#### **COOPERATIVE RESEARCH REPORT**

#### **RAPPORT DES RECHERCHES COLLECTIVES**

NO. 177

### **REPORT OF THE ICES ADVISORY COMMITTEE ON MARINE POLLUTION, 1991**

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The Advisory Committee on Marine Pollution (ACMP) was established by the International Council for the Exploration of the Sea with the task of formulating, on behalf of the Council, scientific advice on marine pollution and its effects on living resources to the Member Governments and to Regulatory Commissions. In its work, the ACMP considers, among other things, the results of work carried out in relevant ICES Working Groups (which also report to their respective Standing Committees during the annual Statutory Meetings). It is a firm procedure within the Council that reports of other subsidiary bodies concerned with pollution pass the ACMP.

The ACMP consists of a number of scientists acting - when they work as Committee members - in their personal capacity as scientists, responsible only to the Council. The membership of the Committee is such that it covers a wide range of expertise related to studies of marine pollution. The members do not act as national representatives. The 1990 membership of the Committee is found on page 1.

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## **REPORT OF THE ADVISORY COMMITTEE ON MARINE POLLUTION, 1991**

#### LIST OF MEMBERS

Dr G. Topping	- Chairman
Dr V. Dethlefsen	- Chairman of the Marine Environmental Quality Committee
Dr (Ms) K. Richardson	- Chairman of the Biological Oceanography Committee
Dr HJ. Brosin	- Chairman of the Hydrography Committee
Prof. H. Ackefors	- Chairman of the Mariculture Committee
Prof. C. Hopkins	- Chairman of the Shellfish Committee

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Dr E. Andrulewicz Dr B.A. Bannink Dr. J.M. Bewers Mr R.G.V. Boelens Dr (Ms) M. Estrada Mr M. Joanny Dr (Ms) J. McDowell Capuzzo Dr S. Patin Dr J.E. Portmann Dr O. Svanberg Prof. R. Wollast

Dr (Ms) J.F. Pawlak, ICES Environment Officer Secretary to the Advisory Committee on Marine Pollution

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#### **OVERVIEW OF THE 1991 ACMP REPORT**

The ACMP report is addressed mainly to the questions posed to ICES by the regulatory Commissions of the Helsinki, Oslo and Paris Conventions. The Executive Summary that follows this overview provides a summary of the report, under three sub-headings, for the Oslo and Paris Commissions broadly corresponding with the groupings under which they record their requests, and a single sub-heading relating to the requests specifically raised by the Helsinki Commission. There is an additional sub-heading for all Commissions relating to items of interest which do not form part of any request.

The Executive Summary is followed by a more detailed report on the progress made in relation to the specific questions raised by the three Commissions. This is intended to direct the reader to the sections of the report likely to be of most interest in relation to a particular question.

It will be noted that in a number of cases the advice or information goes beyond that specifically requested by the Commissions. This additional material is provided, in part, simply for the sake of completing the picture so far as it is practicable at this point in time. As such, it will be of benefit to the wider audience within ICES that ACMP is also expected to advise. It is, however, hoped that the regulatory Commissions will find this material of interest, since it is directly related to the questions they have raised.

#### **Definitions of Terms Used in this Report**

The following terms, used repeatedly throughout this report, are often interpreted in other documents in different ways. For the sake of clarification, in this report the terms should be interpreted as follows:

<u>Pollution</u> - means the introduction by Man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water and reduction of amenities.

<u>Contamination</u> - is used to describe the situation which exists where either the concentration of a natural substance (e.g., a metal) is clearly above normal, or the concentration of a purely man-made substance (e.g., DDT) is readily detectable, but where no judgement is passed as to the existence of pollution (i.e., adverse effects).

<u>Monitoring</u> - is the repeated measurement of an activity or of a contaminant or of its effects, whether direct or indirect, in the marine environment. It may be undertaken either for compliance purposes or with the objective of establishing patterns and trends or for research purposes.

<u>Eutrophication</u> - *sensu stricto* means nutrient enrichment and ACMP uses the term in this context. However, it should be noted that a number of potential effects of eutrophication (for example, increased primary production) are often popularly referred to as "eutrophication".

A full list of acronyms, other than those for the working groups which are given on the first page of the Executive Summary, is given on the final page of this report.

#### **EXECUTIVE SUMMARY**

This Executive Summary provides a brief outline of progress on the work requested by the regulatory Commissions.

The work requested by the Commissions comprises some items that can be completed in a single year, some that require a number of years to prepare an in-depth and authoritative response, and others that require continuing review in the light of improvement in scientific understanding. The annual ICES work programme, therefore, contains some tasks that are carried over from previous years and others that are new. The ACMP report contains both completed responses to individual questions and progress reports on issues receiving longer-term study. Where appropriate, the latter issues are amplified in detailed technical annexes to the report.

At its 1991 meeting, the ACMP considered, inter alia, the most recent reports of the following ICES groups:

SGEEFA	Study Group on Ecosystem Effects of Fishing Activities
SGSSC	Study Group on Seals and Small Cetaceans in Northern European Seas
BEWG	Benthos Ecology Working Group
WGPDMO	Working Group on Pathology and Diseases of Marine Organisms
WGBEC*	Working Group on Biological Effects of Contaminants
SGBSCMS*	Study Group on the Biological Significance of Contaminants in Marine Sediments
MCWG*	Marine Chemistry Working Group
WGMS*	Working Group on Marine Sediments in Relation to Pollution
WGBME*	Working Group on the Baltic Marine Environment
SGCBS	Steering Group for the Coordination of a Baseline Study of Baltic Sediments
WGSSO	Working Group on Shelf Seas Oceanography
WGPME*	Working Group on Phytoplankton and the Management of their Effects
WGSATM*	Working Group on the Statistical Aspects of Trend Monitoring
WGEEMSF	Working Group on the Effects of Extraction of Marine Sediments on Fisheries

\*These groups report directly to ACMP.

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#### Work Requests from the Oslo and Paris Commissions (OSPARCOM)

A brief statement of the progress made by ACMP on the individual tasks requested by the Commissions is given in <u>Section 2</u> of this report, together with the reference to the section of the report which provides a detailed report on the task.

A summary of the progress made on these tasks is presented below under three broad headings - "General Monitoring Issues", "Continuing Responsibilities" and "Specific Issues".

#### **General Monitoring Issues**

A report on the assessment of temporal trends in the concentrations of contaminants in fish liver and mussels was completed during 1990 and published as ICES Cooperative Research Report No. 176 (1991). This report supplements the earlier report on temporal trends in concentrations of contaminants in fish muscle, which was published as Cooperative Research Report No. 162 (1990). Further assessments of temporal trends will be made when more data sets become available.

The ACMP recommends that modifications to the OSPARCOM sampling guidelines for monitoring purposes should not be made until there is firm evidence of the benefits of such changes. However, the Commissions should note that the possibilities of utilizing data collected for one of its purposes for assessment under another of its purposes continues to be reviewed by ACMP.

A report has now been completed on the ICES 1985-1987 Baseline Study of Trace Metals in Coastal and Shelf Sea Waters. This report will be published by ICES in 1991 in its Cooperative Research Report series. The publication of this report is timely for OSPARCOM since it will be available for reference by the North Sea Task Force (NSTF) during the production of the North Sea sub-regional assessments and the overall Quality Status Report in 1992-1993.

A report on the evaluation of biological effects techniques, based on the work carried out at the ICES/IOC Bremerhaven Workshop in 1990, will be available in 1992. A review of all biological and chemical data collected at this workshop will be conducted at a Concluding Workshop in September 1991.

Draft guidelines for the collection and analysis of samples of sea water for nutrient measurements were submitted to the Joint Monitoring Group (JMG) and NSTF during the past year. A supplementary note on the analysis of nutrients is to be published by ICES in its Techniques in Marine Environmental Sciences series. Draft guidelines for sampling strategies for nutrient studies are under preparation.

#### **Continuing Responsibilities**

The ICES/IOC/OSPARCOM programme concerned with the improvement of measurements of chlorobiphenyls (CBs) in marine samples has revealed that a majority of participants do not have their calibration solutions under control. In addition, poor performance in the extraction of CBs from sediments suggests that it is unlikely that current field data for CBs in sediments are comparable. This finding has clear implications for the NSTF/JMG programme of measurements of CBs in sediments in the Baseline Study of Contaminants in Sediments under the NSTF Monitoring Master Plan and the JMP. For instance, the ability to detect spatial variations may be impaired by large differences in the analytical bias of participating laboratories.

A similar programme for polycyclic aromatic hydrocarbons (PAHs) has revealed that bias exists among participants in the measurement of PAHs in calibration solutions. The second phase of this programme is underway and includes analysis of calibration solutions and a sediment extract. Laboratories have been requested to maintain control charts during this phase and to provide control data to the coordinator of the programme when they submit their results for the second phase.

Phase 1 of an intercomparison programme for measurements of trace metals in suspended particulate matter (SPM) has been completed by ICES. A full report is expected to be published by ICES in its Cooperative Research Report series in early 1992.

At present, the Commissions do not consider SPM measurements to be of immediate relevance to their programme of work. However, the Commissions may wish to reconsider this matter in view of the importance of such measurements for studies concerned with inputs and fluxes of metals to the marine environment.

During 1991, work began on the assessment of the comparability of some of the NSTF biological effects measurements, namely, EROD and the oyster embryo bioassay. An intercomparison exercise for the oyster embryo bioassay was conducted in May 1991 and a workshop on EROD measurements is being conducted in September 1991. The results from both of these exercises will be made available to NSTF participants to assist them in the evaluation of data collected during 1991.

The ACMP has continued its work on the examination of contaminants of interest in a marine pollution context by providing an overview on octachlorostyrene and an information note on nonylphenols.

The work on automatic data processing continues to represent a major commitment for ICES as part of its advisory and service work for the Commissions.

The Commissions' attention is drawn to the deadlines which have been set for the submission of data to ICES by NSTF participants in relation to the production of sub-regional assessments and the North Sea Quality Status Report (QSR). The deadlines and agreed timetable for the production of the QSR are extremely tight and contain no allowance for any 'slippage' in the steps leading up to the production of the final QSR in 1993. The ability of ICES to meet its commitments for data processing for the QSR will be seriously at risk if the agreed deadlines are not met by NSTF participants.

The ACMP considers that the deadlines should be rigorously applied and any data submitted after the deadlines should be excluded from the processing procedures.

The Commissions are, therefore, requested by ACMP either to take whatever steps they consider necessary to ensure that member countries meet the agreed deadlines for the submission of data or to request that a more realistic timetable is established for the ICES validation and evaluation of all data that the NSTF regards as necessary for the satisfactory production of the QSR.

Standard protocols and reporting formats for data on biological effects measurements (EROD, oyster embryo bioassay, benthic community studies, and fish diseases) have been finalized during the intersessional period and are now available for NSTF laboratories to report their data to ICES.

#### **Specific Issues**

Progress reports are included in this ACMP report concerning two new ICES groups that have been set up to deal with issues raised by the OSPARCOM and the NSTF, namely, the Study Group on the Biological Significance of Contaminants in Sediments (see Section 7.4) and the Study Group on Ecosystem Effects of Fishing Activities (see Section 19). Preliminary reports on the work of these groups will be given in the 1992 ACMP report.

Some specific guidance is given in this ACMP report on the SACSA request for advice on methods which can be used to assess the dispersion of dredged material disposed at sea (see Section 14.5).

#### Work Requests from the Helsinki Commission

Brief summaries of the progress achieved in answering the questions raised by the Helsinki Commission are presented in Section 3 of this report. Progress has been made on many of the tasks allocated, and a brief outline of the nature of the progress on the main topics is given below.

The preparation of a "Critical Review of Contaminants in Baltic Sediments" has now been completed and this review is being published in the Cooperative Research Report series in late 1991. On the basis of this review, preliminary plans have been developed for a 1993 Baseline Study of Contaminants in Baltic Sediments. Further development of these plans is continuing.

With regard to intercomparison exercises, an intercomparison of measurements of dissolved oxygen in Baltic Sea water was conducted during the Visby Biological Intercalibration Workshop for the BMP in August 1990. Other intercomparison exercises conducted during 1990 covered analyses of (a) chlorobiphenyls (CBs) in sediment and seal blubber extracts, (b) calibration solutions of polycyclic aromatic hydrocarbons (PAHs), and (c) trace metals in suspended particulate matter.

#### Other Issues Not Directly Related to Current Requests But of Interest to the Commissions

A series of papers on the evaluation of data from the 1986 North Sea Benthos Survey will be published by ICES in its Journal of Marine Science in 1992. A summary of the major findings and conclusions from this survey will also be published by ICES in its Cooperative Research Report series in 1991/1992. The detailed papers and the summary will provide useful information for the NSTF, and its Expert Steering Group, during the production of the sub-regional assessments and the QSR (Section 8.1).

Some information on the effects of physical disturbances of the sea floor on benthic and epibenthic ecosystems is presented in Section 8.2 and Annex 1.

A report on the effects of extraction of marine sediments on fisheries will be published by ICES in 1991/1992 in its Cooperative Research Report series. Guidelines for a code of practice, which ensure the balanced and effective protection of fish stocks and marine biota when proposals for extraction are being considered, are also to be published in 1991/1992 (Section 15).

Work is continuing within ICES on the examination of the role of nutrients in phytoplankton-related harmful events, the establishment of a data base for harmful events, and the state of development and routine applicability of methods not based on mammalian bioassays for the detection and quantification of algal toxins (see Section 11).

ICES has established a Study Group on Seals and Small Cetaceans in Northern European Seas to assess the current and future status of seals, dolphins, and harbour porpoises, evaluate the importance of environmental factors on populations, advise on research requirements and data archiving, and advise on management options to ensure a continued healthy population. A progress report is given in Section 18.

ICES is continuing to evaluate the national reports on diseases in wild fish and the relationship between the prevalence of fish diseases and marine environmental quality. The importance of taking into account natural spatial and seasonal variations in disease prevalence rates is a key factor when designing field programmes and evaluating data obtained from them (Section 9).

#### 1. INTRODUCTION

In dealing with requests put to it by Member Governments of ICES and by the regulatory Commissions, the ACMP draws on the expertise of its own members and also on the work of various expert ICES Working Groups. The ACMP considers the reports of these working groups and calls upon them to carry out specific activities.

The ACMP report is structured in terms of the ACMP's overall deliberations on subjects related to contamination and pollution of the marine environment, but specific features relevant to the various Commissions' requests are brought together in an Executive Summary, which is at the beginning of the report, and are further detailed 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

A summary of the progress in the 1991 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 complete information may be found.

A Work which is expected to be undertaken by ICES and reported on in the ACMP report for 1991;

#### A1 To report on the results of the 2nd phase of the intercomparison exercise on CBs in sediments;

This exercise has been completed and the results should be published in full by early 1992. A preliminary report on the results is given in Section 13.2 of this report. The majority of laboratories exhibited difficulties in the preparation of calibration solutions and most of the results for the sediment extracts were disappointing, indicating that the comparability of current NSTF/JMP data for CBs in sediments may be poor.

#### A2 To report on the results of the ICES/IOC Workshop on Biological Effects Techniques;

The ACMP provided a brief review of the preliminary findings of this Workshop in its 1990 report. Most of the biological data from the Workshop have now been evaluated, but a final report cannot be prepared until all the associated chemical analyses have been completed (see Section 7.1). A Concluding Workshop is being held on 11-13 September 1991, at which all data will be fully evaluated. The ACMP expects to report on the overall findings of this Workshop in its 1992 report.

# A3 To prepare a report on the biological availability of contaminants in sediments and the relevance of sediment quality standards;

A progress report on this task is presented in Section 7.4 of this report. The ACMP will include a preliminary report of the first year's intersessional work on this task in its 1992 report. The final report is expected in 1994.

# A4 To provide advice on methods for sampling, storage and analysis of sea water for nutrient measurements;

The ACMP presented basic guidance for the sampling and analysis of nutrients in sea water in its 1990 report. This guidance document was reviewed by JMG in January 1991, and by NSTF in November 1990. Guidelines for sampling strategies for nutrient studies for temporal trend monitoring and other purposes are in preparation.

- **B** Work which is essentially of a continuing nature and on which it is expected that ICES will submit a progress report in the ACMP report for 1991.
- B1 To report routinely on all on-going and planned ICES intercalibration exercises, preferably by means of a full report to JMG on the intercalibration exercises carried out;
- 1) The final report of the fourth ICES Intercomparison Exercise on the Analysis of Nutrients in Sea Water was published in 1991 as Cooperative Research Report No. 174.
- 2) Phase 2 of the ICES/IOC/OSPARCOM Intercomparison Programme on the Analysis of Chlorobiphenyls (CBs) has been completed (see item A1, above, for reference to the sediment component of this exercise, and Section 13.2 of this report for a preliminary evaluation of the results of Phase 2). A report on the results of Phase 2 is expected to be published in early 1992. Plans for Phase 3 of the programme are also presented in Section 13.2 of this report.

## The Commissions should note that many laboratories will have to modify their methodology to improve the comparability of their analytical data.

- 3) The report on the results of the first stage of the Intercomparison Programme on Analyses of Polycyclic Aromatic Hydrocarbons (PAHs) has been completed (see Section 13.1). In view of the apparent limited interest in measurements of PAHs in sediment, the ACMP has decided to await the results of the second stage, which is currently in progress, before publishing the results of both stages in the ICES Cooperative Research Report series.
- 4) A progress report on Phase 1 of the Intercomparison Programme on the Analysis of Trace Metals in Suspended Particulate Matter (SPM) was presented by the ACMP in its 1990 report. The ACMP presents a summary of the outcome of Phase 1 in Section 13.3 of this report. A full report on the results of Phase 1 is expected to be published by ICES in early 1992.

At present the Commissions, through discussion with JMG, do not appear to consider SPM measurements to be of immediate relevance to their current programme of work. However, the Commissions may wish to reconsider this decision in view of the importance of such measurements in studies concerned with inputs and fluxes of metals to the marine environment.

B2 To provide copies of relevant descriptions of methods of sampling and analysis as published in the "Techniques in Marine Environmental Sciences" series;

The titles of the leaflets published to date in this series are listed below. Copies of each have been provided to the OSPARCOM Secretariat.

- No. 1 Cadmium and lead: Determination in organic matrices with electrothermal furnace atomic absorption spectrophotometry
- No. 2 Trace metals in sea water: Sampling and storage methods
- No. 3 Cadmium in marine sediments: Determination by graphite furnace atomic absorption spectroscopy
- No. 4 Lipophilic organic material: An apparatus for extracting solids used for their concentration from sea water
- No. 5 Primary production: Guidelines for measurement by <sup>14</sup>C incorporation
- No. 6 Quality control procedures: Good laboratory practice and quality control
- No. 7 Suspended particulate matter: Collection methods for gravimetric and trace metal analysis
- No. 8 Soft bottom macrofauna: Collection and treatment of samples
- No. 9 Sediments and suspended particulate matter: Total and partial methods of digestion (with a videotape)
- No. 10 Organic halogens: Determination in marine media of adsorbable, volatile, or extractable compound totals

No. 11 - Biological effects of contaminants: Oyster (Crassostrea gigas) embryo bioassay

No. 12 - Hydrocarbons: Review of methods for analysis in sea water, biota, and sediments

The following leaflets are to be published in the second half of 1991:

- No. 13 Biological effects of contaminants: Measurements of ethoxyresorufin-O-deethylase (EROD)
  - An introduction to the study of temporal and spatial trends in contaminant levels in the marine environment, in particular, marine biota
  - Determination of temporal trends in contaminant levels in tissues of Atlantic cod (Gadus morhua)
  - The use of benthic communities in monitoring point-source discharges

The last three titles are working titles only.

B3 To keep under review the experience with the ADP handling of the JMP data and technical problems of access to the JMP data by other computers;

A report on the processing and proposed validation of JMP and NSTF MMP data by ICES is given in Section 21 of this report.

The Commissions' attention is drawn to the deadlines which have been set for the submission of data to ICES by NSTF and JMP participants in relation to the production of sub-regional assessments and the North Sea QSR. The deadlines and agreed timetable for the production of the QSR are extremely tight and contain no allowance for any 'slippage' in the steps leading up to the production of the final QSR in 1993. The ability of ICES to meet its commitments for data processing for the QSR will be seriously at risk if the agreed deadlines are not met by NSTF participants.

The ACMP considers that the deadlines should be rigorously applied and any data submitted after the deadlines should be excluded from the processing procedures.

The Commissions are, therefore, requested by ACMP either to take whatever steps they consider necessary to ensure that member countries meet the agreed deadlines for the submission of data <u>or</u> to request that a more realistic timetable is established for the ICES validation and evaluation of all data that NSTF regards as necessary for the satisfactory production of the QSR.

B4 To keep under review the question of new contaminants that may be of interest to JMG; this should be regarded as a current awareness exercise and implies an expectation that advice will be provided on those contaminants which ICES considers may give cause for concern in the future;

An overview on octachlorostyrene in the aquatic environment is presented in Section 20.1 of this report, and a note on the occurrence and distribution of nonylphenols in the marine environment, requested by NSTF at its November 1990 meeting, is presented in Section 20.2.

# B5 To keep under review and report as appropriate on the results of studies on the relationship between fish diseases and pollution;

Section 9 of this report refers to the results of some studies of diseases in wild fish stocks in European waters.

The ACMP draws the attention of the Commissions to the need to take into account the natural spatial and seasonal variations in disease prevalence rates when assessing the relationship between fish disease and pollution. The Commissions should note that ICES has produced standard protocols and reporting formats for data on fish diseases to be reported by NSTF and JMP laboratories.

B6 To keep under review the question of the bioavailability of contaminants in sediments and dredged material and to provide advice on methods for determining the potential bioavailability of contaminants in sediments and dredged material;

This matter is dealt with under item A3, above, and in Section 7.4 of this report.

- C Special topics, on which it is expected that ICES will carry out an in-depth study.
- C1 To undertake an overview of methods for assessing sediment transport with particular reference to the disposal of dredged material;

The guidance for SACSA on this task is given in Section 14.5 of this report.

- D Work already underway, on which it is expected that ICES will report in the ACMP report for 1990.
- D1 To report on the experience gained from trend monitoring studies, including the results of studies using organs other than fish muscles and liver, and including cases where fish tissues or shellfish have been pooled prior to analysis;

The results of work on statistical analyses of data for temporal trends in contaminants in fish muscle were published as Cooperative Research Report No. 162 in 1989. A brief report on similar work on data on contaminants in fish liver and mussels was given by ACMP in Section 6.5 of its 1990 report, and the full report has been published as Cooperative Research Report No. 176 in 1991.

D2 To provide revised guidelines for the sampling and analysis of biota for purposes (a), (c) and (d) as defined by the Commissions, taking account of the desirability of having a sampling strategy for purposes (c) and (d) that would allow use of only one set of samples;

Advice on this topic was given by ACMP in Sections 6.2 and 6.3 and Annex 3 of its 1990 report. On the basis of this advice, the OSPARCOM guidelines for monitoring were subsequently amended by the JMG in January 1991, with respect to the use of mussels in temporal trend monitoring.

D3 To review evidence of trends in nutrient concentrations in sea water by examining data sets already available to ICES including those provided by the Netherlands, France and Germany;

A report on this task was presented by ACMP in Section 13 of its 1990 report.

D4 To review the proposals (made by the Netherlands in paper JMG 14/Info.17) for quality assurance of metals in sea water analyses in time for any amendments to be incorporated for use in the 1992 baseline survey.

The ACMP reported progress on this work in Section 14.6 of its 1990 report. A document, based on the Dutch proposal and covering the quality assurance aspects of the sampling of sea water for trace metal measurements, is in preparation and will be submitted to the Commissions as an annex to the 1992 ACMP report. (The 1992 baseline rvey has been postponed for other reasons.)

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#### 3. PROGRESS ON TASKS FOR THE HELSINKI COMMISSION

The present status of work on 1991 requests by the Baltic Marine Environment Protection Commission (Helsinki Commission) is as follows:

#### **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 pollution;

As a detailed report on this topic had been provided in the 1990 ACMP report, only a short progress report is contained in this year's report, in Section 18. It should be noted that this work has now been extended to include small cetaceans in the Baltic Sea Area.

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

An overview on octachlorostyrene in the aquatic environment is presented in Section 20.1 and a note on the occurrence and distribution of nonylphenols is provided in Section 20.2.

3. To report routinely on planned and on-going ICES intercomparison exercises, and to provide a full report on the results;

A brief report on the outcome of the intercomparison exercise for measurements of dissolved oxygen, conducted during the Visby Biological Intercalibration Workshop for the BMP in August 1990, is contained in Section 13.4. This exercise was conducted according to a design prepared by ACMP and presented in its 1990 report.

In addition, a brief summary of the results of Phase 2 of the Intercomparison Programme for the Analysis of Chlorobiphenyls in Marine Media is contained in Section 13.2, a brief overview of the results of the first phase of the Intercomparison Programme on the Analysis of Trace Metals in Suspended Particulate Matter is contained in Section 13.3, and a brief overview of the results of the first phase of the Intercomparison Programme on Analyses of Polycyclic Aromatic Hydrocarbons (PAHs) is given in Section 13.1. Laboratories from the Baltic Sea Area participated in all of these intercomparison exercises.

#### Special studies

4. To finalize the work on the Baltic Sediment Assessment and to coordinate the Baseline Study of Contaminants in Sediments in 1993, according to the recommendations from the "Critical Assessment of Contaminants in Baltic Sediments"; this should include the preparation of guidelines for sampling, sample handling and analysis of contaminants in sediments;

The ACMP has reviewed the final version of the "Critical Review of Contaminants in Baltic Sediments" and approved it for publication in the Cooperative Research Report series, as discussed in Section 14.1. In addition, the ACMP has reviewed the preliminary plans for the 1993 Baseline Study of Contaminants in Baltic Sediments, noting that more detailed plans will be available at the 1992 meeting of ACMP. Regarding the guidelines for sampling and analysis of marine sediments, ICES guidelines have already been prepared; a compilation of these guidelines will be available in 1992.

5. To provide in 1992 as detailed information as possible on the environmental impact of mariculture in the Baltic Sea Area, including amounts and impacts of nutrients and organic matter;

The ICES Working Group on the Environmental Impacts of Mariculture is compiling further information on this topic and a full report will be presented in the 1992 ACMP report.

6. To provide information on as quantitative a basis as possible on conditions (physical, chemical and biological) relevant to the potential development of unusual algal blooms in the Baltic Sea Area;

Relevant information on this topic is presented in Section 11.3. Although this information is of general interest in relation to geographical area, several examples from the Baltic Sea Area are included. Owing to the very broad scope of this question, the ACMP considers that this task should be more focussed. A discussion of the revised task could be held at the HELCOM Environment Committee meeting in September 1991.

7. To develop a general scheme for identification of chemical substances that might be of concern to the marine environment based on toxicity, chemical properties, etc., and to provide guidance for its use relevant to the Baltic Sea;

This topic is being handled by the Working Group on Environmental Assessments and Monitoring Strategies and it is hoped that preliminary guidelines will be presented in the 1992 ACMP report.

8. To review proposals for research actions in the Second Periodic Assessment and indicate which research activities ICES would be willing to coordinate;

This matter is addressed in Section 17 of this report.

9. To report on plans for and progress in investigations relevant to the estimation of net inputs of contaminants into the Baltic Sea;

Initial plans for these investigations have been drafted under the Working Group on the Baltic Marine Environment; a brief summary is included in Section 17.

10. To provide advice and to develop a general scheme of study on the relationship between the quality of the environment and the health of the fish;

The ACMP considers that the scope of this task is too broad and the objectives unclear. Accordingly, the ACMP proposes that a discussion to clarify this task be held at the September 1991 meeting of the HELCOM Environment Committee.

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

This task will be assigned to the relevant ICES Working Group for handling during 1992.

#### 4. PROGRESS IN THE WORK OF THE NORTH SEA TASK FORCE

The ACMP noted that considerable progress had been made in the work of the North Sea Task Force (NSTF) since the last meeting of ACMP. In particular, a detailed outline of the first six chapters of the Quality Status Report (QSR) had been prepared, which followed reasonably closely the ACMP proposals as published in its 1988 report (ICES, 1989). In addition, a detailed timetable for the preparation of the QSR had been agreed, including the schedule for the submission of data obtained under the NSTF Monitoring Master Plan to the ICES Data Centre, the submission of the final drafts of the sub-regional assessment reports, and the preparation of the individual chapters of the holistic QSR. According to this schedule, final drafts of holistic Chapter 1 (General Description of the North Sea) and Chapter 2 (Physical Characteristics and Conditions) are to be completed by October 1991. Chapter 3 (Marine Chemistry), Chapter 4 (Marine Biology), and Chapter 5 (Man's Impact on Ecosystems) are to be completed by September 1992. Chapter 6 (Overall Scientific Assessment) should be drafted by December 1992. In addition, at its meeting in May 1991, the NSTF agreed to add a Chapter 7, which is entitled "Conclusions and Outlook". This chapter is intended to summarize changes since 1987, provide information on the effectiveness of measures that have been taken and, in relation to the future, consider new issues relating to monitoring, scientific needs and developments, and the tasks remaining to be done.

Among the ICES-coordinated work of relevance to the preparation of the QSR, the ACMP noted that good progress has been made in the development of a report on the effects of fishing activities on the ecosystem. This work is being coordinated by the new ICES Study Group on Ecosytem Effects of Fishing Activities and is described in greater detail in Section 19 of this report. ICES is also coordinating, via its Study Group on Seals and Small Cetaceans in Northern European Seas, studies on seals and other marine mammals in the North Sea; progress is reported in Section 18, below. In addition, the Marine Mammals Committee will coordinate the development of a reporting format for stranded marine mammals and review the data ultimately reported.

In terms of research-related activities under the NSTF, the ACMP noted that ICES and the Netherlands will co-sponsor a workshop to consider research topics for internationally coordinated studies of the marine environment of the North Sea.

Finally, the ACMP took note of the commitments made by ICES in the handling and initial assessment of data collected under the NSTF Monitoring Master Plan. The ACMP discussion of this topic is covered in Section 21 on data handling activities.

ICES, 1989. Report of the ICES Advisory Committee on Marine Pollution, 1988. ICES Coop. Res.Rep. No. 160, pp. 96-102.

#### 5. MONITORING ISSUES

#### 5.1 Statistical Treatment of Monitoring Data

In the context of continuing work within ICES to develop and refine the statistical methods for analysing data on contaminants in marine media to determine temporal trends, the ACMP reviewed the work by the Working Group on the Statistical Aspects of Trend Monitoring (WGSATM) on this subject.

The ACMP noted with interest that WGSATM was investigating further statistical techniques (e.g., the Kalman-filter model) for application to data collected for purposes of monitoring temporal trends of contaminant levels in biota, in particular, data characterized by significant inconsistency in regression coefficients and variances. Initial indications are that these techniques may offer advantages over the existing statistical methods used in ICES/JMP trend analyses, for example, in improving trend estimates where fish length data are poorly dispersed, and in reducing the influence of outliers. The ACMP was informed that this work, together with studies focussed on the problems of interpreting significant variation between years and assessing the power of the monitoring programmes to detect changes in contaminant levels over time, was continuing and that further information would be available for ACMP to consider in 1992.

The ACMP was also informed that studies are in progress to develop suitable statistical methods for assessing monitoring data collected to establish the spatial distribution of contaminants. The techniques under investigation include comparisons with pre-selected ('reference') values, analysis of variance for the spatial component, and various interpolation techniques for spatial information. Within the last group, the potential usefulness of the Kriging technique is under consideration. Spatial analysis is particularly relevant to on-going studies of contaminants in sediments and, in this regard, the data sets which will be obtained as part of the NSTF/JMP 1990/1991 baseline studies will provide a useful opportunity to test a number of statistical procedures for their applicability in assessing the spatial variation of contaminants in sediments.

The ACMP hopes to report progress on the above topics in its 1992 report.

The ACMP noted that the report entitled "Statistical Analysis of the ICES Cooperative Monitoring Studies Programme (CMP) Data on Contaminants in Fish Liver and *Mytilus edulis* (1978-1988) for the Determination of Temporal Trends" has been published as ICES Cooperative Research Report No. 176. This report continues the publication of results of the ICES CMP temporal trend monitoring programme, the first part of which was contained in Cooperative Research Report No. 162, concerning the analysis of data on contaminants in fish muscle tissue.

The report presents results for sixteen contaminants: trace metals (cadmium, chromium, copper, mercury, nickel, lead, and zinc) and organochlorines (polychlorinated biphenyls as PCBs on a formulation basis and as the individual chlorobiphenyl congener IUPAC No. 153, hexachlorobenzene,  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane, p,p'-DDE, p,p'-DDT, p,p'-TDE, and dieldrin). The data sets, reported by eight countries (Belgium, Denmark, Federal Republic of Germany, France, Netherlands, Norway, Sweden, and United Kingdom), cover 29 species/area combinations for fish liver and 16 areas for *Mytilus edulis*, a total of 273 contaminant time series.

As with the previous analysis of the fish muscle tissue data, the statistical procedure applied produces yearly estimates of the mean contaminant levels along with a statistical interpretation of the trend data for the individual species-area-contaminant combination concerned. The ACMP noted that the report contains a statistical evaluation of the data only; it is not the intention of the ICES analyses to draw conclusions with respect to general trends in environmental contaminant levels in any given area. Such interpretations would require additional comprehensive information on inputs to the areas concerned, as well as on a number of environmental factors and processes operating in the area and improved knowledge about the physiological

and biochemical processes that determine the uptake and metabolism of a contaminant by a particular organism.

The ACMP noted that this report had been presented to the OSPARCOM *ad hoc* Working Group on Monitoring meeting in December 1990 as the background document for their consideration of the temporal trend monitoring results of the biota component of the Joint Monitoring Programme (JMP).

#### 5.2 Optimization of Analytical Costs Through Pooling

In view of the continuing interest in the use of pooled samples (i.e., several specimens bulked together and homogenized prior to chemical analysis) in monitoring programmes, for reasons of economy and to provide adequate material for analysis (see, e.g., ICES, 1990), the ACMP considered the work being conducted by the WGSATM on this issue. The ACMP was informed that no further studies concerning pooling and the optimization of analytical costs through the pooling of samples had been conducted during 1991. However, the ACMP noted that WGSATM was intending to prepare a document compiling previous advice on the subject, and that this will facilitate the design of appropriate sampling and analytical schemes for monitoring programmes. Recognizing the potential usefulness of such a document in bringing together the available information on the subject of pooling, the ACMP looked forward to receive this document, which is intended for publication in the Techniques in Marine Environmental Sciences series.

#### 5.3 Review of Monitoring Guidelines

The ACMP keeps under review the guidelines currently in place concerning the sampling and analysis of marine environmental media. In general, the ACMP does not recommend changes to the guidelines until there is firm evidence demonstrating the benefits of such changes. While there are no immediate proposals from the relevant working groups to modify the guidelines, it is expected that the assessment of the 1990 baseline survey results may lead to recommendations for changes in sampling protocols related to spatial studies of contaminant levels. The question of whether data obtained for one particular monitoring purpose can be used for other monitoring purposes is also under continuing review.

ICES, 1990. Report of the ICES Advisory Committee on Marine Pollution, 1990. ICES Coop. Res. Rep. No. 172, pp. 31 and 126-134.

#### 6. REVIEW OF MEASUREMENTS OF TRACE METALS IN COASTAL AND SHELF SEA WATERS

The ACMP considered the report "Review of Measurements of Trace Metals in Coastal and Shelf Sea Water Samples Collected by ICES and JMP Laboratories during 1985-1987", that had recently been completed, and noted the following principal findings from the review (see also ICES, 1990). Contrary to the conclusions of an ICES-initiated assessment of the baseline distributions of trace metals in sea water conducted in 1978 (Topping *et al.*, 1980), it is now possible to establish baseline levels of selected trace metals for most of the areas of the eastern North Atlantic of major interest to the Oslo and Paris Commissions. There is substantial agreement among laboratories that surveyed metal concentrations in water at two selected reference locations. The data collected under this survey have been presented for areas designated as a result of an earlier physical oceanographic study of the North Sea (ICES, 1983b) in a manner that shows the median and range of metal concentrations. These confirm that the differences between nearshore and offshore waters in the concentrations of metals are not as large as was thought several years ago. In addition, examinations of the relationships between the distributions of some metals and salinity have been used to assess the effective, extrapolated, zero-salinity end-member concentrations and to compare such extrapolations with those for other marine areas.

The ACMP discussed other conclusions that might be drawn from this study in a broader management context. It concluded that routine monitoring of trace metals in filtered sea water in offshore, high salinity areas for either spatial or temporal trend purposes is difficult to justify and may be an unwarranted use of skilled resources. However, the results also confirm the usefulness of an examination of the relationships between dissolved metal distributions and physical oceanographic characteristics, especially those that offer a representation of mixing (i.e., salinity), throughout a broad range of salinities as a means of assessing the effective end-members for mixing in nearshore areas, as advocated earlier by ACMP (ICES, 1988, 1989) and by GESAMP (United Nations Joint Group of Experts on the Scientific Aspects of Marine Pollution) (GESAMP, 1987). A logical and necessary adjunct to such work would be enhanced attention to the gross fluxes of metals in dissolved and particulate form in rivers, as also recommended by ACMP in 1982 (ICES, 1983a). The other major conclusion that may be drawn is that increased attention to the distribution of trace metals in suspended particulate matter is highly desirable, especially in the context of evaluations of the transport and fluxes of metals in estuaries.

- GESAMP IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution, 1987. Land/Sea Boundary Flux of Contaminants: Contributions from Rivers. Rep. Stud. GESAMP, 32. 172 pp.
- ICES, 1983a. Report of the ICES Advisory Committee on Marine Pollution, 1982. ICES Coop. Res. Rep. No. 120, pp. 15-16, and 60-72.
- ICES, 1983b. Flushing Times of the North Sea. ICES Coop. Res. Rep. No. 123. 159 pp.
- ICES, 1988. Report of the ICES Advisory Committee on Marine Pollution, 1987. ICES Coop. Res. Rep. No. 150, pp. 95-97.
- ICES, 1989. Report of the ICES Advisory Committee on Marine Pollution, 1988. ICES Coop. Res. Rep. No. 160, pp. 87-90.
- ICES, 1990. Report of the ICES Advisory Committee on Marine Pollution, 1990. ICES Coop. Res. Rep. No. 172, pp. 33-41.
- Topping, G., Bewers, J.M., and Jones, P.G.W. 1980. A Review of Past and Present Measurements of Selected Trace Metals in Sea Water in the Oslo Commission and ICNAF/NAFO Areas. ICES Coop. Res. Rep. No. 97. 43 pp.

#### 7. BIOLOGICAL EFFECTS OF CONTAMINANTS

#### 7.1 Progress in Evaluating Results from the Bremerhaven Workshop

The ACMP reviewed the report of the Working Group on Biological Effects of Contaminants (WGBEC) and took note of the progress in its work. In this context, the ACMP noted that from 12 to 30 March 1990 an ICES/IOC Workshop on Biological Effects of Contaminants in the North Sea had been held, based at the Alfred Wegener Institute for Polar and Marine Research in Bremerhaven, Germany. During this Workshop:

- 1) biological effects measurements at different levels of biological hierarchy (biochemical, cellular, tissue level) were made simultaneously along a nearshore to offshore transect;
- 2) bioassays were deployed at sea; and
- 3) samples of organisms, sediment and sea water were taken for relevant chemical analyses.

All but a few biological data sets from the workshop have now been collated, analysed and plotted. They have been distributed to all Workshop participants. The patterns shown by data from a number of techniques were consistent and suggested that they were all showing similar responses to the same apparent contamination gradient.

Data on chemical analyses of tissue, water, and sediment samples taken in conjunction with the deployment of the biological techniques are being forwarded to ICES for processing and distribution to Workshop participants. Scientists involved in the Workshop will interpret their biological findings in relation to the results of these chemical analyses. Contributions from all participants will be presented at the Concluding Workshop on Biological Effects Techniques on 11-13 September 1991 in Copenhagen.

An interim report on the Workshop results will be prepared for the 1991 ICES Statutory Meeting. The final report will be published as a special volume of the Marine Ecology Progress Series in 1992.

#### 7.2 The Present State of Biological Effects Monitoring

The ACMP noted that, as a result of several ICES- and IOC-sponsored workshops and various studies reported in the open literature, a few biological effects monitoring methods have been tested comprehensively in both laboratory and field situations. Some are now ready for application and evaluation in pollution monitoring programmes. These are described as Group I methods and are listed below.

The ACMP also noted two other categories of biological effects techniques: Group II, which are at an advanced stage of development, and Group III, which are types of tests which are urgently needed, but for which as yet no detailed proposals exist.

#### **Group I Methods**

The methods identified as currently ready for application in pollution monitoring programmes are:

- 1) Measurements of MFO (Mixed Function Oxidase) activity in fish;
- 2) (Pelagic) invertebrate bioassays based on growth;
- 3) Benthic community structure analysis; and
- 4) Measurement of scope for growth in bivalves.

The procedures currently adopted for biological effects monitoring in the North Sea Task Force Monitoring Master Plan (NSTF MMP) include three of the Group I methods listed above (namely, methods 1, 2 and 3).

The ACMP considered that the review of the strengths and limitations of the present NSTF MMP methods, prepared by the Working Group on Biological Effects of Contaminants, was valuable and, accordingly, the main points are reproduced below.

#### 1) EROD in Dab Liver

The results of field and laboratory experiments show that the induction of EROD (ethoxyresorufin-O-de-ethylase) activity in flatfish is sensitive to the presence of polycyclic aromatic hydrocarbons (PAHs) at the parts per million level in the water column and in sediments. The only other pollutants which are capable of inducing fish hepatic MFOs are polychlorinated biphenyls (PCBs). However, the PCB dose required to cause direct induction of hepatic MFO enzymes is so large that it is likely to occur only in areas of major PCB contamination. Thus, the value of EROD measurements is in indicating the quality of an environment potentially threatened by low levels of PAHs.

#### 2) Oyster Embryo Bioassay

The oyster embryo bioassay has been shown to react very sensitively to a wide range of contaminants in sea water. It is not known to be sensitive to natural influences other than algal toxins and high loads of suspended sediments.

Despite this, the method has demonstrated reduced water quality in only a few estuaries and in the immediate vicinity of certain waste disposal operations. Open North Sea water (including water sampled at the Bremerhaven Workshop) does not prevent normal embryonic development in this species.

This bioassay has been successfully used with sea water elutriates of sediments. These tests indicate that several industrialized estuaries around the North Sea contain sediments from which harmful levels of contaminants can be liberated. The Bremerhaven Workshop data suggest that the bioassay, when used in this way, may have comparable sensitivity with whole sediment bioassays.

#### 3) Diseases in Dab

The use of fish diseases as a technique for monitoring the effects of pollutants in the North Sea shows promise. However, the cause of disease is very complex and epidemiological findings can only be interpreted taking into account many factors other than pollution.

Liver pathology shows the most promise as a direct indicator of the effects of contaminants; for other diseases, the role of pollution is probably indirect (e.g., via immunosuppression).

#### 4) Benthic Community Analyses

Various methods of benthic community analysis have been used for many years to assess the impact of point sources of contamination. Recent advances include the development of statistical techniques, such as abundance-biomass curves (AB) and multidimensional scaling (MDS). In comparison with more commonly used indices, these techniques are more sensitive and robust.

The ACMP considers that the four techniques identified by the NSTF for its Monitoring Master Plan are not necessarily the only ones suitable for monitoring the water quality of the North Sea and has addressed the potential of another technique in this context, namely, scope for growth in mussels. This is a generalized sub-lethal index of stress; it is a measure of the extent to which energy uptake exceeds metabolic requirements under standard conditions. It takes into account the direct action of toxicants on these processes. As a physiological index of stress, it can bridge the gap between a biochemical index, such as EROD, and the more biological indices, like benthic community analysis and fish diseases. However, the ACMP considered that before it could recommend the incorporation of this technique into international programmes, some additional work is necessary. For example, an intercomparison exercise using pure test compounds is desirable, followed by a determination of scope for growth in mussels from one site. It is further necessary to agree upon a standardized methodology, which can be published, e.g., in the Techniques in Marine Environmental Sciences series.

#### Future Approaches to Biological Effects Monitoring

#### **Group II Methods**

Two techniques are at an advanced stage of development and validation, but need additional effort before they can be recommended for inclusion in international programmes:

1) Acetylcholinesterase (AChE) inhibition

Various organic compounds developed as pesticides specifically inhibit acetylcholinesterase, an enzyme responsible for breaking down the neurotransmitter acetylcholine.

At the Bremerhaven Workshop, AChE inhibition in dab showed clear and significant trends that correlated closely with results from a number of other techniques.

2) Metallothionein (MT)

The induction of this metal-binding protein is used as a measure of exposure to metals. It has been tested within the Workshop series and is considered to show promise, which will become clearer when more environmental data are available.

#### **Group III Methods**

Two areas were identified for which there is a requirement to establish new techniques:

- 1) Whole sediment bioassays; and
- 2) Indices of immune function for use in the field.

These techniques are presently applied on a fundamental research basis and their further development for routine application is encouraged.

#### 7.3 Quality Assurance Procedures for Biological Effects Techniques

The ACMP noted that, following a request from the North Sea Task Force to ICES to arrange for quality assurance procedures for the biological effects techniques presently applied in the NSTF context, the ICES Working Group on Biological Effects of Contaminants had reviewed the necessity for quality assurance programmes for each of the four NSTF biological effects methods. The ACMP summarized this review as follows:

#### 1. <u>EROD</u>

An intercomparison exercise workshop for the measurement of EROD activity will be held at the Marine Laboratory in Aberdeen on 4-6 September 1991; it is organized by Dr R. Stagg. This workshop will be an exercise to compare EROD methods among participants who routinely use EROD in monitoring. The scope of the exercise will be confined to intercalibrating EROD measurements on standard homogenates of dab liver.

Three aspects of the EROD assay will be subject to intercomparison:

- a) Resorufin standards;
- b) Assay conditions and instrumentation; and
- c) Protein assay.

ICES and IOC are contributing funds to support this workshop.

The results of the workshop will be assessed at the next meeting of the ICES Working Group on Biological Effects of Contaminants, planned to be held in the first half of 1992.

#### 2. Oyster Embryo Bioassay

The NSTF lead laboratory for the oyster embryo bioassay, the MAFF Fisheries Laboratory at Burnham-on-Crouch, Essex, UK, organized an intercomparison exercise during May 1991. Participating laboratories were from England, Scotland, Norway, France, and the Netherlands.

The intercomparison exercise used a single test compound (tributyltin oxide: TBTO); stock solutions of TBTO, standard reference sea water, sexed and conditioned oysters (*Crassostrea gigas*), and a detailed protocol based on ICES Techniques in Marine Environmental Sciences (TIMES) No. 11 (Thain, 1991) were distributed to the participants. Participating laboratories were expected to conduct the 24-hour test during the week specified and supply the resulting data to the coordinating laboratory. The results will be processed and reported to the participants as well as to ICES in late summer 1991.

3. Fish diseases

The ICES Working Group on Pathology and Diseases of Marine Organisms has developed a standardized methodology for fish disease surveys (ICES, 1989b). It is recommended that this standard methodology, which has been developed at two sea-going workshops, be followed for all studies of fish diseases being carried out in accordance with the NSTF Monitoring Master Plan. Data should be submitted using the proposed Reporting Format for Fish Disease Data (see also Section 9.2, below).

#### 4. Benthic community analysis

The ICES Benthos Ecology Working Group has, in conjunction with the 1986 North Sea Benthos Survey, developed and applied methodologies for benthos studies. This Working Group should, therefore, deal with quality assurance programmes for benthic community studies. The ACMP noted that most NSTF participants are following these guidelines, as recommended in the 1988 ACMP report (ICES, 1989a).

- ICES, 1989a. Report of the ICES Advisory Committee on Marine Pollution, 1988. ICES Coop. Res. Rep. No. 160, pp. 28-45.
- ICES, 1989b. Methodology of Fish Disease Surveys. ICES Coop. Res. Rep. No. 166. 43 pp.
- Thain, J.E. 1991. Biological effects of contaminants: Oyster (*Crassostrea gigas*) embryo bioassay. Techniques in Marine Environmental Sciences No. 11. 12 pp.

## 7.4 Progress in Assessing the Bioavailability and Associated Biological Effects of Contaminants in Sediments

In 1990, the ACMP recommended the establishment of a special study group within ICES to investigate the scientific basis for assessments of hazards associated with the presence of contaminants in sediments. The ACMP noted that this special group, the Study Group on the Biological Significance of Contaminants in Marine Sediments, was established at the 1990 Statutory Meeting and first met in March 1991. The Study Group has begun work on two tasks:

- a) to assess the bioavailability and associated biological effects of contaminants in marine sediments; and
- b) to derive appropriate sediment quality criteria for priority marine contaminants.

The Study Group is expected to report on the results of its work in 1993.

In this connection, the ACMP noted that the new *Ad Hoc* Group on the Assessment of Dredged Materials, proposed by the Standing Advisory Committee for Scientific Advice (SACSA) of the Oslo Commission, has been requested to pay particular attention to the activities of this new ICES Study Group.

#### 8. BENTHOS ISSUES

#### 8.1 Benthic Communities of the North Sea

The ACMP reviewed a draft summary report on the North Sea Benthos Survey prepared by members of the Benthos Ecology Working Group. The report covers the design and major findings of the sampling carried out in the central and southern North Sea in 1986 (197 stations), as well as that carried out in the northern North Sea between 1980 and 1985 (119 stations). These extremely valuable data sets provide a broad picture of the distributions and assemblages of benthic macrofauna and meiofauna of the North Sea between latitudes 51°N and 61°N (see Figure 8.1). Preliminary analysis has been undertaken to relate distributions to selected sediment characteristics and other factors, such as latitude. The results should be of particular relevance to the work of the North Sea Task Force and to the Joint Monitoring Group. Further work is needed to finalize the document, but the ACMP intends to include the summary in its 1992 report. This will complement a more detailed account of the North Sea Benthos Survey to be presented in the ICES Journal of Marine Science, as well as a number of related papers scheduled for publication in the scientific literature.

#### 8.2 Effects of Physical Disturbance of the Sea Floor on Benthic and Epibenthic Ecosystems

The report from the Benthos Ecology Working Group dealing with the effects of physical disturbance of the sea floor on benthic and epibenthic ecosystems was very much welcomed by the ACMP and provided the basis for the following comments, which form ACMP's preliminary advice on the effects of physical disturbance on the sea floor.

#### Introduction

Physical disturbance of the sea floor can be caused by many processes. Natural processes include tidal currents, storm waves, and ice. Anthropogenic processes include aggregate extraction, pipeline installation, disposal of waste at sea, dredging, and fishing activity (trawling and dredging). Knowledge of the effects of these various processes has increased rapidly in recent years with the advent of new technology, such as manned submersibles, remotely operated vehicles (ROVs), underwater video systems and side-scan sonar, which allow direct sensing of the sea floor.

Research on the effects of physical disturbance on benthic organisms is underway in many ICES member countries. This topic is also being considered by the ICES Study Group on Ecosystem Effects of Fishing Activities. As part of this work, an updated bibliography has been prepared on the effects of bottom fishing gear and harvesting techniques on the sea bed and benthic biota (Redant, 1991). In addition, a review of the effects of trawling, dredging and ocean dumping on the eastern Canadian continental shelf sea bed has recently been prepared and is in press (Messieh *et al.*, 1991).

#### **Review of Current Research**

A review of current research being carried out in this field can be found in Annex 1.

#### **Conclusions and Recommendations**

There is widespread interest in understanding the impacts of physical disturbance on the benthic ecosystem. Scientists have the technical tools needed to conduct the necessary research. It is clear from the limited research conducted to date that, under certain conditions, anthropogenic disturbance of the sea floor can affect benthic habitats and organisms. Some of the immediate effects that have been documented include:

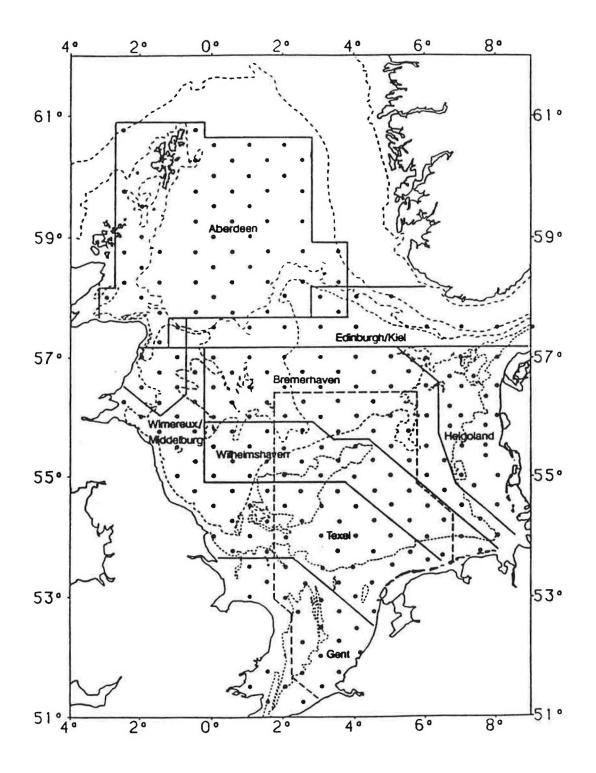


Figure 8.1 Stations sampled by participants of the North Sea Benthos Survey in 1986. Stations in the northern North Sea were sampled between 1980 and 1985.

- Change in the grain size of surface sediments;
- Change in the chemical fluxes between sediments and the overlying water column;
- Change in potential for erosion of surface sediments;
- Mortality of benthic organisms (both on the sea floor and in displaced sediment);
- Relocation of organisms from their preferred habitat;
- Reduction in species diversity;
- Change in the relative abundance of species;
- Physical damage to individual organisms;
- Change in the patchiness of organism distribution; and
- Loss of food sources or shelter essential for survival.

The long-term environmental implications of physical disturbances to the sea floor due to human activities are difficult to predict. However, the ACMP recommends continued research to provide a clearer indication of which activities may harm or devalue living marine resources and which, therefore, may require a greater degree of management and regulation. Initially, the focus of research should be on those practices carried out on a large scale (e.g., beam trawling, dredging, and aggregate extraction) and those which primarily affect particular habitats and substrates.

The ACMP further recommends that, in designing studies of physical impacts on sediments, sufficient care be taken to define clearly the objectives and to ensure that the methodologies adopted are consistent with these objectives. In general, effects on individual organisms and local communities will be of less importance than effects on populations and the productivity and diversity of ecosystems. Thus, studies should address the scaling problems associated with applying experimental results from a specific study site to a large geographical area.

As a general guide, investigations into the physical effects of disturbances on benthos should include detailed descriptions of the type of disturbance, the immediate effects on organisms living in and on the sediment, the rate of recovery (recruitment, migration, re-colonization, etc.) and the long-term impacts. They should also examine the nature and extent of sediment transport in the area, because this exerts a major influence on recovery rates.

Finally, the ACMP emphasizes the need to compare and contrast the impacts of anthropogenic disturbances with the impacts of natural processes (e.g., tidal currents, storm waves, ice, riverine sediment input, etc.) to which an area is subjected, particularly when considering the long-term significance of the changes that occur. In this context, it is important to evaluate the extent to which benthic organisms may have adapted to a pattern of disturbance (i.e., history and frequency of events), either natural or anthropogenic, and whether or not a form of long-term equilibrium has been established.

#### References

- Messieh, S.N., Rowell, T.W., Peer, D.L., and Cranford, P.J. 1991. The effects of trawling, dredging and ocean dumping on the eastern Canadian continental shelf sea bed. Continental Shelf Research, in press.
- Redant, F. 1991. An updated bibliography on the effects of bottom fishing gear and harvesting techniques on sea bed and benthic biota. Working Document to the ICES Study Group on Ecosystem Effects of Fishing Activities, 11 pp.

#### 9. FISH DISEASE ISSUES

#### 9.1 Fish Diseases in Relation to Pollution

The ACMP noted that, in view of the many on-going studies on diseases of marine fish in relation to pollution, there is a need to review published material at regular intervals with the following aims: (1) to monitor the progress made, (2) to revise, if necessary, the advice given to the Commissions, and (3) to recommend further research topics. It noted that, in the most recent review prepared by the Working Group on Biological Effects of Contaminants, more than 50 studies from the North Sea, other European sea areas, and coastal waters of the USA have been reviewed. Generally, greater fish disease prevalences were found in the North Sea as compared to the coastal waters of the USA.

The ACMP considers that this review shows some good examples of cases for which a relationship between pollution and fish disease appears to exist. These are listed below according to the relevant pathologies.

#### Fin Rot

- The prevalence of fin rot in bottom-dwelling fish has been statistically associated with environmental degradation in certain coastal waters of the USA.
- The occurrence of fin rot in perch (*Perca fluviatilis*) has been related to pulp mill effluents in the Baltic Sea.

#### Skeletal deformities

• Skeletal deformities in four-horn sculpin (*Myoxocephalus quadricornis*) have been related to pulp mill and smelter effluents in the Baltic Sea.

#### Skin tumours

• Skin tumours have been associated with organic contaminants (USA).

#### Epidermal papilloma/hyperplasia

• Epidermal papillomas/hyperplasia have been related to waste from the titanium dioxide industry disposed in Dutch and German waters. The fact that two separate study groups found higher levels of epidermal papillomas/hyperplasia at the disposal sites as compared to surrounding areas strongly suggests a causal link. However, both dumping areas are located in the vicinity of heavily contaminated rivers, making discrimination between contamination sources and the general contaminant load difficult.

#### General skin disease

- Positive correlations have been established between skin diseases (ulcers, lymphocystis) in flounder (*Platichthys flesus*) and pollutant levels in Dutch coastal waters.
- Comprehensive studies covering wide areas of the southern and central North Sea have concluded that the spatial pattern of epidermal disease (lymphocystis, epidermal papilloma/hyperplasia) and ulcers in dab (*Limanda limanda*) could, in some localities (i.e., Danish coastal waters, the German Bight), be explained by the impact of chemical contaminants, or oxygen deficiency associated with eutrophication.

#### Liver tumours

• There is evidence of a chemical etiology for liver tumours in marine fish from both the US and Dutch coastal waters.

In contrast to the above, there are numerous examples, especially from studies conducted in offshore waters, where evidence of a relationship between fish disease and marine contamination has been either less convincing or totally absent.

While it is clear that some contaminants can cause disease, the presence of disease in marine areas does not necessarily signify pollution.

The ACMP has previously pointed out that disease induction is multifactorial, involving both natural and anthropogenic factors. Epidemiological studies as presently carried out in many areas, especially in the North Sea and the USA, cannot establish causality because relationships in space and time with contaminants are correlative.

Causality can only be demonstrated in carefully designed experiments. For example, an experiment with fish exposed to contaminated sediments from the Manchester Ship Canal (UK, MAFF) has shown a link between immunosuppression in fish and contaminants present in those sediments. However, particular contaminants responsible for the observed effects have not yet been identified.

#### 9.2 ICES-Coordinated Fish Disease Surveys

Data on diseases of marine fish in the ICES area have been obtained according to a standard methodology for fish disease surveys since 1988 (ICES, 1989). This methodology also includes a data reporting format, which was recently reviewed by the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO). Based on this WGPDMO review, the ACMP recommends the use of two additional codes on the fish disease data reporting formats:

- 1) Use of a presence/absence coding (+/-) for samples smaller than the recommended minimum number in each size group (100 or 50 fish); and
- 2) Use of the code N if a disease is not looked for, 0 (zero) if a disease is looked for but is not present.

The reporting format may be used in two different contexts:

- 1) To report to ICES annually through the WGPDMO on the prevalences of diseases diagnosed according to the standard protocol; and
- 2) To report to WGPDMO any emerging new disease problems, particularly in dab, flounder, or cod (*Gadus morhua*).

In order to ensure a sufficiently broad spread of sampling locations, the ACMP once more encourages each ICES member country to report on diseases of marine fish from at least two stations annually, known for their differences in contamination levels. The revised standard methodology should be applied for these studies and the reporting of results.

In addition, geographically wide-ranging surveys should continue to monitor long-term trends and to examine the relationship between disease and a complex of environmental variables, even though these surveys are unlikely to produce convincing evidence for a cause/effect relationship between disease and pollution. In conducting fish disease surveys, the following points should be considered:

- Observations of liver pathologies should be included whenever possible;
- The measurement of contaminant concentrations in sediments, food organisms, and fish tissues should become an important element of these studies;
- There is a gap in the knowledge of diseases of fish other than dab, flounder, and cod; and
- The diagnosis of any new diseases needs to be standardized before data from different observers, locations, or times of the year can be compared by ICES.

Because difficulties in the interpretation of data on the spatial distribution of diseases of marine fish are partly due to a lack of information on the migration habits of dab and flounder, the information available on the migration habits of these two species has been reviewed by the WGPDMO. Published information on migration is scarce for dab and absent for flounder, although it is acknowledged that more information is available in ICES member countries. From the little information available, it becomes obvious that, for dab, migration can become a major confounding factor in evaluating disease distribution.

More information is needed on:

- 1) The seasonal migration patterns of dab and flounder of the different year classes in the North Sea, the Baltic Sea, and the Irish Sea;
- 2) The residence periods (length of time) of fish in certain areas; and
- 3) Small-scale movements of fish in restricted geographical areas.

ICES, 1989. Methodology of Fish Disease Surveys. ICES Coop. Res. Rep. No. 166. 43 pp.

#### 10. ENVIRONMENTAL IMPACTS OF MARICULTURE

The ACMP noted that the Working Group on Environmental Impacts of Mariculture was working by correspondence during 1991 to complete Technical Reports on "Chemicals Used in Mariculture" and on "Management of the Environmental Impact of Mariculture". This Working Group is also continuing its compilation of information, as detailed as possible, on the environmental impact of mariculture operations in the Baltic Sea Area, including the amounts of nutrients and organic matter arising from these operations. The ACMP will review the information resulting from these Working Group activities in 1992.

The ACMP further noted that there will be a Theme Session on "Medication in Mariculture: Efficacy, Residues, and Environmental Effects" at the 1991 Statutory Meeting. The ACMP will review relevant findings and conclusions from this Theme Session at its 1992 meeting.

# 11. ALGAL BLOOMS AND RELATED ISSUES

# **11.1 Methods for Measuring Primary Production**

With respect to the development of a "standard" method for the measurement of primary production in an environmental monitoring context, the ACMP noted the opinion of the Working Group on Phytoplankton and the Management of their Effects (WGPME) that, with minor modifications, the protocol previously developed by the Working Group would be generally acceptable. However, the ACMP recognizes that any "standard" method must be designed for a specific purpose and developed in cooperation with experts in the field of primary production outside the ICES area (i.e., the Intergovernmental Oceanographic Commission (IOC), the Scientific Committee on Oceanic Research (SCOR)). The ACMP was informed that IOC has contacted ICES to investigate possible ICES interest in the development of a standard method. The ACMP agreed to recommend a positive response from ICES to IOC.

The ACMP also noted that there is an ICES Symposium on 'Measurement of Primary Production from the Molecular to the Global Scale', to be held in La Rochelle, France in April 1992. One of the objectives of this Symposium is "to examine the various approaches that can be used to measure marine phytoplankton production, to state their limits of applicability and to discuss the extent to which the different methods can be said to give consistent results".

# **11.2 Trends in Algal Bloom Incidence**

The ACMP deliberations on problems relating to algal blooms were based on the report of the Working Group on Phytoplankton and the Management of their Effects (WGPME).

With regard to temporal trend analysis of the occurrence of phytoplankton-related harmful events, the ACMP noted that the Working Group had identified 37 time series data sets which may have the potential to be used to examine whether increases in the number or extent of harmful events have occurred in some areas. The ACMP agreed to ask the Statistics Committee to liaise with the WGPME in order to examine one or more of these data sets and identify methods for appropriate statistical treatment of such data.

The ACMP viewed positively the suggestion by the Working Group concerning the establishment of a directory of data bases on phytoplankton-related harmful events that would be potentially suitable for trend analysis, and will ask the WGPME to make recommendations as to how this directory should be constructed.

# 11.3 Role of Nutrients in Phytoplankton-Related Harmful Events

In its report, the Working Group on Phytoplankton and the Management of their Effects included a very comprehensive discussion of the role of nutrients in phytoplankton-related harmful events. Three main conclusions with management implications arise from this review:

- 1. There is clear evidence that some non-toxic but potentially harmful blooms in the ICES area are associated with nutrient enrichment (e.g., *Phaeocystis* in Dutch coastal waters). However, there are also many harmful algal blooms that show no obvious link to nutrient enrichment due to the dominance of physical concentration factors or the high toxicity of small numbers of cells. Thus, there are no generalizations that apply to all types of harmful algal events.
- 2. There is surprisingly little evidence directly linking toxic algal blooms to anthropogenic nutrient enrichment, although this may only reflect a lack of both data and attempts to demonstrate such a relationship.

3. Nutrient supply ratios can affect harmful blooms in several ways: a) by the selection of dominant species (e.g., replacement of diatoms by *Phaeocystis* as silicon is depleted), and b) by altering the toxicity of some species. Evidence supporting the latter mechanism is available from laboratory studies, but lacking from field studies.

The ACMP considered the review produced by the WGPME to be of such potential value in a management context that it is, with some editorial modifications, reproduced here.

# The role of nutrients in phytoplankton-related harmful events

In assessing the role of nutrients in enhancing phytoplankton-related harmful events, two types of events should be distinguished: a) those caused by toxic algal species, which may or may not be present at high levels of biomass, and b) those involving non-toxic species which cause harm as a direct result of their high biomass. Toxic events include episodes of paralytic shellfish poisoning (PSP), diarrhetic shellfish poisoning (DSP), neurotoxic shellfish poisoning (NSP), amnesic shellfish poisoning (ASP), and a variety of fish and marine fauna mortalities caused by known or suspected algal toxins.

Non-toxic species can cause harm as a result of high biomass. Perhaps the most common harmful event caused by non-toxic species is anoxia and the associated mortality of benthic and planktonic organisms due to the decompositional oxygen demand from decaying phytoplankton bloom biomass. Impacts can also be aesthetic, due to the sight and smell of bloom decomposition products on beaches (e.g., *Phaeocystis*). Non-toxic effects can also be mechanical, whereby blooms clog fishermen's nets or coat the nets and make them visible to fish. This is especially the case during blooms of filamentous algae (e.g., *Pilayella littoralis* and *Ectocarpus siliculosus*). A different type of mechanical problem occurs when some phytoplankton species (notably certain species in the diatom genus *Chaetoceros*) irritate fish gills, causing mucous secretions that limit oxygen uptake and cause suffocation. In nearly all cases where these effects have been noted, the affected fish have been caged or caught in gill nets.

Despite this highly diverse spectrum of harmful bloom events, certain common features can be identified. Here the focus will be on the importance of nutrients, especially anthropogenic inputs, to the frequency and magnitude of the harmful events.

# a. Aspects of Toxic Species

Many species of toxic or harmful algae have thrived for thousands of years in waters free from human influence. These species can bloom in "clean" waters (e.g., *Alexandrium* spp. in the Gulf of St. Lawrence or in the Aleutian Islands of Alaska), achieving high biomass sufficient to cause dangerous levels of toxicity using naturally supplied nutrients. Although eutrophication is often invoked to explain the expansion of certain toxic episodes in recent years, convincing evidence linking increased frequency or magnitude of toxic blooms to anthropogenic activities is lacking. In most cases where a toxic species has increased its geographic range or the frequency or severity of its impacts, mechanisms other than growth stimulation through nutrient enrichment can be invoked as alternative explanations. For example, the expansion of the PSP problem within southern New England during the last two decades can be attributed to *Alexandrium* species dispersal through natural bloom advection and cyst deposition just as easily as to nutrient enrichment of Gulf of Maine waters from coastal development. Likewise, the expansion of aquaculture activities may increase the reports of toxic episodes due to the initiation of commercial operations in waters where toxic species are indigenous or to the high level of scrutiny of the commercial product.

Nevertheless, it is evident that anthropogenic activities can provide macro- and micronutrients which can increase the growth rates and standing stock of toxic species. As with all other aquatic plants, increased levels of inorganic macronutrients, such as  $PO_4$  or  $NO_3$ , can stimulate the growth of toxic species if those nutrients are the first to be depleted during normal growth.

Likewise, some toxic species are known to utilize organic N or P as macronutrient sources. Micronutrients, such as trace metals, vitamins, or chelators, are also potentially stimulatory constituents of domestic and industrial effluents.

One example where a link between toxic blooms and anthropogenic activities has been demonstrated is in Finland. A decrease in the abundance of toxic bloom-forming, mostly freshwater cyanobacteria algal species was observed in eutrophic bays in the city of Helsinki following removal of phosphorus from sewage effluents. In contrast, in the outer archipelago areas and open sea, other harmful open sea species have become more abundant and blooms more intense.

These nutrients can stimulate or enhance the impact of toxic species in several ways. For example, toxic phytoplankton may increase in abundance due to nutrient enrichment but remain as the same relative fraction of the total phytoplankton biomass (i.e., all phytoplankton species are affected equally by the enrichment). Alternatively, the nutrient enrichment can differentially enhance either the relative dominance of a toxic species within an assemblage or the level of toxicity of individual cells of that species. In each of these three examples, the net result of nutrient enrichment would be the same, namely, an increased incidence of toxic episodes.

The non-selective stimulation of toxic and non-toxic species alike through nutrient enrichment would result in an elevation of toxicity superimposed on a general background of non-toxic blooms that are more frequent and that reach higher biomass levels. No special mechanisms need to be invoked to explain this pattern of development.

Differential enhancement of the biomass or toxicity of algal species by anthropogenic inputs could occur through several mechanisms. One frequently cited possibility relates to the different requirements that phytoplankton classes or species may have for certain nutrients, such as the silicon requirement of diatoms. Since other classes of algae do not share this requirement, diatoms could be silicon limited when supplies of N and P are sufficient to allow other species to grow and accumulate. An excellent example of this type of "nutrient ratio" effect (reviewed in Smayda, 1990) is found in the long-term monitoring records of Helgoland. Nearly 30 years of very detailed data document a steady increase in the N:Si and P:Si ratios, accompanied by a striking change in the composition of the phytoplankton as the relative proportion of diatoms decreased and flagellates increased. Changing nutrient supply ratios, which presumably reflect the abundance of P and N and the relatively low levels of Si in effluent waters, may thus have had a profound effect on the coastal ecosystem. Since a common assumption has been that diatoms are rarely harmful, the effect of nutrient enrichment may have enhanced the relative abundance and, thus, the impacts of harmful species.

Another example of the importance of nutrient ratio effects is in certain areas of the Baltic Sea where decisions are pending concerning the nature of proposed sewage treatment (e.g., N versus P removal). A controversial and unresolved issue is whether the removal of N will create N:P ratios that favour the growth and dominance of toxic cyanobacteria that possess the unique ability to fix nitrogen (N<sub>2</sub>). Here again, the special nutritional characteristics of one group of harmful algae may permit them to take advantage of favourable nutrient supply ratios and dominate the phytoplankton.

Another mechanism by which nutrient ratios can influence toxic species relates to the effects of different limiting nutrients on the levels of toxicity in certain species. One example is *Alexandrium tamarense*, which can be about 5 times as toxic when grown in P-limited cultures than in nutrient-replete cultures. Severe N-limitation of this species can reduce toxicity several-fold compared to nutrient replete controls. The net effect is that cells limited by these two different nutrients in natural waters could differ in toxicity by an order of magnitude. This has obvious management implications with respect to nutrient loadings to coastal waters because

efforts to reduce P concentrations, for example, might result in higher toxicity cells than before the nutrient control. In this case, even though there may be fewer cells overall, more toxin would be present.

A related phenomenon has been reported in *Chrysochromulina polylepis* cultures, where levels of toxicity were considerably enhanced in P-limited cultures relative to nutrient replete controls. This is consistent with the field data from the 1988 bloom of that species, which caused extensive benthic mortalities when dissolved N:P ratios were very high in the Skagerrak and there was a possibility of P limitation of the algae. Recent preliminary observations indicate that N limitation can also enhance *C. polylepis* toxicity (E. Paasche, unpublished). A related series of observations demonstrates that the toxicity of *Gyrodinium* cf *aureolum* is enhanced in P-limited cultures (Gentien *et al.*, 1991). A possible explanation is that, because the toxins from these two species are glycolipids and lipid synthesis proceeds under both N or P limitation, toxin accumulation would continue after other metabolic pathways for growth have ceased to function.

Another example demonstrating how nutrient ratios may affect algal toxicity is with the pennate diatom *Nitzschia pungens* f. *multiseries*. This species begins to produce the neurotoxin domoic acid when cell division ceases during the stationary phase. However, domoic acid production occurs only when nitrogen is in excess and some other nutrient (e.g., silicon or phosphorus) limits the cell yield at that time (Bates *et al.*, 1991).

In the case of *Gymnodinium catenatum* cultured on K media, changes in the concentration of nitrate (and, therefore, in the N:P ratio) induce important qualitative and quantitative changes in the production of toxins (Reguera and Oshima, 1990). Femtomoles of toxin produced per cell can be more than one order of magnitude higher in cultured cells than in wild populations, and GTX6 can be the predominant toxin in cultures, whereas GTX5 is the more abundant in wild *G. catenatum*.

These observations from cultures emphasize that changing nutrient ratios in coastal waters may induce higher levels of toxicity in the cells of some species.

### b. Aspects of Non-toxic, Potentially Harmful Species

Occurrences of red tides due to intense growth or accumulation of algae predate anthropogenic influences on the marine environment. Such growth results from natural processes of enrichment, such as seasonal upwelling, land runoff, etc. However, it is also evident that a common result of coastal eutrophication has been an increase in the occurrences of massive algal blooms.

In March 1990, an International Conference on Marine Coastal Eutrophication was held in Bologna, Italy to discuss the responses of coastal and estuarine systems to human impacts. Many examples were presented at this conference.

In contrast to the blooms of toxic algal species, for which the link to anthropogenic inputs remains speculative, there are several examples of increasing occurrences of red tides or high biomass blooms of non-toxic algae coincident with intensive coastal development. Examples are the red tides in Hong Kong Harbour, which increased in parallel with the trend of human population growth in that city, and the red tides in the Inland Sea of Japan, which decreased when effluent inputs having a high chemical oxygen demand were reduced through regulatory controls.

As discussed above for toxic algae, the species composition of the blooms can be dependent on the relative supply rates of the major nutrients (i.e., phosphorus, silicon and nitrogen) due to differential uptake capabilities and growth requirements of individual bloom species. An important example of the potential role of nutrient ratios in the relative dominance of non-toxic species concerns the *Phaeocystis* blooms in the German Bight and the southeastern North Sea, which now last 2-3 times as long as was the case prior to 1973. *Phaeocystis* blooms develop after the depletion of silicate by the diatom spring bloom, taking advantage of the high levels of nitrogen and phosphorus which the diatoms are unable to utilize due to silicate limitation. Here again, the relative inputs of N, P, and Si from domestic and industrial effluents may be affecting the dominance of certain species or classes of algae, while providing the additional nutrients required to enhance the biomass of non-toxic species to harmful levels.

Harmful effects from non-toxic blooms are thus controlled in part by the type of nutrient enrichment. In theory, management strategies for the coastal zone could be developed that minimize the likelihood of harmful effects from non-toxic algae or that minimize the magnitude of those impacts. In practice, however, this requires detailed scientific understanding of the nutrient requirements, uptake capabilities, growth potential, and grazing susceptibility of many indigenous species. The task is somewhat simpler in cases where harmful effects are largely due to one or two target species or when a general phenomenon (e.g., anoxia) occurs following blooms of a variety of different non-toxic species. In the former case, knowledge of the growth requirements and bloom mechanisms for those species can be used to design bloom mitigation strategies or to evaluate the potential for other activities to stimulate those species. When the impact is a more general phenomenon not linked to a particular algal species (e.g., anoxia), efforts to reduce effluent inputs can be expected to have a predictable effect by lowering the overall phytoplankton biomass and eliminating some of the oxygen demand responsible for the anoxia.

#### c. Hydrographic and Other Factors

It is important to note that many toxic and non-toxic blooms occur without any direct stimulation from anthropogenic nutrient input. Mechanisms for population development through physical or hydrographic concentration can take a variety of forms. Some blooms are associated with specific hydrographic features, such as <u>fronts</u> (e.g., Ushant Front) and <u>coastal upwelling</u> (e.g., Galician and northern Portuguese coast).

Long-distance <u>transport</u> and delivery of established bloom populations to their impact sites via buoyant <u>plumes</u>, <u>wind-driven</u> flow, etc., are well-established mechanisms that may lead to toxic episodes.

The regular eastward development of the *Phaeocystis* bloom along the southeast coast of the North Sea is another situation in which advective processes contribute to bloom development.

Another case in which the geographic expansion of a toxic species or even the magnitude of bloom populations can be influenced by factors other than nutrient supply concerns species which form dormant <u>resting cysts</u>. The geographic dispersal of cyst-forming species (e.g., *Alexandrium tamarense, Gymnodinium catenatum*) is mainly governed by the advection and deposition of cysts, either during bloom events or during the winter months prior to bloom development. Species dispersal via this mechanism would thus be unrelated to eutrophication. Although field evidence remains weak, advection and resuspension of cysts immediately prior to bloom events can be a major factor in bloom development independent of ambient nutrient levels.

A final consideration in the context of factors that can cause harmful events without linkage to nutrient enrichment is that <u>some algal species are highly toxic</u>. This means that very low concentrations can result in toxicity, i.e., that no enhancement is needed. The best example is *Dinophysis*, which has been shown to cause toxicity in shellfish at concentrations of 200 cells/liter.

Finally, it is important to note the effect that physical processes, such as <u>mixing</u>, <u>dilution</u>, <u>dispersion</u>, and <u>light transmission</u>, have on the observed response of algal populations to nutrient enrichment in the sea. Algae require both light and nutrients to grow. If light becomes limiting, the full growth potential of any nutrient enrichment may not be achieved. Vertical mixing and turbidity in the surface layers reduce the availability of light to phytoplankton. Consequently, in strongly mixed or turbid environments, there may be no algal bloom response to nutrient enrichment. Similarly, there is unlikely to be the local development of algal blooms, even if nutrient enrichment is present, in environments where the growth rate of the phytoplankton cannot produce new cells faster than they are removed by dispersion and dilution (or any other loss) processes. Such factors are particularly important in fjords and estuaries where water exchange is frequently controlled by tidal flushing and circulation driven by freshwater input.

# References

- Bates, S.S., de Freitas, A.S.W., Milley, J.E., Poklington, R., Quilliam, M.A., Smith, J.C., and Worms, J. 1991. Controls on domoic acid production by the diatom *Nitzschia pungens* cf. *multiseries* in culture: nutrients and irradiance. Can. J. Fish. Aquat. Sci., <u>48</u>. (In press).
- Gentien, P., Arzul, G., and Toularastel, F. 1991. Modes of action of the toxic principle of *Gyrodinium* aureolum. International Symposium "Marine Biotoxins", Paris, January 1991. (In press).
- Reguera, B., and Oshima, Y. 1990. Response of Gymnodinium catenatum to increasing levels of nitrate: Growth patterns and toxicity. In Toxic Marine Phytoplankton, pp. 316-319. Ed. by E. Graneli, B. Sundstrøm, L. Edler, and D.M. Anderson. Elsevier, New York.
- Smayda, T.J. 1990. Novel and nuisance phytoplankton blooms in the sea: Evidence for a global epidemic. In Toxic Marine Phytoplankton, pp. 29-40. Ed. by E. Graneli, B. Sundstrøm, L. Edler, and D.M. Anderson. Elsevier, New York.

# 11.4 State of Development and Routine Applicability of Methods for the Detection and Quantification of Phycotoxins

The ACMP noted that a comprehensive review of methods available up to 1989 for the detection and/or quantification of phycotoxins had been produced by the former Working Group on Harmful Effects of Algal Blooms on Mariculture and Marine Fisheries and is expected to be published in the Cooperative Research Report series in 1991.

As there is a rapid development of new techniques in this field, the ACMP noted the new advances in methodology for the detection and quantification of certain marine phycotoxins, and provides the following material as an update on earlier advice:

### a) Diarrhetic Shellfish Poisoning (DSP)

Most ICES countries with DSP problems are using the high performance liquid chromatography (HPLC) technique of Lee *et al.* (1987) to detect the toxins. There is evidence that the extraction and preparation procedures in this method may give rise to considerable variability in results. To avoid some of these problems, an improved technique which uses a different eluent composition and ultrasonification during esterification has been developed by Stabell *et al.* (1991). In addition, the latter method permits the use of an internal standard (deoxycholic acid).

Other improvements have been proposed by Shen *et al.* (1991). The ACMP also noted that a method involving the application of combined Liquid Chromatography-Mass Spectrometry was in use by some workers (Pleasance *et al.*, 1990).

### b) Paralytic Shellfish Poisoning (PSP)

No significant advances have been identified in the routine methods, outlined in previous reports, for the detection and quantification of PSP toxins. However, the ACMP noted the availability of a PSP kit using polyclonal antibodies against STX, neoSTX, GTX1 and GTX3. This "STX test kit" may be more sensitive than HPLC and more specific than mouse bioassays (Cembella and Lamoreux, 1991), but results of intercomparison activities are not yet available.

The ACMP noted that several attempts are being carried out to reduce the number of mouse bioassays used. For example, in the Galician Rfas, where PSP is often due to *Gymnodinium catenatum* and the affected bivalves present a high percentage of the highly fluorescent and low potency toxin, GTX5, a fluorometric technique is being applied for initial screening purposes (Martínez *et al.*, 1991). The ACMP emphasizes that such procedures can only be recommended when the toxin profile is known.

In line with the concerns expressed in its 1990 report, the ACMP noted that, as chemical methods devised for specific toxin profiles replace the mouse test, there is a danger that, if bioassays are completely abolished, the appearance of new toxins may not be detected until after several consumers have become ill. However, the mouse test alone is not a total insurance against this. It is known that the mouse test does give false positive results, i.e., the mouse reacts to chemicals which are not toxic to man. It is equally likely that new toxins will be discovered which affect man but which are not detectable using the mouse test.

### c) Availability of standards

The ACMP noted that an okadaic acid standard is now commercially available from Moana Bioproducts in the USA (purity >97%), and from Boehringer Manheim Ltd. in Europe (purity >97%). It also noted that the National Research Council of Canada (NRC, Halifax, Canada) is planning to produce purified STX, neoSTX, GTX1, GTX4, and a reference mixture prepared from mussel tissue, for HPLC calibration. It further noted that the EEC Community Bureau of References (BCR) is promoting a project to produce toxin standards for PSP and DSP and to provide reference materials.

#### References

- Cembella, A.D., and Lamoreux, G. 1991. La détection des toxines paralytiques de mollusques chez les dinoflagellés marins par essai immunoenzymatique. Rev. Int. Océanogr. Méd. (In press).
- Lee, J.S., Yanagi, T., Kenna, R., and Yasumoto, T. 1987. Fluorometric determination of diarrhetic shellfish toxins by high performance liquid chromatography. Agric. Biol. Chem. 51: 877-881.

- Martínez, A., Reguera, B., Fernández, M.L., Míguez, A. and Cacho, E. 1991. Spatial distribution of PSP toxicity in the mussel rafts of the Galician rías (NW Spain): Some management strategies. International Symposium "Marine Biotoxins", Paris, January 1991. (In press).
- Pleasance, S., Quilliam, M.A., Freitas, S.W., Marr, J.C., and Cembella, A. 1990. Ion-spray Mass Spectrometry of Marine Toxins II. Analysis of Diarrhetic Shellfish Toxins in Plankton by Liquid Chromatography-Mass Spectrometry. Rap. Commun. Mass Spectro., 4: 206-213.
- Shen, J.L., Ganzlin, G., and Luckas, B. 1991. HPLC determination of DSP toxins. International Symposium "Marine Biotoxins", Paris, January 1991. (In press).
- Stabell, O.B., Hormazabal, V., Steffenak, J., and Pedersen, K. 1991. Diarrhetic shellfish toxins: improvement of sample clean-up for HPLC determination. Toxicon, 29(1): 21-29.

### 12. GUIDELINES FOR MONITORING NUTRIENTS

The ACMP reviewed draft guidelines for the sampling and analysis of nutrients in sea water, that had been prepared by the Marine Chemistry Working Group as a combination of a former draft and additions on analytical techniques. The comments made by the Working Group on Shelf Seas Oceanography were also noted by ACMP. The ACMP was reminded that the guidelines which had been requested were required primarily in relation to investigations of the geographical distribution and the temporal trends of nutrients in coastal waters.

The ACMP agreed that the guidelines on analyses provided by the MCWG met those needs but that some clarification of their applicability was required. The ACMP noted, however, that analytical guidelines were being published in the Techniques in Marine Environmental Sciences series and that PARCOM and the NSTF had accepted the preliminary guidelines (ICES, 1990) as being useful as an interim measure. The ACMP, therefore, agreed to work with the Working Group on Shelf Seas Oceanography on the sections dealing with the use of nutrient data and the appropriate sampling strategies during the intersessional period and will report on this issue next year.

ICES, 1990. Report of the ICES Advisory Committee on Marine Pollution, 1990. ICES Coop. Res. Rep. No. 172, pp. 121-125.

## 13. INTERCOMPARISON EXERCISES AND QUALITY ASSURANCE ACTIVITIES

### 13.1 Intercomparison Programme on Analyses of Polycyclic Aromatic Hydrocarbons

The ACMP reviewed a report on stage 1 of the multi-stage Intercomparison Programme on Analyses of Polycyclic Aromatic Hydrocarbons (PAHs), that had been prepared by Mr R.J. Law and Mr M.D. Nicholson and reviewed by the Marine Chemistry Working Group (MCWG). This exercise had been planned from the outset to involve only a limited number of carefully selected laboratories with the ability to carry out analyses of these compounds using either gas chromatography with mass spectrometry (GC/MS) or high pressure (performance) liquid chromatography (HPLC) techniques. Stage 1, which is now complete, involved analysis of a solution of 10 PAH compounds and was conducted in two phases. The first phase had involved 19 laboratories, of which 14 returned results, and the second phase, 18 laboratories, of which 17 returned results. The second phase had been carried out because some participants had reported difficulties with the solvent used (acetonitrile) and with the integrity of the crimp-sealed ampoules used to circulate the sample material. The second phase had, therefore, utilised flame-sealed ampoules and a different solvent (hexane).

The results show that, despite the difficulties encountered in phase 1, the overall level of agreement reached was somewhat better than for phase 2. Taking the two phases together, it is clear that many laboratories achieved a very high level of precision in their results, often less than 3% relative standard deviation (RSD). The overall level of agreement of the results with the nominal concentrations in the distributed solutions was also good. With the general agreement of all participants, a target of 20% bias and 30% interlaboratory variability has now been established. Whilst this may seem high for the first stage, it will be hard to achieve at the later stages when real samples with lower concentrations are used.

In order to establish whether individual laboratories experienced consistent difficulties, or whether particular PAH compounds posed difficulties for most laboratories, a range of statistical treatments has been applied to the results. These served to identify a few common problems with a few compounds analysed by one or other techniques. On the whole, however, the results of these statistical analyses suggest that the majority of the differences encountered appear to be entirely random in nature.

Where difficulties have been encountered by individual laboratories, considerable improvements have been achieved by means of advice provided through the coordinator. To ensure that all laboratories are ready to move on to the next stage, a further phase of stage 1 is being conducted during the first half of 1991 for the few (3) laboratories requiring this assistance.

Plans have been drawn up for the conduct of stage 2 of this exercise in the second half of 1991. This will call for analysis of the same 10 compounds in a cleaned-up sediment extract. The use of this sample matrix recognises the interest of OSPARCOM and the Helsinki Commission as well as the NSTF in surveys of contaminants in sediments. It also takes advantage of the fact that a sediment sample will be easier to stabilise. The second stage will include a requirement for the submission of in-house quality control data in addition to the results of the sample analysis. It is due for completion late in 1991 and it is expected that the report will be ready in 1992.

The ACMP noted that this type of analysis is rather specialised and that a more detailed and easily understood explanation of the statistical treatments used and the results they produce was desirable. Accordingly, it concluded that the reports of stages 1 and 2 together would provide a more complete picture than a report of stage 1 alone and agreed that, if the timetable of stage 2 stays on course, the results of the two stages should be published together in the Cooperative Research Report series. In the meantime, copies of the interim version of the report can be obtained from the ICES Environment Officer.

Outline plans for stages 3 and 4 of the intercomparison programme have been developed. They will be conducted only after the successful completion of stage 2 and will involve analysis of a raw sediment-extract and a fresh sediment. Subsequent stages will provide for analyses of biota and water.

The ACMP recognises that, although the field of PAH analysis is somewhat specialised, there is increasing interest in the concentrations of such substances in environmental samples. It must be recognised in this context that the term PAH covers a very wide range of substances and that, with a few notable exceptions, there is little agreement on which compounds merit most concern in relation to their potential impact on either marine species or man. The ACMP noted that the group of compounds selected for the PAH intercomparison programme had been chosen primarily on the basis of their analytical and chromatographic behaviour. Nevertheless, the ACMP considers that they also represent a reasonable selection of compounds for inclusion in the initial phases of a monitoring programme. The compounds concerned are:

Phenanthrene Fluoranthene Pyrene Benz[*a*]anthracene Chrysene Benzo[*k*]fluoranthene Benzo[*a*]pyrene Benzo[*e*]pyrene Benzo[*ghi*]perylene Indeno[1,2,3-*cd*]pyrene

On the basis of the results of the intercomparison programme achieved so far, it seems likely that experienced laboratories with access to suitable analytical equipment (GC/MS or, to a lesser extent, HPLC) should be capable of producing results that are reasonably comparable among laboratories (20% bias and 30% interlaboratory variability). However, in this context, the ACMP notes the cautionary comments of the coordinators of the exercise concerning the limited objectives of the programme and the danger of over-interpretation of the results. Accordingly, the ACMP emphasises that this statement applies only to the type of laboratory selected to participate in this current programme. The ACMP further notes that the group of compounds concerned only represents a small proportion of the total number of petroleum-derived hydrocarbons and is, even then, only a sub-set of the PAHs which are primarily of fossil-fuel combustion origin. Thus, results from this intercomparison programme should not be extrapolated to predict performance when oil-contaminated samples are being analysed for other specific hydrocarbons.

# 13.2 ICES/IOC/OSPARCOM Intercomparison Programme on the Analysis of Chlorobiphenyls

The ACMP reviewed the report on the results of the second stage of the ICES/IOC/OSPARCOM Intercomparison Programme on the Analysis of Chlorobiphenyls (CBs) in Marine Media, that had been prepared by Drs J. de Boer, L. Reutergårdh, J. van der Meer, and J.A. Calder and reviewed by the Marine Chemistry Working Group. This had involved the determination of the concentrations of 10 CBs (IUPAC Nos. 28, 31, 52, 101, 105, 118, 138, 153, 156 and 180) in an unknown solution, a cleaned-up seal blubber extract, and a cleaned-up sediment extract. For the few participants who had been unable to achieve acceptable results in Stage 1 and for a small number of new participants, an extra requirement was the analysis of an unknown CB solution and a supplied known solution. Sixty-five sets of samples were sent out and 58 laboratories submitted results, although the results from three laboratories were received too late to be included in the statistical analysis of the overall data.

The results fall into three groups:

- **Group 1** All results within 20% of the target or mean values, with the exception of at most one result per solution; acceptable chromatographic performance and calibration.
- **Group 2** More than one unacceptable result per solution or several deficiencies in the calibration procedure and/or the chromatographic system.

**Group 3** Poor chromatographic procedures and/or difficulties with the calibration procedures or with statistical outliers.

Interestingly, only seven laboratories produced results that placed them in Group 1 for all the solutions they analysed, and only four of these laboratories analysed all three solutions. Particularly poor results were obtained with the sediment extract, with only six laboratories achieving Group 1 status and nineteen laboratories falling into Group 3 for this extract.

Several reasons for the poor performance are given in the report. Advice on the improvements necessary and the way to achieve them has been supplied by the coordinators to the laboratories concerned. The two most common problems were unsatisfactory chromatographic conditions, typically too short a column length, and poor preparation of calibration materials including in-house standards. The latter problem revealed that some commercially produced standard solutions are unreliable.

The ACMP noted that, with the exception of the results for CBs 28, 31, 105 and 156, which few analysts determined correctly, the overall results merit a stepwise progression to the next stage. However, the ACMP endorses the requirement that certain minimum standards be met. These are that: commercially prepared standard solutions should not be used, capillary columns should have a minimum length of 50 m and a maximum internal diameter of 0.25 mm, with a recommended preferred maximum of 0.20 mm, and at least two different column coatings should be used. In addition, all laboratories must use internal standards. A number of laboratories which had failed to supply results, even 5 months after the original deadline, will be excluded from subsequent steps. In addition, five laboratories which had failed to achieve anything approaching satisfactory results are being advised not to take part in the next stage.

Subject to these conditions, which participants will be allowed until late 1991 to introduce and achieve the necessary improvements, Stage 3 will start. This will be in two parts. In the first phase, participants will be asked to analyse six times, at approximately weekly intervals, a certified reference material (fish oil or sediment). This will demonstrate the quality of the laboratories' in-house quality control, and satisfactory performance in this phase will have to be demonstrated before the next phase is entered. This next phase will call for the analysis of cleaned-up and raw seal blubber extracts and an uncleaned-up sediment extract.

The ACMP noted that a sediment extract is being included in Stage 3 despite the fact that the overall performance with the cleaned-up sediment extract in Stage 2 is considered to be unsatisfactory. The inclusion of the sediment extract takes account of the fact that OSPARCOM, HELCOM and NSTF are all paying particular attention to the analysis of sediments in their present monitoring studies. The ACMP agreed that this fact does merit the inclusion of the sediment extract and noted that the concentrations of CBs were somewhat lower in the sediment extract than in the seal blubber extract in Stage 2, which may have accounted for the poorer results relative to the seal blubber extract.

Nevertheless, the ACMP is concerned at the implications of the results from Stage 2 of the programme when it comes to the assessment of the results of the analysis of CBs in sediments as part of the NSTF/JMP monitoring programme. It seems likely that, whereas the results from one laboratory may be internally consistent, they may not be comparable with those from another laboratory. This fact must be taken into account at the assessment stage.

The ACMP agreed that, after appropriate editorial attention, the report of the second stage of the CB intercomparison programme should be published in the Cooperative Research Report series. In connection with the conduct of the two components proposed for Stage 3 of this intercomparison programme, the ACMP noted that the satisfactory conduct of both phases, and particularly the conduct of phase 2 of Stage 3, is heavily dependent on the necessary funding being secured to cover the costs of the coordinators of the programme.

## 13.3 Intercomparison Exercise on the Analysis of Trace Metals in Suspended Particulate Matter

The ACMP reviewed a report on the results of the first phase of the Intercomparison Exercise on the Analysis of Trace Metals in Suspended Particulate Matter (SPM), that had been prepared by Mr H. Hovind and Dr J. Skei and reviewed by the Working Group on Marine Sediments in Relation to Pollution (WGMS). This exercise, which assessed the interlaboratory comparability of determinations of trace metals in small amounts (1-5 mg) of sedimentary material (as a substitute for suspended particulate matter), has successfully been completed. A total of 19 laboratories in eleven ICES member countries participated.

The results of this exercise confirm those of an earlier ICES pilot intercomparison exercise, specifically that the determination of a number of trace metals in small particulate samples can be carried out and that, while there are outstanding problems that need resolution, further analytical development and intercomparison are both feasible and desirable. Problems revealed by the exercise are primarily associated with the relatively poor recoveries of analytes from small samples, despite the predominant use of a total digestion method based on the use of hydrofluoric acid, in combination with other oxidizing acids, or other total analysis techniques. The main problems identified are:

- i) The loss of fine particulate material during the weighing step and during transfer of the sample to the digestion apparatus. This results in the analysis of a smaller sample, with differing size distribution, from the weighed original; and
- ii) Difficulties with the accurate and precise weighing of small samples. Such difficulties have been noted in other intercomparison exercises in which larger samples have been used, but are obviously likely to be more severe in the case of samples weighing 1 to 5 milligrams.

Other conclusions of the exercise are:

- a) The use of nitric acid alone is not effective for the determination of all total metal concentrations, and hydrofluoric acid must be used with another oxidizing acid for such purposes;
- b) Slurry sampling, in which particulate material is suspended in glycerine and directly injected into the graphite furnace of an atomic absorption spectrophotometer, provides results for some metals that are remarkably similar to those obtained by total digestion methods;
- c) There may be a need to re-examine procedures for the determination step where boric acid is used for matrix normalization. While the report of the exercise suggests that avoidance of boric acid yields better recoveries, it is possible that the results may simply reflect inadequate final sample dilution; and
- d) Controlling and compensating for moisture uptake by small samples of particulate material appears to be a less severe problem than anticipated, but further examinations of this issue appear warranted.

While there remain concerns about the degree to which well-homogenized sedimentary material is a suitable substitute for marine suspended matter (particularly in respect to homogeneity and size distributions), the intercomparison exercise has enabled some improved insights into the likely difficulties to be experienced with assays of suspended particulate material.

Accordingly, it has been proposed that the conduct of a second phase of this intercomparison programme be based on the use of real marine suspended matter isolated or recovered on filter membranes. This second phase is designed to address the comparability of:

- a) the weighing of filters;
- b) chemical analyses of blank filters; and
- c) chemical analyses of natural suspended matter on filters.

The experimental design of this second phase is shown in Figure 13.3.

Figure 13.3	Design of Phase 2 of the Intercomparison Exercise on the Analysis of Trace Metals in SPM.
FILTERS	LARGE VOLUME OF PRE-FILTERED SEA WATER
WASH	HOMOGENIZE
DRY	
WEIGH	FILTER EQUAL ALIQUOTS OF WATER
	WASH ALL FILTERS
	DRY AND WEIGH FILTERS
	STORE FILTERS
	DISTRIBUTE FILTERS
	DRY AND WEIGH FILTERS
	ANALYSE ALL FILTERS
	REPORT RESULTS TO COORDINATOR

Following a statistical examination of the design of this experiment, it has been recommended that filters be randomly selected and that some preliminary evaluation of the variance of blank filter composition be conducted by a single laboratory. The adequacy of the proposed triplicate replication as a basis for assessing the bias and precision of participating laboratories has also been examined. Accordingly, the selection of replication is likely to be based on the assessment of between-filter variability and some decision as to the level of bias to be detected. The statistical evaluation also included the types of within-laboratory variance to be assessed (i.e., within a single day or over longer periods) because of the mounting evidence that within-laboratory variance is made up of three components (bias, bias variation, and random variation) rather than two (a relatively invariant bias and random variation), as previously believed.

Although the JMG has recently indicated that it has no immediate need for this type of intercomparison exercise, and a similar view has apparently been taken by TWG and SACSA, the ACMP believes that this ignores an important potential interest, namely, the use of measurements of the composition of suspended matter within the context of studies of contaminant transport, flux, and behaviour, and marine environmental assessments (e.g., in relation to gross and net riverine inputs). Accordingly, the ACMP encourages the continuation of studies of the interlaboratory comparability of analyses of suspended particulate matter for ICES purposes and looks forward to receiving the report on the results of the second phase of this exercise.

The ACMP recommended that the report on the first phase of this intercomparison exercise should be published in the ICES Cooperative Research Report series.

### 13.4 Intercomparison Exercise for Measurements of Dissolved Oxygen in Baltic Sea Water

On the basis of a Helsinki Commission request to ICES to develop proposals for an intercomparison exercise on measurements of dissolved oxygen in sea water, the Marine Chemistry Working Group had prepared a draft proposal. Thereafter, the ACMP reviewed and finalized this proposal, and published it in its 1990 report (ICES, 1990).

This proposal was adopted by the ICES/HELCOM Steering Group established for the execution of the intercomparison exercise, which was held during the HELCOM Third Biological Intercalibration Workshop at Visby, Sweden on 27-31 August 1990. Six Baltic Sea countries participated in the exercise, conducting three different tests:

- 1) Test of the variability associated with the use of different sampling equipment;
- 2) Test of the variability associated with the sampling by individual laboratories/participants; and
- 3) Test of the variability associated with the use of different analytical procedures.

The exercise included two different water masses with different oxygen concentrations, taken from 10 m and 80 m depths, respectively. Three replicates were sampled and analysed by participants.

The results of the intercomparison exercise are regarded as positive and they led to the following conclusions:

- 1) The use of different hydrocast bottles does not yield results which differ significantly at the 95% confidence level;
- 2) The use of different persons sampling does not yield results which differ significantly at the 95% confidence level for the samples which are almost saturated with oxygen;
- 3) There are systematic differences, most likely due to titration errors, between laboratories in standardizing their own thiosulphate solutions; and
- 4) All laboratories produced acceptable results (96-104% of the consensus values at high oxygen concentration and 93-104% at the low concentration).

Whilst recognising the good quality of the results achieved, the ACMP noted that the number of replicates analysed (3) was not really enough to provide a basis for a good statistical evaluation of the results.

The ACMP also noted that the Steering Group had taken the opportunity of the Visby Workshop to organise an intercomparison of results of the determination of dissolved hydrogen sulphide. Samples containing dissolved hydrogen sulphide were preserved with cadmium chloride solution. This test failed because none of the laboratories was able to dissolve the precipitate of cadmium sulphide. The ACMP took note of this failure and will pass the question of the feasibility of an intercomparison exercise on hydrogen sulphide determinations for consideration to the MCWG.

ICES, 1990. Report of the ICES Advisory Committee on Marine Pollution, 1990. ICES Coop. Res. Rep. No. 172, pp. 61-62.

### 13.5 Intersessional Work on Nutrient Analyses

The ACMP noted that, since the publication of its basic guidance on the sampling and analysis of nutrients in sea water in its 1990 report, there has been further progress on the development of guidelines for studies of nutrients in sea water. The application of these guidelines has been limited to geographical distribution and trend studies of nutrients.

The ACMP noted that during the Skagerrak Experiment (SKAGEX), participants analysed samples taken along a transect to check the comparability of their results. In most cases, the differences in the results of the nutrient measurements were consistent, but in several cases some form of correction factor will have to be applied to the data. This being the case, it is clear that further efforts must be applied in order to improve analytical performance. The need for reference materials is clearly apparent from the results of such programmes that involve many laboratories, ships, or countries.

Having in mind a number of projects in which nutrient analyses are not possible within a reasonable time after sampling, the ACMP welcomed the activities of the MCWG to study appropriate methods for the preservation and storage of sea water samples for nutrient analysis.

The ACMP further noted that the experience gained in the ICES intercomparison exercise on nutrient measurements in sea water has been successfully applied in the Irish Sea. Under the Northern Seas Action Programme (NORSAP) of the European Community, four UK and two Irish laboratories collaborated in a two-round intercomparison of N and P measurements coordinated by the MAFF/UK Lowestoft laboratory. While initial stages showed that some laboratories were experiencing serious problems, these are now largely resolved and the first phase of an Irish Sea monitoring programme for nutrients was carried out in January 1991. This comprised a network of sampling stations based on selected estuarine salinity gradients and open-sea grids. The results will be evaluated to determine the suitability of the data, and the sampling network, for purposes of monitoring spatial and temporal variations in nutrient concentrations in the Irish Sea. A report on this programme will be finalized during 1991 and will be available from the Fisheries Research Centre, Abbotstown, Co. Dublin, Ireland.

# 13.6 Quality Assurance Protocols for the Analysis of Contaminants in Water, Tissue and Sediment for Use in Data Assessments

There is need for a better balance between the effort applied to Quality Assurance (QA) and that required to evaluate data prior to their interpretation for scientific or management purposes. Deficiencies in either the observance of QA procedures, or their documentation and reporting, result in unnecessary excess demands for effort devoted to data validation and assurance before they can be interpreted with confidence in their reliability. Recent experience within ICES, and particularly that gained from the preparation of the report of the 1985-1987 Baseline Study of Trace Metals in Coastal and Shelf Sea Waters, suggests that it would be useful to provide advice regarding QA protocols and the difficulties that have to be faced if inadequate QA procedures are instituted by laboratories reporting data on conditions in the marine environment. This follows a conviction that many laboratories appear to lack an appreciation that quality control and assurance procedures must be comprehensive and applied to all steps of an analytical operation, from sampling activities to the handling of data.

During the last decade, considerable attention has been paid to analytical problems and the development of quality assurance principles and protocols to encompass the design, execution, and evaluation of monitoring programmes.

Currently, the ACMP considers that there is no need to devise further QA protocols for specific or general purposes. Guidelines for the development and implementation of QA systems in laboratories are now readily available (ICES/TIMES No. 6; ISO No. 25; and EN No. 45001). Furthermore, the reports of the many intercomparison exercises conducted under the auspices of ICES, and other agencies, provide valuable

perspectives on programme design and measurement components that require QA. Attention now needs to be devoted to the implementation of existing guidance into operational programmes.

Quality assurance data required for the proper evaluation of monitoring data are referred to in various documents. In the present context, a good example is the report of the joint NSTF/JMG Workshop on Marine Monitoring Programmes in the North Sea and North East Atlantic, held in London in 1989. Such QA data comprise, *inter alia*:

- data to assess analytical accuracy (results of the analysis of certified reference materials (CRMs));
- data on statistical control within laboratories (control charts); and
- data from intercomparison, or intercalibration, exercises conducted for quality assurance purposes.

Accordingly, it becomes evident that data reporting to ICES must include additional information relating to the QA programmes of each reporting laboratory. It is, of course, incumbent upon those designing and specifying the objectives of interlaboratory measurement operations (including both monitoring programmes and intercomparison exercises) to specify the levels of accuracy and precision that must be met by participating laboratories.

The ACMP recommends that the following information be submitted with all survey, monitoring, or baseline data:

- a) Specification of QA protocols covering sampling, sample storage, sample pretreatment, and analysis;
- b) Analytical Quality Control charts;
- c) Specification and results for CRMs and other control samples; and
- d) The mean and standard deviations derived from each control chart for each sample and each analyte and the degree of sample and analytical replication employed.

If such information is provided, and it is apparent that a contributing laboratory has the analytical process under control and that the requirements for precision and accuracy are being satisfied, the results can be assumed to be reliable.

If only a portion of the required quality assurance information is submitted, the reliability of the results must be questioned. If the assessors still wish to consider such data for interpretation or use in the relevant programme, they must then resort to other information in order to assess the reliability of the data. This indeed was the situation that faced the scientists charged with compiling the results of the ICES 1985-1987 Baseline Study of Trace Metals in Sea Water. The following types of ancillary information can then be used, as they were in the case of the Baseline Study:

- a) the characteristics of the subject area (physical oceanographic, proximity to sources of material, etc.);
- b) pertinent literature (and grey literature) data; and
- c) participation in intercalibration/intercomparison exercises.

All QA data and the above-mentioned ancillary data must be available to the assessors long before they meet to draft their final report, especially because much preliminary assessment must be carried out before they are in a position to examine the entire data set and make final decisions about the rejection or acceptance of data. It should be stressed that such procedures that require the use of ancillary data, which constitute an option that can be invoked by the assessors in the event that inadequate QA reporting occurs, entail considerable additional effort. Furthermore, they do not always unambiguously distinguish between reliable and unreliable data as effectively as can be achieved if appropriate QA data are available.

In summary, the ACMP considers that it is necessary to ensure that QA protocols are laid down and rigidly adhered to in multilaboratory activities of this kind in order that the evaluation of data is both rigorous and expedient. The absence of quality assurance information in data reporting by participating laboratories has placed, and will continue to place, unwarranted demands upon those involved in data assessment and interpretation. It is questionable whether the consideration of incomplete data returns, deficient in QA information, in multilaboratory programmes will be warranted once clear criteria and protocols for associated QA have been established and applied over a few years.

- Vijverberg, F.A.J.M., and Cofino, W.P. 1987. Control procedures: Good laboratory practice and quality assurance. ICES Techniques in Marine Environmental Sciences (TIMES) No. 6.
- International Organization for Standardization (ISO). 1990. Guide 25: General requirements for the competence of calibration and testing laboratories. ISO, Geneva, Switzerland.
- Comité European de Normalisation (CEN). 1989. CEN/CENELEC, European Standard EN45001. General Criteria for the Operation of Testing Laboratories. Brussels, Belgium.

### 13.7 Quality Assurance Procedures under the Baltic Monitoring Programme

The ACMP took note of the appreciation that has been expressed by the Environment Committee of the Helsinki Commission for the ICES work on quality assurance procedures relevant to the HELCOM Baltic Monitoring Programme (BMP), including the coordination by ICES of a large number of intercomparison exercises and programmes that have always been open to participation by BMP laboratories. The ACMP was informed that, as the HELCOM prepares for the Fourth Stage of the BMP, to commence in 1994, ICES has been requested to coordinate quality assurance activities specifically related to the BMP, including the provision of information on any QA procedures or protocols that should be incorporated into the Guidelines for the Fourth Stage of the BMP and guidance on the ultimate use of this QA data in the assessment of the BMP data. The ACMP noted that a mechanism for channelling the ICES information into the HELCOM BMP work has recently been established and agreed to review the functioning of this mechanism, and any draft QA advice it has prepared, at the 1992 ACMP meeting.

### 14. STUDIES OF CONTAMINANTS IN SEDIMENTS

## 14.1 Critical Review of Contaminants in Baltic Sediments and Plans for a Sediment Baseline Study in the Baltic Sea

The ACMP reviewed the final draft of the report entitled "Critical Review of Contaminants in Baltic Sediments", compiled and edited by Drs M. Perttilä and L. Brügmann on behalf of the Sub-Group on Baltic Sediments under the Working Group on the Baltic Marine Environment (WGBME). This report had been prepared in response to a request from the Helsinki Commission and previous drafts had been reviewed and discussed at meetings of the ACMP (1990), WGBME (1990, 1991), and the Working Group on Marine Sediments in Relation to Pollution (WGMS) (1991). This version of the report took into account the main amendments that had been suggested by ACMP in its 1990 report. After review, the ACMP recommended that the report be published in the Cooperative Research Report series.

The ACMP also considered preliminary plans for a 1993 Baseline Study of Contaminants in Baltic Sediments, prepared by the Steering Group for this Baseline Study and reviewed by the WGBME. The ACMP noted that the principal aims of the 1993 Sediment Baseline Study had been defined as:

- a) To provide a description of the distribution of the substances and elements in surface sediments; and
- b) To obtain accurate and representative data which could serve as the first set in a (possible) temporal trend monitoring programme.

In order to meet these aims, a number of individual scientists have been identified to carry out the following practical tasks:

- Selection of regions and stations to be visited;
- Selection of methods and parameters;
- Selection of sampling methods;
- Ship logistics; and
- Selection of laboratories, quality control procedures, and financing.

The ACMP noted that the final proposals will be circulated before the end of 1991 and that the final plans will be reviewed by the Steering Group and the WGMS in 1992.

The ACMP accepted these preliminary plans in principal, but drew the Steering Group's attention to the following points, for consideration in preparing the final plans for the Baseline Study of Contaminants in Baltic Sediments:

- Careful selection should be made of a few representative stations for each area and their sub-division into "primary" and "secondary" stations, with the help of echo-sounding and, if possible, visual inspection of the bottom.
- All possible methods should be used for reliable dating and determination of time-dependent sediment variables.

- A multidisciplinary approach should be adopted aimed at obtaining the maximum possible information about major and trace metals, organic contaminants, nutrients, as well as grain-size parameters, organic matter, carbonate, mineralogical composition, and other characteristics necessary for sediment quality assessment and adequate data interpretation.
- An adequate quality assurance scheme for the collection, storage, and analysis of samples should be implemented.

The ACMP considered that this joint investigation will permit the collection of important new information which will be of relevance to the assessment of the Baltic marine environment and ultimately provide a useful contribution to the Third Periodic Assessment of the Baltic Sea under the Helsinki Commission.

However, while acknowledging the value of sediments as indicators of chemical contamination of the marine environment, the ACMP considers that it would be unwarranted to under-estimate the extreme difficulties of a practical application of this approach for estimating recent anthropogenic trends, especially in relation to trace metals. These difficulties arise not only in relation to those factors discussed in the "Critical Review" (e.g., analytical uncertainty, high variability of types and properties of the bottom sediments, influence of hydrological and physio-chemical parameters at the surface of sediments, diagenetic redistribution of metals within the sediments, bioturbation), but also as a result of a lack of direct coherence of the stock of the metals in the upper sediment layer with the annual anthropogenic flux of the metals into the marine environment. Thus, a simple calculation based on the data reported in the "Critical Review" shows that annual anthropogenic inputs of some trace elements entering the Baltic Sea (from municipal, industrial, riverine, and atmospheric sources) are 10-100 times lower than the stock of the same elements in the upper sediment layers (several cm depth) for all Baltic Sea areas. Accordingly, it is unlikely that such comparatively minor additions resulting from anthropogenic sources, particularly in open sea areas, can be detected and quantified even with long-term monitoring. There are also complications associated with biological and geochemical processes in surficial sediments that influence the vertical distribution of contaminants after deposition.

In view of this, the ACMP considers that the probable outcome of the Sediment Baseline Study will not be the identification of temporal contamination trends, but rather the collection of new information about the relative large-scale spatial distribution of contaminants in surface sediments and the biogeochemistry of Baltic Sea sediments. These considerations should be kept in mind during the development of the plans for the Baseline Study.

# 14.2 Techniques for Comparing Concentrations of Organic Contaminants in Sediments

The ACMP considered the approach developed by the Working Group on Marine Sediments in Relation to Pollution (WGMS) in the examination of two factors that control the concentration of organic contaminants in sediments: contaminant affinity for particles, and the extent to which the particles present have a high affinity for organic contaminants. An examination of contaminant data and sediment characteristics commonly found in US coastal environments concluded that, for sediments having more than 20% fine-grained material (less than 63  $\mu$ m fraction) and having a total organic carbon (TOC) content of less than 4%, a comparison of concentrations of organic contaminants can be accomplished by compensating only for grain-size variability and neglecting the effect of TOC.

The ACMP recognized that techniques to improve the comparability of organic contaminant concentrations in sediments cannot be identical for all areas and that only through evaluations of a real data set from a region of interest could similar specific guidelines be developed for other areas. Such a data set for each region must form the basis for determining whether grain size, TOC, or both, must be used for the normalization of organic contaminant concentrations to improve their comparability. The ACMP recommended that the above-mentioned approach to the techniques for comparing concentrations of organic contaminants in sediments should be an essential element of regional monitoring programmes, e.g., the BMP, and the JMP.

## 14.3 Application of the Guidelines for Normalization of Contaminant Concentrations in Sediments

Following a request from the JMG that ICES consider whether the present sediment monitoring guidelines could be revised, the WGMS had been asked to address this issue in the context of three specific questions at its 1991 meeting, and had reported its findings to ACMP.

The ACMP endorsed the WGMS advice on these three questions concerning the interpretation and application of the Guidelines for the Sampling and Analysis of Sediments under the Joint Monitoring Programme. This advice is as follows:

- The analysis of whole sediment alone will provide sufficient information for a comparison of contaminant concentrations between areas of different grain-size distribution only when supporting data are available to permit normalization for grain-size differences.
- The analysis of organic contaminants in whole sediment from sandy areas can lead to many results being near or below the detection limit. This could be overcome by increased sample weights and improved analytical methods. Neither WGMS nor the ACMP were aware of any validated method of sieving sediments for organic contaminant analysis and were, therefore, unable to recommend that sieving be undertaken.
- The recommendation of only one sampling strategy for sediment monitoring would lead to the selection of the most complete sampling strategy, namely, level III in the JMP guidelines. This would eliminate many of the current JMP and NSTF stations as being unsuitable. It is, thus, recommended that spatial distribution monitoring be carried out at the minimum level I (grab sampling), but the use of small box-corers should be encouraged. Temporal trend monitoring, as envisaged in the Guidelines, requires initial sampling at level III.

The ACMP recognises that a considerable body of new information will be generated via the 1990/1991 Baseline Surveys of Contaminants in Sediments being conducted by the JMG and the NSTF. A careful review of these data may allow revisions to the present guidelines to be made.

# 14.4 Use of Sediments for Temporal Trend Monitoring of Contaminant Concentrations

The ACMP noted that the results of several temporal trend monitoring studies of contaminants in sediments in the Baltic Sea and the Skagerrak had been presented to WGMS, and that some of these have given successful results in assessing increasing or decreasing contamination levels in sediments. These studies took place in depositional areas subject to industrial or municipal discharges. Other studies have shown, as expected, that the use of sediment cores for temporal trend monitoring of metals is possible in chosen areas, provided that bioturbation may be modelled and that the metal in question does not migrate diagenetically.

Because temporal trend monitoring of contaminants in sediments requires the continuous accumulation of sediments and a minimum of disturbance by biological and anthropogenic activities, most of the North Sea, except the Norwegian Trench, is unlikely to be suitable for such trend studies.

As an illustration of the difficulties of detecting changes, a study carried out in the Little Belt in Denmark, characterized by well-determined accumulation rates and mixing parameters, led to the conclusion, based on modelling calculations and field data, that a 50% reduction in metal fluxes to the sediment only shows up significantly 6 years after the reduction occurs.

### 14.5 Preliminary Overview of Methods for Assessing Sediment Transport

The ACMP considered the response of the Working Group on Shelf Seas Oceanography to the request to prepare a preliminary overview of methods for assessing sediment transport, with particular reference to the disposal of dredged material. The Working Group had undertaken a literature review from which it was clear that a great deal of detailed information on this issue was already available (see, e.g., the references listed below). Its conclusion, partly based on an overview of this literature, was that such assessments should be designed to be site specific and in response to specific management questions. Thus, this request can only be dealt with on a case-by-case basis using professional oceanographic and engineering expertise, combining modelling with field work. Because of the large volume of material that is available on this issue, any more detailed overview would require considerable effort which may only be justified if very stringent and clear guidelines are provided by the group requesting this information, SACSA.

- Alzieu, C., and Gallene, B. (Eds.). 1989. Proceedings of the Seminar on Environmental Aspects of Dredging. Nantes, 27 November 1 December 1989. 387 pp.
- National Technical Information Service. 1989. Dredging: Technology and Environmental Aspects (May 1978 July 1989). Citations from the Life Sciences Database, Springfield, VA. 94 pp.

### **15. EFFECTS OF EXTRACTION OF MARINE SEDIMENTS**

The ACMP considered the draft Report on the Effects of Marine Aggregate Extraction on Fisheries, that had been prepared by the ICES Working Group on the Effects of Extraction of Marine Sediments on Fisheries, and agreed that it should be published in the Cooperative Research Report series. This report reviews marine aggregate (sands and gravel) extraction activities in the coastal and shelf environments of ICES member countries, the effects of extraction activities on living resources and fisheries, and the management of aggregate extraction operations. As marine aggregate extraction may result in conflicts with renewable resources (e.g., fisheries and other living assets), the report provides an appropriate and informative synopsis of the field for marine scientists, managers, and the aggregate extraction industry. The text also contains a convenient Executive Summary (describing, *inter alia*, the background and objectives, as well as biotic and other environmental impacts, licensing procedures, progress with aggregate resource mapping, monitoring, and uses of marine aggregates), and a guideline Code of Practice for the commercial extraction of marine minerals.

Bearing in mind the ICES association with fisheries and related aspects of the living environment, the ACMP paid particular attention to the section of the report concerning the identification of biological targets and the nature of biological impacts. The ACMP reiterates that the rationale for the Code of Practice is to promote conduct which ensures a balance in favour of marine biota, and fisheries in particular, when other possibly conflicting and adverse activities are being planned or engaged upon. In this context, the extraction of marine sediments/minerals is relatively short-lived, while fish and shellfish stocks, given an amenable environment, are renewable resources with possibilities for long-term utilization.

Marine aggregate extraction operations are carried out by many ICES member countries. Comparatively few detailed studies on the biological impacts of these operations have been reported and, as a result, our knowledge of the implications of such activities for benthic communities and the fisheries they support remains patchy. Much research still needs to be conducted before definitive statements on the effects on fisheries of marine aggregate extraction can be made. In dredging projects, account should be taken of the relevant guidelines from the ACMP regarding the study of physical disturbances of the sea floor (see Section 8.2, above). In addition, the Working Group has identified a number of areas of research which warrant detailed study, of which the ACMP considers the following to be particularly worthwhile:

- a) The distribution of spawning grounds for bottom-spawning fish, and shellfish overwintering grounds, in areas where marine sediment extraction may occur;
- b) The effects of physical disturbance on gravel biota and communities, as demonstrated by smallscale manipulative experiments conducted under controlled conditions. The impact of repeated disturbances of these communities should also be investigated;
- c) The recolonization by benthos of gravelly substrates following cessation of disturbances or defaunation due to dredging. Time scale is an important consideration;
- d) The effects on local fish and shellfish populations of disturbance due to very large-scale dredging over a short time-span and/or defaunation of an extraction area, e.g., large-scale civil engineering projects: are populations actually reduced or are they simply displaced?
- e) The study of nutrient or suspended solid releases by dredging and effects on growth rates of selected phyla, e.g., shellfish; and
- f) Changes in species dominance following recolonization of disturbed or defaunated substrates, particularly where the substrate type is changed or modified.

### 16. REGIONAL ASSESSMENTS

Under this item, the ACMP reports on any regional or sub-regional assessments of marine environmental quality that have come to its attention during the intersessional period.

The attention of ACMP was drawn to the report "Health of our Oceans: A Status Report on Canadian Marine Environmental Quality", published in March 1991. The report is one of a series of projects that were initiated by the Canadian government in 1985 and is designed 'to bring a new focus and direction to Environment Canada's marine environmental quality programmes, and to achieve a higher government and public profile for marine environmental quality issues in Canada'. The report deals largely with human activities causing contamination and pollution. Canada's major marine areas - the Pacific, the Arctic, and the Atlantic - are treated separately under the headings of Sources, Substances, and Geographic Concerns and an assessment of conditions is given for each area. The report concludes with an overall assessment of current marine environmental quality in Canadian waters and identifies priorities for future action. Copies are available from Dr Peter Wells at the Conservation and Protection Branch of Environment Canada, Queen's Square, Dartmouth, Nova Scotia.

### 17. STUDIES IN THE BALTIC SEA AREA

The ACMP took note of the progress that had been made by the Working Group on the Baltic Marine Environment (WGBME) on the development of plans for a joint study of fluxes in the coastal zones of the Baltic Sea and the development of a long-term strategy plan for the future activities of the Working Group. Some progress had been made by the Working Group in both of these areas, but neither of these proposals has been developed to a stage that the ACMP considers them suitable for general publication. The ACMP recognises that there are many other groups working on environmentally related subjects in the Baltic Sea area. Accordingly, it is important that the WGBME concentrates its activities on topics that are not being addressed by these other groups. The ACMP will attempt to offer further guidance on these issues during the intersessional period and one step in this direction, relevant to the flux studies, is given below.

# 17.1 Conceptual Approach for the Development of a Research Investigation of Fluxes in Coastal Areas of the Baltic Sea

The Baltic Sea is an ideal area for studies designed to improve the understanding of both gross and net riverine fluxes of contaminants. Mechanisms for close collaboration and interaction among scientists from the area have been established and previous work provides a valuable background for further investigations of contaminant fluxes. With the attention currently being paid to marine flux investigations, such as that under SKAGEX, it would seem an ideal area in which to pioneer investigations of land/sea fluxes and mass balances, and this is the primary rationale underlying the ACMP's guidance to the Working Group.

The transport of contaminants into the Baltic Sea and the fluxes and mass balance in the sea is of crucial importance for understanding the development of the conditions in the sea. This problem has to be approached through studies of processes in the coastal zone.

The ACMP believes that there are a number of difficulties in carrying out international projects in coastal waters, as there is usually little interest from countries outside a particular study area and there are obstacles to obtaining permission for the conduct of intensive scientific studies in internal waters of other countries. Furthermore, coastal problems of the whole Baltic Sea cannot be resolved by studying one or two coastal areas, even if they are regarded as the most representative of the entire Baltic Sea. Therefore, the ACMP requests the WGBME to consider the development of coordinated studies in a number of coastal areas: for example, the Odra River and the Gulf of Pomerania, primarily by Germany and Poland; the Vistula River and the Gulf of Gdansk, primarily by Poland and the USSR; the Neva River and the Gulf of Finland, primarily by the USSR and Finland; etc. The focus for such investigations should include primary emphasis on land/sea contaminant flux estimations. After obtaining experience in such coordinated studies, joint international programmes in one or two selected areas devoted to special problems can be developed and conducted.

### 18. SEALS AND SMALL CETACEANS IN NORTHERN EUROPEAN SEAS

The 1989 and 1990 ACMP reports discussed the seal epidemic in 1988 and its impact on affected seal populations (ICES, 1989, 1990). The relationships between contaminant burdens, the attack from the phocine distemper virus (PDV), and the health of the seal stocks were analysed. Although there had been no direct evidence of a connection between environmental contamination and the extent and severity of the epidemic, there was a feeling, among the experts directly involved in the investigations, that such a connection probably existed. Accumulating evidence from studies on other mammalian species concerning the potentially detrimental effects of organohalogens on reproduction and resistance to disease supported this.

The new Study Group on Seals and Small Cetaceans in Northern European Seas met in Texel, The Netherlands on 12-14 March 1991. The ACMP reviewed the report from this meeting and agreed that it provides useful updating information on the status of the seal stocks.

## a. Current status of populations

### Seals

No, or only small, changes have been observed in the number of seals after the 1988 major seal kill, which had affected mainly the common seal (*Phoca vitulina*) and, to a lesser extent, the grey seal (*Halicoerus grypus*) in the North Sea region. Therefore, fears for the viability of seal populations as a result of the epidemic seem to be unjustified. One encouraging indication of recovery is in the Wadden Sea, where improved pup production occurred in 1990 and there was evidence of immigration of young seals from outside the area.

Demographic characteristics of the European common seal populations are now much better known following analysis of the material collected during the epidemic. This makes improved monitoring possible. On-going studies on the diet of seals and on their movement pattern in the sea contribute to knowledge of importance for understanding the interaction between seals and fisheries and other human activities.

The incidence of uterine occlusions, which render animals sterile, appears, from a recent examination of material from small numbers of ringed seals (*Phoca hispida*), to be at about the same level as has been reported previously (ICES, 1988). Additional indications of hormonal imbalance and immunosuppressive effects have come from studies of bone lesions and decalcification in material from common seals in the Wadden Sea and the Baltic Sea. Compared to seal material collected in the Baltic Sea between 1835 and 1935 and held in museums, the present frequency of abnormalities is significantly higher. A high frequency of skull abnormalities has also been observed in Baltic seals.

# Porpoises and dolphins

Information on the population size and dynamics of small cetaceans is still poor. The North Sea is probably the most important area for the harbour porpoise (*Phocoena phocoena*) in the Northeast Atlantic. Although it appears to be abundant in the central and northern North Sea, there is evidence of a marked decline in nearshore and inshore waters. The ACMP considers that there is a variety of possible reasons for this.

Small resident populations of bottlenose dolphins (*Tursiops truncatus*) are found around the British Isles and in the Dutch sector of the North Sea. These groups contain less than one hundred individuals each and there has been a substantial decrease in the populations of these animals during the last decades.

Signs of pathological effects in small cetaceans have been reported, but the existing knowledge on the health of these animals is still very poor. Changes in the adrenal glands of harbour porpoises from the North Sea and tumours in belugas (*Delphinapterus leucas*) in Canada have been reported.

### b. Environmental factors

# Contamination

Mercury and cadmium are found in marine mammals generally. Some mortalities of common seals have been attributed to high concentrations of these metals in some individuals, for example, resulting from exposure to a mercury-contaminated discharge (ICES, 1988). However, high levels have been found in seals from areas where the proportion of the metal burden derived from anthropogenic sources is likely to be small. Accordingly, the ACMP considers that current evidence suggests that present levels of anthropogenic inputs of these elements do not pose a particular threat to seal species.

As previously reported by ACMP, marine mammal tissues, particularly blubber, often contain high levels of organochlorine contaminants. The ACMP recognizes that seals in the Baltic Sea and some parts of the North Sea have body burdens of organochlorine contaminants which are likely to affect their reproductive ability and possibly their resistance to disease. Additional indications of immunosuppressive effects have come from studies of bone lesions and decalcification in material from common seals in the Wadden Sea and in seals aged > 5 years from the Baltic Sea. Seals collected in the Baltic Sea during 1988 had a significantly higher frequency of lesions than those collected between 1835 and 1935. The bone lesions were considered by pathologists to be indicative of hormonal imbalance. A high frequency of skull abnormalities has also been observed in Baltic seals.

# Other factors

It is not possible to rank, in order of importance, the factors influencing marine mammal populations. Fishing activities can have an impact through accidental entanglement of animals in nets, deliberate killing of animals by fishermen, and through changes in the abundance and distribution of prey. Disease agents (like the phocine distemper virus) can be the cause of mass kills at irregular intervals.

Disturbance by noise and shipping, especially during the pupping season, can be the cause of direct and indirect negative effects on the populations. Commercial hunting of seals and small cetaceans has virtually ceased in the area covered by the Study Group (i.e., the English Channel, the Baltic, North and Irish Seas, the Celtic, Hebridean and Færoese Shelves, and the coastal waters of the Norwegian mainland). However, common seals may be hunted in northern Norway during part of the year. In Norway, the UK and Denmark, fishermen and marine fish farmers are also permitted to shoot seals damaging gear or catches.

The recent series of warm winters has emphasized the importance of the duration of the presence of ice for the survival of the pups of ice-breeding seals. This means that climate-related reductions in ice distribution and character within the Baltic Sea will be of critical importance for the pupping success of ice-breeding seals.

# c. Conclusion

The ACMP concludes that decisions taken at the 1990 International Conference on the Protection of the North Sea to reduce inputs of certain persistent contaminants should, in the long term, reduce the threat to marine mammal populations from contamination. However, the effect is likely to be slow because many of the contaminants are persistent and will remain in the sea for many decades.

- ICES, 1988. Report of the ICES Advisory Committee on Marine Pollution, 1987. ICES Coop. Res. Rep. No. 150, pp. 36-52.
- ICES, 1989. Report of the ICES Advisory Committee on Marine Pollution, 1989. ICES Coop. Res. Rep. No. 167, pp. 87-92.
- ICES, 1990. Report of the ICES Advisory Committee on Marine Pollution, 1990. ICES Coop. Res. Rep. No. 172, pp. 70-78.

### **19. ECOSYSTEM EFFECTS OF FISHING ACTIVITIES**

The ACMP examined the first report of the Study Group on Ecosystem Effects of Fishing Activities, which eventually will be used as a component of the 1993 Quality Status Report (QSR) on the North Sea environment. The first report includes an informative overview of the six major sections of the document, of which first drafts have been prepared for large portions of the text. Section 3 considers the direct impacts of fishing activities, comprising: a) the physical reworking and resuspension of the sediment by active gears, e.g., bottom trawls and shellfish dredges, b) the catch and by-catch of benthos, fish, seabirds, and marine mammals, c) damage or mortality arising from animals coming into contact with the fishing gear but which have not been caught/retained, d) dumping of discards and offal, and e) litter (e.g., lost gear and other debris) generated by fishing vessels at sea. Section 4 describes the sources and various measures of fishing effort which may be relevant for identifying trends in the intensity of fishing in the North Sea; it has been proposed that national sets of data be tabulated and included in this section. Section 5 contains a description of the impact of anthropogenic activities other than fishing (nutrient inputs, organic discharges, offshore prospecting and exploitation of sub-seabed resources, mineral and substrate extraction, inputs of heavy metals and radioisotopes, shipping and port activities, and hydrotechnical structures, including platforms, pipelines and well-heads). Section 6 represents the first steps towards a comparison of the direct impacts of fishing with those from other anthropogenic influences and natural processes. Section 7 examines the possible indirect and long-term effects of fishing activities, including trophic changes in species interactions, habitat alterations, and changes in the gene pool of populations. Section 8 provides a preliminary discussion of potential conflicts between fisheries management and other ecosystem management objectives.

The ACMP noted the encouraging progress that has been made so far despite the complexity of the problems the Study Group was asked to consider regarding interactions between fisheries and the marine environment. Having commendably illuminated the factors and issues involved, the ACMP emphasised that the future efforts of the Study Group should concentrate on transforming the report from its present descriptive inclination towards greater quantification. However, recognising that other sections of the QSR will deal in detail with the biological effects of contaminants, the ACMP considers that Section 5 of the report should be limited to describing and quantifying the anthropogenic factors which are likely to impinge more immediately on the benthos and fisheries, e.g., eutrophication/organic enrichment and associated oxygen depletion, oil platforms/well-heads and pipelines, and sediment or aggregate extraction. These factors, besides frequently impeding fisheries operations and goals, are more immediately quantifiable than the effects of contaminants.

The ACMP acknowledged the comments of the Study Group regarding the importance of gaining access to national data bases containing details of fishing effort by area and gear/activity. Although these data generally exist, they are unfortunately rarely available to fisheries scientists. The basic lack of access to these data severely limits the examination of temporal and geographical trends in fishing effort, and the latent relationship with ecosystem change. The ACMP urges the NSTF to bring this to the attention of the relevant national authorities.

The ACMP noted that the Study Group is continuing its work by correspondence prior to its proposed next meeting in the early spring of 1992.

## 20. OVERVIEWS OF CONTAMINANTS IN THE MARINE ENVIRONMENT

## 20.1 Octachlorostyrene in the Aquatic Environment

On the basis of a request for information from the Commissions, the Marine Chemistry Working Group has prepared an overview on the occurrence, distribution, and fate of octachlorostyrene (OCS) in the aquatic environment. This report has been reviewed by the Working Group on Biological Effects of Contaminants and, after minor amendment by the ACMP, is included below. The following brief details summarize the main information presented in the overview.

OCS is formed as a by-product in high temperature industrial processes, such as the electrolytic production of chlorine using graphite electrodes and in magnesium production plants, also with graphite electrodes involved. It is not deliberately produced and has no known uses. It enters the environment via wastewater and is also dispersed by atmospheric transport.

OCS contamination has been reported in, e.g., the St. Clair River between Lakes Erie and Huron, Canada, the Frierfjord on the Norwegian south coast, the River Neckar downstream of Rottweil, the River Elbe downstream of Hamburg, the Rivers Meuse and Rhine, and finally, in the North Sea, where OCS has been detected in water, sediment and biota. Elevated levels have been found in the sediments and biota near the incineration area in the central North Sea.

The degradability of OCS seems to be low, as judged from analyses of dated sediment cores. Like many other chlorinated compounds, it is lipophilic and has a strong potential for bioaccumulation. Sub-lethal physiological effects have been observed in tests with mammals, but its toxicological properties have not been studied extensively. Its acute toxicity is low.

The concentrations of OCS observed in the field seem unlikely to have significance other than in localized areas around point source inputs. The long-term impact of chlorinated styrenes, however, cannot be predicted with current toxicological knowledge. Under these circumstances, unrestricted entry of OCS into the environment is unwise.

The ACMP expresses its appreciation to Dr J. Klungsøyr, Institute of Marine Research, Bergen, Norway, and Mr R. Law, MAFF Fisheries Laboratory, Burnham-on-Crouch, Essex, United Kingdom, for their preparation of this overview. Dr J. Lohse of Okopol, Hamburg, Germany is also acknowledged for supplying Figure 20.1 illustrating data on OCS concentrations in sediments in the North Sea.

# 20.1.1 Introduction

This paper has been prepared in response to a request from the Commissions and gives an overview on the occurrence, distribution, and fate of octachlorostyrene (OCS) in the aquatic environment. OCS was first reported in 1969 in birds from the Dutch coast and the Rhine River (ten Noever de Brauw and Koeman, 1972). In 1976, fish from the Frierfjord in Norway were found to contain OCS and other chlorinated styrenes (Lunde and Ofstad, 1976; Ofstad *et al.*, 1978). That same year, OCS was identified in fish from the Great Lakes in North America (Kuehl *et al.*, 1976). Contamination of the North Sea by OCS was first reported in 1984 by Ernst *et al.* Because of its presence as an environmental contaminant, concern has been raised regarding possible biological effects on humans and animals.

# 20.1.2 **Production and use**

OCS has not been reported to occur naturally and has no commercial use. It occurs as a by-product of some industrial processes. The main source of this contaminant is believed to be from high temperature industrial processes involving carbon and inorganic chlorine (Kaminsky and Hites, 1984).

There are experimental indications that OCS and other organochlorine compounds can be produced during the combustion of, e.g., PVC (Ahling and Lindskog, 1982) or on high temperature pyrolysis of tetrachloroethene (Ballschmitter *et al.*, 1983). The importance of such sources is not well known, however. OCS has also been positively identified in waste products from the production of carbon tetrachloride and tetrachloroethylene (Markovec and Magee, 1984).

# 20.1.3 Physico-chemical properties

The chemical formula of OCS is  $C_6Cl_5CCl=CCl_2$  (Mw 376). Huffmann *et al.* (1984) describe its crystal structure. OCS has a melting point of 99.5-101 °C (Ruetman, 1973). Full information on its physicochemical properties is not readily available. As a fully chlorinated aromatic hydrocarbon, it would be expected to be hydrophobic and, therefore, lipophilic and also resistant to degradation in the environment. A water solubility of only 2.5 to 3  $\mu$ g dm<sup>-3</sup> has been reported for OCS (Bjerk and Brevik, 1980; Bøckman *et al.*, 1981). Literature values for log octanol:water partition coefficients, log P<sub>ow</sub>, range from 5.5 to 7.7 (Veith *et al.*, 1979; Tarkpea *et al.*, 1985), suggesting a strong potential for bioaccumulation.

### 20.1.4 Routes into the environment

The major route of entry into the environment is via wastewater discharges, from industrial rather than municipal sources (Marsalek, 1986). Field measurements at a remote site have confirmed that OCS can be dispersed by atmospheric transport (Swackhamer and Hites, 1988), although the scale of such transport seems to be limited (Sanderson and Weis, 1989; Weis and Barclay, 1985).

## 20.1.5 Methods of analysis

OCS generally behaves in a similar manner to other organochlorine contaminants, such as DDT or PCBs, and is isolated from samples using the methodology developed for those determinands. This usually involves high-resolution capillary gas chromatography with electron-capture detection (GC-ECD). Analysis is not always straightforward, because OCS elutes among the chlorobiphenyls in many analytical procedures. Knickmeyer and Steinhart (1989) showed that OCS elutes among the tetra- and penta-chlorobiphenyls on a SE 54-CB fused silica capillary column. If not carefully controlled, over-estimation of OCS may occur. For unambiguous identification of OCS, the use of GC/MS is essential. Bieniek and Korte (1978) and others have described how OCS can be synthesized, and the compound is also available as a commercial standard.

### 20.1.6 Levels in the environment

OCS contamination has been reported from Europe and North America. Tables 20.1 and 20.2 give information about concentrations found in sediments and biota.

### North America

OCS is produced, along with various other organochlorines, in wastes derived from the electrolytic production of chlorine. In the past, graphite anodes were used, and the wastes resulted from the chlorination of the coal tar pitch binder used in these anodes. Metal anodes are now used instead (Kaminsky and Hites, 1984). The highest concentrations of OCS have been found in the St. Clair River, between Lakes Huron and Erie, adjacent to a chlorine production facility. Kaminsky and Hites (1984) have noted a general association between OCS contamination of fish and sediments and chlorine production facilities in North America.

### Norway

The highest reported concentrations of OCS have been in the Frierfjord area. The local source of chlorinated styrenes is a magnesium production plant, where the compound is formed in two different process stages. In the first stage, magnesium oxide is converted to magnesium chloride at  $1100 \, ^{\circ}$ C by the use of chlorine and coke. The second stage is the electrolytic metal production, where the chlorine formed reacts with the graphite anodes (Bøckman *et al.*, 1981).

Discharges of OCS to the Frierfjord decreased from 2.8 kg week<sup>-1</sup> to 0.6 kg week<sup>-1</sup> between 1976 and 1980 (Bøckman *et al.*, 1981). In 1990, the discharges were further decreased by 90% to 95% due to the installation of a new wastewater treatment plant.

The input of OCS to the Frierfjord has resulted in locally highly elevated OCS levels in biota and sediments (Tables 20.1 and 20.2). In 1975, before discharge reductions, the average level of OCS in cod liver was  $143 \pm 71 \text{ mg kg}^{-1}$  (n=12). These levels have gradually decreased and have been 10-20 mg kg<sup>-1</sup> since 1980 (Knutzen and Green, 1990). The effects of the new strict discharge permit from 1990 have not yet been seen, but it is assumed that it will lead to further reductions in concentrations in the receiving environment.

# Germany

OCS is produced as a by-product of the manufacture of pistons in the city of Rottweil, where chlorine is used in the degassing of molten aluminium alloy (Vogelsang *et al.*, 1986), and has led to the contamination of the River Neckar. Fish in the river contained up to 3.7 mg kg<sup>-1</sup> fat weight of OCS in 1983-1984, and sediments from 1.3 to 6.7  $\mu$ g kg<sup>-1</sup> dry mass (Kypke-Hutter *et al.*, 1986). The Neckar flows into the River Rhine at Mannheim.

In 1983-1985, samples of sediments and suspended particulate material from the Rivers Elbe and Weser, and from the North Sea and Baltic Sea were analysed for OCS. Higher concentrations were found in the Elbe (e.g., 1.4 to 37  $\mu$ g kg<sup>-1</sup> in sediments) than at the other locations (Sturm *et al.*, 1986). The samples were collected downstream of Hamburg, and the highest concentrations of OCS, hexachlorobenzene (HCB), and pentachlorobenzene were found near Stade. Sediment core samples taken from this area in 1983 confirmed the presence of OCS (Eder *et al.*, 1987), but no source has been identified.

# The Netherlands

Dutch investigations in the period 1977-1985 showed that OCS concentrations in eels (Anguilla anguilla) from the Rivers Meuse and Rhine were a factor of 5-10 times higher than in eels from other Dutch fresh waters (Kerkhoff *et al.*, 1986). Between 1977 and 1985, a decreasing trend over time was observed, with concentrations in eels from the Meuse and Rhine declining from 675 to 141  $\mu$ g kg<sup>1</sup> wet weight.

# The North Sea

Samples collected from the vicinity of the German Bight in 1983 showed concentrations of 0.03 to 1.9 ng dm<sup>-3</sup> in water from the Bight and the estuaries of the Elbe and Weser, and sediments in the German Bight contained 0.9 to 1.3  $\mu$ g kg<sup>-1</sup> dry mass of OCS (Ernst *et al.*, 1984). In the same study, liver samples from flatfish from the German Bight contained 2.0 to 90  $\mu$ g kg<sup>-1</sup> wet weight of OCS, and in cod the concentrations were <1 to 67  $\mu$ g kg<sup>-1</sup> (cf. 2.4 to 27  $\mu$ g kg<sup>-1</sup> in 1972). The authors also reported that OCS was not found in the livers of fish from the Red Sea, the North Atlantic, or the Mediterranean Sea.

Lohse (1988b) analysed sediments from the North Sea and the Skagerrak collected in 1984-1986, but OCS was found only rarely. Sediments collected in 1984-1987 showed OCS levels to be low but detectable in the German Bight, low on the Dogger Bank, and at trace levels at the mouth of the River Humber (Lohse, 1988a). OCS concentrations were not given, but Lohse stated that higher concentrations were found, along with high concentrations of HCB, close to an ocean incineration area in the central North Sea. Figure 20.1

shows the distribution of OCS in North Sea sediments, expressed both in ng kg<sup>-1</sup> dry mass (Figure 20.1a) and normalized to total organic carbon (Figure 20.1b). Elevated concentrations of OCS can be seen at the incineration area, in the German Bight, and in the Norwegian Trench/Skagerrak. Büther (1989) has also found significantly higher OCS concentrations in fish and invertebrate species from the incineration area. A distinct spatial trend has been seen for OCS in the livers of cod from the North Sea, with higher levels in the south decreasing to the north. Between 1977 and 1987, a decreasing trend over time has also been seen for OCS in the southern North Sea, with concentrations in cod liver declining from 210 to 33  $\mu$ g kg<sup>-1</sup> fat weight over that period (de Boer, 1989).

### 20.1.7 **Persistence** in the environment

As a fully chlorinated hydrocarbon, OCS is likely to be highly persistent (Norheim and Roald, 1985). Analyses of dated sediment cores from Lake Ontario showed that the deposition of OCS began about 1940, and peaked around 1970. This correlates well with the record of chlorine production in the Great Lakes States in which graphite anodes were used (Kaminsky and Hites, 1984).

## 20.1.8 Bioaccumulation

OCS has a BCF (bioconcentration factor) of 4.52 (cf. 4.27 for HCB and 4.71 for pp'-DDE), equivalent to concentrations in experimentally exposed fish 33,000 times higher than those in water (Veith *et al.*, 1979). Bauer *et al.* (1989) showed experimentally that blue mussels (*Mytilus edulis*) can rapidly accumulate OCS from sea water. Mussels exposed to OCS at a concentration of 1.5  $\mu$ g dm<sup>-3</sup> achieved a constant tissue concentration of 320  $\mu$ g kg<sup>-1</sup> wet weight within 3 days.

In blue mussels and spiny lobsters, the major site of accumulation is the hepatopancreas, and elimination of OCS by mussels takes more than 60 days (Solbakken and Knap, 1986; Ingebrigtsen *et al.*, 1988). In cod and rainbow trout, the main sites of accumulation were the liver and the visceral fat, respectively, reflecting the difference in anatomical localization of lipid reservoirs between the two species. The rate of elimination of OCS was slow in both species, with substantial amounts remaining in the tissues after 90 days. The trial suggested that the major excretory route in both fish species was via bile. The half-life of OCS in the liver of rainbow trout is 143 days (Norheim and Roald, 1985).

The tissue distribution, metabolism, and elimination of OCS have been studied in rats (Chu *et al.*, 1982b). OCS was absorbed from the gastrointestinal tract and distributed in all tissues. The highest concentrations were found in fat, followed by the adrenal glands, skin, and lungs. Most of the OCS absorbed (90%) was eliminated unchanged in the faeces, while negligible amounts were found in the urine. Metabolites of OCS accounted for ca. 10% of the residues excreted in the faeces. A small amount (1%) of the dose was detected in the expired air as carbon dioxide.

Chu et al. (1982b) reported heptachlorostyrene and heptachlorophenylacetic acid as products of OCS metabolism in rats. In a study by Bauer et al. (1989) on blue mussels (*Mytilus edulis*), heptachlorostyrene was not found, but two methylthioheptachlorostyrenes were identified.

# 20.1.9 Effects on biota and man

Effects of OCS on the environment are difficult to evaluate. One of the complicating factors is that elevated OCS concentrations in the environment very often occur alongside elevated concentrations of other groups of contaminants, such as the less chlorinated styrenes, hexachlorobenzene, chlorinated dibenzodioxins, PAHs, etc. (Ofstad *et al.*, 1978; Suns *et al.*, 1983).

Tests have shown that OCS has a relatively low acute toxicity. Chu *et al.* (1982a) reported that no lethal effect was seen when rats were given a single OCS dose of 3710 mg kg<sup>-1</sup>. High doses caused increased liver weight, increased enzymatic activities, and increased serum cholesterol and uric acid levels. Only mild histological changes were seen in the thyroid of the treated animals. Rats fed diets containing 0.5-500 mg kg<sup>-1</sup> OCS for 28 days in a sub-acute study showed no effect on growth rate and food consumption. Liver hypertrophy and hepatic microsomal enzyme induction were observed in animals fed 50 mg kg<sup>-1</sup> OCS and higher concentrations. Elevations in serum cholesterol, total protein, potassium, and sorbitol dehydrogenase occurred in rats fed the 500 mg kg<sup>-1</sup> diet. Histological changes occurred in the liver and thyroid of rats exposed to concentrations as low as 5 mg kg<sup>-1</sup> OCS. The OCS residues accumulated in the fat and liver in a dose-dependent manner. The data of Chu *et al.* (1981a) suggest that OCS can produce biochemical and histological changes in rats after administration of a single dose and/or when fed in the diet. Strik and Koeman (1975) have reported that OCS is a potent porphyrinogen in the rat and Japanese quail. Law and Addison (1981) reported the absence of any hepatic mono-oxygenase induction in brook trout (*Salvelinus fontinalis*) fed OCS.

Concentrations of OCS found in the field seem unlikely to have significant effects, either on fish or their human consumers, in any other than localized areas around point source inputs. The long-term impact of chlorinated styrenes (including OCS) cannot, however, be predicted with current toxicological knowledge (Kaminsky and Hites, 1984). Under these circumstances, unrestricted entry of OCS into the environment is unwise.

## 20.1.10 References

- Ahling, B., and Lindskog, A. 1982. Emission of chlorinated organic substances from combustion. In Chlorinated dioxins and related compounds: Impacts on the environment - Workshop Proceedings. Ed. by O. Hutzinger. Pergamon Press, Oxford, UK, ISBN 0 0802 62562, 165 pp.
- Ballschmitter, K., Zoller, W., Scholz, C., and Nottrodt, A. 1983. Occurrence and absence of polychlorodibenzofurans and polychlorodibenzodioxins in fly ash from municipal incinerators. Chemosphere, 12: 585-594.
- Bauer, I., Weber, K., Ernst, W., and Weigelt, V. 1989. Metabolism of octachlorostyrene in the blue mussel (Mytilus edulis). Chemosphere, 18 (7-8): 1573-1579.
- Bieniek, D., and Korte, F. 1978. Einfache Synthese des Octachlor-styrols. Chemosphere, 7 (9): 729-730.
- Bjerk, J.E., and Brevik, E.M. 1980. Organochlorine compounds in aquatic environments. Arch. environm. Contam. Toxicol., 9: 743-750.
- Boer, J. de, 1989. Organochlorine compounds and bromodiphenylethers in livers of Atlantic cod (Gadus morhua) from the North Sea, 1977-1987. Chemosphere, 18: 2131-2140.
- Bøckman, O.C., Haugerød, O., Haver, E., and Mürer, K. 1981. Heksaklor-benzen og andre organohalogener: Resultater fra arbeidet med et miljøproblem. NORDFORSK Miljövårdsserien, 1: 119-129.
- Bøe, B. 1979. Analyse av klorerte hydrokarboner og kvikksølv i fisk fra Frierfjorden 1978. Fiskeridirektoratet, Bergen, Report 4/79, 8 pp.
- Bøe, B. 1980. Analyse av klorerte hydrokarboner og kvikksølv i fisk fra Frierfjorden 1979. Fiskeridirektoratet, Bergen, Report 6/80, 6 pp.
- Bøe, B. 1981. Analyse av klorerte hydrokarboner og kvikksølv i fisk fra Frierfjorden 1980. Fiskeridirektoratet, Bergen, Report 7/81, 10 pp.

- Büther, H. 1989. Organochlorine compounds in marine organisms from the international North Sea incineration area Preliminary results. ICES, Doc. C.M.1989/E:4, 24 pp.
- Chu, I., Secours, V.E., and Villeneuve, D.C. 1982a. Acute and subacute toxicity of octachlorostyrene in the rat. J. Toxicol. Environ. Health, 10: 285-296.
- Chu, I., Villeneuve, D.C., Secours, V., Benoit, F.M., and Viau, A. 1982b. The tissue distribution, metabolism, and excretion of octachlorostyrene in the rat. Drug Metabolism and Disposition, 10 (6): 632-635.
- Cleland, G.B., Oliver, B.G., and Sonstegard, R.A. 1988. Bioaccumulation of halogenated aromatic hydrocarbons in C57B1/6 and DBA/2 mice following consumption of Great Lakes coho salmon (Oncorhynchus kisutch). Chemosphere, 17 (2): 405-420.
- Durham, R.W., and Oliver, B.G. 1983. History of Lake Ontario contamination from the Niagara River by sediment radiodating and chlorinated hydrocarbon analysis. J. Great Lakes Res., 9 (2): 160-168.
- Eder, G., Sturm, R., and Ernst, W. 1987. Chlorinated hydrocarbons in sediments of the Elbe River and the Elbe Estuary. Chemosphere, 16 (10-12): 2487-2496.
- Ernst, W., Weigelt, V., and Weber, K. 1984. Octachlorostyrene A permanent micropollutant in the North Sea. Chemosphere, 13 (1): 161-168.
- Fox, G.A., Kennedy, S.W., Norstrom, R.J., and Wigfield, D.C. 1988. Porphyria in herring gulls: A biochemical response to chemical contamination of Great Lakes food chains. Environ. Toxicol. Chem., 7: 831-839.
- Huffman, J.C., Kaminsky, R., and Hites, R.A. 1983. Crystal and molecular structure of octachlorostyrene, C<sub>8</sub>Cl<sub>8</sub>, a Great Lakes pollutant. Indiana Academy of Sciences, 93: 145-147.
- Ingebrigtsen, K., Solbakken, J.E., Norheim, G., and Nafstad, I. 1988. Distribution and elimination of (<sup>14</sup>C) octachlorostyrene in cod (*Gadus morhua*), rainbow trout (*Salmo gairdneri*), and blue mussel (*Mytilus edulis*). J. Toxicol. Environ. Health, 25 (3): 361-372.
- Kaminsky, R., Kaiser, K.L.E., and Hites, R.A. 1983. Fates of organic compounds from Niagara Falls dumpsites in Lake Ontario. J. Great Lakes Res., 9 (2): 183-189.
- Kaminsky, R., and Hites, R.A. 1984. Octachlorostyrene in Lake Ontario: Sources and fates. Environ. Sci. Technol., 18 (4): 275-279.
- Kerkhoff, M., de Boer, J., de Vries, A., and Otte, P. 1986. Negen jaren van organochloor-pesticiden onderzoek in rode aal. Netherlands Institute for Fisheries Research (RIVO-DLO), IJmuiden, Report MO 86-02, 21 pp.
- Knickmeyer, R., and Steinhart, H. 1989. Cyclic organochlorines in the North Sea sediments, relation with size and organic matter. Dt. Hydrogr. Z., 42: 43-59.
- Knutzen, J., and Green, N. 1990. Overvåkning av miljøgifter i torsk og blåskjell fra Grenlandsfjordene 1989. Norwegian Institute for Water Research (NIVA), Report 415/90 (ISBN 82-577-1781-9), 41 pp.
- Kruse, R., and Krüger, K.-E. 1989. Kongenere Polychlorierte Biphenyle (PCBs) und Chlorierte Kohlenwasserstoffe (CKWs) in Tischen, Krusten-, Schalen- und Weichtieren und daraus hergestellten Erzeugnissen aus Nordatlantik, Nordsee, Ostsee und deutschen Binnengewässern. Arch. Lebensmittelhygiene, 40: 99-104.

- Kuehl, D.W., Kopperman, H.L., Veith, G.D., and Glass, G.E. 1976. Isolation and identification of polychlorinated styrenes in Great Lakes fish. Bull. environ. Contam. Toxicol., 16 (2): 127-132.
- Kypke-Hutter, K., Vogelsang, J., Malisch, R., Binnemann, P., and Wetzlar, H. 1986. Aufklärung einer Kontamination von Neckarfischen mit Hexachlorbenzol, Octachlorstyrol und Pentachlorbenzol: Entstehung bei einem industriellen Prozess. I. Verlauf der Kontamination im Oberen Neckar. Z. Lebensm. Unters. Forsch., 182: 464-470.
- Law, F.C.P., and Addison, R.F. 1981. Response of trout hepatic mixed-function oxidases to experimental feeding of ten known or possible chlorinated environmental contaminants. Bull. environ. Contam. Toxicol., 27: 605-609.
- Lohse, J. 1988a. Ocean incineration of toxic wastes: a footprint in North Sea sediments. Mar. Pollut. Bull., 19 (8): 366-371.
- Lohse, J. 1988b. Distribution of organochlorine pollutants in North Sea sediments. Mitteil Geologisches-Palaeontisches Institut Universität Hamburg, 65: 345-365.
- Luckas, B., and Harms, U. 1987. Characteristic levels of chlorinated hydrocarbons and trace metals in fish from coastal waters of North Sea and Baltic Sea. Intern. J. environ. Anal. Chem., 29: 215-225.
- Lunde, G., and Baumann Ofstad, E. 1976. Determination of fat-soluble chlorinated compounds in fish. Fres. Z. Anal. Chem., 282: 395-399.
- Markovec, L.M., and Magee, R.J. 1984. Identification of major perchloroaromatic compounds in waste products from the production of carbon tetrachloride and tetrachloroethylene. Analyst, 109: 497-501.
- Marsalek, J. 1986. Municipal sources of selected trace organics in Sarnia. Water Poll. Res. J. Can., 21: 422-432.
- Moksnes, M.T., and Norheim, G. 1986. Levels of chlorinated hydrocarbons and composition of PCB in herring gull *Larus argentatus* eggs collected in Norway in 1969 compared to 1979-81. Environ. Poll., 11: 109-116.
- Norheim, G., and Roald, S.O. 1985. Distribution and elimiation of hexachlorobenzene, octachlorostyrene and decachlorobiphenyl in rainbow trout, *Salmo gairdneri*. Aquatic Toxicol., 6: 13-24.
- Ofstad, E. Baumann, Lunde, G., Martinsen, K., and Rygg, B. 1978. Chlorinated aromatic hydrocarbons in fish from an area polluted by industrial effluents. Sci. Tot. Environ., 10: 219-230.
- Oliver, B.G., and Bourbonniere, R.A. 1985. Chlorinated contaminants in surficial sediments of Lakes Huron, St. Clair, and Erie: Implications regarding sources along the St. Clair and Detroit Rivers. J. Great Lakes Res., 11(3): 366-372.
- Ruetman, S.H. 1973. Synthesis of perchlorinated vinyl compounds. Synthesis, 11: 680-681.
- Sanderson, M., and Weis, I.M. 1989. Concentrations of two organic contaminants in precipitation, soils and plants in the Essex region of Southern Ontario. Environ. Poll., 59: 41-54.
- Solbakken, J.E., and Knap, A.H. 1986. Disposition of phenanthrene and octachlorostyrene in spiny lobsters (*Panulirus argus*) after intragastric administration. Bull. environ. Contam. Toxicol., 37: 747-751.

- Strik, J.J.T.W.A., and Koeman, J.H. 1975. Porphyrinogenic action of hexachlorobenzene and octachlorostyrene. *In* Porphyrin in Human Disease, pp. 418-423. Ed. by M. Doss and M.A.D. Lahn. S. Karger, A.G., Basel, Switzerland.
- Sturm, R., Knauth, H.D., Reinhardt, K.H., and Grandrass, J. 1986. Chlorkohlenwasserstoff-Verteilung in sedimenten und schwebstoffen der Elbe. Vom Wasser 67: 23-38.
- Suns, K., Craig, G.R., Crawford, G., Rees, G.A., Tosine, H., and Osborne, J. (1983). Organochlorine contaminant residues in spottail shiners (*Notropis hudsonius*) from the Niagara River. J. Great Lakes Res., 9 (2): 335-340.
- Suns, K., Crawford, G., and Russel, D. 1985. Organochlorine and mercury residues in young-of-the-year spottail shiners from the Detroit River, Lake St. Clair, and Lake Erie. J. Great Lakes Res., 11 (3): 347-352.
- Swackhamer, D.L., and Hites, R.A. 1988. Occurrence and bioaccumulation of organochlorine compounds in fishes from Siskiwit Lake, Isle Royale, Lake Superior. Environ. Sci. Technol., 22: 543-548.
- Tarkpea, M., Hagen, I., Carlberg, G.E., Kolsaker, P., and Storflor, H. 1985. Mutagenicity, acute toxicity, and bioaccumulation potential of six chlorinated styrenes. Bull. environ. Contam. Toxicol., 35: 525-530.
- ten Noever de Brauw, M.C., and Koeman, J.H. 1972. Identification of chlorinated styrenes in cormorant tissues by a computerized gas chromatography - mass spectrometry system. Sci. Tot. Environ., 1: 427-432.
- Veith, G.D., DeFoe, D.L., and Bergstedt, B.V. 1979. Measuring and estimating the bioconcentration factor of chemicals in fish. J. Fish. Res. Board Can., 36: 1040-1048.
- Vogelsang, J. 1986. Hexachlorobenzene, octachlorostyrene and other organochlorine compounds in wastewater from industrial high temperature processes involving chlorine. Z. Wasser-Abwasser Forsch. 19: 140-144.
- Weis, I.M., and Barclay, G.F. 1985. Distribution of heavy metal and organic contaminants in plants and soil of Windsor and Essex County, Ontario. J. Great Lakes Res., 11: 339-346.

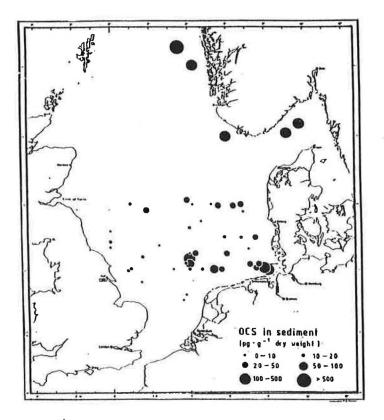
Location	Date	Mean	Range	Reference
Frierford, Norway	1979	62		Bjerk and Brevik, 1982
L. Ontario, N. America	1959-1962	166		Durham and Oliver, 1983
L. Ontario, N. America	1980-1981	4.3		Durham and Oliver, 1983
L. Ontario, N. America	1980	15	0.3-33	Kaminsky et al., 1983
L. Erie, N. America	1982		ND-5.9	Oliver and Bourbonniere, 1985
L. St.Clair, N. America	1982	8.1	5.1-11	Oliver and Bourbonniere, 1985
L. Huron, N. America	1980	0.06	0.02-0.1	Oliver and Bourbonniere, 1985
River Elbe, Germany	1983		0.7-22	Eder et al., 1987 Sturm et al., 1986
German Bight, North Sea	1983	1.0	0.9-1.3	Ernst et al., 1984
River Neckar, Germany	1983-1984	4.1	1.3-6.7	Kypke-Hutter et al., 1986

<u>Table 20.1</u> Concentrations of octachlorostyrene in sediments (in  $\mu g \ kg^{-1}$  wet weight).

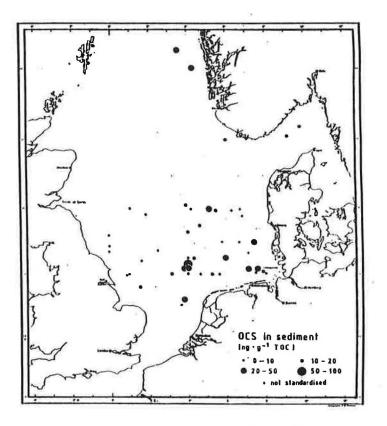
Location	Year	Sample type	Species	Tissue	Mean	Range	Reference
Telemark, Norway	1969	Herring gull	Larus argentatus	Egg	320	20-1200	Moksnes and Norheim, 1986
Telemark, Norway	1979-1981	Herring gull	Larus argentatus	Egg	140	10-1500	Moksnes and Norheim, 1986
Frierfjord, Norway	1978-1979	Saithe	Pollachius virens	Muscle		10-90	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1978-1979	Saithe	Pollachius virens	Liver		2300-19000	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1978-1979	Sprat	Sprattus sprattus	Whole body		20-1600	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1978-1979	Cod	Gadus morhua	Muscle		3-720	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1978-1979	Cod	Gadus morhua	Liver		1300-230000	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1978-1979	Pollack	Pollachius pollachius	Muscle		30-510	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1978-1979	Pollack	Pollachius pollachius	Liver		700-51000	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1978-1979	Whiting	Merlangius merlangus	Muscle		30-2600	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1978-1979	Whiting	Merlangius merlangus	Liver		3200-93000	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1978-1979	Flounder	Platichthys flesus	Muscle		50-570	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1978-1979	Flounder	Platichthys flesus	Liver		320-2000	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1978-1979	Herring	Clupea harengus	Whole body	40	2-160	Bøe, 1979, 1980, 1981
Frierfjord, Norway	1989	Cod	Gadus morhua	Liver		2550-31000	Knutzen and Green, 1990
German Bight	1982	Sea-scorpion	Myoxocephalus scorpius	Liver	82	22-160	Ernst et al., 1984
German Bight	1983	Flounder	Platichthys flesus	Liver	35	6.3-89	Ernst et al., 1984
German Bight	1983	Lemon sole	Microstomus kitt	Liver	9.3	2.4-22	Emst et al., 1984
German Bight	1983	Dab	Limanda limanda	Liver	13	2.0-20	Ernst et al., 1984
German Bight	1983	Plaice	Pleuronectes platessa	Liver	24	8.6-53	Ernst et al., 1984

T	able	20.2	(cont'd)

Location	Year	Sample type	Species	Tissue	Mean	Range	Reference
German Bight	1983	Cod	Gadus morhua	Liver	45	20-66	Ernst et al., 1984
German Bight	1985	Flounder	Platichthys flesus	Muscle	6	3-18	Lucas and Harms, 1987
North Sea	1987	Cod	Gadus morhua	Muscle		ND-1	Kruse and Krüger, 1989
North Sea	1988	Herring	Clupea harengus	Muscle		ND-0.3	Kruse and Krüger, 1989
North Sea	1988	Mackerel	Scomber scombrus	Muscle	0.7		Kruse and Krüger, 1989
Elbe estuary	1985	Flounder	Platichthys flesus	Muscle	151	61-415	Lucas and Harms, 1987
L. Erie, N. America	1982	Coho salmon	Oncorhynchus kisutch	Muscle	3.4		Cleland et al., 1988
L. Ontario, N. America	1982	Coho salmon	Oncorhynchus kisutch	Muscle	27		Cleland et al., 1988
L. Michigan, N. America	1982	Coho salmon	Oncorhynchus kisutch	Muscle	ND		Cleland et al., 1988
L. St. Clair, N. America	1982-1983	Spottail shiners	Notropis hudsonius	Whole body		3-5	Suns et al., 1985
Detroit R., N. America	1982-1983	Spottail shiners	Notropis hudsonius	Whole body		2-10	Suns et al., 1985
L. Erie, N. America	1982-1983	Spottail shiners	Notropis hudsonius	Whole body		ND-5	Suns et al., 1985
L. Michigan, N. America	1985	Herring gull	Larus argentatus	Liver	8		Fox et al., 1988
L. Huron, N. America	1985	Herring gull	Larus argentatus	Liver		27-620	Fox et al., 1988
Detroit, R., N. America	1985	Herring gull	Larus argentatus	Liver	100		Fox et al., 1988
L. Erie, N. America	1985	Herring gull	Larus argentatus	Liver	37		Fox et al., 1988
L. Ontario, N. America	1985	Herring gull	Larus argentatus	Liver		31-48	Fox et al., 1988



a). dry mass



b). normalized to total organic carbon

Figure 20.1 Concentrations of octachlorostyrene (OCS) in sediments of the North Sea (From J. Lohse, Okopol, Hamburg).

#### 20.2 The Occurrence of Nonylphenols in the Marine Environment

This note has been prepared in response to a request from the North Sea Task Force, concerning the finding of nonylphenols in the feathers of 18 dead seabirds in Germany. Although nonylphenols may not have been the primary cause of death, their mere presence raises questions on the occurrence and origin of this MARPOL-category A product. As no information on these compounds was immediately available, ICES was requested to investigate the occurrence of nonylphenols in the marine environment. At the same time, the Paris Commission Working Group on Diffuse Sources was asked to consider possible sources of input to the marine environment. In addition, in connection with on-going OECD work on existing chemicals, a seminar on nonylphenolethoxylates (NPEs) and nonylphenol (NP) was recently held in Stockholm (SEPA, 1991).

The chemical composition of NPEs, with one lipophilic and one hydrophilic component, implies that NPEs have surface tension properties, may accumulate at interfaces (e.g., air/water and water/biological membranes), and could interact with other compounds and influence their bioavailability and toxicity, or could result in physical effects, such as a reduction in the water resistance of the feathers of seabirds. NPs are both more persistent and more toxic than NPEs. Few measurements of the concentrations of NPEs in the natural environment have so far been made; most measurements have been made in fresh water.

Although vast amounts of anionic, cationic, and non-ionic surfactants are released into estuarine and marine systems as a result of domestic and industrial uses, there is little information available concerning their concentrations in nearshore waters. One clearly defined route for surfactant entry to the marine environment is via sewage. It has been shown that nonylphenols (NPs) arise from the breakdown of nonylphenol polyethoxylates (NPEs) in anaerobically digested sewage sludges. NP levels in wastewater of between 2 and 4000  $\mu$ g l<sup>-1</sup> have been reported. Another possible source is from operational discharges from chemical product tankers, although currently no information is available to ACMP on patterns of transport for NP or NPE. Such discharges are controlled under the provisions of MARPOL 73/78. Seabirds have also been reported to be repeatedly harmed by NPE discharges in connection with the cleaning of oil tankers or offshore suppliers.

In the marine environment, concentrations of NPE<sub>n</sub> (0 < n < 13) varying between 0.5 and 4.5  $\mu$ g l<sup>-1</sup> were determined in the waters of the Venice lagoon, which receives inputs of domestic and industrial origin. The highest concentrations were recorded near the Porto Marghera industrial zone, where collective concentrations of NPE<sub>1</sub> and NPE<sub>2</sub> in sediments (0 to 5 cm) varied between 18 and 129  $\mu$ g kg<sup>-1</sup> (dry weight), with an average value of 49  $\mu$ g kg<sup>-1</sup>; concentrations in superficial sediments were higher, varying from 0.2 to 13.7 mg kg<sup>-1</sup> dry weight, with an average value of 2.2 mg kg<sup>-1</sup>. Finally, levels of 0.25  $\pm$  0.15 mg kg<sup>-1</sup> dry weight were determined in macrophytic algae, principally *Ulva rigida*.

The concentration of NPEs found in coastal waters off Barcelona, Spain was 0.85  $\mu$ g l<sup>-1</sup> in the dissolved phase, whereas NPEs were not detected in the particulate phase.

Concentrations of nonylphenols have been measured in the estuary of the River Mersey and in Liverpool Bay. The Mersey receives inputs from a variety of industrial processes and raw and primary treated sewages. Samples of water collected during two cruises in 1989 and 1990 were analysed for concentrations of nonylphenols. It was clear from the few data obtained that the levels of nonylphenols in sea water rapidly decreased away from the sources to values below the detection limit (0.05  $\mu$ g l<sup>-1</sup>). Despite semi-continuous inputs of sewage sludge to the Liverpool Bay disposal ground, no increases in nonylphenol concentrations were measured close to the dumping site. Since the study area described was felt to represent a worst-case scenario, it appears likely that measurable concentrations of nonylphenols would be encountered only in the vicinity of discharge areas.

Bioconcentration factors for NP in mussels up to 2700 have been reported from experiments in the laboratory. Blue mussels (*Mytilus edulis*) caged outside an industrial wastewater discharge on the Swedish west coast accumulated NP to about 400  $\mu$ g kg<sup>-1</sup> fresh weight. Similar levels were found in juvenile eider ducks from the same area.

The acute toxicity of NP to mussels (14-day  $LC_{50}$  140  $\mu$ g l<sup>-1</sup>) occurs at concentrations around 100 times higher than those seen in coastal waters. Sub-lethal effects appear at concentrations above 60  $\mu$ g l<sup>-1</sup>.

SEPA. 1991. Report of the Seminar on Nonylphenolethoxylates (NPE) and nonylphenol (NP). Saltsjöbaden, Sweden. 6-7 February 1991. Swedish Environmental Protection Agency, Report No. 3907.

#### 21. AUTOMATIC DATA PROCESSING (ADP) ISSUES

The ACMP reviewed information on the status of ICES automatic data processing (ADP) activities during 1990/91 in relation to data on contaminants in marine media and the handling of the data from the Joint Monitoring Programme (JMP) of the Oslo and Paris Commissions and the Monitoring Master Plan (MMP) of the North Sea Task Force (NSTF).

#### Review of the processing of 1989 data

In relation to the JMP data handling, the majority of the data submitted in 1990 comprised additional sets of trend monitoring data, in particular, data on contaminants in fish and shellfish. As such, they continue the ICES/JMP time series, some of which now extend from 1978 to 1989.

Assessment of the temporal trend monitoring data on contaminants in fish liver tissue and *Mytilus edulis* represented a considerable commitment for the ICES Secretariat during 1990 (ca. 25 man-weeks). This involved firstly work in support of the initial assessment of the data by the Working Group on the Statistical Aspects of Trend Monitoring (WGSATM) during March and April 1990, and later in updating and finalizing these analyses prior to and during the OSPARCOM's *ad hoc* Working Group on Monitoring (MON) meeting in December 1990. A total of ca. 300 data sets, including data on 16 different contaminants, were analysed in an iterative procedure employing the statistical methodology developed by WGSATM. The resulting ICES analyses are published in ICES Cooperative Research Report No. 176; the *ad hoc* MON report on the interpretation of the JMP trend monitoring data has been proposed for publication in the 1991 annual reports of the Oslo and Paris Commissions.

The ACMP noted that, in connection with the submission of data for the period 1985-1989 for use in NSTF assessments, few additional relevant data have been received beyond the (largely coastal) JMP data sets already routinely processed by ICES; some countries had, however, made a significant contribution, e.g., Belgium's revised submission of 10 years of data on contaminants and nutrients in sea water.

The ACMP was informed that, due to delays in the processing of the Bremerhaven Workshop chemistry samples, the handling of these data by ICES, originally scheduled for January 1991, is now being completed as far as possible during June 1991 due to the urgent need for these results for comparison with the results of the biological effects techniques employed during the workshop. The 'Concluding Workshop' for the Bremerhaven Workshop is scheduled for September 1991.

#### Generic problems associated with the handling and assessment of monitoring data

The ACMP expressed considerable concern over the problems caused by delays in the planned submission of data; these have created, and continue to create, major ADP problems within ICES, in particular in planning the allocation of resources and scheduling activities within the year. As data handling is generally one of the last stages in the data collection process (following planning of monitoring activities, practical field work, laboratory analysis of samples, etc.), it tends to suffer from the cumulative effects of delays in the preceding activities. This is particularly serious in the case of projects with fixed end-points (e.g., the Bremerhaven Concluding Workshop, the deadline for the publication of the QSR, and scheduled assessment meetings).

Extremely large sums of money are involved in conducting the present monitoring programmes of the OSPARCOM and NSTF, however, the resources and finances allocated to subsequently assess and interpret the data obtained are often minimal. Furthermore, because of the time pressures, the assessments often have to be done very hastily.

The ACMP, therefore, urges the Commissions to critically re-examine the mechanisms presently employed to assess monitoring data, reiterating the advice contained in the 1990 ACMP report, which emphasized that, in future, data assessment activities must constitute an integral component of the monitoring programmes.

#### Processing of 1990/1991 data: handling and assessment of NSTF monitoring data

The ACMP was informed that, during 1991/1992 the anticipated Secretariat workload in connection with ADP-related activities is expected to increase greatly, estimated at ca. 80 and 60 man-weeks in 1991 and 1992, respectively. The main reason for this increased workload lies in commitments to handle and assess data for the preparation of the 1993 North Sea Quality Status Report (QSR), including NSTF-MMP, JMP and ICES monitoring data. In addition to handling submissions of NSTF-MMP and JMP 1990 monitoring data (to be submitted by 1 August 1991), it has been agreed that ICES will also receive and include in assessments as much of the 1991 North Sea monitoring data as can be submitted by 31 December 1991.

In consideration of the generic problems associated with the handling and assessment of monitoring data, described above, the ACMP discussed at length the ICES commitments in relation to processing NSTF data for the preparation of the QSR.

- The ACMP noted that, at the fourth (NSTF4, Stockholm) and fifth (NSTF5, Berlin) meetings of the North Sea Task Force in 1990, ICES had undertaken to act as the data centre for NSTF data on contaminants in marine media (fish and shellfish, sediments, and sea water); these data types have routinely been handled within ICES since 1983 in connection with the ICES role as data centre for the JMP.
- In addition, at NSTF4, ICES offered to handle NSTF data on a range of new biological data types: namely, the results of fish disease monitoring surveys, data on marine mammal strandings, measurements of biological effects of contaminants, and benthos community structure. The handling of these data was conditional on the provision of appropriate additional funding to ICES to cover the extra costs involved.
- At NSTF5, a timetable was drawn up for the production of the QSR, including a schedule for the submission of data to ICES, its processing within the ICES data centre, and its subsequent assessment by ICES and OSPARCOM groups. This timetable was subsequently revised by the NSTF's Expert Steering Group (ESG), which in effect brought the final deadlines forward by six months. At NSTF6, it was recognized by all parties that, due to the revised requirement to produce a complete QSR by June 1993 instead of the end of 1993 as originally proposed (North Sea Environment Report No.1), the agreed timetable was extremely tight and contains no allowance for any 'slippage' in the remaining steps for the production of the QSR.
- In connection with this proposed schedule, ICES had pointed out that, for the planned procedures for assessing data to have some chance of producing a scientifically valid product for the QSR, the deadlines for submission of data were absolute; indeed, it has further been pointed out to the NSTF that it would also be very unsatisfactory if all the data were submitted immediately prior to the actual deadline.

The ACMP wishes to make the Commissions and the NSTF aware that, even if deadlines for submitting data are met, data assessment is a lengthy process; some recent data assessments conducted within ICES have taken several years to generate an acceptable product.

Two major assessments planned to contribute to the QSR are:

- the assessment of data from the 1990 JMP (supplementary) Baseline Study on Contaminants in Fish and Shellfish, to be conducted by the OSPARCOM's *ad hoc* MON Group in December 1991; and
- the assessment of the 1990/91 MMP data on contaminants in sediments (including the North Sea component of the 1990/91 JMP sediment baseline study data), to be conducted by a joint ICES/NSTF/OSPARCOM assessment group (largely consisting of a sub-group of the ICES Working Group on Marine Sediments in Relation to Pollution (WGMS)) in March 1992.

In addition, data received on the EROD and oyster embryo bioassay biological effects techniques are due to be assessed by members of the ICES Working Group on Biological Effects of Contaminants (WGBEC) prior to the 1992 meeting of the working group. Data on fish diseases will be reviewed by the ICES Working Group on Pathology and Diseases of Marine Organisms.

In all of these cases, the assessment process requires that consistent data (i.e., data having passed the preliminary validation procedures) are distributed to the relevant members of the assessment groups well in advance of the actual assessment meetings.

The ACMP expressed considerable concern about the ability of ICES to meet its commitments in relation to the data handling for the QSR <u>if</u> the agreed deadlines are not met, especially because during NSTF6 in May 1991 some countries indicated that meeting the deadlines may not be possible.

Past experience has revealed the various problems associated with trying to include late data into ongoing assessments. It was emphasized that, whilst ICES had made definite commitments to handle the NSTF data, it could not accept responsibility for problems arising as a result of countries not meeting their commitments with respect to the agreed timetables. If data assessments were compromised by late submission of data to ICES, this would be the direct responsibility of those countries involved, and the NSTF would have to decide either to ignore the data or to delay production of the QSR.

The ACMP was also informed of a proposal to conduct a two-stage assessment process for NSTF data, to update in 1992/1993 the initial assessments to include evaluations of the 1991 data that are not available for consideration in the first assessment round.

In summary, the ACMP concludes that:

- The ability of ICES to meet its commitments in relation to the data handling for the QSR, which has already been prejudiced by advancing the deadline for the production of the QSR by six months, will be seriously at risk if the agreed NSTF deadlines are not met.
- The deadlines agreed by the NSTF should be rigorously applied; data arriving after the deadlines should be excluded from the assessments.
- The NSTF needs to recognize that, if the present timetable for data submission is compromised, and it is not possible to conclude appropriate assessments of the monitoring data according to the present plans, this will require a revised timetable for the production of the QSR.
- If a two-stage assessment process is adopted, then ICES should meet its data centre commitments to produce the updated assessment products, provided that additional funds are made available for this activity.
- If a second assessment is necessary, then efficient use of limited resources should dictate that the entire process be delayed and a single assessment of the data be conducted when the complete data set is available.

#### Other ADP issues

The ACMP was informed that, as part of the preparation for the various ADP projects, the ICES environmental data reporting formats have been revised in April 1991, in order to:

cover reporting of data on (i) contaminants in fish and shellfish, (ii) contaminants in sediments, (iii) contaminants (and nutrients) in sea water, (iv) selected biological effects techniques (EROD, oyster embryo bioassay), and (v) fish disease surveys, in a more consistent manner; and

- incorporate new variables and items of information, as requested by the NSTF, the Commissions and data assessment groups, and take into account improvements requested by data originators.

Initially, the revised formats will be used for the 1990 NSTF-MMP data submissions, and will subsequently be forwarded to JMG and HELCOM for use in reporting data from their respective monitoring programmes.

#### ANNEX 1

## REVIEW OF CURRENT RESEARCH ON THE EFFECTS OF PHYSICAL DISTURBANCE ON THE SEA FLOOR

This annex provides a review of current research being conducted in ICES member countries and the European Community on the effects of physical disturbances on the sea floor on benthic and epibenthic communities. This represents a summary of information presented at the 1991 meeting of the Benthos Ecology Working Group and accepted by ACMP for inclusion in this annex.

#### Norway

Studies of the effects of Iceland scallop dredging on macrobenthos using photography, underwater video, and benthic sampling equipment show that a single vessel will take on board each day up to 4,000 tonnes of bottom sediment (stones and gravel); this is returned to the sea after processing (which includes heating to 80°C). Dredging has reduced the number of species, the number of individuals per sample, and the biomass. However, some species have become dominant, presumably because of a higher tolerance to physical disturbance. No recovery was apparent two years after the fishery stopped.

#### Sweden

A three-year project is underway to study the effects of trawling on the benthos in the Kattegat using a remotely operated vehicle (ROV). The initial results indicate little difference between trawled and untrawled areas, but the untrawled areas may not be representative of natural conditions because of heavy fishing for *Nephrops*.

#### Germany

The effects of a pipeline channel dredged through glacial till in the Kiel Bight are being studied using various sensing techniques. The track is still visible after five years.

The distribution of sedimentation resulting from the construction of the Danish bridge/tunnel in the Great Belt is being studied using REMOTS (a device that photographs vertical sediment profiles *in situ*).

Experiments are being conducted to measure the mortality of organisms by otter boards. Mortalities are greater in the door tracks than outside. Damage to some species (e.g., the mollusc *Arctica*) appears to be size dependent.

Tracks of bottom trawling gear have been mapped in the Kiel Bight using side-scan sonar records (Krost *et al.*, 1990). Track density is the greatest in mud areas and at depths greater than 20 m. It is estimated that some areas are ploughed at least once a year by the boards alone and that the trawl marks last for at least eight months.

An experiment (DISCOL) has been conducted in the deep Pacific Ocean to examine the influence of sea floor 'ploughing' by manganese nodule dredging (Thiel and Schriever, 1990).

#### Netherlands

Various institutes in the Netherlands are studying the effects of beam trawls on the benthos in the Dutch sector of the North Sea. The results of the 1989 experiment have been published (BEON, 1990). A report on the 1990 experiment is being prepared. A penetration depth of at least 6 cm has been estimated, based on the catch of animals living within the sediments. This is possibly caused by the action of the tickler chains. Work is continuing in 1991.

The mollusc *Arctica* appears to be particularly susceptible to damage from beam trawls. Only 3-5% of trawled shells are complete living animals. Many shells show damage from previous encounters with beam trawls from which the animals presumably recovered. It was suggested that damaged shellfish may serve as an indicator of trawling intensity.

Studies have been conducted on the effects of gravel extraction from the Klaver Bank in the Dutch sector of the North Sea using SCUBA, a ROV, and benthic sampling equipment. Extraction removed on average 35 cm of gravel. Some species were unaffected, while others either disappeared completely or were reduced in abundance. Overall, there was a drop in both species number and biomass. Small animals recovered after one year, by which time the excavated area had completely filled in with new gravel.

#### France

A study on the effects of fishing activity on the benthos has recently started in the Bay of St-Brieuc on the north coast of Brittany. The 300 boats that fish this Bay utilize otter trawls, scallop rakes, and clam dredges. The principle objectives of the study are to evaluate the physical reworking and resuspension of sediments by fishing gear and to determine damage to benthic organisms. Observational methods include side-scan sonar, underwater video, and SCUBA. Preliminary results suggest that the greatest damage is done by clam dredges.

#### United Kingdom

One approach to studying the effects of trawling on the benthos is to sample along gradients away from known wrecks in heavily fished areas. This approach assumes that trawling is not taking place immediately beside the wreck because of potential damage to fishing gear. In March 1991, three such gradients were examined on the Turbot Bank in the North Sea, using a ROV. The results, when available, will indicate whether this approach is valid and practical.

Experiments on the west coast of Scotland show that commercial suction dredges can remove up to 1 m of sediment from the sea floor. Some areas recover quickly, in part due to lateral transport of sand and organisms by storm waves.

#### **United States**

The impacts of scallop dredging on faunal associations have been studied in the western Gulf of Maine using photographs taken along transects from a manned submersible (Langton and Robinson, 1990). Fishing operations appear to reduce the mean densities of megafaunal species (scallops, anemones, and sabellid worms), reduce the mean patchiness in their distribution, and change the faunal associations.

Studies using manned submersibles are also being conducted on Georges Bank. Over the years, strong tidal currents have winnowed away most of the silt and clay in surface sediments from large areas of Georges Bank to create a gravel pavement that appears to be an important habitat for juvenile cod and spawning herring. In areas where this gravel pavement is not trawled, because of the presence of large rocks that would damage fishing gear, epibenthic organisms dominated by tubiculous polychaetes are present. Trawled areas, in contrast, are quite different. Tubiculous polychaetes are much less abundant and reworked sand coats the surface of the gravel pavement. It is not known whether trawling has adverse effects on juvenile

cod and herring egg beds or how long it takes to re-establish the gravel pavement and re-colonize epibenthic organisms.

Experiments have been conducted in shallow estuarine habitats off the coast of North Carolina to test the impact of clam raking and mechanical harvesting on clams, seagrass, benthic macroinvertebrates, and the bay scallop (Peterson *et al.*, 1987). Harvesting did not significantly affect clam recruitment, but did reduce the biomass of seagrass, and recovery ranged from one year to more than four years. Small benthic macroinvertebrates were not affected, presumably because of their capacity for rapid re-colonization. Bay scallop abundance decreased with the decline in seagrass biomass. The results indicate that the clam fishery should be managed to minimize the intensity of harvest within seagrass beds.

#### Canada

All existing side-scan sonar records (collected primarily by geological programmes) from the Bay of Fundy, the Canadian sector of the Gulf of Maine and Georges Bank, and the Scotian Shelf have been examined for evidence of sea floor disturbance by fishing activity. Just 1.5% of the available 13,000 km of records (a relatively small amount of the total area) had visible sea floor disturbance. Approximately 90% of the disturbance observed was caused by the boards of otter trawls, 7% by scallop rakes, and 3% by hydraulic clam dredges. No disturbance was visible in high energy environments with bedforms. A report will be available soon. An identical study is currently being conducted on the Grand Banks. These studies do not provide any information on the geographical extent of physical disruption, biological effects, or recovery times.

The impact of an otter trawl on benthic organisms was investigated in the autumn of 1990 in the intertidal zone of the Minas Basin, Bay of Fundy. Furrows from both the doors and rollers persisted for the entire experimental period despite storms. However, no effects on either chlorophyll or macrobenthos numbers and biomass (predominately polychaetes) could be detected, even in the trawl track, which was up to 4 cm deep. This experiment will be repeated in the summer of 1991, when biological activity in the sandflat will be greater.

A new project will begin in May 1991 to investigate the impacts of trawling on benthic communities on both the Scotian Shelf and the Grand Banks. It will utilize side-scan sonar, underwater video, and traditional benthic sampling methods. Field work will focus on two sites which are closed to mobile fishing gear. This project will run for at least five years and experimental trawling within the closed area may be considered.

#### **European Community (EEC)**

A new joint project within the EEC has been started with the Netherlands State Institute for Fisheries, the Netherlands Institute for Sea Research, the Delta Institute for Hydrobiological Research in the Netherlands, the Marine Laboratory in Aberdeen, Scotland, the University of Kiel in Germany, and the Fisheries Institute in Ostende, Belgium. The project aims at studying the environmental impact of beam and otter trawling and starts in May 1991. Traditional sampling will be complemented by video and sonar investigations.

#### References

- BEON. 1990. Effects of beam trawl fishery on the bottom fauna in the North Sea. Netherlands Institute for Sea Research, Netherlands Institute for Fishery Investigations, Netherlands North Sea Directorate. Policy Linked Ecological Research North Sea and Wadden Sea (BEON) Report No. 8. 57 pp.
- Krost, P., Bernard, M., Wener, F., and Hukriede, W. 1990. Otter trawl tracks in Kiel Bay (Western Baltic) mapped by side-scan sonar. Meeresforsch., 32: 344-353.

- Langton, R.W., and Robinson, W.E. 1990. Faunal associations in scallop grounds in the western Gulf of Maine. J. Exp. Mar. Biol. Ecol., 144: 157-171.
- Peterson, C.H., Summerson, H.C., and Fegley, S.R. 1987. Ecological consequences of mechanical harvesting of clams. Fishery Bulletin, 85: 281-298.
- Thiel, H., and Schriever, G. 1990. Deep-Sea Mining. Environmental Impact of the DISCOL project. Ambio, 19(5): 245-250.

### ANNEX 2

### ACMP ADVICE ON A TOPIC BASIS FOR THE YEARS 1991 - 1980

Numbers in table refer to sections of the ACMP report from 1991 to 1984 and to paragraphs in the report from 1983 to 1980. \*Signifies major advice on that topic

Topic	Sub-topic	1991	1990	1989	1988	1987	1986	1985	1984	1983	1982	1981	1980
Monitoring	Strategy				*4								
	Multi-purpose		6.2										
	Benthos	8.1	9	*An.1	*7.1	8							
	NSTF-MMP		9.3	4									
	Sediments - Guidelines			*14			15		*An.2	45-49	42-45		
	H H									An.2			
	Sed. data normalization			*14.1	14.1	15.2	16						
	Sensitivity of sediments				14.6								
					An.2								
	Metals/sediments				12.6								
	Tissue sample storage										52-55		
	Matrix tables - gen. (JMP)		*An.1	*6.1	4								
	" - organic		6.1										

Topic	Sub-topic	1991	1990	1989	1988	1987	1986	1985	1984	1983	1982	1981	1980
Monitoring	Matrix tables - NSTF		6.1										
(ctd.)	Use of seaweeds		6.8	6.3					4.6				
	CMP Guidelines										23-25		
	Review of CMP									16-19		28-33	10-14
	JMP Guidelines						4.5						
	BMP Guidelines					*12	4.4			90-91			
	Mussel Watch											41	15-16
												An.3	
	Trend monitor. Guidelines				5.2	6.2	*4.1	4.1	4.5	25-26	22/25		30-33
						6.3	An.1						
	" " Nutrients				11.1								
	" " Fish - JMP	5.1	6.2				An.1						
	" " Fish - CMP	5.1	6.5	*6.4	5.1	6.1	An.1	4.2	4.1	25-26		34-40	
	" " Mussels	5.1	*An.3			6.3							
	" " Pooling		6.7	6.4.3		6.2.1							
	H H H		An.5							0			
	" " Precision			6.4.4									
	" " Sed. Storage				14.2								
	" " Sea water		6.6		A supervision of the second se	6.5	4.2			27-28			

Topic	Sub-topic	<b>199</b> 1	1990	1989	1988	1987	1986	1985	1984	1983	1982	1981	1980
Monitoring	Trend Monitor. Sediments				5.3	6.5	4.2						
(ctd.)	н и н				An.2								
Biological	Monitoring Strategy							5	5.1	33-37	41	64-66	42-45
Effects											An.3		
	Concepts			*7.1									
	Methods	7.2											
	Pathology						5.1						
	Oslo Workshop						5.2						
	A. Dohrn Workshop								5.2				
	Bremerhaven Workshop	7.1	8.1	7.2	6								
	Fish egg bioassays						5.3						
Mariculture	Impacts		*11	10	9	10	10						
	Nutrient inputs Baltic		11.1	10.4									
	Drug use control		An.6										
Algal	Primary production meths.	11.1	12.1		10.2								
Blooms	Initiating factors	11.3	12.2				8						
	Exceptional algal blooms	11.2					8	*8	9	43-44	58	88-90	
										*An.1			
	Red tides												61-63

Topic	Sub-topic	<b>1991</b>	1990	1989	1988	1987	1986	1985	1984	1983	1982	1981	1980
Blooms	Phycotoxins/measurements	11.4	12.3		10.1		9						
(ctd.)	C. polylepis bloom			*11.1	10.3								
Regional	Guidelines		5		*20.1					53-55	46-51		
Assessments	11									An.3			
	Preparation plans			5		21.4		10	10				
	Irish Sea					*21.1	24.2			An ann an Anna Anna Anna Anna Anna Anna			
	Skagerrak/Kattegat					21.2	24.1						
	North Sea QSR	4	5			21.3	23						
	Baltic Sea			5								77-78	48-51
	Baltic fish		17.2	17.3			•						
	Canadian waters	16											
	Nutrient trends - N. Atl.		13	12		16.1							
Baseline	1985 Baseline Fish					*4	4.3.1		4.2	20-21			
Studies									11.4	86			
	" " Plans								An.9				
	ICES Baseline TM/SW	6	*7	6.5	13	5	4.3.2	7.2.1	4.3	22-24			
	Contams. in Baltic seds.	14.1	15.1			15.1							
Fish	Relation to pollution	9.1		9.3			5.1	6.2	5.4		34-40		
Diseases	Survey methods	9.2			8.2				5.3				

Topic	Sub-topic	1991	1990	1989	1988	1987	1986	1985	1984	1983	1982	1981	1980
Fish	Training guide		10										
Diseases (ctd.)	Immunocompetence		10										
(0.0.)	Survey results			9.1	8.1	9	6	6.1					
Quality	Philosophy	13.6									12-18		
Assurance	Good lab. practice					13.5	11.5	An.1					
	Reference materials	-		13.1	12.8		11.4	7.3					
	Oxygen in water		14.5	13.6									
	Hydrocarbons			13.7									
	Cd, Pb det'n limits												21
	NSTF		14.7										
	Biological effects techs.	7.3											
	Sed. quality criteria		15.2	22.2									
Intercal-	Status		An.9	An.2	An.3						An.1	4-10	4-7
ibration	11											An.1	25-29
	Nomenclature										*4		
	Nutrients - sea water		14.1	13.4	11.3	16.2	19						
	Lindane ( $\gamma$ -HCH)						*13						
::	Specific hydrocarbons					13.3	11.1	7.1.2					
	Hydrocarbon biol. tissue			13.7				7.1.2	6.5	14-15	10	20-22	5-6

Topic	Sub-topic	1991	1990	1989	1988	1987	1986	1985	1984	1983	1982	1981	1980
Intercal-	2-3HC/BT								6.5				
ibration (ctd.)	Hydrocarbons in sediments			13.7								20-22	5-6
(000)	Hydrocarbons in sea water			13.7			*12	7.1.2			9	23	
	PAHs - standards	13.1	14.2	13.2	12.1								
	PCBs/CBs in biota	13.2			12.3			7.1.1					
	Organochlorines								6.4	11-13	8	7-10	
	5/OC/BT								6.4				
	CBs in sediments	13.2				14	14						
	CBs - standards		14.3	13.3	12.2		14						
	TMs in sea water					13.1		7.2.2	6.2	5-8	6-7	68-70	26-29
	5/TM/SW					·			6.2	5-8			
	6/TM/SW					13.1							
	TMs in sediments				12.5		11.2.1	7.2.4	6.3				
	11 11 11						11.2.2	7.4					
	1/TM/MS						11.2.1						
	Baltic sediment intercal.							7.4	11.3	52			
	TMs in biological tissue					13.2		7.2.1	6.1	9-10	5-6	11-19	
	7/TM/BT					13.2		7.2.1					
	Diss. oxygen in sea water	13.4	*14.5										

Topic	Sub-topic	1991	1990	1989	1988	1987	1986	1985	1984	1983	1982	1981	1980
Intercal-	Methyl Hg in biol. tissue				12.4	13.4							
ibration (ctd.)	TMs in SPM	13.3	14.4	13.5	14.4		18.2	7.2.3					
(c.u.)	17 17 19				An.1								
	Primary production				10.2								÷.
Marine	Contaminants/effects					*11.1	7.2						
Mammals	Seal epidemic 1988		*18	*18.1									
	Baltic seal stocks					11.3	*7.1		12				
									An.8				
	Populations - N. Atl.	18											
Classif'n	Human health		19										
Overviews	Arsenic					*17.2							
	Cadmium											*An.4	
	Mercury			*19.1									*An.2
	Zinc								*An.7				
	Lead										*An.5		
	PCBs											An.4	
	НСВ		*20.1										
	Lindane ( $\gamma$ -HCH)		*20.1			1							
	HCBD									*An.5			

Topic	Sub-topic	1991	1990	1989	1988	1987	1986	1985	1984	1983	1982	1981	1980
Overviews	PCDDS and PCDFs			*19.2					An.4				
(ctd.)	PAHs						*20.2						
	Phthalate esters					+		*13.2					
	Organo-tin and -lead								*An.5				
	Polychlorinated terphenyls								*An.6				
	Octachlorostyrene	20.1											
	Toxaphene									*An.4			
Sand/gravel	Code of Practice		16										
extraction	Effects	15	16	15	15								
Methods	SPM in sea water						18.1						
	Trace metals in SPM						18.2						
	Total nitrogen						19.4						
	Nutrients in sea water	13.5	*An.4				19						
	Low DO in sea water			13.6									
	Sediment normalization	14.2,3		*14.1	14.1	15.2	16						
	Analysis of total OCs				12.7								
Special	Context of ACMP advice		An.7	*21		22	25					*An.2	
Topics	Patchiness in Baltic Sea			17.1	19.1	20.1	22.1	12.1	11.1	84	85	75	
	Nutr. trends OSPAR area		13	12	11.1	16.1							

Topic	Sub-topic	1991	1990	1989	1988	1987	1986	1985	1984	1983	1982	1981	1980
Special	Nutrients & eutrophication	*11.3			10.4							-	
Topics (ctd.)	Eutrophication in Baltic										*An.7		
(0.01)	Sediments German Bight					An.1			7.4.2	50			
	Sediments Kattegat					An.2							
	Sediments Skagerrak								7.4.1	50			
	Sediments Baltic	14.1	15.1	14.2	19.3	15.1	22.2	12.2	7.4.3	51-52			
	Bioavailability/sediments	7.4		7.3			17						
	Release of sed. contams.			14.3									
	Oil spill combatting									*An.6			
	Oil dispersants											91-93	
	Effects of low-level HCs							*9					
	Oxidation prods. of HCs								14.6				
	Effects of TiO <sub>2</sub> wastes								*8	41-42		82-85	
									*An10				
	Incineration at sea			1							29-33	87	46-47
	Acid rain studies/effects			20	17	19							
	Estuar. transport/processes											*An.5	
	Gross riverine input				16.1	18.2		14	*An.1		61-65	67	17-20
	11 17 11										*An.6		

Торіс	Sub-topic	1991	1990	1989	1988	1987	1986	1985	1984	1983	1982	1981	1980
Special	Net riverine inputs			16	16.2	18.3	21		*An.1				
Topics (ctd.)	Atmospheric inputs				16.3	18.1				96-98			17-20
(0001)						*An.3							
	Selection of dumpsites										*An.2	79-81	
	Capping dredge spoils									99			
										An.7			
	Specimen banking										56	60-61	39-40
											An.4		
	Effs. disturb. on benthos	8.2											
	Ecosystem effects fishing	19											
	North Sea flushing times											52-56	
Data	Nutrients						19.5						
Manage- ment	Contaminants		×					4.3			26-27		
	BMP format												52
	NSTF	*21	22				- C						
	ICES format						4.6		4.7	29-32			

#### **ANNEX 3**

#### OVERVIEW OF INTERCALIBRATION/INTERCOMPARISON EXERCISES 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 North Sea laboratories in Cooperative Research Report No. 80 (1978) and for Baltic laboratories in Cooperative Research Report No. 63 (1977).

Third ICES Intercalibration Exercise on Trace Metals in Biological Tissue (3/TM/BT) 1975

Coordinator	4	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 North Sea laboratories in Cooperative Research Report No. 80 (1978) and for Baltic laboratories in Cooperative Research Report No. 63 (1977).

## 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).

	Sixt	h 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. 110 (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.

Report on results in preparation.

#### 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 Samples		J.M. Bewers, J. Dalziel, P.A. Yeats, and J.L. Barron, Canada. 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 Participation		Cd, Cu, Mn, Fe, Ni, Pb, and Zn. 43 laboratories from 13 ICES member countries plus Monaco.		
Results published	d ir	n Cooperative Research Report No. 105 (1981).		
Fifth ICES Intercalibration Exercise for Trace Metals in Sea Water (5/TM/SW) 1982				
Coordinators	:	J.M. Bewers, P.A. Yeats, S.S. Berman, D. Cossa, Canada; C Alzieu, P. Courau, France.		
Samples	:	<ul> <li>(a) sea water samples, filtered and acidified, for analysis of metals except Hg, and</li> <li>(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.</li> </ul>		
Metals analysed Participation		Cd, Cu, Pb, Zn, Ni, Fe, Mn. 59 laboratories from 15 ICES member countries plus Monaco.		

Results published in Cooperative Research Report No. 136 (1986).

Exercises on trace metals in sea water coordinated by ICES for the Joint Monitoring Group of the Oslo and Paris Commissions (1979)

### Cadmium

Coordinator Samples Participation	<ul> <li>Y. Thibaud, France.</li> <li>(a) Natural sea water,</li> <li>(b) sea water with a low Cd spike, and</li> <li>(c) sea water with a high Cd spike.</li> <li>33 laboratories from all 13 member countries of the Oslo and Paris Commissions plus Canada and Monaco.</li> </ul>
Mercury	
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**

F	Firs	t 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) Poltic mud addiment "MDSS" (from Poltic Sediment Intercelibration Francisco)
		(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: Intercomparison of Analyses of Reference Samples ABSS and MBSS, 1985.

Coordinators	:	L. Brügmann, German Democratic Republic and L. Niemistö, Finland.					
Samples	:	wo 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.

Step 2: Intercomparison of Analyses of Sliced Wet Cores, 1984.

d, and P. Pheiffer
dating by Pb-210

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 (Phase 1) (1/TM/SPM-1) 1989

Coordinator	:	H. Hovind and J. Skei, Norway.
Samples	:	Standard reference materials from the National Research Council of Canada:
-		(a) PACS-1, (b) MESS-1, and (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.

Report on results in preparation.

#### **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	2	A.V. Holden, United Kingdom.
Sample	:	Fish oil (capelin).
Analytes	1	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	7	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 to be published in Cooperative Research Report series.

		ICES/IOC/JMG 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 (Netherlands) (for ICES), J.C. Duinker (Federal Republic of Germany) (for IOC), J. Calder (USA) (for JMG).
Samples	ť	<ul> <li>(a) Standard solution of 10 CBs in iso-octane,</li> <li>(b) solution of the 10 CBs in iso-octane at unknown concentration,</li> <li>(c) internal standard: octachloronaphthalene in iso-octane, and</li> <li>(d) blank: iso-octane.</li> </ul>
Analytes	:	CB Nos. 28, 31, 52, 101, 105, 118, 138, 153, 180, 189.
Participation	:	57 laboratories from 17 countries.
Report on resul	lts to	be published in 1991. ICES/IOC/JMG Intercomparison Programme on the Analysis of Chlorobiphenyls in Marine Media - Step 2 (7/0C/BT-2 and 1/0C/MS-2)
Coordinators	:	J. de Boer (Netherlands) (for ICES), J.C. Duinker (Federal Republic of Germany) (for IOC), L. Reutergårdh (Sweden), and J.A. Calder (USA) (for JMG).
Samples	:	<ul> <li>(a) standard solution of all CBs (in iso-octane) to be analysed;</li> <li>(b) seal blubber extract in iso-octane;</li> <li>(c) sediment extract in iso-octane;</li> <li>(d) internal standard solution in iso-octane; and</li> <li>(e) blank (iso-octane).</li> </ul>
Analytes	:	CB Nos. 28, 31, 52, 101, 105, 118, 138, 153, 156, 180.

Participation : 58 laboratories from 16 countries.

Results will be published in late 1991.

#### 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 (nC7-nC33), and several aromatic
		hydrocarbons.
Participation	:	36 laboratories from 12 ICES member countries and Bermuda.

Results published in Cooperative Research Report No. 117 (1982).

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#### 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	<ul> <li>(a) Three samples of frozen, freeze-dried mussel homogenate,</li> <li>(b) reagent grade chrysene,</li> <li>(c) methylene chloride solution of n-alkanes,</li> <li>(d) methylene chloride solution of aromatic hydrocarbons, and</li> <li>(e) Arabian Light Crude Oil standard.</li> </ul>
Analytes Participation	<ul> <li>Aliphatic hydrocarbons (nC15-nC32) and selected aromatic hydrocarbons.</li> <li>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).</li> </ul>

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
		(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 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 will be published in 1991.

#### 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	•	<ul> <li>(a) Natural oceanic water, with no preservatives or pre-treatment,</li> <li>(b) natural shelf sea water, filtered, bottled in glass and autoclaved, and</li> <li>(c) sea water depleted in nitrate and phosphate, then filtered and bottled (blanks for nitrate and phosphate).</li> </ul>
		intrate 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 Cooperative Research Report No. 174.

### ANNEX 4

### RECENTLY PUBLISHED RELEVANT COOPERATIVE RESEARCH REPORTS

No.	Title
160	Report of the ICES Advisory Committee on Marine Pollution, 1988
162	Statistical Analysis of the ICES Cooperative Monitoring Programme. Data on Contaminants in Fish Muscle Tissue (1978-1985) for Determination of Temporal Trends
163	Baltic Sea Patchiness Experiment PEX '86 Volumes 1 and 2
165	Current Meter Data Quality
166	Methodology of Fish Disease Surveys
167	Report of the ICES Advisory Committee on Marine Pollution, 1989
170	Report of the ICES <sup>14</sup> C Primary Production Intercomparison Exercise
172	Report of the ICES Advisory Committee on Marine Pollution, 1990
174	Report on the Results of the Fourth Intercomparison Exercise for Nutrients in Sea Water
175	The Chrysochromulina polylepis Bloom in the Skagerrak and the Kattegat in May-June 1988: Environmental Conditions, Possible Causes, and Effects
176	Statistical Analysis of the ICES Cooperative Monitoring Programme Data on Contaminants in Fish Liver Tissue and <i>Mytilus edulis</i> (1978-1988) for the Determination of Temporal Trends

#### ACRONYMS

ADP	2	Automatic Data Processing
BCR	-	Community Bureau of Reference of the Commission of the European Communities
BMP	-	Baltic Monitoring Programme of the Helsinki Commission
CBs		Chlorobiphenyls
СМР	-	Coordinated ICES Monitoring Studies Programme
GEEP	-	IOC/UNEP Group of Experts on the Effects of Pollutants
GESAMP	•	IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution
IOC	-	Intergovernmental Oceanographic Commission
JMG	-	Joint Monitoring Group of the Oslo and Paris Commissions
JMP	-	Joint Monitoring Programme of the Oslo and Paris Commissions
MMP	-	Monitoring Master Plan of the North Sea Task Force
NSTF	-	North Sea Task Force
РАН	-	Polycyclic aromatic hydrocarbons
PEX	-	Joint Multi-Ship Investigation on Patchiness in the Baltic Sea (1986)
QA	-	Quality assurance
QSR	Ť	Quality Status Report
SKAGEX	-	Joint Investigation of the Skagerrak Area (1990)
SPM	-	Suspended particulate matter
UNEP	-	United Nations Environment Programme

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