REPORT OF THE ICES ADVISORY COMMITTEE ON MARINE POLLUTION. 1985

International Council for the Exploration of the Sea
Palægade 2-4, DK-1261 Copenhagen K
Denmark

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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 matters must 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 1985 membership of the Committee is found on page 1.
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REPORT OF THE ADVISORY COMMITTEE ON MARINE POLLUTION

LIST OF MEMBERS

Dr. J M Bewers  Chairman
Dr. B I Dybern  Chairman, Marine Environmental Quality Committee
Dr. J Meincke  Chairman, Hydrography Committee
Dr. K Sherman  Chairman, Biological Oceanography Committee

COOPTED MEMBERS

M. C Alzieu
Dr. (Ms.) M C de Barros
Dr. L Brügmann
Prof. I Dundas
Dr. (Ms.) E Egidius
Dr. J Lassig
Dr. M Parker
Dr. J E Portmann
Dr. H Rosenthal

Dr. (Ms.) Janet F Pawlak, ICES Environment Officer
Secretary to the Advisory Committee on Marine Pollution
This report begins with a brief summary of the progress made in respect to work requested by the Oslo and Paris Commissions and the Helsinki Commission. It then summarizes activities within ICES on trend monitoring in biological tissues stressing the considerable progress that has been achieved with respect to statistical techniques. This is followed by a summary of the strategy and application of biological effects techniques to environmental monitoring programmes and an analysis of issues related to fish diseases that form the background to discriminating between natural disease and the biological effects of contaminants. The results of recently conducted quality assurance intercalibrations for the measurement of different types of contaminants in various marine matrices are then presented. Special attention is given to the resolution of problems associated with the measurement of organic contaminants, such as PCBs and hydrocarbons. Considerable progress is being made towards the improvement of these techniques and a status report, including the identification of specific chlorobiphenyl congeners for quantification in monitoring, is included in this material. A detailed proposal for the conduct of an intercalibration for metals in estuarine waters, requested by JMG, is presented. The results of a Special Meeting on the Causes, Dynamics, and Effects of Exceptional Marine Blooms and Related Events, held in Copenhagen in October 1984, are described and analysed. In response to some concerns expressed about the potential effects of chronic oil contamination of the marine environment, an evaluation is presented of the effects of long-term, low-level introductions of oil into the sea. A summary of the results of regional investigations, with particular emphasis on the Baltic Sea, is provided and, finally, as one in a series of overviews on specific contaminants in the marine environment, an overview of phthalate acid esters is included in this report.
EXECUTIVE SUMMARY

This Executive Summary provides a brief summary in respect to work requested by the regulatory Commissions, separate from the body of the report.

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

At its 1985 meeting, the ACMP considered, inter alia, the most recent reports of the following ICES groups:

- Marine Chemistry Working Group (MCWG);
- ICES/SCOR Working Group on the Study of the Pollution of the Baltic;
- Working Group on Marine Sediments in Relation to Pollution (WGMS);
- ad hoc Group of Statisticians Assisting WGMPNA on Trend Monitoring Issues;
- Study Group on Biological Effects Techniques;
- Working Group on Pathology and Diseases of Marine Organisms;

Work Requests from the Oslo and Paris Commissions

Brief summaries of the progress made in response to questions raised by the Commissions are presented, under the topic headings assigned by the Commissions, in Section 2 of this Report. For the benefit of readers not wishing to study the detailed report, a brief elaboration of the main topics is presented below under three headings: 'General Monitoring Issues', 'Specific Problems' and 'Continuing Responsibilities'.

General Monitoring Issues

In further work aimed at developing appropriate methods for the detection of temporal trends in contaminant concentrations, general guidelines have been issued for the statistical analysis of data pertaining to the incidence of contaminants in fish.
These guidelines provide for a sequential analysis of such data, with interim checks to ensure that appropriate results are being obtained at each step in the procedure. The application of these guidelines will be tested during 1985 and the results reported in 1986.

During 1985, a Baseline Study of Contaminants in Fish and Shellfish is being conducted in various areas of the North Atlantic and the Baltic Sea. In addition, surveys for the construction of baselines for trace metals in coastal and shelf sea water are being conducted and some pilot applications of biological effects techniques may be included.

A number of problems have been encountered in the development of techniques that can be used to study biological effects over wide geographical areas. These various problems are outlined in the report. They include difficulties associated with the inherent variability of biological materials, technique standardization and the substantial effort required to convert a laboratory-based method to one suitable for field application. The report contains proposals for achieving progress in this field and makes a specific recommendation for close cooperation with the IOC Group of Experts on the Effects of Pollutants (GEEP).

Considerable progress has been made in respect to agreement on specific chlorobiphenyl congeners that should be detected and quantified in surveys of PCB contamination in the marine environment. A discussion of continuing difficulties in this field is presented. It is stressed that appropriate standards are urgently needed and that limitations imposed by inadequate laboratory quality control still must be overcome. Experience with the analysis of chlorobiphenyl congeners in fish and shellfish tissues will have to be gained before further proposals for appropriate intercalibrations can be made. Although collaborative work is not possible due to problems with intercalibration, useful work by individual laboratories is not precluded. To this end, a number of suggestions are made as to how this can be achieved pending solution of the intercalibration problems.

The results of the Second and Third Intercomparison Exercises on Petroleum Hydrocarbons in Biological Tissues have been reviewed. It was concluded that, while a large number of laboratories are clearly interested in determining contamination of the marine environment by hydrocarbons, there remain a number of analytical problems to be resolved before a cooperative monitoring programme can be instituted for petroleum hydrocarbons in biological tissues. It appears that satisfactory interlaboratory comparability can only be ensured through the use of a common method of analysis. As in the case of chlorinated compounds, appropriate standards are urgently needed and it is recommended that ICES be involved in activities within the IOC/UNEP forum addressing this problem. However, the UV-F method does provide a means of surveying, in broad terms, the total hydrocarbon levels in sea water.
In respect to trace metals, good interlaboratory comparability has been achieved for a number of metals, including copper, zinc, cadmium and mercury in biological tissues. Analytical problems with lead and arsenic still exist, as illustrated by the results of the Seventh Round Intercalibration for Trace Metals in Biological Tissues. Charts depicting the performance of participating laboratories in this exercise have been prepared in order to assist the Joint Monitoring Group in evaluating the quality of data submitted as part of monitoring programmes. Similar charts, depicting bias and precision in the analysis of sea water for trace metals, have been prepared on the basis of the results of the Fifth Round Intercalibration for Trace Metals in Sea Water. It is pointed out that data quality requirements for participation in cooperative monitoring programmes can only be established on the basis of the design and objectives of specific programmes, but ACMP maintains a willingness to assist the Joint Monitoring Group in these respects.

In response to a request by the Joint Monitoring Group, formulated at its 1985 meeting, a detailed proposal for the conduct of an intercalibration for trace metals in estuarine water has been prepared and is included in this report. This experiment can be conducted in early 1986 and final planning will be carried out by the coordinators in conjunction with the Joint Monitoring Group.

A review is presented of the preliminary results of two intercalibrations on the analysis of marine sediments, namely the First Intercalibration for Trace Metals in Marine Sediments and the Baltic Sediment Intercalibration. Although the results suggest that there exist minor difficulties in the analysis of sediments using strong acids for most metals, problems have been encountered with respect to mercury and cadmium. The problems associated with cadmium analysis appear to have been identified and further intersessional work among the members of the Working Group on Marine Sediments in Relation to Pollution will be undertaken to resolve them. A first pilot intercalibration on trace metals in suspended particulate matter in sea water has also been undertaken. The results of this exercise suggest that relatively good intercomparability for such analyses can be achieved among experienced laboratories.

Specific Problems

An important topic under this heading is the problem of unusual phytoplankton blooms. The results of a Special Meeting on this subject were reviewed and it was concluded that there exists little evidence for any increasing trend in the incidence of blooms in North Atlantic waters. This conclusion, however, must be tempered by an appreciation that relevant data are extremely sparse. Changes in species composition have been observed in some areas, but the reasons for these changes remain unclear. The development of exceptional blooms stems from the combination of, and interaction between, physical, chemical and biological processes. While the role of biological factors is becoming clearer, information on chemical factors remains scarce. The major detrimental effect of exceptional algal blooms is of an economic nature resulting from interference with molluscan
fisheries and mariculture.

An assessment of the consequences of the impact of long-term, low-level discharges of oil to the ocean is also presented in the report. This analysis concludes that there exists no real evidence for significant degradation of the marine environment as a consequence of such releases but advocates the continuing restriction of discharges of oil in view of possible deleterious effects associated, inter alia, with the combined influences of oil and other contaminants. It also provides advice on the types of investigation needed to gain more authoritative understanding of the subject.

Continuing Responsibilities

A review of experience gained in the first year of automated data processing (ADP) of the Joint Monitoring Programme data has been conducted. Several amendments to the reporting formats and output tables were suggested by the Joint Monitoring Group, and these have now been implemented in the ICES ADP system. Plans are now being made for revising the reporting format for contaminants in sea water to take account of new analytes that have been added to the Joint Monitoring Programme.

Another continuing item is to keep under review, and to report on, 'new' contaminants of interest to the Joint Monitoring Programme. In this connection, an overview on phthalate acid esters is included in this report and a further list of subjects for such overviews has been prepared for early attention within ICES.

In addition to these topics, the continued appraisal of the effects of titanium dioxide wastes has been requested of ACMP. Advice on this topic was included in the 1984 ACMP report and it is not anticipated that further authoritative evaluation of the subject can be made until 1987 at the earliest. Finally, the subject of the bioavailability of substances in dredge spoils, upon which a request for advice has been received from the Oslo and Paris Commissions, is being dealt with in the work of ICES Working Groups and pertinent advice will be developed as soon as possible.

Work Requests from the Helsinki Commission

During its 1985 session, the ACMP addressed three specific requests from the Baltic Marine Environment Protection (Helsinki) Commission. Progress in respect to these topics is outlined in Section 3 of this Report.

The first of these requests requires ICES to develop reporting formats for data on contaminants in sea water and sediments. Work is being carried out to meet the request that they be made compatible with the ICES hydrographic/hydrochemistry data reporting forms.
The second request concerns the preparation of a specific assessment of contaminants in sediments in the Baltic Sea. Plans have been developed to prepare this specific assessment on the basis of a critical review of data on geochemical and sedimentological analyses of recent cores from the Baltic Sea, together with the results of the Baltic Intercalibration Exercise. Recommendations for monitoring contaminants in sediments will also be given, as appropriate.

Regarding the third request, the estimation of changes in seal populations in the Baltic Sea and assessment of their condition in relation to pollution, a meeting of the Baltic Seals Working Group was held in October 1985 and the results of this meeting will be reported in the 1986 ACMP Report.
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 Committee's overall deliberations on pollution matters, but specific features relevant to the various Commissions' requests are drawn out into an Executive Summary, which is at the beginning of the Report, and are further itemised 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 IN THE WORK REQUESTED BY THE OSLO AND PARIS COMMISSIONS FOR 1985

A summary of the progress in the 1985 programme of work requested by the Oslo and Paris Commissions is given below, along with a reference to the relevant paragraphs and annexes of the report or an indication of the status of the work:

i) to report on the experience gained from trend monitoring studies, including the results of studies using organs other than fish muscle and liver;

A set of general guidelines for the statistical analysis of trend monitoring data has been prepared. These guidelines provide for a sequential analysis of the data, with checks at each stage to ensure that the next step is appropriate. These guidelines will be tested intersessionally and the experience gained in using them will be reported next year. See Sections 4.1 and 4.2 of the report.

ii) to report on the experience with biological effects and biological monitoring, in particular the outcome of the two workshops held in 1984 and to recommend those techniques which, having been tested, appear useful for general application;

A statement summarizing the present position with regard to the application of biological effects techniques to marine pollution monitoring is contained in Section 5 of the report. ICES will seek to cooperate with the new IOC Group of Experts on the Effects of Pollution (GEEP) in an effort to develop more specific recommendations on appropriate techniques.

iii) to report on the detailed plans for the conduct of the 1985 baseline study of contaminants in fish and shellfish: areas to be examined, substances to be measured and any associated studies on water, sediments or biological effects, and to report on the outcome in due course;

Detailed plans for the 1985 Baseline Study have been provided to the Commissions in the 1984 ACMP report. Steps have been taken to ensure the evaluation of the data from the Baseline Study during 1987. It appears that the contributions to the Baseline Study may be more extensive than originally expected, both in regard to measurements of contaminants in fish and shellfish and also in sea water, although in some cases minor reductions to contributing programmes have been notified to ICES.

iv) to further advise on the methods of sampling to determine the input of contaminants to the marine environment via rivers, with particular reference to net inputs;
This question has remained on the work programme for several years. Information on methods for assessing gross riverine discharges of contaminants has been provided in the 1982 ACMP report. In addition, some approaches to the methods of assessing net inputs have been described in the 1984 ACMP report. No response from the Commissions has yet been forthcoming as to the usefulness of the latter advice. However, the ACMP recognises that further, more specific advice on this topic would be desirable and will therefore request the MCWG to place greater emphasis on this topic in their 1986 and 1987 meetings to assist ACMP in formulating a more comprehensive response to the Commissions in the 1987 ACMP report. The ACMP noted that a GESAMP Working Group will be reporting on this topic in 1986 and the conclusions of that report will be considered.

v) to report routinely on all on-going ICES intercalibration exercises and, in particular, on the outcome of the ICES Fifth Round Intercalibration Exercise on Sea Water, concerning, in particular, methods of sampling and pretreatment;

The intercalibration exercises coordinated under ICES during the past two to three years include the following:

a) the Fifth Round Intercalibration on Trace Metals in Sea Water (5/TM/SW),

b) the Seventh Intercalibration on Trace Metals in Biological Tissue - Part A (7/TM/BT(A)),

c) the Fifth Intercomparison Exercise on Organochlorines in Biological Tissue (5/OC/BT),

d) the Second Intercomparison on Petroleum Hydrocarbons in Biological Tissue (2/HC/BT),

e) the Third Intercomparison on PAHs in Biological Tissue (3/HC/BT),

f) the First Intercalibration Exercise on Trace Metals in Marine Sediments (1/TM/MS),

g) the Baltic Sediment Intercalibration Exercise, and

h) the Pilot Intercomparison of Trace Metal Analyses in Suspended Particulate Matter.

All of these intercalibration exercises have been completed and the results will be published in the Cooperative Research Report series. It should be noted, however, that the analysis of the data obtained in the First Intercalibration on Trace Metals in Marine Sediments is still in an early stage, so the published report will not be available before early 1987.
Descriptions of methods of sampling and analysis are also being prepared, including _inter alia_ procedures for the determination of trace metals in biological tissues and sea water and sampling methods for sea water analysis. These will be completed in a timely fashion and made available to the Commissions.

Finally, an intercalibration exercise for trace metals in estuarine water has been designed and planned to satisfy the Commissions' request for such an exercise. A proposal for the conduct of this experiment has been made to the Joint Meeting of the Oslo and Paris Commissions in Brussels in June 1985.

**vi** to report on progress made in studies of sediments and pollution, by providing information on the progress of the first and second steps of the pilot survey, the outcome of the two intercalibration exercises in which ICES is involved and to advise on the detailed methods of sampling and analysis which have been tried and tested and found to give satisfactory results;

Progress reports on the Pilot Study of Sediments in the Skagerrak and the Pilot Study of Sediments in the German Bight were included in the 1984 ACMP report. Further progress in the conduct of the Pilot Study in the Skagerrak has been hampered due to funding difficulties; the Pilot Study in the German Bight is continuing and a progress report should be available in 1986. A summary of the results of the Baltic Sediment Intercalibration Exercise is given in Section 7.4 of this report;

It is anticipated that detailed descriptions of suitable methods for the sampling and analysis of sediments for geochemical and pollution purposes will be prepared after results of the various sediment intercalibrations have been fully evaluated. A leaflet on a method for the determination of cadmium in sediments is now being prepared and should be available for distribution during 1986. In addition, work has begun concerning sediment quality criteria.

**vii** to report on the progress towards the conduct of an intercalibration exercise on the measurement of petroleum hydrocarbons in sea water and the outcome of the work on intercalibration of petroleum hydrocarbons and PAHs in biological tissues;

The ACMP is anxious to ensure that the design of an intercalibration exercise for hydrocarbons in sea water suitable for JMG purposes will be available by 1986, so that a proposal could be submitted to JMG at its 1987 meeting. The ACMP has therefore requested the MCWG to undertake suitable planning for this work in order to meet the time-frame proposed.

**viii** to produce, as soon as practicable, a method for the calculation of the concentration of PCBs in environmental samples based on capillary gas chromatographic techniques. If necessary, on an interim
basis this advice could involve only a few selected isomers of PCB. To include in this advice the extent to which data provided by the new method of calculation will be compatible with the already available data produced by packed column gas chromatographic techniques;

Section 7.1.1 of this report contains an evaluation of the substantial progress made by MCWG on this issue during 1985. Methods of analysis based upon the use of single congener standards and reference materials are proposed and it is hoped that such materials will become available in the near future. The MCWG will continue its deliberations of these new methodologies and the ACMP will provide further advice on this topic, when available.

ix) to consider the feasibility of conducting an intercalibration exercise for PCBs in sediments, and to advise accordingly. If appropriate, to draw up plans for and conduct such an exercise, reporting on the results in due course;

It is not yet feasible to design an intercalibration exercise for the measurement of PCBs in sediments. The Working Group on Marine Sediments in Relation to Pollution, in association with the Marine Chemistry Working Group, will plan an intercalibration as soon as it is possible. In the interim, measurements of PCBs in sediments can be based upon the use of single congener standards and reference materials.

x) to report on the experience gained in the first application of ADP to the input of JMP environmental quality data and their output. The advice should include identification of any problems encountered with a view to eventual modification of the interim formats to meet the needs identified during the trial period;

A discussion of the experience gained in the ADP handling of JMP data occurred at the 1985 JMG meeting and amendments to the input formats and output tables requested at that time have been made. Information on the further development of reporting formats for sea water and sediments is given in Section 4.3.

xi) to provide further advice on the effects of the disposal of TiO₂ wastes at sea, whether originating from dumping activities or discharges from land-based sources;

The 1984 ACMP report contains an evaluation of the extent of the hazards posed by the discharge and dumping of wastes from the TiO₂ industry. The ACMP does not expect to be able to provide additional substantive advice on this issue until 1987, when a further analysis of the situation will be made, provided that sufficient new material is available at that time.
xii) taking account of the report of and the information available to, the Working Group of the Paris Commission responsible for assessing the input of contaminants from the atmosphere to the sea and to advise on the most appropriate methodologies for quantifying inputs from this source;

The ACMP takes note of the activities within the Paris Commission and also the Helsinki Commission on measurements of contaminant deposition from the atmosphere. The ACMP would like to review the results of these studies.

xiii) to examine, as a priority issue, the problem of unusual phytoplankton blooms, evaluate the possible causative factors including the role of nutrients and hydrographic conditions, and review the environmental effects;

Section 8 of this report contains an analysis of the issues related to this topic based upon the results of the Special Meeting on Causes, Dynamics and Effects of Exceptional Marine Blooms and Related Events, held in Copenhagen in October 1984. This is part of a much larger issue concerning primary production in the sea, and the ACMP has proposed that various activities be carried out under the Biological Oceanographic Committee. The results of these activities will be reported when available. The ACMP intends to provide further advice on this topic in due course.

xiv) 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;

Section 13.2 of this report contains an overview on phthalate acid esters in the marine environment. In addition, several classes of "new" contaminants are noted in Section 13.1 and the Marine Chemistry Working Group has been requested to prepare overviews on some of these.

xv) to assess the importance of the bioavailability of organohalogen compounds in dredged spoils dumped in the Oslo Convention area and to advise on the role of interstitial water in determining the bioavailability of organohalogen compounds and metals in sediments;

This topic has been taken up by the Working Group on Marine Sediments in Relation to Pollution and a draft paper was given preliminary consideration. The current work relates only to the bioavailability of metals in sediments, but it is anticipated that it may also be possible to provide some advice on the availability of organic contaminants. It is anticipated that a status report will be made available by the Working Group in 1986.
xvi) to advise on the extent to which the fat content of fish tissue is associated with the concentration of contaminants found in fish tissues and the most appropriate procedures for accommodating such variations in analysing data for trend monitoring purposes;

The ACMP has referred this issue to the ad hoc Group of Statisticians Assisting WGMPNA on Trend Monitoring Issues for the preparation of an initial response which the ACMP will then consider in order to provide advice on this topic.

xvii) to provide advice on methods for monitoring dumping grounds and coastal areas affected by land-based discharges by means of studies of the composition of the benthic communities.

The ACMP has requested the Biological Oceanography Committee to develop a mechanism to review the use of benthic community studies in monitoring and provide the results to ACMP as soon as practicable.
3 PROGRESS IN WORK REQUESTED BY THE HELSINKI COMMISSION

The ACMP took note of the current requests by the Baltic Marine Environment Protection Commission (Helsinki Commission) and reviewed the present status of this work.

1) The development of formats for reporting data on contaminants in sea water and sediments.

These reporting formats are being developed in consultation with the future users of these formats. It is hoped that the sea water format will be completed in 1986 and the sediment format by mid-1987. (See Section 4.3).

2) The preparation of a report on the results of the Baltic Sediment Intercalibration Exercise and the conduct of a specific assessment on sediments.

The final report on the results of the first part of the Baltic Sediment Intercalibration Exercise has been reviewed and approved for publication. The report on the second part is still under review and is expected to be approved in early 1986. Plans have been developed for the preparation of a critical review of data on contaminants in sediments and this critical review, together with the reports on the results of the intercalibration exercise, will form the basis for the specific assessment. (See Sections 7.4 and 12.2).

3) The continuation of the work on evaluating the size of the seal populations in the Baltic Sea and assessing their condition in relation to pollution.

The Baltic Seals Working Group met in October 1985. The results of this meeting will be reviewed by ACMP in 1986.
4 MONITORING ISSUES

4.1 Trend Monitoring

Expert advice on this topic was available to ACMP through the activities of an ad hoc Group of Statisticians Assisting the WGMPNA on Trend Monitoring Issues. In recent years there has been considerable discussion over the choice of an appropriate multiple linear regression model for analysing temporal trends of contaminants in fish. Problems will obviously arise if an inappropriate multiple linear regression model is selected, but the variables to be included in the model cannot be selected solely on the basis of statistical procedures alone, rather, important variables must be identified and investigated. At this point in time, it is apparent that the protocol recommended for sampling and treatment of fish samples for analysis when the objective is temporal trend assessment has substantially improved the usefulness of the data obtained. It is also apparent that frequently the key variable is size of the fish and that it makes little difference which indication of size is used, although length, which is easiest to measure, usually seems to be adequate. The effect of seasonal changes in concentrations of contaminants on trend studies is under discussion and therefore it has not been possible to establish whether sampling during the same annual period will compensate for this effect. As one possible means of resolving this situation, it is recommended that data on contaminant burdens in tissues be used in order to compensate for the differences which arise in contaminant concentrations in tissues when tissue masses change during the course of the year. Other possible means of dampening the annual fluctuations in contaminant concentrations in tissues should also be sought, e.g., by establishing a better understanding of the physiological processes governing uptake and loss.

In the light of the deliberations of this expert group, the ACMP concluded that there was no reason to change the recommended protocol for sampling and analysis for temporal trend assessment purposes; indeed, its use should be encouraged. The ad hoc Group will be invited to continue its activities and to report on the outcome of the first three years of investigations undertaken according to this protocol as soon as the third set of data becomes available. Meanwhile, the ACMP recognized that, for further progress to be made in the work on monitoring for time trends in contaminants using fish, a better understanding must be obtained of the biological processes influencing the uptake, metabolism and excretion of contaminants in fish and other organisms, and the transfer of contaminants through food chains. While expensive, a great deal of information would be obtained through the establishment of a long-term, high intensity monitoring station to examine the cyclical and seasonal changes in marine organisms and their uptake and retention of contaminants as a background to the analysis of time trends of contaminants on an annual basis. Investigations on these lines are therefore to be encouraged.
4.2 Results of the Cooperative ICES Monitoring Studies Programme

Regarding the data from the Cooperative ICES Monitoring Studies Programme, it was noted that the ad hoc Group of Statisticians Assisting WGMPNA on Trend Monitoring Issues had prepared general guidelines for the statistical analysis of these data, whereby a sequential analysis of the data should be carried out with checks at each stage to ensure that the next step is a sensible one. This analysis involves testing a linear model relating concentrations of the contaminant to biological variables to determine whether the model agrees with the data. If it does, a simpler model is then used to establish whether the relationship between the contaminant levels and the biological covariates is the same for the years under consideration. Finally, if the biological relationships are constant, the next step is to test for differences between years in the average contaminant levels adjusted for the biological variables. It was agreed that (a) efforts should be made to interpret current ICES data sets; (b) there is a necessity for a better understanding of the movement of contaminants through fish individuals/populations and food webs; (c) there is a need for longer-term data collection, as opposed to the two to four years currently available; and (d) there is a need to tie input data to levels in stocks. It was noted that the ad hoc Group had also considered the issue of the use of pooling techniques in trend monitoring in terms of the statistical costs of analysing pools prepared from the fish in each stratum of a length stratified sampling scheme rather than analysing individual fish. A number of problems that may occur with pooling were identified and the ICES Secretariat was requested to investigate the data from the Coordinated ICES Monitoring Studies Programme to develop further insights into the advantages and disadvantages of pooling.

Having considered this report, the ACMP felt that it showed evidence of considerable and satisfactory progress in the analysis of trends in contaminant concentrations in fish stocks. Further work carried out by the ad hoc Group of Statisticians assisting WGMPNA on Trend Monitoring Issues is expected to result in further progress in trend monitoring determinations and the ACMP looked forward to reviewing the results of this work.

4.3 Reporting Formats for Data on Contaminants in Marine Media

The ACMP reviewed the progress in the development and use of formats for reporting monitoring data on contaminants in different marine media. The Interim Reporting Format for Contaminants in Fish and Shellfish had been used for the first time in 1984 for reporting data for the Cooperative ICES Monitoring Studies Programme, the Joint Monitoring Programme and the Baltic Monitoring Programme. Although some problems had been encountered in the use of this format, they were not serious. Several amendments have been made to the format based on this year's experience and it is expected that this format will continue to be used for the next few years.

A Preliminary Interim Reporting Format for Contaminants in Sea Water had been developed to meet the needs of the Joint Monitoring Programme. This format was used in 1984 and is being used in 1985, but the inclusion of additional contaminants to the JMP
will make its use in 1986 impractical. Accordingly, a major revision of this format is needed.

Another problem with the sea water format is that the Scientific-Technological Committee of the Helsinki Commission has not considered it to be suitable for reporting data from the Baltic Monitoring Programme. The system for reporting BMP data is based on the ICES hydrographic/hydrochemistry formats; this includes the Biological Data Reporting Format, which was developed to be compatible with the hydrographic formats. The Preliminary Interim Reporting Format for Contaminants in Sea Water was developed to be compatible with the Interim Reporting Format for Contaminants in Fish and Shellfish and, accordingly, is not compatible with the hydrographic format.

The ACMP noted that the ICES Secretariat was examining the overall question of formats, in response to Council Resolution 1984/4:20, and had preliminarily concluded that a system based on the Helsinki Commission/ICES Biological Data Reporting Format, which can be integrated with the ICES hydrochemistry format, would seem the most appropriate for a variety of purposes. The Secretariat considered that it should be possible to expand these formats to include data on contaminants in sea water and possibly sediments. It was noted, however, that the Marine Data Management Working Group at its 1985 meeting had recorded reservations with regard to the latter point, although they endorsed the use of this format for physical/chemical and biological data. The ACMP felt that if the format were to be designed in such a way that small subsets can be extracted for specific users, then the system might be more acceptable and user-friendly. The ACMP also believed that, bearing in mind the likely large extension in parameters, especially those of an oceanographic nature, to be reported along with the data on contaminants in sea water, it seemed more logical to develop the format for contaminants in sea water using the hydrographic/hydrochemical format as a basis rather than developing it in a completely separate self-contained system. This would minimise the risk of duplication of effort in developing the formats, and will also greatly assist the ICES Secretariat in streamlining its computer software for handling these data. Accordingly, the ACMP requested the Secretariat to try to overcome the reservations of the Marine Data Management Working Group and, especially, of potential users, by discussing these issues with users of the contaminant formats. In particular, it should be made absolutely clear that only data items required by the monitoring programmes should be filled in, with completion of the other fields in the format left optional. Finally, the ACMP noted that an early decision was essential, as obligations to the JMG and the Helsinki Commission had to be met by the end of the year.

The ACMP was informed that the development of reporting formats for contaminants in sediments had proceeded more slowly than originally envisaged, owing to the difficulty in obtaining agreement among potential users. The approach to the development of this format will be reconsidered when the problems regarding the sea water format have been resolved.
5 THE USE OF BIOLOGICAL EFFECTS TECHNIQUES IN POLLUTION MONITORING PROGRAMMES

On this issue, the ACMP had available to it the report of the Study Group on Biological Effects Techniques, which had been established at the 1984 Statutory Meeting to review and evaluate the extent to which existing biological effects techniques serve (a) to identify and quantify the presence and effects of potentially harmful anthropogenic inputs or activities, including at the population or community level, and (b) to identify the causes of the effects detected. The extent to which the techniques reviewed allow discrimination between natural changes and those which are anthropogenically induced should also be determined. The Study Group had additionally considered the extent to which the results of the application of biological effects techniques permit an assessment to be made of the impact of human activities on the marine environment and its resources.

5.1 Consideration of Reasons for Previous Lack of Progress

Previous work in both ICES and GESAMP has provided a general strategy for the application of biological effects techniques, critical reviews of available techniques, and criteria for the selection of techniques.

There has been general agreement on the reasons for, and the value of, applying biological effects techniques to pollution monitoring. It has also been agreed that a number of candidate techniques were available. Nevertheless, outside the Baltic Sea, little progress has been made in using such methods in national or international pollution monitoring programmes. It is necessary to be aware of the reasons for this lack of progress, if a more appropriate strategy is to be developed to realise the potential of biological effects techniques in monitoring.

Monitoring programmes incorporating biological effects techniques face all the problems associated with chemical monitoring programmes, but, in addition, there are problems which are due to the inherent variability of the biological material used for the assays. Furthermore, biological methods tend to be very time and labour consuming, to require highly trained personnel and to be more difficult to standardise and automate than analytical chemical methods.

Even after a biological effects technique has been developed to the stage where it may yield useful data in laboratory-based experimental research, additional effort is necessary to develop it into a method useful for environmental monitoring in the field. Scientists may be loath to expend this effort, which may not be as highly regarded as more basic research.

Developing any promising methodological principle into a useful environmental monitoring technique also requires economic resources which funding agencies, already committed to supporting expensive analytical programmes and equipment, are reluctant to invest.
The multifactorial nature of the problems and the consequent need to develop not only one but a whole suite of new techniques is also a probable reason for the lack of progress in including biological effects techniques in pollution monitoring programmes.

Probably the most important reason for the lack of progress in applying biological techniques to environmental monitoring is that both biologists and environmental regulators appear to have had excessive expectations that the application of simple biological effects techniques would readily permit an assessment to be made of the impact of human activity on the marine environment and the resources it supports, while in reality most of the available methods provide at best only comparative scales of measurement of biological change. The general disillusionment due to these excessive expectations may even have resulted in an underappreciation of the real value of such comparative data.

5.2 Strategy for the Application of Biological Effects Monitoring Techniques

GESAMP has already outlined a strategy (Reports and Studies No. 12) recognising three phases in biological monitoring:

Phase I - identification: detecting a change in time and/or space;

Phase II - quantification: establishing the degree or extent of the change;

Phase III - causation: determining the cause of the observed change.

In 1982, the ACMP endorsed this strategy, but, in reviewing the GESAMP approach in 1985, it was agreed that Phases I and II are closely interconnected and require a similar approach (baseline and monitoring studies), while Phase III, studies of causation, usually requires an experimental research approach. Moreover, the ACMP considered that a crucial fourth phase, that of the assessment of the consequences of observed effects, was missing from the original strategy. This assessment step recognises that most biological techniques used in the identification and quantification phases provide only comparative scales of measurement and cannot be immediately or simply related to consequences of direct concern to regulatory authorities; this is especially true of techniques utilising measurements at the individual level, which are often difficult to interpret in terms of population or community. The assessment phase provides the essential link between the observation of biological change and management action.

There are many techniques available to identify and quantify biological changes in the sea (including those occurring at the population and community levels). Management action requires an indication of either the causes and/or the consequences of observed changes. It was recognised that it is frequently difficult to establish clear cause-effect relationships. It is often, at best, possible to establish only the probability that a given contaminant, in concert with other contaminants and
natural variables, has such a relationship; however, this should be sufficient information for management decisions regarding the control of inputs of that contaminant. Where clear evidence of causal relationships is lacking, but an assessment of the observed change indicates that either the observed change or some consequence of that change is deleterious and significant, this should be sufficient indication to regulatory agencies that caution should be exercised before further inputs are permitted to such an area.

The causes of biological change (and the discrimination between natural and anthropogenically induced change) may be examined by the use of correlation of effects and environmental variables, by manipulation experiments with bio-assays, by the use of defined biological responses to specific contaminants, and by relating response thresholds to field data on contaminant levels.

In order to assess the consequences of measured effects, the following criteria are among those of relevance:

a) the reversibility of the effect (and time-scale of reversibility);

b) the immediate ecological significance of the measured effect (particularly to valued species or communities);

c) the relevance of the effect to other levels of biological organisation (i.e. usefulness for extrapolation to population and/or community levels);

d) the relevance to a range of taxa;

e) trends in recorded effects.

It must be re-emphasized that no single technique will fulfill the requirements of all phases. Normally, a suite of techniques must be chosen, including techniques selected on the basis of their ability to facilitate assessment of the consequences of observed effects and techniques selected to determine the causes of observed effects. Each selected technique must be suited to providing answers to part of the specific pollution problem and the selected suite must be appropriate to the actual phase of the monitoring strategy, the aims and needs of management, and the indigenous biota.

5.3 Future of Biological Effects Techniques in Pollution Monitoring

The ACMP recognized that future progress on this issue is dependent on both short-term and long-term developments in methodology and strategy. In the long term, a better understanding of interactions among physical, chemical and biological components of the ecosystem is necessary. This requires continued effort in both basic and applied interdisciplinary ecosystem research. In the meantime, pressing practical problems require a pragmatic approach which provides at least partial solutions. Since pollution is defined, inter alia, in terms of deleterious biological effects, it is
obviously necessary to use biological effects techniques in its assessment.

The ACMP agreed that efforts should be made to control the natural variability of biological assay material as a first step towards method standardisation. The guidelines for the measurement of primary production in the ICES area (Doc. C.M.1981/L:46) provide a good example of this approach. The ACMP also noted that an intercalibration of sampling techniques had been reported to the Biological Oceanography Committee (Doc. C.M.1985/L:19), demonstrating that this could successfully be carried out with complex biological studies. When promising methods have been developed to the stage of "laboratory prototypes", an effort must be made to evaluate their potential for inclusion in interdisciplinary ecological research and in pollution monitoring programmes. An important step in such an evaluation could be their inclusion in practical workshops dedicated to biological effects techniques.

The ACMP recommended that close co-ordination of activities on biological effects monitoring be maintained between ICES and the Group of Experts on Effects of Pollution (GEEP) operating under IOC's GIPME (Working Committee for the Global Investigation of Pollution in the Marine Environment) programme. ICES should not duplicate the GEEP activity, but should seek information on its programme and progress from members of GEEP also involved in ICES activities and should encourage the participation of laboratories in ICES member countries.

For future work on this topic, the ACMP proposed that an ICES Working Group or Study Group review the outcome of the 1986 GEEP Workshop on Biological Effects Techniques and the results of biological effects studies during the 1985 Baseline Studies. On the basis of this review, it should provide information on techniques suitable for application to pollution monitoring in local and national contexts, and how selected techniques could be used in cooperative international monitoring programmes, taking into consideration procedures for standardization and intercalibration.

In addition, the ACMP recognised that progress in relating biological effects to changes at the population and community levels within marine ecosystems has been limited, and that a contributory factor is the need for greater multidisciplinary work by physiologists, pathologists, geneticists, biochemists, microbiologists, ecologists, and other marine scientists in a focussed effort. Accordingly, the ACMP agreed that consideration should be given to the establishment of a Working Group to focus on the effects of contamination on the reproductive success of, and recruitment to, fish stocks. This work should include the development of a strategic approach to the study of the effects of contamination on reproductive success and recruitment, utilising an experimental matrix including observations ranging from the cellular to the population level and inclusive of all life stages.
This proposal was made with cognizance of the growing interest of fish stock assessment biologists, oceanographers, chemists, fishery ecologists, and other marine scientists in the recruitment problem, thereby presenting an opportunity for multidisciplinary biological and environmental studies on reproductive success, a process of key importance to ICES.
6 RESULTS OF STUDIES ON FISH DISEASES AND DISEASES IN OTHER MARINE ORGANISMS

6.1 General Studies of Fish Diseases

On the question of fish diseases, the ACMP had available to it the report of the 1985 meeting of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO). This Working Group had also held a joint meeting with the Study Group on Biological Effects Techniques. From the reports of these two meetings, it is apparent that there is still not enough attention being paid to the collection of information on disease conditions in wild-fish populations. The ACMP strongly encourages the establishment of baseline levels of disease in wild fish and is proposing that fish stock assessment cruises be used to obtain this kind of information.

An examination of national reports on disease studies revealed several instances where there is evidence of a cause and effect relationship between disease incidence and a pollution event or contamination stress. For example, the final report on the effects of the Amoco Cadiz oil spill showed that oil produced effects on oysters, but no correlation could be found between oil contamination and the oyster parasite infection in the region, nor did tumours occur. A Swedish report mentioned the observation of fin abnormalities in perch associated with pulp and paper mill effluents. Experimental studies have been conducted on this type of effluent and showed the same effect. A Belgian-Dutch cooperative research program on eel disease concluded that there was no direct causative effect of contamination on this disease; however, the presence of contamination resulted in higher levels of specific bacterial species which, in combination with possibly lowered resistance in the fish, may cause higher disease levels. Studies on the impact of fish culture on the environment and vice versa have arrived at the same conclusions. A report from the Federal Republic of Germany on the results of studies of disease in fish in areas receiving waste from titanium dioxide production concluded that no specific effect could be attributed to the dumping of this waste. Increased disease levels in this area were due to a combination of different factors and it was important to attempt to determine the role of each of these factors. Although fish disease surveys cannot establish cause-effect relationships, they can, in combination with fishery and chemical studies, provide indications concerning possible effects of different factors, including contamination.

A set of slides of pathological material taken from fish collected in the Irish Sea between the late 1890s and the early 1920s has recently been re-examined. This material provides information relevant to several topics which are presently in focus in terms of pathological and environmental studies, such as tumours and tumour-like lesions, teratologic lesions and parasite infections.
There has been much discussion on the value of recording observations of fish pathology as a monitoring technique. These observations could be considered as an epidemiological study and have value as such. However, with the monitoring techniques presently used, no direct proof for a relation to contamination can be obtained. Proofs in this field can only be obtained by experimental investigations.

During 1984, ten new leaflets for identification of fish diseases were published by ICES, bringing the total number published to twenty. In addition, another ten leaflets are ready for publication and about 20 are under preparation. A system for classification of tumours has been established within ICES.

The disease surveys carried out during recent years clearly show the necessity for a discussion of statistical approaches and methodology for collecting and analysing data. This work was started in 1984 and it was concluded that epidemiological experts should be consulted in the planning of further work.

Finally, the larval pathology of cultivated fish was discussed with a view to applying the experience obtained in that field to studies of mortality at early life stages in wild populations. It was felt that this would provide a valuable insight into what may occur in the environment.

While both mariculture and pollution monitoring have presented useful initiatives to the work on diseases of marine organisms, it is often forgotten that disease also is a natural part of the life history of marine populations, as it is in terrestrial populations. If fish pathology is to be of any use in environmental monitoring, the establishment of baseline values is essential.

Another question is the time delay between the observation of a pathological condition at the tissue level, for example, and the appearance of effects at the individual or population level. Another example of such a delay could be the time between the observation of pathology at the larval tissue level and the detection of a subsequent effect on the mature fish or on the next generation or subsequent generations. This time component is extremely important and makes the cause-effect relationship very difficult to assess.

Concern has been expressed about the possible transfer of pathological conditions in fish to humans, especially in regard to neoplasia. It is uncertain at present whether there are real grounds for such concerns. It has been shown that fish in sewage-contaminated waters can carry human pathogens for short intervals. However, these pathogens do not affect the fish, as they are unable to multiply. In addition, fish pathogens from northern waters generally have optimum temperatures around 15-20°C; they are not able to multiply at human body temperature and thus present no threat to humans.
6.2 The Possible Relation of Fish Diseases to Pollution

Several reasons have been advanced as to why fish disease studies could be a useful component of monitoring programmes, for example:

1) Unlike many of the other possible indices of biological change, diseases affect commercially important fishery resources at the level of the individual and possibly also at the population level. Thus, if a cause/effect relationship could be established, this would be a measure of effects of real significance to regulatory authorities. Furthermore, given the geographical ranges of many fish species, it could be important at an international as well as a local level.

2) The interest in fish diseases by environmental scientists rests on an analogy with human epidemiological studies of environmentally-induced disease and stress syndromes. This analogy has not been adequately tested. The basis for human epidemiological studies of this type is the establishment of baselines of natural conditions (for selected geographical areas, age groups, social groups, etc.) and the identification of sub-groups in which a syndrome or disease occurs at a higher than normal frequency. Most fish disease studies have been carried out in selected 'hot spots' of contamination, without any attempt to examine the 'natural' level of incidence in areas believed to be unaffected by pollution.

3) However, this analogy does lead to testable hypotheses. If the principle hypothesis, that environmental factors are among the factors concerned in the aetiology of some diseases of fish, holds good (which seems likely) then fish disease incidence studies offer a possible tool for monitoring pollution or water quality.

4) If the effect of contaminant inputs is a generalised exertion of stress on fish, rendering them more susceptible to certain classes of disease or resulting in the appearance of stress syndromes, then fish disease incidence could be a useful tool in wide-scale baseline surveys of environmental quality. Furthermore, if the role of disease in population dynamics could be better understood, this approach might provide a direct measure of impact on stocks. At present, both of these are very hypothetical.

5) Alternatively, specific contaminants might give rise to specific responses (e.g., cancer induction or piscine equivalents of asbestosis). Such possibilities would need to be examined on the basis of laboratory studies and would probably relate not to mean environmental concentrations of waste, but probabilistically to the occurrence of extreme concentrations. Again, if such associations could be established, it might be possible to predict impact on fish stocks.

In considering these arguments, the ACMP noted that they are
often formulated as two closely related questions: (1) does pollution cause diseases among aquatic life forms, and (2) can fish pathology be used to monitor the biological effects of marine pollution? There is a serious risk, however, that questions cast in these terms lead to a dangerously misleading oversimplification of highly complex interactions.

It should be clearly understood that diseases, defined broadly or narrowly, are multifactorial in origin and/or development. Furthermore, clinical signs are often not specific to one disease. Similarly, “pollution” is also a collective term covering a complex range of agents or events which includes, among others, such diverse elements as waste heat, a lengthy list of both organic and inorganic chemicals, microbial agents, turbidity, increased sediment burdens, etc., in highly varied combinations and concentrations which either singly or in combination may influence fish health.

There are well-documented examples from experimental situations where external agents or man-induced changes have been shown to impair or eliminate resistance, substantially interfere with metabolic processes or otherwise pre-dispose animals to disease. Undoubtedly this, on occasion, also occurs in nature, but the sweeping assumption that contamination necessarily causes disease is too all-encompassing to be acceptable or useful.

It must be recognised that the mere presence of disease at high or low levels coincident with the presence of contaminants is not necessarily indicative of a cause-and-effect relationship because diseases are multifactorial in origin and/or development. A linkage would not be suspected unless there has been a sudden or dramatic change in background levels or characteristics of the diseases consistent with changes in degree of contamination. The simple comparison of two areas (without taking natural and anthropogenic factors into consideration) in which one area shows a high frequency of disease and the other shows a low frequency should not be taken to indicate that the area with the high disease rate is necessarily highly polluted or even polluted at all; there are many causes for disease and many factors controlling the levels.

It must also be remembered that disease studies deal with the more subtle part of the life scale rather than with those areas of dramatic or major change which result in massive kills and a major reduction in the numbers of organisms or the creation of biological deserts. Effects on these scales are observable or determinable by population scientists; the massive reduction or elimination of important species will not remain undetected.

It should be remembered that contamination is not studied for its own sake, but rather because it has, or may have, an impact on the biological entities or cause a reduction in the aesthetic value of an area. These biological effects include a reduction in or elimination of stocks of aquatic life forms of commercial or recreational value or an interference with various elements of the food web. At this stage it seems advisable that a selection be made, on the basis of first principles, of those features which serve best the studies of man-induced changes as well as those studies concerned with the more fundamental aspects of diseases and their impacts on populations. In the
meantime, an answer to those concerned with environmental quality is that until the underlying causes of disease are clearly understood, the greatest degree of caution should be observed in the use of diseases as an indicator of pollution.

The most likely general effect of pollution is the non-specific lowering of disease resistance, resulting in the appearance of variable symptoms, rather than the specific induction by a contaminant of an identifiable syndrome (analogous to environmentally induced diseases in man). Accordingly, at the present time it seems likely that, at best, the occurrence of unusually high levels of incidence of a fish disease cannot be immediately interpreted as reflecting poor environmental quality, but environmental parameters should be considered when studying the causes of such incidence.

To meet the needs of environmental scientists, two possible approaches to disease surveys can be envisaged. Both are of an epidemiological nature.

a) Demographic studies of variations in disease prevalence, e.g., to establish baseline data on normal levels of prevalence and also to identify disease "hot-spots". This approach could be applied to non-migratory populations locally or on a larger scale to entire fish stocks throughout their migratory range. As with human epidemiological studies, significant sample size is important and such studies could best be associated with stock assessment cruises (ref. ICES C.Res.1982/4:5).

b) Alternatively, focused observational studies on stressed populations in contamination hot-spots (together with controls) may allow the detection of a correlation between disease symptoms/prevalence and environmental factors. In these circumstances, attention should focus on the most sensitive species, regardless of possible significance as economic resources. It is essential that for this sort of study there be a full understanding of all possible sources of pollutants and their nature. In the absence of such information, wrong assumptions may be drawn.

In either type of survey it is important to try to establish the rate of infection rather than simply to make observations on prevalence, because diseases with low prevalences may be the result of high mortalities and, conversely, diseases with high prevalences may be the result of low mortalities. In addition, for long-term trend studies, it is better to investigate non-lethal diseases.

Three principal target organs or tissues which might display pollution responses were identified, namely, the skin, liver and haematopoietic tissues. External lesions of the skin (such as ulcers) have the advantage of ease of detectability by personnel with relatively brief training (this is not the same as easy identification), but difficulties of clear diagnosis probably render such lesions as fin rot less useful for such work, while other pathological effects, such as lymphocystis and epidermal papillomas, are amenable to examination only by trained personnel. Similarly, while the haematopoietic tissues offer theore-
tically good target organs, in practice, specific haematological parameters may show too much variability and sampling is relatively difficult. Liver lesions probably offer the best possibilities for correlation with body burdens of contaminants, while some skin lesions may be more closely related to ambient environmental contamination (water, sediments). Due to the ability of sedentary molluscs to accumulate large quantities of foreign material, environmental changes can be detected by histological examination.

Since the basic mechanism of neoplasia (uncontrolled cell proliferation) induction may be similar in all animal species (certain human neoplasias are thought to be induced by specific environmental contaminants), neoplasias seem to have a potential as long-term indicators of environmental change.

The above points are largely theoretical because existing practical information is limited. Little is known on a broad scale about the normal levels of disease incidence, although the pathologists are now considering how to map the data presented at their annual meetings. Both groups considered that there was an urgent need to include epidemiologists and statisticians in their discussions to assist in developing statistically correct sampling programmes that would yield interpretable results. Little is known, except in rare cases of epizootics, about the impact of diseases on fish populations.

Nevertheless, it was agreed that, while many unrealistic expectations concerning the immediate usefulness of fish pathology techniques in pollution monitoring have been corrected, there were possibilities for using pathology in the biological effects monitoring strategy.
7 INTERCALIBRATION EXERCISES AND ANALYTICAL ISSUES

7.1 Organic Compounds

7.1.1 Polychlorinated biphenyls

The ACMP discussed the proposals and conclusions presented by the Marine Chemistry Working Group (MCWG) and the meeting of its Sub-Group on Trace Organic Compounds. Advances in analytical methodologies for the determination of PCBs and other organochlorine residues were considered and a review was made of the results of the ICES intercalibration for PCB congeners and the EEC study on methods of PCB analysis.

A further study of the results of the Fifth Intercomparison Exercise on the Determination of Organochlorine Residues in Fish Oil (5/0C/BT) showed that, although problems with identification and quantification of individual chlorobiphenyls (CBs) were present, most of the error in the PCB analysis might be associated with several steps in the analytical methods prior to gas chromatography. The modern automated, dedicated capillary gas chromatograph is a very reliable instrument and is capable of producing excellent chromatographic results provided it is operated correctly. At this stage it is not possible to identify all possible sources of analytical error, but, among others, problems may arise when the analyst attempts to present to the instrument a sample which has not been fractionated or sufficiently or effectively cleaned-up, relying on the capillary column to do the work. Whilst this is obviously not good analytical technique, it is a not uncommon practice and is bound to result in significant qualitative and quantitative errors. On the other hand, within each laboratory, other, more systematic, errors are likely to occur, but in many instances, a careful check of procedures could result in substantial improvements. For this reason, it is essential that standards of good laboratory practice be maintained and quality assurance programmes be carried out. The MCWG has proposed that it consider a set of guidelines for quality assurance procedures and performance criteria for trace organics determination.

It should be noted that the use of data may be severely prejudiced if their accuracy and precision (quality) cannot be assured. Accordingly, analytical procedures must be proven initially and assured throughout their use. It has been suggested that quality assurance procedures might consume as much as 20% of an analytical laboratory's resources. The ACMP strongly recommends that adequate quality assurance schemes be maintained by laboratories involved in ICES programmes. The scientific literature on quality assurance in analytical laboratories should be consulted by all analysts engaged in trace organic analysis and a list of appropriate bibliographic references, as formulated by MCWG, has been reproduced in Annex 1.
The results of a special intercomparison exercise for PCB congeners showed that the coefficients of variation for chlorobiphenyl analysis in fish oil by different laboratories are decreasing, but the values obtained are still too high for a coordinated monitoring programme to be practical. The availability of certified reference materials and of adequate standards may improve the situation in the near future and reference to known sources of these materials is presented later in this report. The implementation of a quality assurance scheme in each laboratory will further contribute to the comparability of analyses.

The determination of PCBs in environmental samples will be more accurately performed through the use of capillary column chromatography, as was referred to in the 1984 ACMP report. The ACMP noted with satisfaction that agreement has been reached on the identity of the major chlorobiphenyls that should, for the time being, be used in the quantification of PCB residues.

It should be stressed that the decision on exactly which congeners should be quantified depends on the purpose of the planned study. A particular contamination problem with PCBs of a special chlorination pattern or studies of bioaccumulation, degradation or metabolism may warrant consideration of other CBs than those to be quantified when the aim of the study is general surveillance or monitoring of environmental levels. It must also be recognised that it is possible that, in the future, new information will be acquired which will require a change in the selection of congeners currently recommended.

Considering monitoring situations using biological tissues, the ACMP advises that the following chlorobiphenyls should be quantified in the first instance:

IUPAC Nos. 28, 52, 101, 118, 153, 138, 180

and that, when appropriate, depending on the sample source, the following additional CBs should also be quantified:

IUPAC Nos. 18, 31, 44, 66/95, 110, 149, 187, 170.

However, when using these congeners for identification and quantification, careful consideration should be given to the possibility of the occurrence of unknown co-eluting components and of the overlapping of a number of CBs. These problems will be easier to overcome if two columns of different polarities are used to check routinely or repeatedly the separation of chlorobiphenyls. The current literature provides appropriate guidance, but in each laboratory the actual performance of the complete analytical methodology needs to be studied and adequate checks of reproducibility and resolution should be performed routinely.

The ACMP noted that several relevant studies are still under way and that more precise advice on the analytical methodology, as well as on identification and quantification procedures, will soon be made available. It should be borne in mind in the meantime that the current preoccupation with the development of quantification techniques for individual PCB congeners represents a departure from the traditional methods of analysis.
As such, it should be recognised that the results obtained are quite incompatible with those which have been produced by the older packed column techniques. It is often forgotten that in the hands of an experienced analyst these can produce consistent data. Thus, if properly used, without methodological changes, over long periods they can produce useful and reliable data for trend monitoring purposes, provided only one laboratory is involved in doing the work for the area concerned.

Some analysts are attempting a compromise solution which takes advantage of the better resolution achievable using capillary columns but still uses summation of several more readily identifiable single peaks. With the increasing use of modern integrators and larger laboratory data systems, it is a relatively simple task to employ two or more methods of quantitation without a significant increase in effort on behalf of the analyst. If such techniques are available to the analyst, the production of data based on a summation of carefully selected peaks using formulations alongside data based on a mixture of CBs (both analysed on a suitable capillary column) is a viable option. This approach would be especially useful if, as seems possible, the number and structure of CBs recommended for quantitation are likely to change, which would obviously lead to the production of data over a period of time which would not be comparable, whereas the use of peak summation using a standard formulation on capillary columns, whilst not a perfect solution, will at least produce comparable data.

The ACMP considers that this approach might be the most suitable if the objective of continued analysis involves comparison of levels measured today and in the future with those measured in earlier years.

For a further understanding of the fate of PCBs already present in the environment, detailed and more accurate knowledge about the actual prevalence and concentrations of several PCB congeners is essential. This knowledge is also essential to assess, in the future, through field and/or experimental studies, the effects of PCBs on marine ecosystems. It is in these areas that the ability to achieve accurate qualitative and quantitative analysis of individual PCB congeners, which is made possible by the new capillary column gas chromatography techniques, is likely to be particularly fruitful. Accordingly, if the objective of study is in these areas, the method of choice must be the use of individual congener standards and, on the basis of present knowledge, they should be selected from the collection previously mentioned, as appropriate to the specific study being conducted.

It will be apparent from the foregoing that the analyst has a number of options open to him. What to select will clearly depend on the equipment he has available, but it is also important that the particular objective be clearly established before the choice is made and analysis is undertaken.

The potential dangers arising as a consequence of the persistent nature of PCBs and their widespread distribution are widely appreciated. This has resulted in regulation of the production and use of such compounds and the control of their release to the environment has been sought. Analytical procedures for PCBs
have been developed and improved to the stage where data obtained by any competent single laboratory allow for the study of temporal and spatial trends provided that appropriate sampling strategies have been followed. The assessment of spatial and temporal trends on larger scales involves several laboratories and requires effective intercomparison of analytical results. Even with the use of agreed lists of PCB congeners for quantification by capillary column gas chromatography, several problems remain unsolved. An effective comparison cannot therefore yet be carried out. However, since trends may be expressed as changes in relative values, the data presently available from several laboratories will satisfy the needs of regulatory conventions for assessing the effect of present restrictions on the release of PCBs.

7.1.2 Hydrocarbons

The ACMP discussed the results of two intercomparison exercises on the analysis of petroleum hydrocarbons. The ICES Second Intercomparison Exercise on Petroleum Hydrocarbons in Biological Tissue (2/HC/BT), conducted jointly with the IOC, was devised to explore the comparability of several methods of analysis for petroleum hydrocarbons in a biological tissue, namely, a mussel homogenate. In this exercise, about 60% of the laboratories that requested samples returned results and the overall picture was encouraging, demonstrating the international interest in improving the comparability of data. However, this comparability is still low. The intralaboratory precision of measurements for 5 to 8 sub-samples of tissue homogenate ranged from 5 to 50% coefficient of variation, depending on the parameter or compounds being measured. If the lower molecular weight naphthalenes are discounted, the range in the intralaboratory coefficients of variation is lowered to 5-20%.

A few problems that may explain some of the discrepancies in the results were identified. First, it was noted that freeze-drying led to losses of some of the hydrocarbons, mainly the components measured as chrysene units; this was probably due to the loss of volatile aromatic hydrocarbons such as highly alkylated benzenes, naphthalenes or methyl-naphthalenes during the freeze-drying process. It was also found that the recovery of internal standards was lower in freeze-dried samples than in wet homogenates. This problem certainly needs further investigation and must be kept in mind when interpreting data from freeze-dried samples. Concentrations of some PAHs based on column chromatographic separations on silica and subsequent GC-FID determinations were unusually high, apparently because of interference from alkenes of biological origin. On the basis of this exercise, it was concluded that future intercalibrations should require that data be reported for certain specified parameters and certain compounds, but it was recognized that much work is still needed to identify which parameters and compounds yield the most useful data for assessing petroleum contamination. There also remains considerable controversy on which methods to apply. Simple, inexpensive and non-discriminatory methods (e.g., ultraviolet fluorescence (UV-F)) are available and some researchers advocate their use in survey or monitoring type studies. Others recommend the use, in most instances, of more sophisticated, more expensive and highly
discriminatory methods (such as glass capillary gas chromatography/mass spectrometry computer-based methods), which allow for the measurement of a suite of specific target compounds.

The results of the Third Intercomparison Exercise on Polynuclear Aromatic Hydrocarbons (PAHs) in Biological Tissues (3/HC/BT) were discussed. Only ten out of the original twenty-five participants supplied quantitative data and only a few of these analysed for the wide range of PAHs in the two samples distributed. Both intra- and inter-laboratory precision were poor and it is obvious that a considerable number of analytical problems need to be solved before any cooperative research programme can be launched. Progress in achieving satisfactory interlaboratory error levels is likely to be achieved only if an agreed method (e.g., a method already tested in other intercalibration studies) is applied by each laboratory along with its own method. The availability of accurate qualitative and quantitative standards is considered extremely important. For future intercalibration work, it was considered that a procedure similar to that used in other intercalibration series should be applied, i.e., a first round on the analysis of a standard solution should precede the analysis of a fish or shellfish oil matrix sample and a bivalve tissue homogenate.

The ACMP took note of the UK Oil Pollution Research Unit intercalibration exercise for hydrocarbons in sediments, in which several ICES laboratories have participated. The results will be presented to the 1986 meeting of the Marine Chemistry Working Group and their interpretation of the results of this exercise will be examined by ACMP.

The preliminary results of the IOC/GEMSI Hydrocarbon Intercalibration Workshop demonstrated that UV-F measurements in sea water intercalibrate well even in areas where the concentrations are low. This study also stressed the need to extend UV-F measurements to include synchronous scanning of excitation and emission wave-lengths to cater for cases of very high contamination. Certain information concerning the nature of the contaminating substances can thus be obtained with relative ease and reference materials can be chosen to reflect the actual situation. This will require modifications to the fluorescence method, as described in the IOC Manuals and Guides No. 13.

At present, it seems possible to conclude that UV-F is a good technique for screening large numbers of samples to identify which samples should be explored in depth, but that by itself UV-F will not provide enough information on the extent and magnitude of petroleum hydrocarbon contamination except at specific sites where the potential source of input is periodically well characterised by a higher resolution methodology. On the other hand, gas chromatographic analysis does not provide a reliable quantitative indication of the degree of contamination by compounds of concern to human health, e.g., PAHs, which are also important from the perspective of effects on marine organisms. In this case, the use of high performance liquid chromatography (HPLC) and/or gas chromatography/mass spectrometry (GC/MS) is necessary. It is worth noting that, by virtue of its sensitivity and ease of use, the UV-F method provides a means of conducting surveys to establish in broad terms the levels of total hydro-
carbons present in sea water, although it does not provide an accurate indication of their origin.

The analysis of individual PAHs in tissues from marine organisms other than bivalve molluscs, and possibly selected crustacea and polychaetes, will not be an accurate measure of their exposure to biologically available PAHs in the habitat because of the probability of the induction of enzymes capable of metabolising PAHs.

It was noted that more research is needed to determine whether PAH metabolites induced by enzyme metabolic activity are of concern from a human health perspective and that analytical methodology for quantification and identification of body burdens of such metabolites is in the development stage.

In view of the present situation in regard to inter- and intra-laboratory errors, it was considered that a Fourth Intercalibration Exercise for PAHs in Biological Tissue is necessary with the proviso that two rounds be conducted, that laboratories participating test a common method along with their own method, and that HPLC and/or GC/MS techniques are used. Careful guidelines for analysis and reporting requirements are necessary. The two rounds referred to will consist of: (a) the analysis of a standard solution of a suite of non-alkylated PAHs, and (b) the analysis of both a fish or shellfish oil matrix sample and of a bivalve tissue homogenate. It was proposed that the common method to be tested be an appropriately modified version of the method published by Grimmer and Bohnke (J. Assoc. Off. Anal. Chem. 38: 125-132).

With regard to the preparation of a proposal for a possible intercalibration exercise on the analysis of petroleum hydrocarbons in sea water, as requested by the Oslo and Paris Commissions, the ACMP considered two proposals for procedures which could possibly be used to prepare replicate samples for this type of intercalibration. Noting that both procedures had advantages and disadvantages, the ACMP requested the Marine Chemistry Working Group to reconsider these proposals in the light of the results of the intercalibration conducted by the UK Oil Pollution Research Unit and by the IOC and provide ACMP with recommendations next year for the early conduct of an appropriate intercalibration exercise.

7.2 Trace Metals

7.2.1 Trace metals in biota and sea water

The ACMP considered the assessment of the results from Part A of the Seventh Round Intercalibration of Trace Metals in Biota (7/TM/BT). The report, prepared by the Coordinator, Dr. S Berman, pointed out that:

- copper, zinc, cadmium and mercury were analysed accurately and the results were comparable among the majority of the 49 participants,
- the results for cadmium at levels <0.1 mg/kg and lead, even at the high level of 2 mg/kg, showed that there are problems in accuracy and reproducibility,

- half of the participating laboratories had submitted results on arsenic, of which about 50% were accurate.

It was felt that these results were very useful for the comparison of monitoring data obtained by different laboratories.

The ACMP considered the request of the Joint Monitoring Group (JMG) for criteria which could be used to evaluate satisfactory performance in 7/TM/BT as well as in the Fifth Round Intercalibration on Trace Metals in Sea Water (5/TM/SW). The ACMP agreed that the diagrams and tables contained in the reports on the results of 7/TM/BT and 5/TM/SW provide specifications of laboratory analytical performance which can be used, in conjunction with the objectives and design of monitoring programmes, to determine acceptable performance criteria. As concluded by the Marine Chemistry Working Group, however, the required performance criteria can only be decided in the context of the objectives and design of specific programmes. Some illustration of the reasons for this is perhaps useful.

Bias represents the systematic deviation of a result (or the mean of a series of individual determinations) from the true value. In most cases, this true value is established through the application of some standard or independent technique. If the bias of a laboratory for a particular measurement, e.g., copper in plaice muscle, is constant, it is possible to normalise the results from that laboratory by a simple correction factor in order to reflect accurate or standardised concentrations. However, bias can vary with matrix composition, concentration, and time, among other factors (e.g., instrument conditions, analyst, etc.). Thus, bias has to be assessed over a range of matrices and concentrations and times that circumscribe the corresponding ranges in the programme. It is for this reason that 7/TM/BT is based upon the use of three different matrices having different element concentrations. Similarly, this is the reason that the second stage of this intercalibration will be carried out over the period of the 1985 Baseline Study of Contaminants in Fish and Shellfish. If a confident expression of bias and its dependence upon various factors can be developed for individual laboratories, it will be possible to normalise data to improve interlaboratory comparability.

Precision is an expression of the reproducibility of determinations. Its improvement requires the reduction of random influences on the entire determination procedure. Precision, as reflected in the specification of Relative Standard Deviation (RSD), will also vary with factors such as matrix, concentration and time. It is usually possible to compensate for poor precision by increasing the degree of replication in sampling and analyses within a programme. Thus, while improvements in the precision of individual determinations are always desirable, it is possible to assess confidence intervals essential for the attainment of programme objectives and achieve these through the judicious application of analytical
improvements and replication. It will normally be more cost-effective to devote greater effort to the improvement of individual measurement precision in cases where substantial replication is necessary to achieve the desired envelope of uncertainty in programme results; however, some degree of replication is usually desirable to meet quality assurance specifications.

It is clear from the foregoing that specification of acceptable performance can only be judged in the context of the unambiguously stated objectives of a field programme and some preliminary information on the types of matrix to be sampled and the incidence of analytes within them. If any of the concentrations reported are below the level of detection of the method used, it is essential that the methods be improved or changed in order to allow corrections for bias or precision to be implemented.

Having provided the above information, the ACMP agreed that histograms giving Relative Standard Deviation (RSD) and Relative Bias for each element, matrix and concentration level for each laboratory, prepared on the basis of the results of 7/TM/BT (Part A) and 5/TM/SW, should be transmitted to the JMG together with the final reports of these exercises.

The ACMP noted that the second stage (Part B) of the Seventh Intercalibration Exercise on Trace Metals in Biological Tissues was currently being conducted in connection with the 1985 Baseline Study of Contaminants in Fish and Shellfish. In addition, although no overall intercalibration activities were planned in association with the Baseline Study of Trace Metals in Coastal and Shelf Sea Waters, specific sites in the Skagerrak, the Bay of Biscay, an area off the northwest coast of Scotland and in the Sargasso Sea were accepted as trace metal Reference Stations because their deep water trace metal profiles were considered to be relatively stable over the period of the Baseline Study. The locations of these reference stations are as follows:

(1) Bay of Biscay: 46°00'N 6°00'W at 3000 m
(2) Sargasso Sea: 32°10'N 64°30'W at 1750 m Panulirus Station
(3) Off Northwest coast of Scotland: 60°30'N 5°00'W at 950 m
(4) Skagerrak: 58°10'N 9°30'E at 640 m Swedish Station M6

7.2.2 Trace metals in estuarine water

In response to a request from the JMG, the ACMP considered plans for an intercalibration exercise on the analysis of mercury, cadmium, copper and zinc in estuarine water, which had been prepared by MCWG. According to these plans, water samples should be obtained that are representative of estuarine waters commonly monitored in the Joint Monitoring Programme. These samples would be taken from either the Western Scheldt estuary or the Rhine estuary.

The ACMP recommended that, during the sampling cruise, a transect should be planned in order to estimate the ranges in concentrations of trace metals along the estuary.
The ACMP discussed the choice of the National Research Council of Canada (NRCC) as one of the coordinating laboratories. It was concluded that, since NRCC was already equipped with the necessary capital equipment and was able to undertake the experiment at an early date, the selection of NRCC was preferable to the designation of a European laboratory which might require a considerable amount of time and effort to acquire the specialized equipment necessary for the conduct of this intercalibration. Thus, the choice of NRCC offered the most expedient and efficient avenue for the early conduct of the intercalibration. A proposal for the design and conduct of this intercalibration is given below; this proposal was submitted to the Joint Meeting of the Oslo and Paris Commissions in Brussels, 6-7 June 1985.

**Intercalibration Exercise on the Determination of Trace Metals in Estuarine Waters**

A request has been made to ICES by JMG for the conduct of an intercalibration exercise on the analysis of trace metals in estuarine waters. This request followed an evaluation of the results of the ICES Fifth Round Intercalibration for Trace Metals in Seawater during which it was suggested that the levels of metals in waters 30-40 km off St. Nazaire in the Bay of Biscay might be atypical of the levels prevailing at most of the JMP coastal and estuarine monitoring stations.

As a result of the request from JMG, ICES has formulated a proposal for the conduct of an intercalibration based upon the use of low salinity water (salinity 10-20 o/oo) collected from a North Sea estuary.

The intercalibration exercise is intended for participation by all JMG laboratories and other interested laboratories in ICES member countries. Additional participation by experienced laboratories with proven ability will be sought by the coordinators, in order to ensure that reliable estimates of the concentrations can be made for reference purposes.

**Selection of Sampling Area and Determinands**

The exercise will be performed on filtered and acidified water from either the Scheldt or Rhine estuary. Analysis for Hg, Cu, Cd and Zn in the samples will be mandatory; the determination of other elements, in particular Pb, Ni and Cr, will be requested on a voluntary basis.

The JMG meeting in January 1986 will be requested to indicate desired concentration ranges for Hg, Cu, Cd and Zn, and to possibly express a preference for the Rhine or Scheldt estuary as the sampling area. A suitable location for collection of the water will then be determined on the basis of the known characteristics of water in the chosen estuary and a preliminary on-site survey.

**Sampling**
The National Research Council of Canada (NRCC) will provide sampling material, chemicals and containers, which all will be transported from Canada to the Netherlands. The collection of the samples will be performed by the NRCC with the assistance of the Rijkswaterstaat. This assistance comprises the provision of a ship for approximately one week, and laboratory facilities, including a clean working area with a laminar flow bench and an AAS instrument with background correction. At least 400 litres of water will be collected and filtered through 0.45 μm filter membranes. Half of this water will be required to prepare samples for the determination of mercury, the other half is needed for the samples for the analyses of the remaining elements. During the course of the sample collection programme, one or more transects will be sampled along the estuary and offshore to determine the distribution of certain metals in waters of the area.

The water will be shipped in bulk to Canada. At the NRCC laboratories in Ottawa, the water will be blended and bottled in polyethylene (metals excluding Hg) and borosilicate containers (Hg). The interbottle homogeneity will be tested by NRCC prior to sample distribution.

It is intended that 100 samples for the analyses of mercury and a further 100 samples for the determination of the other elements be prepared. The samples for mercury will be contained in bottles with a smaller volume.

**Sample Distribution and Data Manipulation**

The samples will be distributed by NRCC, which will also undertake the receipt, compilation and evaluation of the results on behalf of ICES.

**Financial Aspects**

The National Research Council of Canada and the Rijkswaterstaat of the Netherlands will not charge for personnel or associated capital equipment costs. The NRCC will request reimbursement only for the other operating expenses, comprising bottles, chemicals, shipping, mailing, travel and subsistence. It is expected that four people from the NRCC will be required to travel to the Netherlands to undertake the field sampling and initial analytical work. The total cost is estimated to be 15,000 US dollars.

**Time-table**

This time-table has been devised in order to make possible a discussion of the results and draft report during the MCWG meeting in February 1987. The following target dates are proposed, subject to the approval by the Oslo and Paris Commissions of this proposal, including financial aspects, at their meeting in June 1985. (This approval was given at the Joint Meeting.)

- **October 1985**  Determination of sampling period.
- **January 1986**  Indication by JMG of the desired concentrations of Hg, Cd, Cu and Zn in the samples.
Selection of the estuary for sampling.

March/April 1986 Notification of intention to participate to Oslo/Paris Commissions Secretariat and ICES.

April/May 1986 Collection of water.

June 1986 Distribution of samples; establishment of deadline for receipt of results.

September 1986 Submission of results to the NRCC by participants.

January 1987 Presentation of a draft report to JMG.

February 1987 Presentation of a draft report by the Coordinators to the MCWG meeting for review and comment.

June 1987 Review of final report by ACMP, prior to transmission to the Oslo and Paris Commissions.

In order to be able to present a draft report early in 1987, it is imperative that the participants adhere strictly to the deadline for the return of results, which will be set prior to the distribution of samples.

Coordination of the Exercise and Use of Results

The coordination of the exercise will be undertaken by the National Research Council of Canada (Dr. S S Berman), the Marine Pollution Laboratory, Denmark (Dr. A. Jensen) and the Government Institute for Sewage and Water Works (Rijkswaterstaat), the Netherlands, (Dr. W. Cofino). Dr. Berman will represent the interests of ICES and will be the overall coordinator, Dr. Jensen will represent the interests of JMG and Dr. Cofino will assume responsibility for the on-site shipboard and land facilities.

Alternative laboratories to the NRCC were considered for the role of primary coordinator of the exercise. A number of other laboratories, including several in Europe, potentially have the ability to carry out this work but all would need to make substantial capital investments in special equipment and facilities, which are already available to NRCC. This would not only make the exercise more expensive, but it would also take longer to complete. Thus, for the timely and cost-effective execution of the exercise, NRCC was chosen for the coordinating role which they were fortunately willing to assume.

The results of this exercise should enable a more reliable assessment to be made of the accuracy, precision and inter-comparability of JMP data pertaining to the incidence and distribution of metals in coastal and estuarine waters. Furthermore, assuming JMP data are made available, it will be possible to examine the extent and confidence with which differences among stations and areas exist. If necessary, information can also be provided on the extent to which, and how, modifications to analytical procedures may be made to
improve the reliability and resolution of JMP data.

7.2.3 Trace metals in suspended particulate matter

The ACMP was informed about the results of a pilot intercomparison exercise on the analysis of metals in suspended particulate matter, which had been carried out by eight selected laboratories from seven countries. The exercise was based on the analysis of material prepared by the organizers, Dr. P A Yeats and Dr. J A Dalziel, by the filtration of Canadian inshore and harbour waters through pre-weighed 0.4 µm Nuclepore filters. The basic conclusions of the exercise were that the participating laboratories had been able to carry out the appropriate measurements without difficulty and that the sampling must have been done in a reproducible way. The ACMP noted that the Working Group on Marine Sediments in Relation to Pollution (WGMS) was developing plans to carry out a new exercise with a broader range of laboratories which aimed to intercompare different techniques for collecting and processing the samples. The ACMP considered that it was first necessary to develop and intercompare methods for a reproducible determination of the concentration of particulate matter itself in sea water and requested the WGMS to coordinate this work.

7.2.4 Trace metals in marine sediments

The ACMP noted the preliminary results of the First Intercalibration Exercise for Trace Metals in Marine Sediments (1/TM/MS) organised by Dr. D Loring. This exercise was designed to evaluate the suitability of four different sample treatment procedures (dissolution using hydrofluoric acid (HF), treatment with aqua regia, and weaker leaching by 1N HCl (hydrochloric acid) and 25% acetic acid) for determining the total, partial and weakly bound metal contents in three sediment samples and to assess the analytical comparability among laboratories in ICES member countries. Thirty-nine laboratories from ten countries submitted results. The preliminary compilation of these data show again (see results of the Baltic Sediment Intercalibration, section 7.4, below) that many laboratories have problems in determining precisely the concentrations of mercury, cadmium, nickel, and chromium. Another initial conclusion was that the aqua regia treatment removes large (80% to 100%), but sample dependent, amounts of zinc, iron, lead, copper, and nickel and much lesser amounts of titanium, aluminium, and chromium than the HF dissolution procedure. It was noted that a complete analysis of the large set of data obtained in this intercalibration was presently underway and the results will be reported in 1986.

7.3 Standards and Reference Materials

The ACMP noted with satisfaction the attention that has been given to quality assurance problems within the Marine Chemistry Working Group and the Working Group on Marine Sediments in Relation to Pollution. The primary focus of discussions and activi-
ties within these Working Groups on this topic has been to seek better means to assess and improve the accuracy, precision and intercomparability of measurements of trace metals, hydrocarbons and chlorinated organic compounds in marine biological tissues, water and sediments in order to satisfy the needs of both the ICES community and the regulatory Commissions. The problems of standardization of methodologies have become considerably more widespread in the field of marine sciences and are now the subject of increased interest in other agencies. Most notably, the IOC and UNEP, through their joint sponsorship of the Group of Experts on Methods, Standards and Intercalibration (GEMSI), have started a detailed assessment of marine chemical reference materials and standards. The ACMP noted this with interest and would like to ensure that ICES is intimately involved in these activities, not only to bring to the attention of other agencies relevant ICES activities and successes, but also to spread more evenly the effort associated with the preparation and distribution of such materials.

It was also noted that additional certified reference materials for trace metal analysis are, or will soon be, available from the National Research Council (NRC) of Canada, through the Marine Analytical Chemistry Standards Program. These include a nearshore sea water sample certified for ten trace metals (currently available), samples of dogfish muscle and liver (available by the end of 1985), and samples of river water from the St Lawrence (also available by the end of 1985).

Reference materials for trace organic compounds (organochlorine pesticides, chlorobiphenyls, PAHs) at various levels and in various matrices are still lacking. It was expected that the NRC of Canada would issue a set of such materials for the analysis of PAHs in sediments in the near future. The Marine Chemistry Working Group is also currently seeking the preparation of reference materials for the analysis of biological tissues for trace organics. Fish oil and shellfish tissue are considered as the appropriate matrices. At present, samples from a single batch of Aroclor 1254 and a batch of Phenochlor DP5 are available for distribution to interested laboratories. A frozen mussel homogenate is also available from the U.S. National Oceanic and Atmospheric Administration to be used as a reference material, but shipping problems will have to be solved before its distribution is possible.

Analytical standards of mixtures of chlorobiphenyls (CBs) are now available from the NRC of Canada and will also soon be available from the Community Bureau of References (BCR) of the European Economic Community and from the United States National Bureau of Standards. Individual organochlorine pesticides, a few PCB congeners and PAHs can be purchased from various private suppliers.

The ACMP agreed that the development of reference materials and their appropriate use are of the utmost importance in improving the analytical capability of laboratories in ICES member countries. The ACMP strongly urged ICES and its member countries to support this initiative.
7.4 Baltic Sediment Intercalibration Exercise

The ACMP noted that the first part (Part A/1) of the Baltic Sediment Intercalibration Exercise, in which two dry, homogenised muddy sediments (ABSS and MBSS) were analysed for a suite of metals and organic and inorganic carbon, has been completed. A final draft report was accepted at the 1985 meeting of the ICES/SCOR Working Group on the Study of the Pollution of the Baltic. After incorporating minor amendments, the report on the results of this part of the intercalibration will be ready for publication in the ICES Cooperative Research Report series.

Owing to the poor results obtained for mercury and cadmium in Part A/1 of the intercalibration, a second round for both elements was organised by Dr. A Jensen in 1984/1985 for Baltic participants only. Pre-digested sediment samples, including the Canadian reference material MESS-1, were distributed together with blanks, standard solutions and a solid ABSS/MBSS mixture to 14 laboratories of which 11 responded. The report on their results (Part A/1/2) showed that (a) there was a considerable improvement in analyses for cadmium (relative standard deviation decreased to around ±10%, after exclusion of outliers), (b) normalisation procedures which took into account the results obtained from the certified reference material (MESS-1) were successfully applied, (c) the problems with cadmium analyses are most probably associated with the final flameless AAS measurement and not with the digestion step, and (d) no improvement was achieved in the analyses for mercury, for which the relative standard deviation was still around 40%-55%.

Noting that a revised draft of the report of this part of the intercalibration is under final review, the ACMP supported the proposal of the ICES/SCOR Working Group that this report on the mercury and cadmium intercomparison should be published as an annex to the report on Part A/1 of the Baltic Sediment Intercalibration Exercise.

The ACMP noted further that a preliminary draft report on the results of the geochemical and sedimentological analyses conducted by eight laboratories participating in the second step (Part A/2) of the intercalibration exercise had been prepared by Dr. L Brügmann and Dr. L Niemistö. The samples for this part of the intercalibration exercise were dissected fresh 20 cm sediment cores from the Arkona Basin. Similar cores were also analysed using radiochemical dating techniques and the results submitted by eight participating laboratories were compiled separately by Dr. P. Pheiffer Madsen. This report (Part A/2/2) showed that (a) the analytical determination of Pb-210 and Cs-137 seemed to cause only minor problems, (b) the substantial mixing of the cores to a depth of 10 cm to 17 cm was probably due to bioturbation, and (c) the problems created by this mixing could be overcome by the application of a mathematical model which resulted in the estimation of comparable linear (1.3 ± 0.2 mm.y^{-1}) and mass accumulation rates (36 ± 5 mg.cm^{-2}.y^{-1}).
The mixing observed in the sediment cores also created problems for the interpretation of the data submitted on geochemical and sedimentological analyses. The results were rather scattered due to both the natural variability and analytical problems. While the vertical profiles for several determinands reported by some laboratories were relatively similar, other laboratories were unable to resolve such distribution patterns for single determinands due to insufficient precision. As was the case in Parts A/1 and A/1/1, severe problems were again evident in the mercury and cadmium analyses.

The ACMP looked forward to reviewing the report on the results of the geochemical and sedimentological analyses of Part A/2 of the intercalibration, including also the final report on the radiochemical dating results.


8 EXCEPTIONAL ALGAL BLOOMS

8.1 Introduction

As a result of a growing concern regarding the occurrence of unusual phytoplankton blooms, ICES held a Special Meeting on the "Causes, Dynamics and Effects of Exceptional Marine Blooms and Related Events" on 4-5 October 1984, prior to the Statutory Meeting. The summary report of this meeting is available as Doc. ICES C.M.1984/8:42, and the papers will be published in the Rapports et Procès-Verbaux des Réunions series. The following paragraphs provide the main conclusions of the Special Meeting, as amended and endorsed by ACMP. These conclusions will be of interest to the regulatory Commissions and should be considered as a response to the request from the Oslo and Paris Commissions to examine the problem of unusual phytoplankton blooms.

8.2 Definition of Terms

Considerable confusion surrounds the use of terms such as "blooms", "exceptional blooms" (in French: efflorescence; floraison), hypernutrification and eutrophication (in French: eutrophication).

In scientific usage, the term "bloom" is used to refer to an outburst of growth in the plankton, resulting in (and usually recorded by the presence of) a high biomass. The term is particularly applied to the spring and autumn outbursts of growth which are a normal feature of many sea areas and are known as the spring and autumn blooms.

"Exceptional" blooms are those which are noticeable, particularly to the general public, directly or indirectly through their effects, such as visible discoloration of the water, foam production, fish or invertebrate mortality or toxicity to humans. Such effects may be due to outbursts of plankton growth (blooms in the sense used above), but this is not always the case; severe toxicity of shellfish may result from a relatively low biomass of toxic algae. Although these latter are not blooms in the true sense, they are included here because of their noticeable effects and because often the same types of organisms are involved in both types of event. "Exceptional" blooms are only exceptional in terms of their noticeability, i.e., their effects. In some sea areas, they may be common and even more or less regular features, and have been noted in historical records since such records began.

There are two reasons why such events are of concern. One is their economic and public health impact; the other more recent concern has been that anthropogenic influences, especially on coastal areas, might cause an increase in their incidence. In relation to a discussion of the effects of anthropogenic influences on the incidence of exceptional blooms, it is also necessary here to define the terms "hypernutrification" and "eutrophication".
Hypernutrification involves substantial and measurable increases in concentrations of dissolved nutrients (which may include inorganic and organic compounds of nitrogen, phosphorus, silicon, iron and other trace metals and vitamins). Current practice is generally to use measurements of inorganic nitrogen and phosphorus because of their relative ease of measurement. It should be noted, however, that laboratory investigations of phytoplankton have shown that a wide range of substances can control growth, including not only substances which can be considered as nutrients, but also substances such as toxic metals and materials which control their availability to phytoplankton.

Hypernutrification can in theory lead to increased phytoplankton biomass and production in regions and at times in which nutrients are limiting to phytoplankton growth. In freshwater ecosystems, there is a stage in the natural evolution of lakes in which such increased phytoplankton production occurs and which is known as eutrophication. This term is sometimes applied, by analogy, to the effects of hypernutrification in marine systems, but it is useful to make a distinction between eutrophication sensu stricto and hypertrophication, which implies the anthropogenic acceleration of primary production, with concomitant deleterious effects, as a result of nutrient inputs. This latter term is used in the rest of this report.

8.3 The Incidence of Exceptional Blooms

There are very few long time-series data sets on exceptional bloom incidence. In assessing such data as are available, a distinction needs to be made between oceanic and open shelf waters on the one hand and, on the other, coastal and estuarine waters where terrestrial influences may be more marked.

Since the mid-1960s, the dinoflagellate Gymnodinium aureolum has occurred in European coastal and shelf waters; it has given rise to exceptional blooms in many areas and has caused fish kills. The causes for its recent upsurge are unknown, but it has been suggested that it is a recently introduced species to European waters; newly introduced species may thrive excessively in the first years following their introduction.

Apart from the special case of G. aureolum, it is more difficult to point to trends in inshore waters of the Atlantic. There has been a southward extension over a long time-scale of Paralytic Shellfish Poisoning (PSP) problems associated with both low and high biomasses of Gymnodinium tamarensis on the east coast of Canada and the USA, apparently for rational climatic reasons. Fluctuations in the degree of toxicity of shellfish in the Bay of Fundy have been correlated with long time-scale oceanographic and meteorological changes and with the 18-year lunar cycle on tidal mixing activity with varying degrees of success. In Europe, exhaustive studies failed to identify trends in blooms in the Oslofjord, although changes in species composition have been noted. On the east coast of the United Kingdom, PSP toxin has been recorded each year since 1968, but no trends in toxicity have been observed; shellfish toxicity is known to have occurred in this area earlier in the century. In the German
Bight, where blooms of *Ceratium* spp. and other species have caused concern recently, it is also known that such events have occurred at intervals over the last century.

It is worth comparing these results with information on inshore areas outside the North Atlantic, such as the Seto Inland Sea of Japan, where clear trends in bloom incidence have been associated with trends in pollution.

Exceptional blooms must be seen against the general background of the normal cycle of phytoplankton biomass. Data from the Continuous Plankton Recorder for the Northeast Atlantic suggest a downward trend in the incidence of periods of higher than normal biomass of diatoms and *Ceratium* spp. in the last 20 years, with an increase since the mid-1970s of the more generalised "Phytoplankton Colour" index. These trends may be superimposed on general downward trends in zooplankton and phytoplankton abundance.

In conclusion, there is little evidence in North Atlantic waters for any rising trend in bloom incidence, although the data are very sparse. Changes in species composition have been observed, although the reasons for these changes are unclear.

### 8.4 Causative Factors in the Development of Exceptional Blooms

Recent research has stressed understanding the importance of physical factors in bloom incidence. The widespread extent of observed changes in the plankton indicates the important role of long-term and wide-scale climatic and oceanographic changes, though how these might be related to bloom incidence is not well understood.

On a smaller scale, areas of high biomass or production are associated with boundaries (pycnoclines and fronts) and upwelling areas. This is also true of inshore areas where the effect of river inputs, in addition to tidal mixing and other coastal influences on the stability of the coastal waters, may be an important factor, especially in exceptional blooms of diatoms early in the year. Later in the year, as nutrient levels decline, dinoflagellate populations which are a normal component of the summer plankton are noticeably high at boundary systems, and the incidence of summer storms followed by calm weather is related to the incidence of exceptional blooms.

The influence of wind-induced current events on sea sediments is also an important factor, for example with respect to the re-suspension of resting stages (cysts) of some dinoflagellates from the sea bed into the water column.

The role of biological factors is clearly important. A full understanding of exceptional bloom events depends on a thorough knowledge of the life cycles of the organisms concerned; such information is often lacking.

Among other relevant biological factors, reduced grazing pressure, such as occurs particularly in response to inhibitory properties of some dinoflagellates, may be important to the development of large populations of algae. The role of vertical
migration in ensuring both effective nutrient and light utilisation and concentration in surface waters aided by physical mechanisms may be a key to the development of surface "red water". Some bloom species appear to be well adapted to a changeable light environment.

The role of nutrient enrichment is not clear. Certainly, where nutrient levels are high, production will occur somewhere, though nutrient-rich coastal waters are often highly turbid and well-mixed, which reduces the opportunity for exceptional growth. Similarly, it is clear that in many cases it is the flux of nutrients rather than their concentration which is important to the development of algal populations, although relatively low fluxes may be sufficient to sustain already existing large populations. Some long-term data sets on inorganic nitrogen and phosphorus nutrient concentrations are available, but data on the fluxes of nutrients are far more limited and the roles of inputs or of recycling through grazers, bacteria or the sediments are poorly understood. Current understanding suggests that the physical structure of the water column and its relationship to the distribution and availability of nutrients is a major factor in bloom development.

In conclusion, the development of exceptional blooms is the result of a special combination of, and interactions between, physical, chemical and biological factors. Of these, the role of biological factors is becoming clear, although detailed information on individual species is often lacking; the role of chemical factors is much less clear.

8.5 Hypernutrification and Hypertrophication

If high nutrient levels affect algal populations, they might do so in three ways: (a) by directly increasing overall annual biomass, perhaps by extension of the growth season, (b) by leading to sporadic exceptional outbursts of growth, and/or (c) by changing the composition of species. The latter effect would be particularly hard to distinguish from natural changes in species' composition which occur all the time, such as for example those noted in Continuous Plankton Recorder data throughout the eastern North Atlantic. As stated earlier, there is little evidence to suggest that actual increases in exceptional bloom incidence other than G. aureolum have occurred in Atlantic waters. Equally, it is hard to find any evidence for overall measurable increases in biomass in these waters, though the data available are very limited. If such effects were to occur, they would be most likely to occur in areas where the spatial and temporal scales of enrichment were such as to allow time for algal growth, i.e., in enclosed embayments or estuaries or in coastal areas affected by major river inputs. Even in these areas it might be difficult to separate nutrient effects from purely physical ones (e.g., the effect of fresh-water input on stability). Such areas might include the New York Bight, the German Bight and southern North Sea, the Kattegat, parts of the Baltic Sea and areas such as the Oslofjord. While nutrient inputs compared with the available 'pool' are undoubtedly high in these areas, it is still not easy to point to clear examples of hypertrophication. The availability of phosphate in summer may allow increased production by nitrogen-fixing blue-green
algae in the Baltic Sea, and the high level of production of *Phaeocystis* in the southeastern North Sea may point to a case of hypertrophication. Equally, if elevated nutrient concentrations occur, exceptional meteorological and hydrographic conditions may permit outbursts of growth.

The case mentioned earlier of the Seto Inland Sea raises a further question in relation to hypertrophication and especially the potential role of anthropogenic influences. There are many field and laboratory data that point to the significance, on the one hand, of vitamins and growth factors in determining species' composition and, on the other hand, to the role of natural organic chelating agents in controlling the toxicity and nutritional availability of metals to algae. Recent research suggests that the metal complexing compounds in sewage effluent may be chemically similar to naturally occurring humic and fulvic acids. Since dinoflagellate growth is often stimulated by the addition of soil extracts or similar enrichments containing humic acids, it is possible that pollution of coastal areas could enhance bloom development due to the input of organic rather than inorganic compounds. The Seto Inland Sea experience suggests that bloom incidence there was at least partially related to organic inputs as well as nutrient inputs, but there are few data available on either the natural levels of such substances or the levels of inputs and fluxes in Atlantic waters.

It can be concluded, on the basis of data on exceptional blooms, that there is little evidence for the existence of large-scale hypertrophic effects in North Atlantic waters. However, it should be stressed that such effects are more likely to be observed through a study of annual phytoplankton biomass as a whole, rather than exceptional bloom incidence. Suitable data sets are not available for most areas; in particular, biological data and long time-series data sets are lacking. Attention should be addressed especially to the areas identified above and to other estuarine areas receiving large natural or anthropogenic inputs of nutrients, whether organic or inorganic. Further research is needed on the role played by organic enrichment.

8.6 Predictability

The understanding of the physical environmental factors affecting bloom incidence is now sufficient to identify areas, either on the basis of long time-series data or a knowledge of physical structure present, in which there is a high probability of bloom occurrence. Models incorporating physical parameters and variables associated with blooms and related events, e.g., hypoxia, are capable of predicting conditions which can lead to bloom circumstances and events. Relatively simple biological models incorporating data particularly on grazing rates and the behaviour and physiology of bloom-forming species and the dominant nutrient flux can also be used to predict the probability of bloom events in given areas. Prediction of the group of species (diatoms, dinoflagellates, flagellates) likely to dominate the bloom is feasible on the basis of the degree of turbulence/stability of the water column, though it is more difficult to make predictions as to particular species dominance.
since information on the life histories and specific growth rates of many species is lacking. However, these models may be extended to prediction of harmful effects either through estimation of the effects of biomass on oxygen consumption or through the relationships which are beginning to be established between toxicity and nutrient status of the cell.

Such predictability is purely probabilistic, since the actual concentrations or values of physical, chemical and biological factors that lead to a particular bloom cannot be predicted absolutely through the application of such models. Probabilistic prediction, however, is probably adequate for overall environmental management purposes and should be used at this stage as a means of directing resources to the longer-term monitoring of areas theoretically likely to have a higher incidence of blooms. On the other hand, mariculture and shellfish fishery managers require prediction of actual events over much shorter time, and smaller spatial, scales; this can only come from a system of monitoring at the areas to be protected.

Predictive capabilities could be improved by

a) an improved knowledge of the biology and life histories of blooming species, and

b) the collection of long time-series data on selected phytoplankton, species composition and biomass in the areas identified above. One source of historical data would be the recent (10^6 years) sediment record of cysts and pigments which could be obtained from areas of high natural sediment accumulation and low bioturbation.

Satellite and aircraft remote sensing may provide useful support for field programmes, especially in synopticity, but their use in gathering long time-series data needs further investigation. Automated methods for the continuous collection of biological data also need further development.

In conclusion, the understanding of exceptional bloom incidence is now sufficient to predict areas likely to be subject to exceptional blooms. Prediction of actual events can currently only be made on short time scales on the basis of monitoring data.

8.7 Effects of Algal Blooms

Half of the Special Meeting was concerned with a discussion of the effects of exceptional blooms. Most exceptional blooms have no ill effects beyond minor aesthetic problems. Problems are associated with a limited number of species, for which the major effects are toxicity of shellfish to human consumers and kills of wild and/or cultured fish and shellfish. Economic losses go beyond the immediate loss of stock or sales, because the sales of seafood products other than those directly affected often decline as a result of ill-informed public perceptions of the effects of blooms.
The Special Meeting commenced the task of drafting advice on the management of bloom problems (see sections 4 and 5 of Doc. ICES C.M.1984/E:42). This task has subsequently been taken up by the Working Group on Exceptional Algal Blooms, which was established at the 1984 Statutory Meeting in response to recommendations of the Special Meeting. This Working Group will be concerned with the preparation of advice to fishery and mariculture managers on monitoring, site selection, prediction, site management and management options during bloom events.

Among the problems identified by the Special Meeting was the need to identify the toxins produced by some species and to provide suitable analytical tools to enable toxin production and accumulation to be measured. The most commonly used tools are broad-spectrum bio-assays. Progress is being made in the development of chemical techniques, although these have the disadvantage of being specific to particular toxins; many species produce more than one toxin and sometimes produce different toxins under different conditions. The ACMP also raised the possibility that antibody techniques might have some use in this field. Analytical matters will be explored further by the Biological Oceanography Committee.

It was concluded that the main significance of exceptional algal blooms lies in their economic impact on molluscan fisheries and mariculture. ICES is taking active steps to provide management advice to overcome these impacts.

8.8 General Conclusions on Exceptional Algal Blooms

The above paragraphs give a summary of the current state of knowledge, as presented to the Special Meeting. It is evident that an understanding of the problems of exceptional blooms, and related questions concerning hypernutrification and hypertrophication, cannot be divorced from a better understanding of coastal and shelf seas primary production in general. Future attention, therefore, needs to focus on overall variations in the pattern and quantity of annual production, with particular reference to enriched coastal areas. There is an urgent need to establish long time-series of data on primary production and nutrient fluxes in addition to exceptional bloom incidence.

Basic research is needed on, inter alia, the biology and life cycles of blooming species and the role of organic factors as well as inorganic nutrients in primary production.

ICES will soon publish the first of a series of keys to the identification of dinoflagellates, which will help to dispel taxonomic confusion. The Council has also agreed that a Workshop on primary production methodology should be held in 1986. It was anticipated that a leaflet describing a method for the measurement of primary production will be published by ICES in mid-1986.

Noting the above information, the ACMP agreed that there is an urgent need to develop and extend the methods currently applied to studies of primary production and encouraged the Biological Oceanography Committee to initiate an appropriate programme.
9 EFFECTS OF LONG-TERM LOW-LEVEL RELEASES OF OIL

9.1 Introduction

In earlier reports, the ACMP has considered the damage caused to the marine environment by large-scale local releases of oil such as occur in the event of tanker collisions (ACMP, 1977). Information has also been collected on the nature, effectiveness and side effects of measures for reducing the impact of various cleanup techniques used for such spillages (ACMP, 1983). The conclusion reached by these earlier reviews and similar major national reviews (NRC, 1975, 1985; RCEP, 1981) were that large releases of oil to the sea have a catastrophic local impact on amenities, sea birds and marine organisms generally. However, in all but extremely cold environments, or when the spill is of a heavy fuel or crude oil, degradation and recovery are remarkably rapid and the effects are essentially transient.

These conclusions have not eliminated concern over the impact of oil on the marine environment and interest has recently been increasingly turned towards the possible effects of large volume continuous releases of effluents containing low to medium concentrations of oil. It has been suggested that these releases might have adverse effects because the quantities of petroleum hydrocarbons discharged can be quite large when taken on a total basis and because the inputs are centred on point outlets, such as oil-producing platforms. Several investigations have now been undertaken to assess the impact of such discharges and the ACMP reviewed the outcome of these studies. The conclusions reached are given in the following paragraphs.

9.2 Sources and Nature of Oil Inputs

9.2.1 Shipping and other offshore discharges

Oily discharges to the sea are subject to control by international agreements and national legislation, so that large quantities of oil at high concentrations are usually released to the sea only as a result of accidents or illegal discharges. Offshore oil-producing platforms discharge large quantities of "oily-water", but this is treated by oil separation systems until the residual oil concentration is very low. The "interim standard" imposed by the Paris Commission for such discharges is an average of 40 parts per million and the total North Sea oil input from this source was only 2,000 tonnes in 1983. Such dilute solutions and suspensions should be readily dispersible into the water column, rapidly reaching concentrations which are indistinguishable from ambient levels. However, the measured oil concentrations represent only a fraction of the total organic load of discharged waters and while the bulk of that not measured seems to consist of simple organic acids of low toxicity, more attention is being paid to the composition and behaviour of the plumes from oil-production platforms offshore.
The restricted methods of treatment of oil-based drill-cuttings on offshore oil and gas platforms, although legally controlled, means that large quantities of waste containing high concentrations of oil (5-20% by weight) are discharged from such platforms. This provides a large input of oil to bottom sediments (ca. 20,000 tonnes to the North Sea from UK platforms in 1984) which can be considered as a long-term, low-level source of local oil pollution, but only very restricted areas of the seabed are expected to show persistent effects once the drilling, and hence the input, ceases.

Accidental releases of oil from ships, platforms or pipelines are usually reported rapidly to the appropriate authorities and clean-up procedures are applied where they are necessary and practicable. Unless there is a threat to sea birds or coastal amenities, such oil is best left to degrade and disperse naturally over wide areas of open sea. Such releases are likely to be of crude oil or refined products, susceptible to heavy losses of light fractions to the atmosphere, but also containing water-soluble toxins.

Illegal discharges are often not detected until oil arrives inshore or causes damage to sea birds and amenities. The majority of such discharges is probably derived from tank washings or bilge-pumping by ships at sea. As such, they will usually consist of heavy fuel and lubricating oils and waxy or asphaltene-rich residues from crude oils. These present a threat to sea birds and to coastal amenities. It is usually agreed that they cannot be considered a major source of water-soluble toxins because, unlike the crude oil and refined product spills, they contain few hydrocarbons in the low and middle boiling point ranges.

Legal ship discharges consist of oily waters whose very low concentrations of oil are strictly controlled and which can be relied on to dilute and disperse very rapidly in the open sea. Although rich in water-soluble toxins, the majority of these will be mono- or di-aromatic hydrocarbons liable to loss to the atmosphere from surface waters.

The implementation of national regulations under the provisions of the recently implemented MARPOL 73/78 convention should reduce both controlled oil-water discharges from ships and (by better provision of reception facilities for tank-washings, etc. ashore) illegal discharges from ships. Evidence for these reductions may already be appearing (Robertson-Smith and Knap, 1985). In any case, it is unlikely that ship discharges (apart from large accidental releases) form a significant oil input to the sea. For instance, Whittle et al. (1982) estimated that only 4,000 to 5,000 tonnes, out of an annual total of 70,000 to 74,000 tonnes of oil to UK waters, were contributed by operational ship discharges.

9.2.2 Other sources

Long-term, low-level oil inputs may be classified as diffuse or point-source, but the distinction between them is largely one of locality and scale. The two major sources of diffuse inputs are
generally regarded as the atmosphere and rivers. Even in the case of the atmosphere, the land-based sources of oil hydrocarbons, by evaporative loss and partial pyrolysis, and the prevailing patterns of atmospheric circulation and deposition, will make some sea areas the repositories of much greater atmospheric hydrocarbon inputs than others. Little is known of the actual atmospheric return to the sea, either quantitatively or in terms of its chemical composition, or how either vary in time and space. Estimates of inputs have been largely based on estimates of land-based losses to the atmosphere and conjectures about the proportion returning to the sea. Whittle et al. (1982) estimated that 1,462,000 tonnes are emitted annually by the UK with only 2% to 20% returning in unchanged form; RCEP (1981) estimated only 8,000 to 9,000 tonnes annual input. It is assumed that losses to the atmosphere will suffer extensive photolysis and photo-oxidation before redeposition, but whether this makes the final input of more or less environmental concern than the parent compounds is debatable. It is clear that photolytic degradation of oil films on the sea surface can produce compounds far more toxic to algae and the phytoplankton than the original oils (Tjessam and Palmork, 1984), but it is not known whether this also occurs before atmospheric redeposition. It is also argued that atmospheric inputs will be largely trapped in the surface micro-layer, where they combine with and scavenge other contaminants such as heavy metals, oil-soluble pesticide residues and PCBs. There is a particular population at risk from these inputs, namely the neuston, planktonic organisms living within a few centimetres of the sea surface, but once again we are largely ignorant of its composition, variation with time and space or its importance to the marine food web and recruitment. The surface layer of the sea is a phase through which the life-stages of many marine organisms will pass at some time (Davenport, 1982). All that can reasonably be said is that if monitoring of particular enclosed sea areas, such as the Baltic or the Mediterranean, showed the extent, thickness and chemical composition of the surface micro-layer to be altering, then concern for nondispersive stages of the neuston might be appropriate.

The second major chronic input to the sea usually regarded as a diffuse source is that of rivers. UK returns to the Paris Commission for 1982 estimate an annual oil input to the sea from rivers of 5,000 tonnes, compared to an annual UK total input of some 30,000 to 40,000 tonnes. However, a major source to coastal waters that could also be considered diffuse is that of general coastal discharges from land runoff and municipal wastes. This is estimated at 8,100 tonnes for the UK in 1982 and does not include point source inputs of 3,500 tonnes from coastal refineries, 1,000 tonnes from reception facilities and oil terminals, 3,000 to 4,000 tonnes from dredge spoils or 7,000 tonnes from sewage sludges dumped at sea. The input from general coastal runoff is probably larger than that from rivers alone, but whether it is considered as a diffuse source to coastal waters in general, or comprised of a series of minor, local point sources (drains, storm sewers, streams, ditches) is a matter of perspective. However, the same can be said of rivers. Much of their oil load received inland will be highly modified, degraded and adsorbed onto suspended solids by the time it reaches the sea and the bulk of this material will be sedimented out and trapped in the estuary. Only major rivers can be
considered sources of oil to the seas beyond coastal waters, where their inputs, compared with atmospheric deposition, must be minor.

9.3 Effects of Low-Level Releases

The remaining inputs will be from legally controlled point sources where both the concentrations and quantities of oil will be restricted, but generally only to avoid acute biological effects or visible deterioration of amenities. Even where diffusers are used and discharges made at particular states of the tide to promote dilution, in estuarine and coastal waters the trapping of oil onto solids and its sedimenting out is a very efficient process and most point-source inputs will enter the surrounding sediments. The long-term effects of this will depend on the hydrography, sediment regime and biological community in the receiving locality. However, the rapid degradability of oil in oxygenated waters coupled with the ability of many estuarine and coastal species to adapt, within limits, to elevated concentrations of xenobiotics indicate that only in exceptional circumstances (demanding revision of the discharge procedures and consents) will severe long-term damage occur. Chronic effects on physiology, biochemistry, and such effects as "reduced scope for growth" can certainly be measured in communities around such point sources of oil and hydrocarbons, but even where "scope for growth" and fecundity are affected, it is very difficult to demonstrate population changes or ecological effects outside natural variability. The chances of measuring or validly predicting adverse changes over wide areas due to effects from diffuse sources or combinations of local sources are very low. It is also important to recognize that while oil is not considered a major pollutant in its own right, compared with, e.g., PCBs or heavy metals (RCEP, 1981), it is recognized to be a general stressor on marine organisms, lowering their resistance to disease, other contaminants and natural hazards. Further, it is usually particularly in those areas where major contaminants are present, e.g., industrialised estuaries, that oil concentrations are high. Oil in combination with other contaminants is therefore far more of a threat than oil alone, providing another reason to reduce oil inputs where possible.

In addition to the neuston, considered above, there will always be certain marine species or populations more susceptible to oil than others. These include rare species and populations of species at the extremes of their geographical range which may require special protection on aesthetic, if not ecological, grounds. Similarly, sea birds are particularly at risk from persistent, floating oil residues. In the UK there appear to be no sea bird populations whose decline can be positively linked to oil pollution and many populations are actually on the increase; nevertheless, for aesthetic and humanitarian reasons the prevention of sea bird oiling is widely demanded. While deaths directly due to oiling may not account for all the oiled sea bird corpses recorded on coasts (floating and beached corpses will retain oil encountered after death), even minor oiling will contribute to increased mortality of sea birds from other, including natural, causes by increased susceptibility due to lower thermal insulation, irritation of the gut, altered
9.4 Conclusions

The more extreme concerns expressed by both scientists and the public about potential large-scale environmental damage caused by major oil spills now seem unjustified. The grounds for continued concern about the effects of long-term, low-level oil releases, as opposed to acute effects, stem from the relative ignorance of the significance, or even the existence, of largely unseen and unmeasurable chronic effects. Diffuse sources of oil, however defined, form only a minor component of total oil inputs to the sea and oil from point sources is unlikely to exert detectable effects outside the immediate receiving environment. Some serious anxieties about potential environmental damage by chronic low-level oil inputs have not been verified, mainly because of analytical difficulties in separating effects of such oil inputs from environmental stress caused by other contaminants.

Thus, there seems to be no real evidence of significant deterioration of marine communities due to long-term, low-level oil pollution, but it must be admitted that such deterioration probably could not be detected even if it occurred, until gross changes were apparent. It is because of this present inability that existing measures to reduce oil inputs should be maintained. The importance of some of the damage which it is envisaged might be caused by chronic oil contamination is such that further work, to verify the extent to which it actually occurs, is warranted. Of the various concerns still expressed about the potentially damaging effects of low-level chronic oil contamination, those which ACMP considered deserve further investigation are:

1) The effects of oil on the formation, prevalence, composition and role of surface films, in relation to their importance (positive or negative) for marine biota, including eggs and larvae of fish, and

2) The possibility of bioaccumulation of persistent components of oil or oil degradation products on the grounds that this may cause deleterious effects.

Other concerns about possible effects of low-level, chronic oil contamination seem less important and should be given lower priority:

1) the effect of oil as an additional environmental stressor (organic load) on benthic communities likely to be subjected to oxygen depletion;

2) the possibility of toxic or otherwise damaging compounds being released in conjunction with low-level chronic oil discharges and interacting with other contaminants in the environment;

3) the effects of oil on limiting the extension range of biota (animals and plants) at the extreme of their geographical environmental range, alone or in
conjunction with other contaminants.

It does, however, seem warranted to continue monitoring for low-level oil concentrations in order to spot anomalies in oil distribution and to verify that existing restrictions are complied with. Action to minimise further such discharges would be justified if important damage to the marine environment can be shown to be probable or if the cost of such action is relatively low. Similar measures might also be considered whenever chemical monitoring shows that levels of oil contamination are increasing in areas of known discharges.

9.5 References


9.6 Acknowledgement

The material on which the preceding review was based was prepared by Dr R A Blackman (Fisheries Laboratory, Burnham-on-Crouch, UK). Additional material has, however, been added and some amendments and rearrangements have been incorporated in the process of its adoption by ACMP.
10 REGIONAL ASSESSMENTS

The ACMP reviewed the status of the preparation of documents assessing the state of the marine environment on a regional basis. It was noted that the assessment of the environment in the Skagerrak and Kattegat was nearing completion. In addition, basic information has been collected in preparation for the compilation of a suitably condensed assessment of the state of the mid-Atlantic Shelf area off the east coast of the United States. Note was also taken of the fact that the Helsinki Commission has almost completed its First Periodic Assessment of the State of the Baltic Sea.

The work undertaken in preparation for the International Conference on the Protection of the North Sea (Bremen, 1984) had included an assessment of the state of knowledge on the conditions and resources of the area. It was suggested that it might be possible to utilise the background material for this Conference to produce a regional assessment document on the North Sea. However, given that further information will become available as a result of a number of studies being carried out in the North Sea, including work which had been commissioned following the North Sea Conference, it was decided to await the outcome of these investigations before such an assessment is attempted by ICES.

It was also suggested that, in the light of recent interest in the Irish Sea, a regional assessment of this area should be undertaken as a matter of priority. In this connection, it was noted that the United Kingdom had initiated a review of the available information on the Irish Sea. This would use as its basis the outline format proposed by ICES. The information collected could be made available to ICES, possibly in time for the 1986 mid-term ACMP meeting. The ACMP welcomed this initiative and agreed that in order to extend the study to cover all aspects required for a full regional assessment of the area, requests would be made to the Shelf Seas Hydrography Working Group and the Irish Sea and Bristol Channel Working Group to ensure that the sections on hydrography and fish stocks are adequately covered for the whole area.

The First Periodic Assessment on the State of the Baltic Sea, being carried out under the Helsinki Commission, comprises General Conclusions based upon a background document that had been prepared by a number of scientists from the countries around the Baltic Sea. The ACMP looked forward to seeing these General Conclusions and the Background Document when they have been published.
11 POLLUTION STUDIES IN THE NORTH SEA

The ACMP reviewed the Declaration from the International Conference on the Protection of the North Sea (Bremen, 31 October - 1 November 1984) and noted that the Conference had clearly recognised the North Sea as an ecosystem that must be protected from the input of contaminants via all sources. In noting the various problems identified by the Conference as requiring specific action, the ACMP agreed that it was in a position to provide relevant information and advice on a number of these issues. This included the preparation of assessments on harmful substances; the ACMP has already completed several such assessments and has others in preparation. Another area is the preparation of advice on which chemical and biological characteristics of the marine environment should be monitored and the most appropriate methods for use in such monitoring.

In conclusion, the ACMP stated that it is prepared to receive requests from the relevant Commissions to provide appropriate advice on the follow-up action recommended by the Conference.
12 PROGRESS IN THE STUDY OF THE BALTIC SEA

12.1 Patchiness Studies

The ACMP reviewed the progress in the study of the inhomogeneity/patchiness in the distribution of physical, chemical and biological properties in the Baltic Sea, which is being coordinated by the Study Group on Patchiness Investigations in the Baltic Sea under the ICES/SCOR Working Group on the Study of the Pollution of the Baltic. The Baltic Marine Biologists are also supporting this programme, and the ACMP agreed that support should also be sought from the Helsinki Commission.

The ACMP was informed that in preparation for the Multi-ship Joint International Study of Heterogeneity/Patchiness in the Baltic Sea (scheduled for April-May 1986), a pre-study (PRE-PEX) had been carried out in the southern Gotland Basin (near the BOSEX area) on 16 - 25 April 1985. Four research vessels, from the Federal Republic of Germany, Poland, Sweden and the USSR, participated testing methods that will be used in the full-scale experiment. The measurements taken included: standard meteorological and physical hydrographic parameters, oxygen, phosphate, nitrite and nitrate, silicate, ammonium, chlorophyll-a, primary production, phytoplankton biomass, zooplankton biomass and plankton identification. This experiment had been very successful and had provided valuable information on how to conduct the main experiment in 1986.

It was noted that the results of PRE-PEX will be reviewed at a meeting in Tallinn in October 1985 and the final plans for the multi-ship international experiment will be agreed at a Study Group meeting in early 1986. From nine to thirteen research vessels from all countries around the Baltic Sea are expected to take part in the Patchiness Experiment, which will be one of the largest investigations in the North Atlantic area.

12.2 Sediment Studies

The ACMP took note of the progress in the Pilot Sediment Study in the Baltic Sea, which is being conducted under the ICES/SCOR Working Group on the Study of the Pollution of the Baltic. The first component of this Pilot Study, namely, the Baltic Sediment Intercalibration Exercise, has now been completed and the reports on the results are being finalised (see Section 7.4, above). The next step in this work will be the compilation of data on sedimentological and geochemical analyses of recent sediment cores and their evaluation based on the results of the intercalibration exercise, the influence of bioturbation, etc. This information will be used to prepare a critical review of the results on contaminants in sediments, from which will be developed recommendations on further work.
Noting that the Helsinki Commission has requested ICES to prepare a specific assessment on sediments in the Baltic Sea to be used to assist the Commission in deciding whether, when and how sediment investigations should be included in the Baltic Monitoring Programme, the ACMP agreed with the ICES/SCOR Working Group that the critical review of contaminants in sediments should constitute one component of this assessment.

12.3 Other Studies in the Baltic Sea

The ACMP reviewed the results of a series of related discussions in the ICES/SCOR Working Group with regard to the study of the conditions in the Baltic Sea, including monitoring in the coastal zone, studies of the transport and flux of substances from the coast to the open sea, and investigations of effects of contaminants or excess nutrients in the coastal zone and/or open sea. In terms of coastal zone studies, the Working Group had considered two types of monitoring, long-term low-frequency monitoring on a dense network of coastal stations versus high-frequency monitoring of a small number of stations in an area to relate inputs of nutrients to transport and production. The importance of relating conditions in the coastal zone to those in the open sea was emphasized and the Working Group encouraged monitoring along sections or transects from the coast to the open sea Baltic Monitoring Programme stations and other stations. Information on results obtained using different frequencies of monitoring in open sea areas was considered and it was noted that for the Kattegat notable differences were observed between the results obtained using a high monitoring frequency and those obtained using a low monitoring frequency. For the Baltic Sea, there were not enough observations to be able to draw conclusions, but the information available did not indicate such large variations in results between high and low frequencies of observations. Concerning biological effects of contaminants, it was noted that studies are being carried out in Finland on effects of the discharge of wastes from a titanium dioxide industry in the Bothnian Sea. A detailed report on the results of these and other studies will be presented at the 1986 ACMP meeting.

In the context of possible hypertrophication in the open Baltic Sea, given that several scientists have reported trends of a long-term increase in nutrient concentrations in the surface water layer during the winter, the results of biological monitoring were examined to determine whether a similar trend could be observed in production and related parameters. An analysis of biological data from the southwestern Baltic for the summer season alone revealed a statistically significant increasing trend over the period 1975 to 1983 in mean values of chlorophyll-a and primary production. While this was not a strong increase in production, the ACMP encouraged the ICES/SCOR Working Group to initiate similar studies in other areas of the Baltic Sea.

The ACMP took note of the concern expressed by the ICES/SCOR Working Group on the need to obtain data on the input of substances to the Baltic Sea on relevant time scales (i.e., monthly or less) and the need for these data to include all sources (e.g., ground water seepages). The ACMP understood that the
Working Group will consider relevant scientific questions and appropriate methods for obtaining such input data in the course of its future work.

12.4 Second International Baltic Year

In completing the discussion of the activities coordinated by the ICES/SCOR Working Group on the Study of the Pollution of the Baltic, the ACMP noted that ICES, with the support of the Helsinki Commission, has designated 1985 and 1986 as the Second International Baltic Year. This underscores the importance of the three major studies being carried out during these years, namely, the Multi-Ship Joint International Study of Heterogeneity/Patchiness, the Baseline Studies of Contaminants in Fish and Shellfish and Sea Water, and the ongoing study of sediments in the Baltic Sea.

12.5 Baltic Seals

A meeting of the Baltic Seals Working Group was held in October 1985 and the report was considered by the Marine Mammals Committee at the Statutory Meeting. The ACMP will consider this report at its 1986 meeting and prepare advice, as appropriate.
13 REVIEWS OF MARINE CONTAMINANTS

13.1 General

The ACMP continued its work of reviewing current knowledge about selected contaminants on the basis of the overviews being prepared for it by the Working Groups and their members. It was noted that several of these were in the course of preparation, but only one was considered to be in a form which could be utilised directly by ACMP. This concerned phthalate esters and the completed text, as amended by ACMP, is contained in Section 13.2, below. The main conclusions arising from the overview are that phthalate esters are now very widely distributed in the marine environment, but there is little or no evidence to suggest that present levels are likely to cause adverse effects, except in areas very close to point sources of input or in mariculture when new plastic tanks are first brought into use. In both these situations, concentrations can be extremely high and cannot be regarded as typical of the marine environment as a whole.

The ACMP then considered other contaminants that might be the subject of future overviews. A number of chemical and biological contaminants that might be important to consider in the context of their effects upon the marine environment were suggested and discussed. As a result of these discussions, the ACMP concluded that it concurred with the plans of MCWG to provide overviews for polynuclear aromatic hydrocarbons (PAHs), phenols, lindane, and organosilicon compounds.

It further believed that, in particular, an evaluation of organosilicon compounds was necessary and requested the MCWG to accelerate its attention to this class of substances, taking account of relevant discussions within GESAMP, the London Dumping Convention Scientific Group and the Oslo Commission.

The ACMP also considered that overviews on copper and chromium would be valuable due to the increased interest of the JMG in the inclusion of these metals in the Joint Monitoring Programme and their addition to Annex II of the Oslo Convention. In addition, it was decided that nickel should be included as an element worthy of overview attention on the grounds that it had been identified as a substance of interest by the International Conference on the Protection of the North Sea (Bremen, 1984). Such overviews could be started initially from either the marine chemical or the toxicological aspects independently. However, it suggested that MCWG should also consider these three elements from the marine biogeochemical perspective in the near future. A further element discussed from the perspective of JMG interest was arsenic. The preparation of an overview on arsenic would be extremely valuable and the ACMP agreed to pay early attention to this element.
Finally, a further list of contaminants was discussed, namely short-chain aliphatic organohalogens, organosulphur compounds (e.g., mercaptans), steroids, selenium, chlordane isomers, and surface-active substances. It was concluded that this list should be borne in mind by MCWG and other appropriate Working Groups when planning their future overview work, but that, of these substances, the most important for early attention is surface-active substances.

13.2 The Analysis and Occurrence of Phthalate Esters in the Marine Environment

13.2.1 Production and Use

Industrial phthalate esters are usually those of 1, 2-benzene dicarboxylic acid, or ortho-phthalic acid. They are manufactured from phthalic anhydride, which is obtained by the oxidation of either naphthalene or ortho-xylene in the presence of vanadium pentoxide (Graham, 1973). Esterification of phthalic anhydride and the appropriate alcohol (or mixture of alcohols) is carried out in the presence of sulphuric acid or para-toluene sulphonic acid as catalysts, or non-catalytically at high temperatures (Pierce et al., 1980). The world-wide production of phthalate esters is currently around 2 million tonnes per annum (Ehrhardt and Derenbach, 1980).

The main use of phthalate esters is as plasticizers in various plastics and resins, notably PVC, in which the phthalate esters may be present in concentrations as high as 100 parts phthalate ester per 100 parts resin (Pierce et al., 1980). They are also used as insect repellents and insecticides, and are constituents of perfumes, cosmetics, inks, lacquers, explosives, and other products. Their uses are indeed so widespread that in the USA the annual production rate of DEHP, the most widely used phthalate ester, has been shown to closely parallel that of all synthetic organic chemicals (Peterson and Freeman, 1982).

There is some evidence to suggest that phthalate esters may also be produced biosynthetically, but the problems of contamination attendant on such investigations make it impossible to estimate the size of any contribution from natural sources to the total phthalate ester budget (Pierce et al., 1980).

13.2.2 Analytical Methodology

The major problem encountered when analysing for phthalate esters is that of contamination, both during sample collection and subsequent laboratory analysis. Commonly used laboratory materials such as wooden spatulas, aluminium foil, paper towels, teflon tape, as well as distilled water, solvents, chemicals and adsorbents have been shown to contain unacceptably high levels of phthalate esters and to require extensive cleaning or purifi-

<1> For a list of abbreviations used, see section 13.2.9
cation before use. Even then great care must be taken to prevent recontamination of uncapped solvents and adsorbents, and the adsorption of phthalate esters onto the surface of exposed glassware from laboratory air (Ehrhardt and Derenbach, 1980; Giam \textit{et al.}, 1975; Pierce \textit{et al.}, 1980; Waldock, 1983). The best analytical methods are those with the smallest number of steps and which use the minimum of solvents, chemicals and adsorbents.

The storage of samples prior to extraction and analysis may lead to substantial under-estimates of the quantities of phthalate esters present. Schouten \textit{et al.} (1979) demonstrated the rapid loss by biodegradation of DnBP and DEHP in stored samples of river water. At 50 $\mu$g l$^{-1}$, 90% of DnBP was lost in 3 days and 50% of DEHP in 5 days. Rapid microbial degradation of DnBP was also shown to occur in estuarine water and sediments (Walker \textit{et al.}, 1984). It is therefore preferable to extract samples taken for phthalate ester analysis as soon as possible after collection.

For the identification of phthalate esters, gas chromatography (GC) is the most commonly used technique, with flame ionisation detection (FID) (Schouten \textit{et al.}, 1979), electron capture detection (ECD) alone (Musial \textit{et al.}, 1981) or following chemical derivatisation (Giam \textit{et al.}, 1976b and 1978), or more commonly by gas chromatography/mass spectrometry (GC/MS). This is usually operated in the electron impact ionisation mode (Ehrhardt and Derenbach, 1980; Peterson and Freeman, 1982; Waldock, 1983), the phthalate esters exhibiting very weak molecular ions but a strong base peak at m/z 149, deriving from the fragmentation and rearrangement:

\[
\begin{align*}
\text{OR}_1 & \quad \text{OR}_2 \\
\text{m/z 149} &
\end{align*}
\]

where R$_1$ and R$_2$ are alkyl groups.

All phthalate esters give this strong base peak except DMP, which may be conveniently monitored via its base peak at m/z 163. Although capillary GC with detection by electron impact mass spectrometry on non-polar or low polarity columns is the most reliable method used for the analysis of phthalate esters,
a number of other techniques have been proposed.

The use of chemical ionisation with isobutane reagent gas has been proposed as a technique with advantages for the identification of phthalate esters as it provides molecular weight information, with the formation of abundant quasi-molecular ions \([M+H]^+\) (Addison, 1979), but no quantitative data on environmental samples have so far been reported which have been derived by this technique.

High-performance liquid chromatography (HPLC) with UV detection has been used both quantitatively (Schouten et al., 1979), and as a purification step prior to confirmation of the identity of a phthalate ester by proton nuclear magnetic resonance spectroscopy (NMR) (Musial et al., 1981).

Whenever further work on phthalates is undertaken, intercalibration between laboratories is urged as a means of testing and validating analytical methods and precautions taken against contamination.

13.2.3 Transport Mechanisms and Deposition to the Marine Environment

When phthalate esters are used as plasticizers, they are not chemically bonded to the plastics, but only physically incorporated. Significant volatilisation of the esters may occur, particularly if high temperatures are encountered during manufacture, storage, use or disposal (Pierce et al., 1980). Many plastics are burnt or incinerated after disposal, and phthalate esters have been detected in air samples collected near to incinerators, implying that they may not always be degraded completely during incineration. Their presence in the atmosphere over the Gulf of Mexico (Giam et al., 1976a) and in precipitation samples collected in Norway (Lunde et al., 1977) raise the possibility that long-range aerial transport occurs, but this has not yet been adequately studied. Mass balance calculations for the Gulf of Mexico by Giam et al. (1977) showed that at least 70% of the DEHP measured was attributable to inputs via atmospheric deposition. Atmospheric deposition would seem therefore to be a very significant route of input to the marine environment.

Although the solubility of phthalate esters in water is low, they can become associated with colloidal materials and thereby mobilised and distributed on a fairly wide scale. The disposal of plastics and other products containing phthalates in landfill sites will lead to releases to the atmosphere and leaching of phthalate esters into ground water, and their subsequent entry into the marine environment. The extent to which this occurs will depend upon the degree of degradation which occurs in the landfill site or en route to the marine environment. If degradation does not occur, eventual escape and entry to the marine environment is inevitable.
13.2.4 Movement and Fate within the Marine Environment

As they are relatively hydrophobic, phthalate esters will adsorb onto particulate materials and ultimately be deposited in the sediments. Studies of phthalate ester concentrations in dated sediment cores from the Chesapeake Bay have shown increases in the concentrations of a number of different phthalate esters (particularly DEHP) over the last 60 years, and at one site the rise in concentration of DEHP in sediments was shown to closely parallel its rising annual production rate (Peterson and Freeman, 1982).

Chemical hydrolysis of phthalate esters can occur by step-wise ester hydrolysis to yield first the mono-ester and finally orthophthalic acid, but the reaction rates are slow. The main process of degradation in the environment is therefore likely to be enzymatic, and indeed rates of enzymatic hydrolysis have been found to be rapid in fungi, bacteria, fish and mammals (Pierce et al., 1980).

13.2.5 Distribution and Levels in Water, Sediment and Biota

There are many reports of concentrations of particular phthalate esters being detected in marine samples. However, for the reasons stated earlier, not all data can be considered with equal confidence. Accordingly, only a few selected sources have been used in the following citations of concentrations which might be regarded as typical.

In the open waters of the Gulf of Mexico mean concentrations of DnBP and DEHP were 90 ng l⁻¹ and 80 ng l⁻¹, whereas coastal samples had 70 ng l⁻¹ and 130 ng l⁻¹, respectively (Giam et al., 1977). DEP, DiBP and DnBP were determined at 1, 20 and 80 ng l⁻¹, respectively, in the open water of the Kiel Bight (Ehrhardt and Derenbach, 1980), and in estuarine samples from the Crouch estuary, DMP, DEP, DiBP, DnBP and DEHP were found at 6.4, 50, 30, 30 and 60 ng l⁻¹, respectively (Waldeck, 1983). These concentrations are approximately an order of magnitude lower than those found in freshwater rivers in the Netherlands, where DEHP concentrations average 1,000 ng l⁻¹ in the Rhine, Meuse and IJssel, with DnBP concentrations of 300, 500 and 2,000 ng l⁻¹, respectively, in these rivers (Schouten et al., 1979).

Mean phthalate ester concentrations in marine sediments have been determined for the coastal areas of the Gulf of Mexico, where DnBP and DEHP were found at 7.6 and 6.6 ng g⁻¹, wet weight, respectively, with 3.4 and 2.0 ng g⁻¹ being measured offshore (Giam et al., 1977). Estuarine sediment levels of DnBP, DnBP and DEHP were 1.8 to 11.5 ng g⁻¹, 3.9 to 15 ng g⁻¹, and 11 to 26 ng g⁻¹, respectively, in the River Crouch (UK) (Waldock, 1983). Maximum mean concentrations of DEP, DiBP, DnBP and DEHP in surface sediments from the Chesapeake Bay were 42, 5.6, 89 and 180 ng g⁻¹ dry weight, respectively, (Peterson and Freeman, 1982). These concentrations are all much lower than those reported for the sediments of three Netherlands rivers, DnBP and DEHP being reported as <500 to 16,000 ng g⁻¹ and 7,000 to 72,000 ng g⁻¹ (wet weight), respectively, in the Rhine, <500 to 8,000 ng g⁻¹ and 3,000 to 36,000 ng g⁻¹ in the IJssel, and <500 to 2,000 ng g⁻¹ and 1,000 to 17,000 ng g⁻¹ in the Meuse (Schwartz et al.,...
Concentrations of DEHP in marine biota from the Gulf of Mexico were <1 to 135 ng g\(^{-1}\) wet weight, the highest concentration being found in the whole tissue of a starfish. Samples of muscle from various fish species contained <1 to 20 ng g\(^{-1}\) wet weight DEHP (Giam et al., 1978). In fish from Tees Bay, a heavily industrialised estuary, DEHP concentrations were ca. 10 and ca. 50 ng g\(^{-1}\) in samples of plaice and whiting muscle, respectively, and ca. 80 and ca. 50 ng g\(^{-1}\) in plaice and whiting liver, respectively, whilst neither DiBP nor DnBP were found at concentrations significantly higher than the blanks. Samples of dab muscle from the Crouch Estuary contained DiBP and DnBP at concentrations of 6.3 and 4.1 ng g\(^{-1}\), respectively, with somewhat higher levels in the livers. Higher concentrations of DEHP were found in the digestive glands of the bivalve Scrobicularia plana, 80 to 200 ng g\(^{-1}\), with 20 to 40 ng g\(^{-1}\) in the rest of the body. Ostrea edulis had significant quantities of DEP, DnBP, and DEHP in the digestive gland, at 10, 2 and 6 ng g\(^{-1}\), respectively. Only the DnBP concentration of ca. 1 ng g\(^{-1}\) was significant in the rest of the body (Waldock, 1983).

Although there is some bioaccumulation of phthalate esters under conditions of continuous exposure, biomagnification is not expected to be significant (Pierce et al., 1980). The detection of DnHP in herring and mackerel at concentrations of 17 to 27 \(\mu g\) g\(^{-1}\) wet weight, respectively, has indicated the possibility of selective bioaccumulation because, although it is not a major industrial phthalate ester, the concentrations of DnHP far exceeded those of DnBP and DEHP, which are the two major industrial products (Musial et al., 1981).

### 13.2.6 Toxicological Aspects

Phthalate esters are used in so many forms with which man comes into direct contact (e.g., in insect repellent gels and creams and in plastics used in surgery) that it has generally come to be accepted that they present little danger to human health, whether absorbed through the skin, inhaled or ingested. Most of the mammalian toxicity data justify this view. Recently, however, some concern has been expressed about the possible consequences of long-term continuous exposure to certain phthalate esters, as there are indications that some may have carcinogenic properties under particular exposure conditions (Kluwe et al., 1982). There has, however, been no suggestion that restrictions on either the use of phthalate esters or their release to the environment are necessary in order to protect human health.

The literature based on the toxicity of phthalate esters is not extensive. However, the information available on short-term LC50 values indicates that mortalities among fish or shellfish populations are very unlikely to occur as a result of exposure to even the highest concentrations indicated in the preceding section as being likely to be present in most marine environments (Pierce et al., 1980). The only evidence that phthalates might be responsible for damage to marine organisms stems from some preliminary observations in connection with unexpected failures in hitherto successful commercial
mariculture operations. Investigations have linked these failures to the introduction of new plastic tanks and pipework and high concentrations of certain phthalate esters have been found in the waters passing through such plastic hardware. Separate laboratory tests have shown that prolonged exposure to such relatively high concentrations, ca. 0.4 mg l⁻¹, may cause mortalities (Waldock and Thain, pers. comm.). These concentrations are higher than those known to produce sub-lethal effects on a variety of marine organisms, which are usually of the order of 0.1 mg l⁻¹ (Randall et al., 1983; Ozretich et al., 1983).

13.2.7 Conclusions

It is apparent that extremely large quantities of phthalate esters have been, and are continuing to be, produced. The class of materials includes numerous individual compounds, but only a few are produced and used in large amounts, of these DEHP is the most widely used. All are produced and used in comparatively pure form and the problems of analysis are not brought about because of use as multi-compound formulations, as is the case for PCBs, but because their widespread utilisation throughout the developed world and in many articles in common laboratory use is liable to cause severe contamination of samples prior to or during analysis.

As a consequence of their widespread use and the ease with which they escape to the environment, it is possible to detect phthalate esters in most marine environmental samples. The comparatively uniform concentrations found suggest that atmospheric transport is the major route of input to the marine environment. Where unusually high concentrations are encountered, as for example in parts of Chesapeake Bay, they probably indicate the predominance of a local source and/or that biodegradation systems may be inhibited by high concentrations of phthalates.

There is little evidence that current levels of contamination present a hazard either to man or marine organisms and, except in areas close to point sources where concentrations in sediments might build up, there is little evidence of accumulation. There is clearly a need to keep the situation under review, but there is little evidence to suggest that large-scale investigations into toxicity or environmental presence can be justified.

13.2.8 Acknowledgement

The information contained in this review is based on material originally prepared by Mr. R J Law (Fisheries Laboratory, Burnham-on-Crouch, UK). A substantial proportion of the review was discussed by the MCWG and amendments were incorporated at their suggestion before presentation to ACMP, which further amended and added to the material now included in the above text.
13.2.9 Abbreviations

DMP \hspace{1cm} \text{dimethyl phthalate}
DEP \hspace{1cm} \text{diethyl phthalate}
DiBP \hspace{1cm} \text{di-iso-butyl phthalate}
DnBP \hspace{1cm} \text{di-\(\eta\)-butyl phthalate}
DnHP \hspace{1cm} \text{di-\(\eta\)-hexyl phthalate}
DEHP \hspace{1cm} \text{bis (2-ethyl hexyl) phthalate}
GC \hspace{1cm} \text{gas chromatography}
FID \hspace{1cm} \text{flame ionisation detection}
ECD \hspace{1cm} \text{electron capture detection}
HPLC \hspace{1cm} \text{high-performance liquid chromatography}
NMR \hspace{1cm} \text{nuclear magnetic resonance spectroscopy}
UV \hspace{1cm} \text{ultraviolet absorption spectrophotometry}
PVC \hspace{1cm} \text{polyvinyl chloride}
GC-MS \hspace{1cm} \text{gas chromatography - mass spectrometry}

13.2.10 References


The ACMP considered a report entitled "Determination of Pollu­tants in Effluents: Estimates of the Mass of the Six List I and Six List II Substances Discharged to the Tidal Waters in the United Kingdom". It was concluded that this type of study is valuable in assessing the magnitudes of, and relationships between, inputs of contaminants from various sources. The report covered discharges of contaminants from UK rivers, sewage and industrial/trade wastes (excluding cooling water).

It was noted that the river inputs are at least comparable with, and in some areas greater than, the aggregate inputs from sewage and trade effluents. Some doubt was expressed as to the extent to which the comparative differences noted were really correct when account was taken of the manner in which the objectives of the programme for river monitoring had been translated into quality assurance criteria and procedures, as described in various papers published in the Analyst (1985). It was recognised that the data on contaminant concentrations in river waters had been utilised in a rather different way from that originally intended when the analytical quality control programme was established. However, bearing in mind the purpose to which the data were now being put, the ACMP expressed the hope that the quality assurance criteria and the activities associated with the assessment of laboratory performance and data quality would continue to be improved to provide greater confidence in the assessment of contaminant discharges from freshwater courses to the coastal environment. For example, the cadmium concentration in pristine rivers is currently reported to be in the range 2 to 50 ng l\(^{-1}\), with 10 to 20 ng l\(^{-1}\) being the most likely concentration of cadmium in rivers unaffected by human or industrial activity. The performance criteria for cadmium in the UK Harmonized River Monitoring Programme, however, involve values of bias and precision higher than these concentration levels. The criteria for laboratory performance and data reliability in this programme should continue to be reappraised in the context of the prevailing levels of the subject contaminants in both pristine and anthropogenically influenced freshwater courses.

Nevertheless, the ACMP noted that the information contained in the document had been prepared as an attempt to give at least an order of magnitude indication of the scale of inputs from land-based sources. This activity was welcomed and it was hoped that other countries would adopt similar programmes, while endeavouring to ensure that the quality of the data on concentrations of contaminants in river water are as high as possible.
In connection with this subject, the ACMP considered that it might be useful to national authorities embarking on river monitoring programmes if some indication of the concentrations of metallic contaminants that might be encountered in river water were provided. Such information is most pertinent to the specification of the detection limits, accuracies and precisions required for reliably estimating gross contaminant discharges (or fluxes) from rivers. As has already been noted above, in at least one such monitoring programme, the selected uncertainty criteria (Analytical Quality Control Committee, 1985a,b,c) are considered inappropriate to the stated objectives of the programme, namely, to make accurate estimates of river discharges of contaminants. The following table provides information on the ranges of metallic contaminants likely to be encountered in rivers. Meaningful averaging of data from either spot determinations or regular and continuous sampling requires that the full range of concentrations be measured accurately. The sampling and analytical methods employed must therefore be suitable for the accurate determination of the analytes of interest in these rivers.

It should be stressed that some of the rivers from which these data have been derived are considered to be receiving significant quantities of metals through discharges of domestic and industrial wastes. Furthermore, in most cases the values are based upon spot (or grab) sample determinations. Thus, in only a few cases has account been taken of spatial or temporal variability in composition, which may be quite substantial for rivers having a large variability in hydrologic conditions. Finally, evaluation of these data is also complicated by the improvement in sampling and analytical methodology that has occurred during the past decade. The first and latter factors will probably result in the most recent data for pristine rivers being the most useful indication of the lowest concentrations that need to be detectable within any river monitoring programme. This should be borne in mind when setting criteria for the accuracy and precision (and thereby detection limits) of procedures to be applied for the measurement of contaminants in rivers.

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<1> The term 'flux' as commonly used in this context means the rate, in units of mass/time, of the discharge of contaminants from rivers. By convention, in physics, flux is defined in units of mass/area/time. Thus, 'flux' as used here is really a spatial integral, over a two-dimensional section, of a conventionally defined flux.
### Ranges of Dissolved (Filtered) Contaminant Concentrations in Rivers

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Concentration units</th>
<th>Reported concentrations</th>
<th>Overall ranges of concentrations</th>
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<tr>
<td>Hg</td>
<td>ng.l⁻¹</td>
<td>&lt;3&lt;sup&gt;1a&lt;/sup&gt; 70&lt;sup&gt;15&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>ng.l⁻¹</td>
<td>110&lt;sup&gt;1b&lt;/sup&gt; 90&lt;sup&gt;2a&lt;/sup&gt; 14&lt;sup&gt;2b&lt;/sup&gt; 390&lt;sup&gt;3&lt;/sup&gt; 9-25&lt;sup&gt;4&lt;/sup&gt; 2-400</td>
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<tr>
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<td>μg.l⁻¹</td>
<td>8.6&lt;sup&gt;1b&lt;/sup&gt; 10&lt;sup&gt;2a&lt;/sup&gt; 54&lt;sup&gt;3&lt;/sup&gt; 6-7&lt;sup&gt;4&lt;/sup&gt; 17 13.2&lt;sup&gt;8&lt;/sup&gt; 1-50</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>μg.l⁻¹</td>
<td>2.5&lt;sup&gt;1b&lt;/sup&gt; 10&lt;sup&gt;2a&lt;/sup&gt; 6.3&lt;sup&gt;3&lt;/sup&gt; 1.1-1.4&lt;sup&gt;4&lt;/sup&gt; 1.5&lt;sup&gt;5a&lt;/sup&gt; 0.3-10</td>
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<tr>
<td>Ni</td>
<td>μg.l⁻¹</td>
<td>1.5&lt;sup&gt;1b&lt;/sup&gt; 1.6&lt;sup&gt;2a&lt;/sup&gt; 0.7-0.9&lt;sup&gt;4&lt;/sup&gt; 0.27&lt;sup&gt;5a&lt;/sup&gt; 2&lt;sup&gt;7&lt;/sup&gt; 0.25-4</td>
<td></td>
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<tr>
<td>Co</td>
<td>ng.l⁻¹</td>
<td>150&lt;sup&gt;1b&lt;/sup&gt; 30&lt;sup&gt;10&lt;/sup&gt; 100&lt;sup&gt;12&lt;/sup&gt; 80&lt;sup&gt;13&lt;/sup&gt; 100&lt;sup&gt;14&lt;/sup&gt; 30-200</td>
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</table>

**NOTE:** The superscripts refer to the references, given on the following pages.
References

Text

Analytical Quality Control (Harmonised Monitoring) Committee, 1985a. Accuracy of determination of cadmium, copper, lead, nickel and zinc in river waters, Analyst 110, 1-10.


Table

1. St. Lawrence


2. Mississippi


(b) Trefry, J H , Metz, S, and Trocine, R P, 1983. Decreased inputs of cadmium and lead to the Gulf of Mexico. Transactions of the American Geophysical Union 64, 244.

It should be noted that the Cd value provided in Ref. 2(a) is likely to be incorrect and the value given in Ref. 2(b) should be considered the more reliable.
3. Rhine


4. Göta


5. Amazon

(a) Grant, B, Ming-hui, Hu, Boyle, E, and Edmond, J, 1982. Comparison of the trace metal chemistry in the Amazon, Orinoco, and Yangtze plumes, Transactions of the American Geophysical Union 63, 48.


6. Yangtze

Grant, B, Ming-hui, Hu, Boyle, E, and Edmond, J, 1982. Comparison of the trace metal chemistry in the Amazon, Orinoco, and Yangtze plumes, Transactions of the American Geophysical Union 63, 48.

7. Mackenzie


8. Volga

9. Ob


10. Columbia


11. Zaire


12. Yukon


13. Neuse


14. Rhône


General


In reviewing the discussions in the Marine Chemistry Working Group (MCWG), the ACMP noted that a broad range of subjects should be dealt with by that Working Group, namely basic chemical oceanography, in support of fisheries studies or as an auxiliary science to physical oceanography, and marine chemistry as the science of substances in the marine environment, studying the chemical compositions of the sea and the various changes that occur. The MCWG also should carry out work to evaluate the actual significance of the chemical data produced for the marine environment, regardless of whether the data are for nutrients, trace metals, organohalogens or other chemicals in the sea.

The ACMP took note of the MCWG views with regard to nutrient analysis. Present methodology is considered adequate, though it should be recognised that the regular use of auto-analysers may weaken the accuracy of these analyses since the effects due to sample turbidity are not measured. This should be further investigated by the MCWG. The problems related to standards were discussed and the suitability of the Sagami standards was agreed. There is a need for a suitable seawater reference standard for alkalinity measurements, as these determinations are required for several types of studies, such as those relating to CO₂ processes and carbon fixation, for which the current IOS standard seawater is not appropriate. Plans for the preparation of a standard sodium carbonate solution will be discussed, and an intercalibration exercise may need to be conducted at a later stage.

With regard to the possible inclusion of lindane in the list of analytes for the Joint Monitoring Programme, it was noted that, while the identification of these pesticides is relatively easy if appropriate methodology is used, accurate quantification is as difficult as for any other organochlorine. The relative standard deviation for lindane from the Fifth Intercalibration Exercise on Organochlorines in Marine Biota was 77% and it is known that routine detection of this compound will require extra clean-up steps of the extracts in view of the high incidence of materials that interfere with lindane chromatography. In these circumstances, it might be preferable to develop further the present studies on PCBs before considering the inclusion of lindane in the coordinated programme. The above-mentioned relative standard deviation from the previous intercalibration exercise also highlights the need for a revision of the analytical methodology before these determinations can usefully be incorporated in international monitoring programmes.
ANNEX 1

LIST OF PAPERS ON GOOD LABORATORY PRACTICE WITH REFERENCE TO DETERMINATIONS OF TRACE ORGANIC COMPOUNDS


Hill, R H jr., 1981. Control of hazardous and highly toxic materials in the laboratory. Amer. Lab. 11, 14-20.


Indication of spine colours

Reports of the Advisory Committee on Fishery Management .......................... Red
Reports of the Advisory Committee on Marine Pollution .............................. Yellow
Fish Assessment Reports ...................................................... Grey
Pollution Studies ............................................................... Green
Others ................................................................. Black

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