Sicily. All these remote disseminations are probably due to the fact that these algae are transported via the anchoring systems of yachts and fishing boats. The alga develops on all substrates (rock, sand, mud, water plants) between 1 and 30 metres depth. It was also discovered at 30 to 99 m depth, but in much weaker densities. It adapts to all environmental conditions (in waters far away from any source of pollution as found in harbours), and to all coastal outlines and protected bays. It can survive three months at 10° C. This physiological property is one of the differences that makes it possible to distinguish *Caulerpa taxifolia* introduced to the Mediterranean from that of the *Caulerpa taxifolia* in the tropical seas. Its development and survival in the Mediterranean are consequently not linked to the possible warming up of the waters or of the climate.

The development of the alga continues until it covers the entire substrate. This permanent vegetation rapidly suppresses most of the other algae and affects the water plant Posidonies. The fauna associated with the original vegetation suffers from profound changes such as regression of certain species which then promotes other species. Globally, in the typical Mediterranean ecosystems overrun *Caulerpa taxifolia*, one notices a decline in the biodiversity.

The alga contains toxins which play an adverse role on the herbivorous fauna and which can influence the

spores, the eggs, the micro-flora and the micro-fauna. The ecological impact is increased by the characteristics which dominate this algae.

The above evaluation represents four years of research of which the latest results have been presented to the Second International Seminar on *Caulerpa taxifolia*.

Even though it is not yet possible to foresee all the consequences of the spreading of *Caulerpa taxifolia* on the coastal environment of the Mediterranean. and even if certain hypotheses have not yet been clarified, the present collected data confirm that there is a major risk with regard to the biodiversity, the ecological equilibrium and the exploited resources.

The scientists carry out their research and accept the responsibility to alert the authorities. It is now up to the governments of the countries in question, as well as the international organisations in charge of the environment (PNUE, Barcelona Convention, UICN) to instigate preventive measures (as taken into account by the Rio de Janeiro Convention) and to define a coherent international strategy with regard to the problem in question.

Barcelona, 16 December 1994

This text has been approved by the scientists present during the Plenary Assembly of the Second Seminar on *Caulerpa taxifolia* which took place in Barcelona from 15–17 December 1994.

**Steering Committee of the DG XI Life Programme of the European Union on the "Expansion of the Algae *Caulerpa taxifolia* in the Mediterranean"**

## ANNEX 7

### OVERVIEW OF INTERCALIBRATION/INTERCOMPARISON EXERCISES ON CHEMICAL ANALYSES COORDINATED BY ICES

#### TRACE METALS IN BIOTA

##### First ICES Intercalibration Exercise on Trace Metals in Biological Tissue (1/TM/BT) 1972

Coordinator : G. Topping, United Kingdom.  
Sample : Fish flour prepared from commercial fish meal.  
Metals analysed : Hg, Cu, Zn, Cd and Pb.  
Participation : 8 laboratories from 7 countries around the North Sea.

Results published in *Cooperative Research Report* No. 80 (1978).

##### Second ICES Intercalibration Exercise on Trace Metals in Biological Tissue (2/TM/BT) 1973

Coordinator : G. Topping, United Kingdom.  
Samples : Fish flour prepared from unskinned muscle of inshore cod and acidified solution of metals.  
Metals analysed : Hg, Cu, Zn, Cd and Pb.  
Participation : 15 laboratories in 11 countries around the North Sea and the Baltic Sea.

Results published for Baltic Sea laboratories in *Cooperative Research Report* No. 63 (1977) and for North Sea laboratories in *Cooperative Research Report* No. 80 (1978) and

##### Third ICES Intercalibration Exercise on Trace Metals in Biological Tissue (3/TM/BT) 1975

Coordinator : G. Topping, United Kingdom.  
Samples : (a) Fish flour prepared from skinned muscle of distant water cod, and  
(b) individual reference standard solutions for each metal.  
Metals analysed : Hg, Cu, Zn, Cd and Pb.  
Participation : 29 laboratories in 17 ICES Member Countries.

Results published for Baltic Sea laboratories in *Cooperative Research Report* No. 63 (1977) and for North Sea laboratories in *Cooperative Research Report* No. 80 (1978).

##### Fourth ICES Intercalibration Exercise on Trace Metals in Biological Tissue (4/TM/BT) 1977

Coordinator : G. Topping, United Kingdom.  
Samples : Same fish flour as in 3/TM/BT.  
Metals analysed : Cd and Pb.  
Participation : 12 of the laboratories which had participated in 3/TM/BT.

Results published in *Cooperative Research Report* No. 108 (1981).

**Fifth ICES Intercalibration Exercise on Trace Metals in Biological Tissue**  
(5/TM/BT) 1978

Coordinator : G. Topping, United Kingdom.  
Samples : (a) Fish flour prepared from skinned muscle of distant water cod, and  
(b) the same fish flour extracted to produce a lower Hg concentration.  
Metals analysed : Hg, Cu, Zn, Cd and Pb.  
Participation : 41 laboratories, including those associated with the Joint Monitoring Programme, from all 18 ICES Member Countries plus several laboratories in Australia.

Results published in *Cooperative Research Report* No. 108 (1981).

**Sixth ICES Intercalibration Exercise on Trace Metals in Biological Tissue**  
(6/TM/BT) 1979

Coordinator : G. Topping, United Kingdom.  
Samples : (a) White meat of edible crab freeze-dried and ground into powder,  
(b) commercial fish meal freeze-dried and ground into powder, and  
(c) digestive gland of Canadian lobster treated and ground into powder.  
Metals analysed : Hg, Cu, Zn, Cd and Pb.  
Participation : 52 laboratories from 17 ICES Member Countries plus Australia.

Results published in *Cooperative Research Report* No. 111 (1981).

**Seventh ICES Intercalibration Exercise on Trace Metals in Biological Tissue – Part 1**  
(7/TM/BT-1) 1983

Coordinators : S.S. Berman and V.J. Boyko, Canada.  
Samples : (a) Lobster hepatopancreas homogenized, spray-dried and acetone extracted,  
(b) scallop adductor muscle freeze-dried and ground, and  
(c) plaice muscle freeze-dried and ground.  
Metals analysed : Hg, Cu, Zn, Cd, As and Pb.  
Participation : 51 laboratories from 17 ICES Member Countries.

Results published in *Cooperative Research Report* No. 138 (1986).

**Seventh ICES Intercalibration Exercise on Trace Metals in Biological Tissue – Part 2**  
(7/TM/BT-2) 1985

Coordinators : S.S. Berman and V.J. Boyko, Canada.  
Samples : (a) Cod liver, acetone-extracted and freeze dried,  
(b) dogfish muscle, acetone-extracted and freeze dried,  
(c) dogfish liver, acetone-extracted and freeze dried,  
(d) whole dogfish, spray-dried, and  
(e) *Mytilus edulis* soft material, freeze dried.  
Metals analysed : Hg, Cu, Zn, Cd, As and Pb.  
Participation : 49 laboratories from 16 ICES Member Countries.

Results published in *ICES Cooperative Research Report* No. 189 (1992).



## TRACE METALS IN SEA WATER

### First ICES Intercalibration Exercise for Trace Metals in Sea Water (1/TM/SW) 1976

Coordinator : P.G.W. Jones, United Kingdom.  
Samples : Two standard solutions of metals.  
Metals analysed : Hg, Pb, Ni, Co, Fe, Cr, Cu, Cd, Zn and Mn.  
Participation : 41 laboratories from 14 ICES Member Countries.

Results published in *Cooperative Research Report* No. 125 (1983).

### Second ICES Intercalibration Exercise for Trace Metals in Sea Water (2/TM/SW) 1976

Coordinator : J. Olafsson, Iceland.  
Samples : Two natural sea water samples and a mercury-spiked sea water sample, all acidified.  
Metal analysed : Hg  
Participation : 14 laboratories from 10 ICES Member Countries.

Results published in *Cooperative Research Report* No. 125 (1983).

### Third ICES Intercalibration Exercise for Trace Metals in Sea Water (3/TM/SW) 1977

Coordinator : P.G.W. Jones, United Kingdom.  
Samples : Two frozen samples of filtered sea water, one from open North Sea waters and one from coastal waters.  
Metals analysed : Co, Fe, Ni, Pb, Cd, Cr, Cu, Mn, and Zn.  
Participation : 49 laboratories from 14 ICES Member Countries.

Results published in *Cooperative Research Report* No. 125 (1983).

### Fourth ICES Intercalibration Exercise for Trace Metals in Sea Water (4/TM/SW) 1978

Coordinators : J.M. Bowers, J. Dalziel, P.A. Yeats, and J.L. Barron, Canada.  
Samples : Sets of six sea water samples consisting of four replicate sea water samples, one sample spiked with relevant metals and one dummy. Samples were frozen and acidified.  
Metals analysed : Cd, Cu, Mn, Fe, Ni, Pb, and Zn.  
Participation : 43 laboratories from 13 ICES Member Countries plus Monaco.

Results published in *Cooperative Research Report* No. 105 (1981).

### Fifth ICES Intercalibration Exercise for Trace Metals in Sea Water (5/TM/SW) 1982

Coordinators : J.M. Bowers, P.A. Yeats, S.S. Berman, D. Cossa, Canada; C. Alzieu, P. Courau, France.  
Samples : (a) Sea water samples, filtered and acidified, for analysis of metals except Hg, and  
(b) sea water samples, natural and spiked, for analysis of Hg. In addition, 6 laboratories participated in an intercomparison of filtration procedures for coastal sea water samples.  
Metals analysed : Cd, Cu, Pb, Zn, Ni, Fe, Mn.  
Participation : 59 laboratories from 15 ICES Member Countries plus Monaco.

Results published in *Cooperative Research Report* No. 136 (1986).

**ICES/JMG Intercalibration for Cadmium in Sea Water**  
(ICES/JMG/1/CD/SW) 1979

Coordinator : Y. Thibaud, France.  
Samples : (a) Natural sea water,  
(b) sea water with a low Cd spike, and  
(c) sea water with a high Cd spike.  
Participation : 33 laboratories from all 13 Member Countries of the Oslo and Paris Commissions plus Canada and Monaco.

**ICES/JMG Intercalibration for Mercury in Sea Water**  
(ICES/JMG/1/HG/SW) 1979

Coordinator : J. Olafsson, Iceland.  
Samples : (a) Two samples of natural sea water,  
(b) sea water with a low Hg spike, and  
(c) sea water with a high Hg spike.  
Participation : 36 laboratories from all 13 Member Countries of the Oslo and Paris Commissions plus Canada, Japan, and the United States.

Results of both intercalibration exercises published in *Cooperative Research Report* No. 110 (1981).

**TRACE METALS IN MARINE SEDIMENTS**

**First ICES Intercalibration Exercise for Trace Metals in Marine Sediments**  
(1/TM/MS) 1984

Coordinator : D.H. Loring, Canada.  
Samples : (a) Estuarine calcareous sandy mud sediment,  
(b) harbour sediment, and  
(c) Baltic mud sediment "MBSS" (from Baltic Sediment Intercalibration Exercise).  
Metals analysed : Cd, Cr, Cu, Ni, Pb and Zn.  
Optional metals : Ti, Fe, Mn and Al.  
Participation : 40 laboratories from 11 ICES Member Countries.

Results published in *Cooperative Research Report* No. 143 (1987).

**Baltic Sediment Intercalibration Exercise—Step 1**  
(Reference Samples ABSS and MBSS) 1983

Coordinators : L. Brügmann, German Democratic Republic, and L. Niemistö, Finland.  
Samples : Two mud sediments ("ABSS" and "MBSS") from different locations, dried and homogenized.  
Analytes : Cu, Pb, Zn, Cd, Mn, Fe, Cr, Ni, and organic C.  
Optional : Hg, Co, Al, inorganic C, P and N.  
Participation : 42 laboratories from 15 ICES Member Countries.

Additional Exercise on Hg and Cd, 1985.

Coordinator : A. Jensen, Denmark.  
Samples : Six samples, some of which were pre-treated.  
Metals analysed : Hg and Cd.  
Participation : 8 (Hg) and 10 (Cd) laboratories from 6 countries around the Baltic Sea.

**Baltic Sediment Intercalibration Exercise—Step 2**  
(Sliced Wet Cores) 1984

|               |  |
|---------------|--|
| Coordinators  | : L. Brüggmann, German Democratic Republic, L. Niemistö, Finland, and P. Pheiffer Madsen, Denmark. |
| Samples       | : 20 cm cores, sliced into 1-cm slices and deep frozen.  |
| Main analytes | : Cu, Cr, Zn, Pb, Mn, Cd, Fe, Ni, Al, Co, Hg, dry matter content, dating by Pb-210 technique.      |
| Optional      | : Cs-137, organic C, N, P, clay minerals.  |
| Participation | : 11 laboratories from 6 countries around the Baltic Sea.  |

Results for the entire exercise published in *Cooperative Research Report* No. 147 (1987).

**TRACE METALS IN SUSPENDED PARTICULATE MATTER**

**First ICES Intercomparison Exercise for Trace Metals in Suspended Particulate Matter**  
(1/TM/SM) 1984

|               |   |
|---------------|---|
| Coordinators  | : P. Yeats and J.A. Dalziel, Canada.  |
| Samples       | : Suspended particulate matter collected on pre-weighed 0.4 mm Nuclepore filters. |
| Analytes      | : Al, Fe, Mn, Zn, Cu, Pb, Ni, and Cd.   |
| Participation | : 8 selected laboratories from 7 countries.                                       |

Results published in *J. Cons. int. Explor. Mer*, 43: 272-278 (1987).

**Second ICES Intercomparison Exercise for Trace Metals in Suspended Particulate Matter—Phase 1**  
(2/TM/SM-1) 1989

|               |   |
|---------------|---|
| Coordinators  | : H. Hovind and J. Skei, Norway.  |
| Samples       | : Standard reference materials from the National Research Council of Canada:<br>(a) PACS-1,<br>(b) MESS-1, and<br>(c) BCSS-1, from which participants should weigh out 1, 3, and 5 mg samples for analysis. |
| Analytes      | : Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn.   |
| Participation | : 19 laboratories from 11 countries.  |

Results published in *ICES Cooperative Research Report* No. 184 (1992).

**Second ICES Intercomparison Exercise for Trace Metals in Suspended Particulate Matter—Phase 2**  
(2/TM/SM-2) 1993

|               |   |
|---------------|---|
| Coordinator   | : C. Pohl, Germany.   |
| Samples       | : Suspended particulate matter collected on pre-weighed 0.4 mm Nuclepore filters. |
| Analytes      | : Al, Cd, Cu, Fe, Li, Mn, Ni, Pb, Zn.   |
| Participation | : 24 laboratories from 13 countries.  |

Report on results to be published in *ICES Cooperative Research Report* series.

## ORGANOCHLORINES IN BIOLOGICAL TISSUE

### First ICES Intercalibration Exercise for Organochlorine Residues in Biological Tissue (1/OC/BT) 1972

Coordinator : A.V. Holden, United Kingdom.  
Samples : (a) Natural fish oil, and  
(b) same fish oil spiked with selected organochlorines.  
Analytes : pp'-TDE, pp'-DDE, pp'-DDT, PCBs, dieldrin,  $\gamma$ -HCH  
Participation : 9 laboratories from 7 ICES Member Countries.

Results published in *Cooperative Research Report* No. 80 (1978).

### Second ICES Intercalibration Exercise for Organochlorine Residues in Biological Tissue (2/OC/BT) 1974

Coordinator : A.V. Holden, United Kingdom.  
Samples : (a) unspiked maize oil, and  
(b) same maize oil spiked with selected organochlorines.  
Analytes : pp'-TDE, pp'-DDE, pp'-DDT, PCBs, dieldrin,  $\gamma$ -HCH  
Participation : 30 laboratories from 13 ICES Member Countries.

Results published in *Cooperative Research Report* No. 80 (1978) and, for Baltic laboratories, in *Cooperative Research Report* No. 63 (1977).

### Third ICES Intercalibration Exercise for Organochlorine Residues in Biological Tissue (3/OC/BT) 1978

Coordinator : A.V. Holden, United Kingdom.  
Sample : Fish oil (capelin).  
Analytes : pp'-TDE, pp'-DDE, pp'-DDT, PCBs, dieldrin,  $\alpha$ -HCH,  $\gamma$ -HCH.  
Participation : 30 laboratories from 16 ICES Member Countries.

Results published in *Cooperative Research Report* No. 108 (1978).

### Fourth ICES Intercalibration Exercise for Organochlorine Residues in Biological Tissue (4/OC/BT) 1979

Coordinators : J.F. Uthe and C.J. Musial, Canada.  
Samples : (a) Fish oil prepared from herring muscle tissue and  
(b) same oil spiked with PCBs.  
Analytes : PCBs  
Participation : 23 laboratories from 12 ICES Member Countries.

Results published in *Cooperative Research Report* No. 115 (1982).

**Fifth ICES Intercalibration Exercise for Organochlorine Residues in Biological Tissue**  
(5/OC/BT) 1982

Coordinators : J.F. Uthe and C.J. Musial, Canada.  
Samples : (a) Herring oil, and  
(b) same oil spiked with individual chlorobiphenyls (CBs).  
Analytes : Individual CBs.  
Participation : 30 laboratories.

Results published in *Cooperative Research Report* No. 136 (1986).

**Sixth ICES Intercalibration Exercise for Organochlorine Residues in Biological Tissue**  
(6/OC/BT) 1983

Coordinators : L. Reutergårdh and K. Litzén, Sweden.  
Samples : (a) Standard solution of 12 pure CBs,  
(b) solution of an internal standard, and  
(c) herring oil.  
Analytes : Individual CBs.  
Participation : 12 laboratories.

Results published in *ICES Cooperative Research Report* No. 183 (1992).

**ICES/IOC/OSPARCOM Intercomparison Programme**  
**on the Analysis of Chlorobiphenyls in Marine Media—Step 1**  
(7/OC/BT-1 and 1/OC/MS-1) 1989

Coordinators : J. de Boer, The Netherlands (for ICES), J.C. Duinker, Federal Republic of Germany (for IOC),  
J.A. Calder, United States (for JMG).  
Samples : (a) Standard solution of 10 CBs in iso-octane,  
(b) solution of the 10 CBs in iso-octane at unknown concentration,  
(c) internal standard: octachloronaphthalene in iso-octane, and  
(d) blank: iso-octane.  
Analytes : CB Nos. 28, 31, 52, 101, 105, 118, 138, 153, 180, 189.  
Participation : 57 laboratories from 17 countries.

Results published in *ICES Cooperative Research Report* No. 183 (1992).

**ICES/IOC/OSPARCOM Intercomparison Programme**  
**on the Analysis of Chlorobiphenyls in Marine Media—Step 2**  
(7/OC/BT-2 and 1/OC/MS-2) 1990

Coordinators : J. de Boer, The Netherlands (for ICES), J.C. Duinker, Federal Republic of Germany (for IOC),  
L. Reutergårdh, Sweden, and J.A. Calder, United States (for JMG).  
Samples : (a) Standard solution (in iso-octane) of all CBs to be analysed;  
(b) seal blubber extract in iso-octane;  
(c) sediment extract in iso-octane;  
(d) internal standard solution in iso-octane; and  
(e) blank (iso-octane).  
Analytes : CB Nos. 28, 31, 52, 101, 105, 118, 138, 153, 156, 180.  
Participation : 58 laboratories from 16 countries.

Results published in *ICES Cooperative Research Report* No. 207 (1995).

**ICES/IOC/OSPARCOM Intercomparison Programme  
on the Analysis of Chlorobiphenyls in Marine Media—Step 3a  
(7/OC/BT-3a and 1/OC/MS-3a) 1991**

Coordinator : J. de Boer, The Netherlands.  
Sample : Certified Reference Material CRM 349 cod liver oil (from the Community Bureau of Reference (BCR) of the European Community).  
Analytes : CB Nos. 52, 153, 156.  
Participation : 45 laboratories from 15 countries.

Report on results will be published in the *ICES Cooperative Research Report* series.

**ICES/IOC/OSPARCOM Intercomparison Programme  
on the Analysis of Chlorobiphenyls in Marine Media—Step 3b  
(7/OC/BT-3b and 1/OC/MS-3b) 1992**

Coordinators : J. de Boer and J. van der Meer, The Netherlands.  
Samples : (a) A cleaned and an uncleaned sediment extract;  
(b) a cleaned and an uncleaned seal blubber extract; and  
(c) a standard solution.  
Analytes : CB Nos. 28, 31, 52, 101, 105, 118, 138, 153, 156, 180.  
Participation : 46 laboratories from 15 countries.

Report on results will be published in the *ICES Cooperative Research Report* series.

**ICES/IOC/OSPARCOM Intercomparison Programme  
on the Analysis of Chlorobiphenyls in Marine Media—Step 4  
(7/OC/BT-4 and 1/OC/MS-4) 1993**

Coordinators : J. de Boer and J. van der Meer, The Netherlands.  
Samples : (a) Seal oil,  
(b) sediment,  
(c) Atlantic cod muscle,  
(d) standard solution.  
Analytes : CB Nos. 28, 31, 52, 101, 105, 118, 138, 153, 156, 180.  
Participation : 43 laboratories from 15 countries.

Report on results will be published in the *ICES Cooperative Research Report* series.

**HYDROCARBONS IN MARINE SAMPLES**

**First ICES Intercomparison Exercise on Petroleum Hydrocarbons in Marine Samples  
(1/HC/BT and 1/HC/MS) 1980**

Coordinators : R.J. Law and J.E. Portmann, United Kingdom.  
Samples : (a) Crude oil standard,  
(b) aliphatic fraction of crude oil standard,  
(c) marine sediment, and  
(d) mussel homogenate.  
Analytes : Total hydrocarbons, aliphatic hydrocarbons ( $nC_7$ – $nC_{33}$ ), and several aromatic hydrocarbons.  
Participation : 36 laboratories from 12 ICES Member Countries and Bermuda.

Results published in *Cooperative Research Report* No. 117 (1982).



**ICES/IOC Intercomparison Exercise on Petroleum Hydrocarbons in Biological Tissues**  
(2/HC/BT) 1984

|               |  |
|---------------|--|
| Coordinators  | : J.W. Farrington, A.C. Davis, J.B. Livramento, C.H. Clifford, N.M. Frew, A. Knap, United States.  |
| Samples       | : (a) Three samples of frozen, freeze-dried mussel homogenate,<br>(b) reagent-grade chrysene,<br>(c) methylene chloride solution of n-alkanes,<br>(d) methylene chloride solution of aromatic hydrocarbons, and<br>(e) Arabian Light Crude Oil standard. |
| Analytes      | : Aliphatic hydrocarbons (nC <sub>15</sub> –nC <sub>32</sub> ) and selected aromatic hydrocarbons.   |
| Participation | : 38 laboratories from 13 ICES Member Countries and 12 laboratories from 11 IOC Member Countries (most, if not all, ICES Member Countries are also members of IOC).  |

Results published in *Cooperative Research Report* No. 141 (1986).

**Third ICES Intercomparison Exercise on Polycyclic Aromatic Hydrocarbons in Biological Tissue**  
(3/HC/BT) 1984

|               |  |
|---------------|--|
| Coordinators  | : J.F. Uthe, C.J. Musial, and G.R. Sirota, Canada.   |
| Samples       | : (a) Acetone powder of lobster digestive gland, and<br>(b) the oil extracted during the preparation of this powder. |
| Analytes      | : 21 selected polycyclic aromatic hydrocarbons.  |
| Participation | : 11 laboratories from 7 ICES Member Countries.  |

Results published in *Cooperative Research Report* No. 141 (1986).

**Fourth ICES Intercomparison Exercise on Polycyclic Aromatic Hydrocarbons in Marine Media—Stage 1**  
(2/HC/MS) (4/HC/BT) 1988–1990

|               |  |
|---------------|--|
| Coordinator   | : R.J. Law, United Kingdom.  |
| Samples       | : Solutions of 10 PAHs in acetonitrile (for HPLC analysis), or solutions of 10 PAHs in hexane (for GC analysis).   |
| Analytes      | : Phenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[e]pyrene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, and indeno[123-cd]pyrene. |
| Participation | : 17 laboratories from 9 countries.  |

Report on results published in *ICES Cooperative Research Report* No. 207 (1995).

**NUTRIENTS IN SEA WATER**

**Fourth ICES Intercomparison Exercise for Nutrients in Sea Water**  
(4/NU/SW) 1989

|               |   |
|---------------|---|
| Coordinators  | : D. Kirkwood, United Kingdom, A. Aminot, France, and M. Perttilä, Finland.   |
| Samples       | : (a) Natural oceanic water, with no preservatives or pre-treatment,<br>(b) natural shelf sea water, filtered, bottled in glass and autoclaved, and<br>(c) sea water depleted in nitrate and phosphate, then filtered and bottled (blanks for nitrate and phosphate). |
| Analytes      | : Nitrate + nitrite, phosphate, silicate, nitrite, ammonia, total nitrogen and total phosphorus.  |
| Participation | : 68 laboratories from all 18 ICES Member Countries.  |

Report on the results published in *ICES Cooperative Research Report* No. 174 (1991).

**Fifth ICES Intercomparison Exercise for Nutrients in Sea Water**  
(5/NU/SW) 1993

Coordinators : D. Kirkwood, United Kingdom, and A. Aminot, France.  
Samples : Six samples of sea water (three for nitrate + nitrite determinations and three for ammonium and phosphate determinations).  
Analytes : Nitrate + nitrite, ammonium, phosphate.  
Participation : 132 laboratories from 31 countries.

Report on results will be published in the *ICES Cooperative Research Report* series.

## ANNEX 8

## ACME/ACMP ADVICE BY TOPIC FOR THE YEARS 1984–1995

Numbers in the table refer to sections of the present report and of the ACMP or ACME reports from 1984 to 1995, in reverse chronological order.

\*Signifies major advice on that topic.

| Topic      | Sub-topic                                   | 1995 | 1994          | 1993           | 1992         | 1991 | 1990    | 1989    | 1988           | 1987 | 1986 | 1985 | 1984   |
|------------|---|------|---------------|----------------|--------------|------|---------|---------|----------------|------|------|------|--------|
| Monitoring | Strategy                                    | 5.1  | *4<br>*Ann. 1 | 5              | 5.1          |      |         |         | *4             |      |      |      |        |
|            | Programme evaluation                        |      | 4.2           |                |              |      |         |         |                |      |      |      |        |
|            | Multi-purpose                               |      |               |                |              |      | 6.2     |         |                |      |      |      |        |
|            | Benthos                                     |      |               |                | 8<br>*Ann. 6 | 8.1  | 9       | *Ann. 1 | *7.1           | 8    |      |      |        |
|            | NSTF/MMP                                    |      |               | 5.2            |              |      | 9.3     | 4       |                |      |      |      |        |
|            | Sediments/guidelines                        |      | 5.5           | 6.1<br>*Ann. 1 |              |      |         | *14     |                |      | 15   |      | *Ann.2 |
|            | Sediment data normalization                 |      | 5.5           |                |              |      |         | *14.1   | 14.1           | 15.2 | 16   |      |        |
|            | Sediment sensitivity, variance factors      | 5.6  |               |                |              |      |         |         | 14.6<br>Ann. 2 |      |      |      |        |
|            | Metals/sediments                            | 5.6  | 5.5           |                |              |      |         |         | 12.6           |      |      |      |        |
|            | Matrix tables                               |      |               |                |              |      |         |         |                |      |      |      |        |
|            | •general (JMP)                              |      |               |                |              |      | *Ann. 1 | *6.1    | 4              |      |      |      |        |
|            | •organic                                    |      |               |                |              |      | 6.1     |         |                |      |      |      |        |
|            | •NSTF                                       |      |               |                |              |      | 6.1     |         |                |      |      |      |        |
|            | Use of seaweeds                             |      | 5.1           |                |              |      | 6.8     | 6.3     |                |      |      |      | 4.6    |
|            | Spatial monitoring                          | 5.3  | 5.1           |                |              |      |         |         |                |      |      |      |        |
|            | Organic contaminants in biota and sediments | 6.6  | 6.8           |                |              |      |         |         |                |      |      |      |        |
|            | JAMP/JMP guidelines                         | 5.4  |               |                | 13.3         |      |         |         |                |      | 4.5  |      |        |
|            | BMP guidelines                              | 5.4  |               | 5.3            |              |      |         |         |                | *12  | 4.4  |      |        |
|            | AMAP  |      | 5.4           |                |              |      |         |         |                |      |      |      |        |
|            | Effects of nutrient enrichment              | 5.8  |               |                |              |      |         |         |                |      |      |      |        |

| Topic  | Sub-topic                | 1995           | 1994          | 1993           | 1992    | 1991 | 1990          | 1989  | 1988          | 1987       | 1986           | 1985 | 1984 |
|--|--------------------------|----------------|---------------|----------------|---------|------|---------------|-------|---------------|------------|----------------|------|------|
| Temporal trend monitoring                        | Strategy                 |                | *4<br>*Ann. 1 |                |         |      |               |       |               |            |                |      |      |
|  | Guidelines               |                | 4<br>5.2      |                |         |      |               |       | 5.2           | 6.2<br>6.3 | *4.1<br>Ann. 1 | 4.1  | 4.5  |
|  | Data analysis            |                | 5.2           | 6.2            | 5.2     |      |               |       |               |            |                |      |      |
|  | Nutrients                |                |               | 6.3            |         |      |               |       | 11.1          |            |                |      |      |
|  | Fish/JMP                 |                |               |                |         | 5.1  | 6.2           |       |               |            | Ann. 1         |      |      |
|  | Fish/CMP                 |                |               |                |         | 5.1  | 6.5           | *6.4  | 5.1           | 6.1        | Ann. 1         | 4.2  | 4.1  |
|  | Biota/BMP                | 7.3            |               |                |         |      |               |       |               |            |                |      |      |
|  | Mussels                  |                |               |                |         | 5.1  | *Ann. 3       |       |               | 6.3        |                |      |      |
|  | Pooling                  |                |               |                |         |      | 6.7<br>Ann. 5 | 6.4.3 |               | 6.2.1      |                |      |      |
|  | Precision                |                | 5.2           |                | *Ann. 1 |      |               | 6.4.4 |               |            |                |      |      |
|  | Sediment storage         |                |               |                |         |      |               |       | 14.2          |            |                |      |      |
|  | Sea water                |                |               |                |         |      | 6.6           |       |               | 6.5        | 4.2            |      |      |
|  | Sediments                |                |               |                |         |      |               |       | 5.3<br>Ann. 2 | 6.5        | 4.2            |      |      |
|  | Statistical requirements | 4.3            |               |                |         |      |               |       |               |            |                |      |      |
| Integration of<br>biol./chemical<br>measurements | Sediment quality         | 4.2<br>Ann. 2  | 5.4           | 6.4<br>*Ann. 2 |         |      |               |       |               |            |                |      |      |
| Biological effects                               | Monitoring strategy      | 4.1<br>*Ann. 1 |               |                |         |      |               |       |               |            |                | 5    | 5.1  |
|  | Concepts                 |                |               |                |         |      |               | *7.1  |               |            |                |      |      |
|  | Methods                  | Ann. 1         |               |                | 6.2     | 7.2  |               |       |               |            |                |      |      |
|  | Molecular techniques     | *5.2           |               |                |         |      |               |       |               |            |                |      |      |
|  | Pathology                | 8.4            | 9.4           |                |         |      |               |       |               |            | 5.1            |      |      |
|  | Workshop results         |                |               |                | 6.1     | 7.1  | 8.1           | 7.2   | 6             |            | 5.2            |      | 5.2  |
|  | Fish egg bioassays       |                |               |                |         |      |               |       |               |            | 5.3            |      |      |
|  | Data analysis            |                |               |                |         |      |               |       |               |            |                |      |      |
|  | • general                |                |               |                | 6.3     |      |               |       |               |            |                |      |      |
|  | • EROD                   |                |               |                | *Ann. 2 |      |               |       |               |            |                |      |      |
|  | • oyster bioassay        |                |               |                | *Ann. 2 |      |               |       |               |            |                |      |      |

| Topic                | Sub-topic                            | 1995 | 1994 | 1993 | 1992 | 1991  | 1990   | 1989  | 1988  | 1987  | 1986  | 1985  | 1984        |
|----------------------|--------------------------------------|------|------|------|------|-------|--------|-------|-------|-------|-------|-------|-------------|
| Mariculture          | Interactions                         | 14   | 13   |      | 9.1  |       | *11    | 10    | 9     | 10    | 10    |       |             |
|                      | Nutrient inputs/Baltic               |      |      |      | *9.2 |       | 11.1   | 10.4  |       |       |       |       |             |
|                      | Drug use control                     |      |      |      |      |       | Ann. 6 |       |       |       |       |       |             |
| Algal blooms         | Primary production methods           |      |      | 6.5  | 11   | 11.1  | 12.1   |       | 10.2  |       |       |       |             |
|                      | Initiating factors                   |      |      |      |      | *11.3 | 12.2   |       |       |       | 8     |       |             |
|                      | Dynamics                             |      | 8    | 10   |      |       |        |       |       |       |       |       |             |
|                      | Exceptional blooms                   |      |      |      |      | 11.2  |        |       |       |       | 8     | *8    | 9           |
|                      | Phycotoxins/measurements             |      |      |      |      | 11.4  | 12.3   |       | 10.1  |       | 9     |       |             |
|                      | <i>C. polylepis</i> bloom            |      |      |      |      |       |        | *11.1 | 10.3  |       |       |       |             |
| Regional assessments | Guidelines                           |      |      |      |      |       | 5      |       | *20.1 |       |       |       |             |
|                      | Preparation plans                    |      |      |      |      |       |        | 5     |       | 21.4  |       | 10    | 10          |
|                      | Irish Sea                            |      |      |      |      |       |        |       |       | *21.1 | 24.2  |       |             |
|                      | Skagerrak/Kattegat                   |      |      |      |      |       |        |       |       | 21.2  | 24.1  |       |             |
|                      | North Sea QSR                        |      |      | 4.1  | 4    | 4     | 5      |       |       | 21.3  | 23    |       |             |
|                      | Baltic Sea                           | 7.2  | 7.3  |      |      |       |        | 5     |       |       |       |       |             |
|                      | Baltic fish                          | 7.2  | 7.3  |      |      |       | 17.2   | 17.3  |       |       |       |       |             |
|                      | Canadian waters                      |      |      |      |      | 16    |        |       |       |       |       |       |             |
|                      | Nutrient trends<br>•North Atlantic   |      |      |      |      |       | 13     | 12    |       | 16.1  |       |       |             |
| Baseline studies     | 1985 Fish baseline                   |      |      |      |      |       |        |       |       | *4    | 4.3.1 |       | 4.2<br>11.4 |
|                      | 1985 Baseline plans                  |      |      |      |      |       |        |       |       |       |       |       | Ann. 9      |
|                      | ICES Baseline TM/SW                  |      |      |      |      | 6     | *7     | 6.5   | 13    | 5     | 4.3.2 | 7.2.1 | 4.3         |
|                      | Contaminants in<br>•Baltic sediments | 7.1  | 7.1  | 8.1  | 13.2 | 14.1  | 15.1   |       |       | 15.1  |       |       |             |
|                      | •North Sea sediments                 |      |      |      | 13.1 |       |        |       |       |       |       |       |             |
|                      | HCH in sea water                     |      |      |      | 14   |       |        |       |       |       |       |       |             |

| Topic                            | Sub-topic                                      | 1995              | 1994   | 1993   | 1992   | 1991   | 1990   | 1989   | 1988   | 1987 | 1986 | 1985   | 1984 |
|----------------------------------|--|-------------------|--------|--------|--------|--------|--------|--------|--------|------|------|--------|------|
| Fish diseases and related issues | Relation to pollution                          | 8.4               | 9.4    |        |        | 9.1    |        | 9.3    |        |      | 5.1  | 6.2    | 5.4  |
|                                  | Survey methods                                 |                   |        |        |        | 9.2    |        |        | 8.2    |      |      |        | 5.3  |
|                                  | Training guide                                 |                   |        |        |        |        | 10     |        |        |      |      |        |      |
|                                  | Baltic fish                                    | 8.1<br>8.2<br>8.3 | 9.3    |        |        |        |        |        |        |      |      |        |      |
|                                  | Survey results                                 |                   |        |        |        |        |        | 9.1    | 8.1    | 9    | 6    | 6.1    |      |
|                                  | Data analysis                                  |                   | 9.5    | 9.4    | 7      |        |        |        |        |      |      |        |      |
|                                  | M-74 in Baltic salmon                          | 7.4               | 9.1    |        |        |        |        |        |        |      |      |        |      |
| Quality assurance                | Philosophy                                     |                   |        |        |        | 13.6   |        |        |        |      |      |        |      |
|                                  | Good laboratory practice                       |                   |        |        |        |        |        |        |        | 13.5 | 11.5 | Ann. 1 |      |
|                                  | Reference materials                            |                   | *6.9   | 7.11   |        |        |        | 13.1   | 12.8   |      | 11.4 | 7.3    |      |
|                                  | Oxygen in water                                |                   |        |        |        |        | 14.5   | 13.6   |        |      |      |        |      |
|                                  | Quality/comparability<br>•organic contaminants | *6.6              | *6.8   |        |        |        |        |        |        |      |      |        |      |
|                                  | Hydrocarbons                                   |                   |        |        |        |        |        | 13.7   |        |      |      |        |      |
|                                  | Lipids   | 6.4               | 6.5    |        |        |        |        |        |        |      |      |        |      |
|                                  | NSTF   |                   |        |        |        |        | 14.7   |        |        |      |      |        |      |
|                                  | Biological effects<br>techniques               | 6.2               |        | 7.1    |        | 7.3    |        |        |        |      |      |        |      |
|                                  | Sediment quality criteria                      |                   |        |        |        |        | 15.2   | 22.2   |        |      |      |        |      |
|                                  | QA of sampling                                 |                   |        |        | *12.8  |        |        |        |        |      |      |        |      |
| Intercalibrations                | QA info. in data bank                          |                   | 6.10   |        |        |        |        |        |        |      |      |        |      |
|                                  | Status   | Ann. 7            | Ann. 6 | Ann. 5 | Ann. 8 | Ann. 3 | Ann. 9 | Ann. 2 | Ann. 3 |      |      |        |      |
|                                  | Nutrients/sea water                            | 6.5               | 6.6    | 7.8    | 12.4   |        | 14.1   | 13.4   | 11.3   | 16.2 | 19   |        |      |
|                                  | Lindane ( $\gamma$ -HCH)                       |                   |        |        |        |        |        |        |        |      | *13  |        |      |
|                                  | Specific hydrocarbons                          |                   |        |        |        |        |        |        |        | 13.3 | 11.1 | 7.1.2  |      |
|                                  | Hydrocarbons in<br>•biota                      | 6.7               |        |        |        |        |        | 13.7   |        |      |      | 7.1.2  | 6.5  |
|                                  | •sediments                                     |                   |        |        |        |        |        | 13.7   |        |      |      |        |      |
|                                  | •sea water                                     |                   |        |        |        |        |        | 13.7   |        |      | *12  | 7.1.2  |      |
|                                  | PAHs/standards                                 |                   |        |        | 12.2   | 13.1   | 14.2   | 13.2   | 12.1   |      |      |        |      |



| Topic                        | Sub-topic                         | 1995       | 1994       | 1993           | 1992            | 1991 | 1990  | 1989  | 1988           | 1987  | 1986             | 1985         | 1984         |
|------------------------------|-----------------------------------|------------|------------|----------------|-----------------|------|-------|-------|----------------|-------|------------------|--------------|--------------|
| Intercalibrations<br>(cont.) | PCBs/CBs in biota                 | 6.6<br>6.7 | 6.3<br>6.4 | 7.5            | 12.1            | 13.2 |       |       | 12.3           |       |                  | 7.1.1        |              |
|                              | Organochlorines in biota          | 6.6<br>6.7 |            |                |                 |      |       |       |                |       |                  |              | 6.4          |
|                              | CBs/standards                     |            |            |                |                 |      | 14.3  | 13.3  | 12.2           |       | 14               |              |              |
|                              | CBs in sediments                  | 6.6        | 6.3        | 7.5            |                 | 13.2 |       |       |                | 14    | 14               |              |              |
|                              | Metals in<br>• sea water          |            |            |                |                 |      |       |       |                | 13.1  |                  | 7.2.2        | 6.2          |
|                              | • sediments                       |            |            |                |                 |      |       |       | 12.5           |       | 11.2.1<br>11.2.2 | 7.2.4<br>7.4 | 6.3          |
|                              | • biological tissue               |            |            |                |                 |      |       |       |                | 13.2  |                  | 7.2.1        | 6.1          |
|                              | • SPM                             |            | 6.7        | 7.9            | 12.3            | 13.3 | 14.4  | 13.5  | 14.4<br>Ann. 1 |       | 18.2             | 7.2.3        |              |
|                              | Baltic sediment                   |            |            |                |                 |      |       |       |                |       |                  | 7.4          | 11.3         |
|                              | Dissolved oxygen in<br>sea water  |            |            |                | 12.5            | 13.4 | *14.5 |       |                |       |                  |              |              |
|                              | Methyl Hg in<br>biological tissue |            |            |                |                 |      |       |       | 12.4           | 13.4  |                  |              |              |
|                              | Primary production                |            |            |                |                 |      |       |       | 10.2           |       |                  |              |              |
|                              | Oyster embryo bioassay            |            |            |                | Ann. 4          |      |       |       |                |       |                  |              |              |
|                              | EROD                              |            |            |                | 12.6<br>*Ann. 3 |      |       |       |                |       |                  |              |              |
| Marine mammals               | Contaminants/effects              |            |            |                |                 |      |       |       |                | *11.1 | 7.2              |              |              |
|                              | Seal epidemic 1988                |            |            |                |                 |      | *18   | *18.1 |                |       |                  |              |              |
|                              | Baltic seal stocks                |            | 10.2       |                | *18             |      |       |       |                | 11.3  | *7.1             |              | 12<br>Ann. 8 |
|                              | Populations/N. Atlantic           |            | 10.1       | 11.1           | *18             | 18   |       |       |                |       |                  |              |              |
|                              | Pathogens                         |            |            | 11.2<br>Ann. 3 |                 |      |       |       |                |       |                  |              |              |

| Topic                               | Sub-topic                          | 1995            | 1994 | 1993 | 1992 | 1991 | 1990  | 1989  | 1988 | 1987  | 1986  | 1985  | 1984    |
|-------------------------------------|------------------------------------|-----------------|------|------|------|------|-------|-------|------|-------|-------|-------|---------|
| Classification/<br>assessment tools | Human health                       |                 |      |      |      |      | 19    |       |      |       |       |       |         |
|                                     | Hazardous substances               | 12.3            |      |      | *15  |      |       |       |      |       |       |       |         |
|                                     | Background concentrations          | 12.1            |      |      |      |      |       |       |      |       |       |       |         |
|                                     | Ecotoxicological reference values  | 12.2            |      |      |      |      |       |       |      |       |       |       |         |
| Overviews                           | Arsenic                            |                 |      |      |      |      |       |       |      | *17.2 |       |       |         |
|                                     | Mercury                            |                 |      |      |      |      |       | *19.1 |      |       |       |       |         |
|                                     | Zinc                               |                 |      |      |      |      |       |       |      |       |       |       | *Ann. 7 |
|                                     | HCB                                |                 |      |      |      |      | *20.1 |       |      |       |       |       |         |
|                                     | Lindane ( $\gamma$ -HCH)           |                 |      |      |      |      | *20.1 |       |      |       |       |       |         |
|                                     | Benzene/<br>alkylated benzenes     | 10.2<br>*Ann. 5 |      |      |      |      |       |       |      |       |       |       |         |
|                                     | Chlorinated alkanes                | 10.1<br>Ann. 4  |      |      |      |      |       |       |      |       |       |       |         |
|                                     | PCDDs and PCDFs                    |                 |      |      |      |      |       | *19.2 |      |       |       |       | Ann. 4  |
|                                     | PAHs                               |                 |      |      |      |      |       |       |      |       | *20.2 |       |         |
|                                     | Phthalate esters                   |                 |      |      |      |      |       |       |      |       |       | *13.2 |         |
|                                     | Organo-tin and -lead               |                 |      |      |      |      |       |       |      |       |       |       | *Ann. 5 |
|                                     | Polychlorinated<br>terphenyls      |                 |      |      |      |      |       |       |      |       |       |       | *Ann. 6 |
|                                     | Octachlorostyrene                  |                 |      |      |      | 20.1 |       |       |      |       |       |       |         |
|                                     | Toxaphene                          |                 | 12.3 |      |      |      |       |       |      |       |       |       |         |
|                                     | Atrazine                           |                 | 12.1 |      |      |      |       |       |      |       |       |       |         |
| Sand/gravel<br>extraction           | Code of Practice                   |                 |      |      |      |      | 16    |       |      |       |       |       |         |
|                                     | Effects                            |                 |      |      |      | 15   | 16    | 15    | 15   |       |       |       |         |
|                                     | Environmental impact<br>assessment | *15             | *15  | 13   |      |      |       |       |      |       |       |       |         |

| Topic          | Sub-topic   | 1995          | 1994 | 1993          | 1992  | 1991         | 1990   | 1989 | 1988    | 1987   | 1986 | 1985 | 1984          |
|----------------|---|---------------|------|---------------|-------|--------------|--------|------|---------|--------|------|------|---------------|
| Methods        | SPM in sea water  |               |      |               |       |              |        |      |         |        | 18.1 |      |               |
|                | Trace metals in SPM   |               |      |               |       |              |        |      |         |        | 18.2 |      |               |
|                | Total nitrogen  |               |      |               |       |              |        |      |         |        | 19.4 |      |               |
|                | Nutrients in sea water  |               |      |               |       |              |        | 13.5 | *Ann. 4 |        | 19   |      |               |
|                | Low DO in sea water   |               |      |               |       |              |        |      |         | 13.6   |      |      |               |
|                | Sediment normalization  |               | 5.5  |               |       | 14.2<br>14.3 |        |      |         | *14.1  | 14.1 | 15.2 | 16            |
|                | Analysis of total OCs   |               |      |               |       |              |        |      |         |        | 12.7 |      |               |
| Modelling      | Radioactive contaminants/Baltic Sea                                   |               |      |               | *17.1 |              |        |      |         |        |      |      |               |
|                | Use in monitoring and assessment                                      |               | 16   |               | 17.2  |              |        |      |         |        |      |      |               |
| Special topics | Context of ACMP advice  |               |      |               |       |              | Ann. 7 | *21  |         | 22     | 25   |      |               |
|                | Patchiness in Baltic Sea  |               |      |               |       |              |        | 17.1 | 19.1    | 20.1   | 22.1 | 12.1 | 11.1          |
|                | Nutrient trends in OSPAR area   |               |      |               |       |              | 13     | 12   | 11.1    | 16.1   |      |      |               |
|                | Nutrients and eutrophication  | 5.8           |      | 6.3           | 10    | *11.3        |        |      | 10.4    |        |      |      |               |
|                | Sediments<br>• Baltic<br>• German Bight<br>• Kattegat<br>• Skaggeerak | 7.1           | 7.1  |               |       | 14.1         | 15.1   | 14.2 | 19.3    | 15.1   | 22.2 | 12.2 | 7.4.3         |
|                |   |               |      |               |       |              |        |      |         | Ann. 1 |      |      | 7.4.2         |
|                |   |               |      |               |       |              |        |      |         | Ann. 2 |      |      |               |
|                |   |               |      |               |       |              |        |      |         |        |      |      | 7.4.1         |
|                | Sediments<br>• bioavailability  | 4.2<br>Ann. 2 | 5.4  | 6.4<br>Ann. 2 |       | 7.4          |        | 7.3  |         |        | 17   |      |               |
|                |   |               |      |               |       |              |        |      |         |        |      |      |               |
|                | • release of contaminants   |               |      |               |       |              |        | 14.3 |         |        |      |      |               |
|                | Effects of low-level HCs  |               |      |               |       |              |        |      |         |        |      | *9   |               |
|                | Oxidation products of HCs   |               |      |               |       |              |        |      |         |        |      |      | 14.6          |
|                | Effects of TiO <sub>2</sub> wastes                                    |               |      |               |       |              |        |      |         |        |      |      | *8<br>Ann. 10 |
|                | Acid rain studies/effects   |               |      |               |       |              |        | 20   | 17      | 19     |      |      |               |
|                | Coastal zone fluxes   |               |      | 8.2           |       |              |        |      |         |        |      |      |               |

| Topic                          | Sub-topic                            | 1995        | 1994           | 1993 | 1992    | 1991 | 1990 | 1989 | 1988 | 1987            | 1986 | 1985 | 1984    |
|--------------------------------|--------------------------------------|-------------|----------------|------|---------|------|------|------|------|-----------------|------|------|---------|
| Special topics<br>(cont.)      | Riverine inputs                      |             |                |      |         |      |      |      |      |                 |      |      |         |
|                                | • gross                              |             |                |      |         |      |      |      | 16.1 | 18.2            |      | 14   | *Ann. 1 |
|                                | • net                                |             |                |      |         |      |      | 16   | 16.2 | 18.3            | 21   |      | *Ann. 1 |
|                                | Inflow to Baltic                     |             |                | 8.3  |         |      |      |      |      |                 |      |      |         |
|                                | Atmospheric inputs                   |             |                |      |         |      |      |      | 16.3 | 18.1<br>*Ann. 3 |      |      |         |
|                                | Effects of disturbance on<br>benthos | 9<br>Ann. 3 | 11.1           |      | 8.3     | 8.2  |      |      |      |                 |      |      |         |
|                                | Ecosystem effects of<br>fishing      |             | 18             |      | *19     | 19   |      |      |      |                 |      |      |         |
|                                | Seabird/fish interactions            |             | 19             |      |         |      |      |      |      |                 |      |      |         |
| Data banks and<br>management   | North Sea Benthos<br>Survey          | 9           |                |      | *Ann. 5 |      |      |      |      |                 |      |      |         |
|                                | Nutrients                            |             |                |      |         |      |      |      |      |                 | 19.5 |      |         |
|                                | Contaminants                         | 17          | 2.2            | 2.2  |         |      |      |      |      |                 |      | 4.3  |         |
|                                | NSTF                                 |             |                |      | 20      | *21  | 22   |      |      |                 |      |      |         |
|                                | ICES format                          |             |                |      |         |      |      |      |      |                 | 4.6  |      | 4.7     |
|                                | ICES databases                       |             |                | 14   |         |      |      |      |      |                 |      |      |         |
| Introductions and<br>Transfers | Benthos database                     |             | 11.2<br>Ann. 4 |      |         |      |      |      |      |                 |      |      |         |
|                                | Code of Practice                     | 13.1        | 14.1           | 12.1 |         |      |      |      |      |                 |      |      |         |
|                                | Accidental transfers                 | 13          | 14.2           | 12.3 |         |      |      |      |      |                 |      |      |         |
|                                | Genetically modified<br>organisms    |             |                | 12.2 |         |      |      |      |      |                 |      |      |         |

## ANNEX 9

### RELEVANT VOLUMES OF RECENTLY PUBLISHED ICES COOPERATIVE RESEARCH REPORTS

| No. | Title   |
|-----|---|
| 177 | Report of the ICES Advisory Committee on Marine Pollution, 1991   |
| 178 | A Review of Measurements of Trace Metals in Coastal and Shelf Sea Water Samples Collected by ICES and JMP Laboratories during 1985–1987   |
| 180 | Review of Contaminants in Baltic Sediments  |
| 181 | Effects of Harmful Algal Blooms on Mariculture and Marine Fisheries   |
| 182 | Effects of Extraction of Marine Sediments on Fisheries  |
| 183 | Report on the Results of the ICES/IOC/OSPARCOM Intercomparison Exercise on the Analysis of Chlorobiphenyl Congeners in Marine Media–Step 1, and the Intercomparison Study of the Determination of CBs in Herring Oil  |
| 184 | Report of the Second ICES Intercomparison Exercise on the Determination of Trace Metals in Suspended Particulate Matter   |
| 186 | Report on the Eighth Dialogue Meeting, 13–14 September 1991   |
| 189 | ICES Seventh Round Intercalibration for Trace Metals in Biological Tissue, ICES 7/TM/BT (Part 2)  |
| 190 | Report of the ICES Advisory Committee on Marine Pollution, 1992   |
| 194 | Atlas of North Sea Fishes   |
| 197 | Ninth Dialogue Meeting–“Atlantic Salmon: A Dialogue”  |
| 198 | Report of the ICES Advisory Committee on Marine Environment, 1993   |
| 200 | Report of the Study Group on Ecosystem Effects of Fishing Activities  |
| 201 | Patchiness in the Baltic Sea (Symposium proceedings, Mariehamn, 1991)   |
| 202 | Chemicals Used in Mariculture   |
| 203 | Joint Report of the ICES Advisory Committee on Fishery Management and the Advisory Committee on the Marine Environment  |
| 204 | Report of the ICES Advisory Committee on Marine Environment, 1994   |
| 207 | Report on the Results of the ICES/IOC/OSPARCOM Intercomparison Programme on the Analysis of Chlorobiphenyls in Marine Media–Step 2, and the Intercomparison Programme on the Analysis of PAHs in Marine Media–Stage 1 |
| 208 | Results of the 1990/1991 Baseline Study of Contaminants in North Sea Sediments (Edited by S.M. Rowlett and I.M. Davies)   |
| 209 | Underwater Noise of Research Vessels: Review and Recommendations (Edited by R.B. Mitson)  |

