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REPORT OF THE ICES ADVISORY COMMITTEE ON MARINE POLLUTION, 1986

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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 1986 membership of the Committee is found on page iv.

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REPORT OF THE ADVISORY COMMITTEE ON MARINE POLLUTION

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OVERVIEW OF THE 1986 ACMP REPORT

report begins with a brief summary of the progress made in respect to the work requested by the Oslo and Paris Commissions and the Helsinki Commission. It then provides a summary of further progress in the development of guidelines for the determination of temporal trends in the incidence of contaminants in marine biota, procedures for the analysis of relevant data from both the Joint Monitoring Programme and the ICES baseline study, and future plans relating to the evaluation of trends for contaminants in sea water and sediments. Progress in the development, application and revision of reporting formats for data on contaminants in marine media is also outlined. The report contains an updated evaluation of techniques for determining biological stress induced by contaminants with specific reference to the potential application of pathology in this field. Progress in investigations of fish disease and the association between contaminants and disease in marine mammals is described. This includes an assessment of trends in the populations of, and the incidence of diseases in, Baltic seals together with proposals for further attention to methods of relating such diseases to marine contaminants. Sections follow on exceptional algal blooms, methods for the analysis of toxins derived from blooms of toxic algae and an assessment of the future development of culture and related environmental concerns. Several sections of the report deal with methodological and intercalibration specifically addressed are the feasibility and procedures for intercalibration of petroleum hydrocarbons in sea water, marine biota, sediments and sea water, and polychlorinated biphenyls in marine sediments. Three further sections deal simplified guidelines for the use of sediments in monitoring, techniques for the normalization of data pertaining to metallic contaminants in sediments, and an analysis of various approaches to determining the bioavailable fractions of contaminants sediments. Methods are described for the reliable determination of suspended particulate matter in sea water and procedures outlined for future work on the analysis of suspended particulate material for trace inorganic constituents. The report also contains an overview of the incidence and toxicological significance of polycyclic aromatic hydrocarbons in the marine environment. Various other issues are discussed, including regional environmental assessments and patchiness studies in the Baltic Sea. report concludes with a statement of the philosophy of ACMP respecting the potential use of the so-called "assimilative concept marine environmental management and capacity" in describes how ACMP intends to undertake further development of several relevant regulatory principles.

EXECUTIVE SUMMARY

This Executive Summary provides a brief summation of progress in relation to work requested by the regulatory Commissions, separate from the main 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 develop an authoritative response, and others that require continuing review in the light of improvements in scientific understanding. An annual work programme therefore contains a mixture of items, some carried over from 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 sometimes amplified in detailed technical annexes to the report.

At its 1986 meeting, the ACMP considered, <u>inter alia</u>, the most recent reports of the following ICES groups:

Marine Chemistry Working Group (MCWG);

ICES/SCOR Working Group on the Study of Pollution of the Baltic;

Working Group on Marine Sediments in Relation to Pollution (WGMS);

<u>Ad hoc</u> Group of Statisticians Assisting the WGMPNA on Trend Monitoring Issues;

Working Group on Pathology and Diseases of Marine Organisms (WGPDMO);

Working Group on Pollution-Related Studies in the Skagerrak and Kattegat;

Working Group on Baltic Seals.

Brief summaries of the progress made in respect to questions raised by the Oslo and Paris Commissions are presented in Section 2 of this report, itemized in the form of the requests for advice received from the Commissions. Similarly, summaries of progress made on requests from the Helsinki Commission are contained in Section 3. For the benefit of readers not wishing to study the detailed sections of the report, a brief elaboration of the main topics is presented below under the headings "Monitoring of Contaminants in Biota", "Biological Effects Measurements and Disease Studies", "Monitoring of Contaminants in Sediments and Suspended Particulate Material", "Other Monitoring and Quality Assurance Issues", "Overviews of Marine Contaminants", and "Other Matters".

Monitoring of Contaminants in Biota

Further work has been conducted on the development and proving of methods for determining temporal trends in the incidence of con-

taminants in fish and shellfish. A set of statistical guidelines has been established for the elucidation of trends fish tissue and these guidelines have been tested through their application to the analysis of a number of data The approach adopted seeks to devise a procedure amenable to routine application without excessive human intervention. procedure and the results of its application to a particular data set are described in an Annex to this report. The potential role determinations of fat content of marine biological tissue is also discussed. Further analyses of monitoring data pertaining to the incidence of metallic contaminants in fish tissue is planned. In addition, it is intended to extend this work by examining ways in which trends in contaminant concentrations in sea water and sediments might be elucidated.

A major item of discussion pertained to planning for the overall assessment of results from the 1985 Baseline Study of Contaminants in Fish and Shellfish, that is to be commenced early in 1987. The associated intercalibration work, essential for quality assurance and for comprehensive evaluation of the data, is well in hand and the results will be available prior to the first stage of the assessment process.

Biological Effects Measurements and Disease Studies

This report contains an assessment of the manner in which fish and shellfish pathology can be included in studies of the effects of contaminants, but stresses the need for better information on the prevalence of diseases in relation to fish populations gathered through the medium of broad areal and seasonal surveys as a prerequisite to unambiguous use of disease prevalence measurements in monitoring.

Special attention is given in the report to an evaluation of the status and trends in Baltic seal populations and the possible effects of contaminants on these species. Greater attention to other marine mammal populations in terms of disease and fecundity relation to organic contaminant levels is warranted and further study of this subject is currently being undertaken jointly by ICES and the Intergovernmental Oceanographic Commission (IOC). Steps have been proposed to follow up on earlier appraisals exceptional algal blooms and their causes through the establishment of a new ICES Working Group to pay specific attention to research that might throw more light on the physical, chemical and biological factors that result in the initiation and sustenance of exceptional algal blooms. The associated need for greater attention to the accuracy of primary production measurement techniques is referred to in this context. Chemical procedures for the measurement of diarrhetic and paralytic shellfish poison toxins, which are potentially applicable to other algallyderived toxins, are also discussed.

Monitoring of Contaminants in Sediments and Suspended Particulate Material

The report contains a summary of the results of the First Intercalibration for Trace Metals in Marine Sediments, which has recently been completed. Plans have been made by the Working Group on Marine Sediments in Relation to Pollution to evaluate collectively the results of a number of intercalibrations for metals in sediments, which have used some common samples, in order to determine the overall similarity of the results of these experiments and to obtain a more comprehensive assessment of the accuracy and precision of analytical methods.

The Guidelines for the Baltic Monitoring Programme are under revision and the role of ACMP in this revision process is outlined in the report. The report also contains an evaluation of the status of reporting formats for contaminant data.

The report also contains a simplified re-statement of the lines for the use of sediments as a monitoring medium for marine contaminants advanced by ACMP in earlier reports. This is accompanied by a description of normalization techniques that assist in quantifying anomalies in the incidence of contaminants sediments and in quantifying the extent of contamination of marine areas. A further section of the report also addresses the bioavailability of contaminants in marine sediments and outlines some potential approaches to quantifying the bioavailable tions of contaminants through chemical and biological tests. Attention has also been paid to both the determination of suspended particulate matter in sea water and to its analysis. A technique for suspended matter determination is briefly described following the successful conclusion of the recent pilot intercomparison for trace metal determinations in suspended matter, it is pointed out that a further full-scale intercomparison could be conducted should the Commissions so wish.

Other Monitoring and Quality Assurance Issues

Approaches to the intercomparison and evaluation of techniques for the determination of petroleum hydrocarbons in sea water, lindane in biota, sea water and sediments, and polychlorinated biphenyl compounds in sediments are described based upon the application of a strategic framework for such activities outlined in Section 13 of the report.

Recent developments relevant to the measurement of nutrients in sea water are described. New information, specifically arising from the programme of studies of patchiness in the Baltic (PEX), will be examined to determine if there exists a need for further intercalibration of nutrient methods.

Overviews of Marine Contaminants

A number of overviews of the incidence, distribution and biological significance of contaminants in the marine environment have been issued in previous ACMP reports. Section 20 of the current report contains an overview of polycyclic aromatic hydrocarbons which concludes that these compounds are unlikely to present problems of acute toxicity but should continue to be of concern in respect to sub-lethal effects on marine organisms in contaminated areas and potential chronic effects on man as a consumer of marine foodstuffs. The report also contains a discussion of sub-

stances for which overviews of their incidence, distribution and toxicity in the marine environment are warranted. The plans of the Marine Chemistry Working Group to address such substances in the preparation of overviews are also provided.

Other Matters

Recent pollution-related studies in the Baltic Sea, the role of ICES in the International Conference on the North Sea, two soon-to-be completed environmental assessments for regional marine areas within the ICES jurisdictional area, the need for reference materials and the specification of good laboratory practice in marine analytical work, and a description of the status of measurements of net influxes of contaminants from rivers are subjects that receive attention in the report.

An assessment of current aquaculture production and a prognosis on the future growth of this industry is outlined in Section 10 of the report. The anticipated growth in this industry is likely to result in a variety of environmental problems that could affect both the cultured fish and adjacent wildfish populations. Concern is expressed with regard to the use of certain vaccines, antibiotic and chemotherapeutic agents in fish farming (aquaculture) and reference is made to the spread of parasitic organisms through stock transfers among countries.

Finally, Section 25 of the report contains a statement of the philosopy adopted by the ACMP in respect to the subject of the derivation and use of the so-called "oceanic assimilative capacity" which has been the subject of a number of reports and papers during the last year. This statement embraces the wider subject of environmental management and regulation and concludes that the most appropriate approach to such subjects is one based upon the application of three regulatory principles, namely, justification, compliance with dose limits, and optimization. These principles are explained and their importance in the context of the use of the assimilative capacity concept in environmental management is explained.

1 INTRODUCTION

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

The ACMP Report is structured in terms of the ACMP's overall deliberations on subjects related to contamination and pollution of the marine environment, but specific features relevant to the various Commissions' requests are brought together in an Executive Summary, which is at the beginning of the Report, and are further detailed in Sections 2 and 3, where the individual work items from each Commission are listed and related to relevant sections of the main text.

2 PROGRESS IN THE WORK REQUESTED BY THE OSLO AND PARIS COMMISSIONS FOR 1986

A summary of the progress in the 1986 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; to extend the report to cover all aspects of trend monitoring related to seawater and sediments;

Guidelines on statistical methods for temporal trend analysis of data on contaminants in fish tissues are described in Section 4.1 and given in detail in Annex 1 of this report. These guidelines are similar to those described in the 1985 ACMP Report, but have been somewhat modified on the basis of experience gained during the past year. The ACMP recommends the use of these guidelines for the statistical analysis of the JMP trend monitoring data on contaminants in fish and shellfish.

Regarding the portion of this request concerning trend monitoring of contaminants in sea water and sediments, a short progress report is given in Section 4.2 of the report. It is intended that more detailed information will be given in the 1987 ACMP Report.

ii) to report on the experience with biological effects and biological monitoring and to recommend those techniques which, having been tested, appear useful for general application;

Section 5.1 of this report contains a summary statement of the present position on the potential use of studies of pathological conditions in fish and shellfish as techniques for monitoring the biological effects of contaminants. A number of other biological effects monitoring techniques have been tested at the Workshop on Biological Effects Techniques coordinated by the IOC Group of Experts on the Effects of Pollutants (GEEP) in Oslo in August 1986 (see Section 5.2 of the report); the results of this Workshop will be reported in due course.

iii) to report on the progress 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;

Detailed plans for the 1985 Baseline Study of Contaminants in Fish and Shellfish were provided in the 1984 ACMP Report. The results of this Baseline Study will be evaluated in the first instance by a joint ICES/OSPARCOM

group in February 1987. Representatives of the Helsinki Commission will possibly also join this group. Section 4.3 of this report contains further information on this topic.

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;

Some approaches to the estimation of the net input of contaminants to the marine environment via rivers were described in the 1984 ACMP Report. In a dialogue with the Technical Working Group, it has been reported that the advice required by the Paris Commission is in relation to techniques for measuring net fluxes at estuarine and nearshore boundaries, rather than at the continental shelf break, as ACMP had earlier assumed. Although it is understood that this is not regarded an an urgent issue, the ACMP has taken steps to ensure that further work on this subject will be undertaken. A brief discussion of this topic is contained in Section 21 of the report.

v) to report routinely on all on-going and planned ICES intercalibration exercises preferably by means of a full report to JMG on the intercalibration exercises carried out; to plan an intercalibration exercise for Hg, Cd, Cu, Zn in estuarine waters;

The report on the results of the ICES Fifth Round Intercalibration on Trace Metals in Sea Water (5/TM/SW) has been published in Cooperative Research Report No. 136, along with the report on the results of the Fifth Intercomparison Exercise on the Determination of Organochlorine Residues in Fish Oil (5/OC/BT). The report on the results of Part 1 of the Seventh Intercalibration Exercise on Trace Metals in Biota (7/TM/BT(1)) has been published in Cooperative Research Report No. 138.

Reports on the results of the Second Intercomparison Exercise on Petroleum Hydrocarbons in Biological Tissue (2/HC/BT) and the Third Intercomparison on PAHs in Biological Tissue (3/HC/BT) have been published as Cooperative Research Report No. 141 and the report on the Baltic Sediment Intercalibration Exercise will be published in the same series in winter 1986/87. The report on the Pilot Intercomparison of Trace Metal Analyses in Suspended Particulate Matter will be published in the Journal du Conseil.

The report on the results of the First Intercalibration on Trace Metals in Marine Sediments has now been completed and will be published in the Cooperative Research Report series in early 1987.

Concerning the plans for an intercalibration exercise for Hg, Cd, Cu, and Zn in estuarine waters, these plans were presented in Section 7.2.2 of the 1985 ACMP Report. The samples were collected for this exercise in late spring

1986 and the first draft report on the results should be available in early 1987.

vi) to report on progress made in studies of sediments and pollution, by providing information on the progress of the various pilot surveys, the outcome of the relevant 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;

A summary of the results of the First Intercalibration Exercise on Trace Metals in Marine Sediments (1/TM/MS) is given in Section 11.2.1 of the report. More detailed information on the implications of the results of this intercalibration, and other relevant intercalibrations, will be given in the 1987 ACMP Report.

As a result of a request of the 1986 meeting of the Joint Monitoring Group, streamlined guidelines for monitoring contaminants in sediments have been developed, based on the earlier advice of ACMP on this subject. These streamlined guidelines are contained in Section 15 of the report.

At its 1986 meeting, the Technical Working Group requested information on normalization techniques for comparing data on contaminants in sediments from different areas. A report on this topic is given in Section 16 of the report.

Finally, reports on the results of the Pilot Sediment Study in the German Bight and the Pilot Sediment Study in the Skagerrak are expected to be available in 1987.

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;

Information relevant to the conduct of an intercalibration exercise on the measurement of petroleum hydrocarbons in sea water is contained in Section 12 of the report. This section provides two possible alternative approaches to intercalibrating analyses of petroleum hydrocarbons in sea water, for decision by the Commissions.

Information relevant to future work on analyses of petroleum hydrocarbons, including PAHs, in biological tissues is contained in Section 11.1.

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 PCB-congeners;

A recommended method for the determination of PCBs in environmental samples, based on the estimation of individual chlorobiphenyl congeners, was presented in Section 7.1.1 of the 1985 ACMP Report. A small amount of additional information is contained in Section 11.4 of the present report. At present, the ACMP recommends no changes to these procedures.

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

The ACMP agreed that it is now feasible to conduct an intercalibration exercise on the analysis of PCBs in marine sediments. An approach to such an intercalibration is outlined in Section 14. If the Commissions agree that such an exercise should be carried out, further details of the exercise will be developed in conjunction with the coordinator, after one has been chosen.

x) to consider the feasibility of conducting an intercalibration exercise for γ -HCH in biota and sediments, and to advise accordingly. If such an exercise is feasible, to draw up plans for and conduct such an exercise, reporting on the results in due course:

The ACMP decided that it is feasible to carry out intercalibration exercises for γ -HCH (lindane) in sediments, sea water and marine organisms, but felt that the most appropriate medium for the purposes of the JMP was sea water. An approach to the conduct of intercalibrations for lindane in marine materials is contained in Section 13 of this report. The ACMP will await the decision of the Commissions as to whether they approve the conduct of such intercalibrations before developing further plans.

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

No major problems have been experienced in the ADP handling of the JMP data. However, with the continually increasing amounts of data that must be handled, the importance of submission of data on, or preferably before, the deadline must be strongly stressed. The submission of data on magnetic tapes, when prepared according to the appropriate format, is also encouraged.

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, to review knowledge on 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 noted that a report on this topic is under preparation in the Marine Chemistry Working Group and looked forward to reviewing this report at its 1987 mid-term meeting.

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;

A report on this topic, based on the results of the ICES Special Meeting on Causes, Dynamics and Effects of Exceptional Marine Blooms and Related Events, was given in Section 8 of the 1985 ACMP Report. Section 8 of the present report contains a short update on this topic; Section 9 contains some information on the development of new methods for the analysis of the toxins involved in paralytic shellfish poisoning (PSP) and diarrhetic shellfish poisoning (DSP).

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 20.1 of this report contains an overview paper on polycyclic aromatic hydrocarbons (PAHs) in the marine environment. The main conclusions arising from this overview are that PAHs are unlikely to pose an acute toxic hazard to marine organisms; the main cause for concern stems from their potential long-term effects because of their accumulation in marine organisms and their carcinogenic and mutagenic properties.

xv) 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 recommended that measurements of the fat content of the tissues analyzed should be made, especially in those tissues where the fat content varies significantly. In terms of analyzing data for trend monitoring purposes, the statistical procedure recommended can include the addition of fat content as a biological variable in those data sets for which this is required. Further information is contained in Sections 4.1.2 and 4.1.1 of the report.

xvi) 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 noted that information on this topic is being developed by the Benthos Ecology Working Group and looked forward to receiving a report from this Group next year.

xvii) to review the new documents submitted to the Paris Commission Working Group on Titanium Dioxide, any further research results which are published in the scientific literature or become available from other sources, and to consider whether the ACMP's initial conclusions need to be modified in any respect.

The ACMP provided information on this topic in its 1984 Report; it believed that insufficient information existed to warrant a reconsideration of its advice at the present time.

Special topic

To consider the problem of bioavailability of contaminants in sediments and report on how this should influence the monitoring programmes of the Commissions. In addition, the bioavailability of contaminants arising out of the dumping of dredged spoils should also be taken into account.

The ACMP considered this topic in detail at this meeting. It noted that there is no single technique for measuring the bioavailability of contaminants in sediments. Research has shown that bioavailability is not only a function of the substance itself, but is related to the structure and composition of the sediment and the physical and chemical conditions of the surrounding medium. In Section 17, guidance is given on certain aspects of bioavailability assessment to help in the evaluation of data from sediment monitoring programmes and to assist in predicting the consequences of dumping contaminated dredged materials.

3 PROGRESS IN THE 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.

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

The ACMP noted that the Interim Reporting Format for Contaminants in Sea Water had been substantially revised to permit easier automatic handling of the data, to reduce the amount of repetition of certain types of information, and to permit the reporting of data on a greatly expanded list of contaminants and also nutrients. In this context the Sea Water Master Form had been rearranged to meet the needs of the Helsinki Commission for closer correlation with the ICES Oceanographic Data Formats. The new sea water formats have been available since June 1986.

Reporting formats for contaminants in sediments will be developed in late 1986 for review during the first half of 1987. This format will be structured along lines similar to the new format for data on contaminants in sea water. (See Section 4.6.)

ii) 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 reports on both Parts 1 and 2 of the Baltic Sediment Intercalibration Exercise have been reviewed and approved for publication. They are presently in press and will be published in the Cooperative Research Report series in early 1987.

Work on the conduct of the specific assessment on contaminants in Baltic Sea sediments is underway in the ICES/SCOR Working Group on the Study of the Pollution of the Baltic, as described in Section 22.2.

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

The report of the 1985 meeting of the Working Group on Baltic Seals is contained in Section 7.1, along with the conclusions of that Group. The ACMP concurred with all these conclusions.

iv) To review the results of the Patchiness Experiment (PEX) in terms of any possible implications on sampling schemes used in the BMP;

The Patchiness Experiment took place in April-May 1986. Data from PEX are presently being compiled at the ICES data centre. The initial overall evaluation of these data is expected to take place during 1987. When the general evaluation of these data has been completed, a review will be carried out to determine the possible implications on sampling schemes with regard to the BMP. (See Section 22.1.)

v) To review the BMP Guidelines for monitoring contaminants in marine organisms and prepare proposals for amendments, as required, taking into account new methods for analysis of individual PCB compounds.

The review of the BMP Guidelines is being carried out under the ICES/SCOR Working Group on the Study of the Pollution of the Baltic. The schedule for and substance of this review is described in Section 4.4 of the report.

vi) To provide advice on reliable, intercomparable methods to determine concentrations of suspended particulate matter in sea water.

Information relevant to this item is contained in Section 18.1 of the report. Further work will be conducted in 1987.

4 MONITORING ISSUES

4.1 Trend Monitoring

The ACMP reviewed the report of the <u>ad hoc</u> Group of Statisticians assisting the WGMPNA on Trend Monitoring Issues. This report addressed a number of issues relevant to the development of procedures for the statistical analysis of temporal trend monitoring data. These included: (1) modifications to the guidelines for analysing trend monitoring data, (2) the inclusion of fat content to normalize contaminant concentrations in tissue, and (3) the pooling of samples prior to analysis. The results of the ACMP's consideration of each of these issues is contained in the following sections.

4.1.1 Modifications to the Guidelines for Analysing Trend Monitoring Data

Introduction and Overview

In the report of the 1985 meeting of the <u>ad hoc</u> Group of Statisticians (C.M.1985/E:10, Annex 4), guidelines were established for the analysis of temporal trends in the concentrations of contaminants in fish tissue. A corresponding statistical procedure was described in which a series of increasingly simpler models are applied sequentially. The use of a simpler model can be justified if this does not result in a significant increase in the value of the residual sum of squares. Initially, the models investigate the effect of biological variables on contaminant levels. If it can be established that these relationships are consistent throughout the data series, contaminant levels, suitably adjusted for these biological influences, can be used to investigate the nature of any trends which may exist in the levels (e.g., concentrations and burdens) of contaminants.

The procedure described allows for the inclusion of any number of biological variables as covariates in the models and could be extended to include 'factor' type variables, such as sex, in addition to more 'continuous' measured variables, such as length, weight, etc.

Preliminary application of the procedure

The ACMP noted that preliminary investigations of a number of data sets using the procedure described above gave rise to the following conclusions:

- the procedure provided a clear and logical approach to the analysis of the available trend monitoring data for contaminants in fish.
- the 'step-wise' nature of the analysis was valuable, both in defining a consistent treatment for the different data sets and in identifying the logic behind the analysis.

- whilst application of the models and conducting the statistical analysis using computers presented no serious problems, the procedure does include a number of assumptions about the nature of the data available.
- investigations of the data characteristics to ensure that they complied with the assumptions could not readily be computerized. Considerable human intervention could be required to ensure that the analysis maintained its statistical validity, for example, in subsequently determining which parameters (biological variables) should be retained as significant covariates in any single analysis and in correctly handling or rejecting data that did not fully comply with the assumptions.
- particular problems were identified in association with a routine application of the procedure to a wide range of different data sets, where detailed preliminary investigations of the data sets would not be practicable and where each data set contained a different range of inconsistencies and partial incompleteness.

In the light of these observations, it was recognized that the procedure required some modification and extension if it were to be suitable for routine application to a wide range of data sets with different characteristics, without excessive intervention by persons with statistical expertise, and at the same time retain its statistical validity. These modifications are incorporated in the modified procedure described in Annex 1.

Modifications to the Procedure

The modified procedure retains the basic models and logic previously described in C.M. 1985/E: 10, Annex 4.

In recognition of the need for a procedure that could be readily applied to a number of different data sets without recourse to excessive human intervention, provision was made to develop a system for computerised application of the procedure which would at the same time attempt to ensure that the statistical validity of the approach was not compromised.

A major revision to the procedure involved the selection of a 'key' biological variable for inclusion in the models as a single biological parameter, as opposed to the inclusion of a range of different parameters (because a number of the biological covariables, such as those associated with fish size, are frequently mutually correlated, e.g., length, weight, age). Thus, a single covariate will often be as effective as several acting together in defining the biological relationships. However, the possibility of including other biological variables at a later stage is not excluded, and the modified procedure includes a step to determine whether or not this is necessary.

For this procedure, which has only been used on data on trace metals thus far, length was selected as the most appropriate biological variable, as it is simple to measure and, even when considering these contaminants in liver tissue, length was found to be appropriate in comparison with, for example, liver weight,

as a single 'key' variable in the models. Length is also a convenient variable in relation to defining the sample characteristics, by means of the length-stratified sampling strategy. There may be circumstances in which other biological variables become more important than length, e.g., fat content of cod liver in relation to organochlorine contaminants.

This approach offers a number of advantages: (i) it is possible to develop computer programs which can conduct this analysis on any data set, irrespective of the range of different measurements it includes, (ii) length is unlikely to be missing as a component in any data set, and (iii) use of a single covariate considerably simplifies the procedures involved in ensuring that the data meet the assumptions implicit in the analysis.

A series of routines were built into the system to provide a graphical output which can be quickly checked to identify any potential major problems in the data.

Additional models are described which allow the new assumptions relating to the choice of the 'key' covariate 'length' to be checked and to indicate when it is necessary to carry out a more detailed analysis, involving the inclusion of additional covariates. There is thus a need to measure other biological variables, e.g., liver weight, fat content, so that they can be included in the application of the models when necessary.

The system automatically applies the sequence of models, carries out the appropriate comparisons and tests and produces a summary report of the analysis suitable for an assessment of the results (e.g., identifying the evidence of trends) and provides an indication of the additional steps which may be required by experienced statisticians to continue the analysis in cases where, for example, data assumptions are violated.

The ACMP agreed that this system should make it possible for the ICES Secretariat to conduct a valid analysis of the Cooperative ICES Monitoring Studies Programme data as defined within the procedure, for subsequent assessment by an expert group.

4.1.2 The Inclusion of Fat Content to Normalize Contaminant Concentrations in Tissue

Addressing the question of the importance of fat content as a parameter in trend monitoring studies, the ACMP noted that results have indicated that in some circumstances, particularly in the case of contaminants in those tissues where the fat content varies significantly, fat content is a significant parameter for inclusion in trend monitoring studies.

If measurement of the neutral lipid content is not possible, it may be possible to use 'weight of extracted solids' as an alternative, to describe fat content for trend purposes. This would considerably reduce the analytical burden associated with measurements of neutral lipid content; analysts could conduct routine weighing of extracted solids (either as part of their organochlorine measurements or as a separate determination).

Thus, it is recommended that the measurement of fat content (preferably as neutral lipid) be included in monitoring programmes, especially in the type of situation noted above.

The modified procedure for analysis of temporal trends of contaminants in fish tissue, described in Section 4.1.1, above, essentially incorporates the ability to include fat content into the trend analysis by treating it as an additional biological variable. Although the procedure is based on the use of length as the primary biological variable, it includes a built-in component which will indicate whether or not it is appropriate to include additional variables such as fat content in any particular analysis.

4.1.3 Pooling of Samples

The pooling of samples prior to analysis is of potential benefit in trend monitoring studies as a means of reducing the analytical commitments involved. The <u>ad hoc</u> Group of Statisticians assessed the implications of such pooling strategies on the quality of the statistical analysis. This was achieved by artificially constructing pooled samples from a set of Canadian lobster data and by subsequent comparison of the analysis of the pooled data with that of the original unpooled data.

As expected, the results of such a comparison show that there is a loss in data quality (loss of statistical efficiency, i.e., variance estimations increase) as a result of pooling, however, in general the results of the analysis are consistent and thus pooling is potentially applicable. The implications of a number of different pooling strategies were considered and some basic guidelines for acceptable pooling strategies were established.

The conclusions also indicated that data quality could be maintained in pooled samples by increasing the total number of individuals sampled. Whilst this would not significantly affect the advantages of pooling in terms of contaminant analyses, it was pointed out that some of these advantages would be offset by the increased sampling and sample preparation effort required. Similarly, the need to establish the biological relationships of the sampled community on the basis of individual analyses before devising a pooling strategy and then periodically to investigate these biological relationships was stressed.

It was agreed by ACMP that the study of the effects of pooling by artificially constructing pools from available data sets should be extended to fish, as pooling of fish represents the largest potential savings on analytical commitments. This study should be carried out within the ICES Secretariat.

Ultimately, the usefulness of pooling will represent a compromise between the gains in sampling and analytical commitment and losses in terms of data quality. It will depend upon the situation at individual laboratories and on the communities sampled. Further information, including the results of the pooling studies on fish, is required before establishing any firm guidelines.

4.1.4 Conclusions on Trend Monitoring of Contaminants in Fish

In concluding its discussion on the statistical analysis of temporal trends of contaminant concentrations in fish, the ACMP agreed that the method described in Section 4.1.1, above, and in Annex 1 represented a good method for trend analysis and approved its use in the analysis of data collected for trend monitoring in the Cooperative ICES Monitoring Studies Programme. Noting that there is also some information on the statistical consequences of pooling specimens prior to analysis, the ACMP decided to await the results of the study of the pooling of fish before providing advice on this topic.

4.1.5 Analysis of the Joint Monitoring Programme Data on Trends

ACMP was informed that the ICES Secretariat, in its capacity as data centre for the Oslo and Paris Commissions' Joint Monitoring Programme (JMP) data, has been requested to conduct statistical analyses of the JMP data collected for trend monitoring purposes in preparation for a meeting of the ad hoc Group on Monitoring of the Joint Monitoring Group (JMG) that will take place ICES headquarters in December 1986. The ACMP agreed that the ICES Secretariat should undertake statistical analyses of the JMP data on mercury, cadmium and, where adequate valid data are available, PCBs in plaice, flounder and cod using the statistical methods approved for the ICES monitoring programme. The ACMP felt that it would be extremely useful if several people from the ICES ad hoc Group of Statisticians Assisting WGMPNA on Trend Monitoring Issues could also attend this meeting and, accordingly, couraged the attendance of as many members of this Group as possible at the meeting in December.

4.2 Trend Monitoring in Sea Water and Sediments

In response to the request from the Oslo and Paris Commissions for advice on methods for the statistical analysis of temporal trends in data on contaminants in sea water and sediments, the ACMP noted that the Marine Chemistry Working Group (MCWG) had discussed this request in terms of the design of a programme for monitoring trends in contaminants in sea water. The ACMP noted that the MCWG was in the process of preparing a document on monitoring to determine temporal trends in trace metals in sea water, which should be available in 1987, and intended to prepare a similar document on nutrient measurements, in conjunction with the Hydrography Committee and the ICES Hydrographer, at the 1987 meeting. It was noted, however, that these documents would concern measurements in offshore waters only, as the often extremely variable conditions in nearshore waters and estuarine environments made measurements of temporal trends of substances in these waters very difficult if not impossible.

With regard to the measurement of temporal trends of contaminants in sediments, the ACMP noted that the Working Group on Marine Sediments in Relation to Pollution was considering this topic and intended to have a relevant paper available also in 1987.

The ACMP looked forward to discussing these documents at its 1987 mid-term meeting.

4.3 1985 ICES Baseline Studies of Contaminants in the North Atlantic

4.3.1 Baseline Study of Contaminants in Fish and Shellfish

With respect to the evaluation of the data from the Baseline Study of Contaminants in Fish and Shellfish, the ACMP discussed the progress made by the MCWG on the validation of contaminant data collected in this study. The ACMP noted that the MCWG had completed the first phase of the second part of the Seventh Intercalibration on Trace Metals in Biota (7/TM/BT, Part II) and that the second phase was nearing completion. Based on a preliminary examination of the results submitted to date, the MCWG had reported that there was evidence of improvement in the metals, but that problems with the analysis of analysis of all lead at levels less than 1 ppm still existed. In general, the 'baseline or monitoring' laboratories have performed well and those that had participated in Part I had produced much better in phase 1 of Part II than those that had not participated in Part I. The ACMP noted that a full report of the exercise will be available for evaluation by the MCWG at its 1987 meeting.

The ACMP noted that the MCWG had discussed the validation of organochlorine data to be collected during the Baseline Study. The MCWG had expressed concern over the problems associated with the distribution of a mussel homogenate that could have served as a reference material and provided some means of comparing measurements made by different laboratories. Given that this material had not been distributed, and in the absence of measurements on any other reference materials during this exercise, the ACMP agreed that it would be difficult to evaluate the comparability of baseline data on organochlorines. It accepted that it was too late to distribute reference samples for this programme since many of the baseline data would already have been produced. The ACMP stressed the need for such reference materials to be included in any future baseline exercise organised by ICES or other organizations.

The ACMP discussed the recommendation made by the Marine Chemistry Working Group that a sub-group of MCWG should meet immediately prior to the 1987 MCWG meeting to evaluate the results of the ICES Baseline Study of Contaminants in Fish and Shellfish. In view of the interest of the Oslo and Paris Commissions and the Helsinki Commission in this study, the ACMP agreed that the initial evaluation of the Baseline Study data should be done jointly by representatives of all interested parties. The ACMP noted that many of the potential participants in this meeting were common to both the MCWG and the ICES/SCOR Working Group on the Study of the Pollution of the Baltic and were also likely to act as representatives for the other organizations. The ACMP concurred with the recommendation of the Oslo and Paris Commissions that Dr J.E. Portmann should chair the group that will carry out

this evaluation. After this first evaluation, the report to ICES will be reviewed by the MCWG and the ICES/SCOR Working Group and finally by the ACMP.

4.3.2 <u>Baseline Study of Trace Metals in Coastal and Shelf Sea</u> Waters

The ACMP noted that the validation of trace metal data from this baseline study would be based on the results of measurements made at the reference stations listed in the 1985 ACMP report (Coop. Res. Rep. No. 135, p.37). As the time period for this study would extend through 1987, only a preliminary evaluation of the data received by late 1986 could be made during early 1987.

4.3.3 Biological Effects Studies Carried out in Connection with the Baseline Study

The ACMP agreed that plans for the evaluation of the results of biological effects studies carried out in association with the Baseline Study should be developed when the exact type and amount of these data are known.

4.4 Review of Guidelines for the Baltic Monitoring Programme of the Helsinki Commission

The ACMP was informed that the Helsinki Commission, through its Group of Experts on Monitoring (GEM), which met in March 1986 in Tallinn, had requested ICES to review the sections of the present Guidelines for the Baltic Monitoring Programme (BMP) for which ICES had originally provided advice. This advice, prepared in 1977 and 1978, consisted of guidelines for monitoring a number of contaminants in marine organisms in the the Baltic Sea, including recommended methods for sampling, sample preparation and analysis. ICES had also coordinated the development of a Biological Data Reporting Format and had, more recently, developed formats for reporting data on contaminants in several marine media.

The ACMP noted that GEM and the Scientific-Technological Committee (STC) of the Helsinki Commission wished to be able to review proposals for major changes to existing chapters or annexes of the BMP Guidelines and suggestions for new sections in September 1986. Drafts of the revised sections and new proposals should be available for final discussion in GEM in April 1987, with subsequent review by the STC in September 1987. The Helsinki Commission is scheduled to adopt the revised Guidelines in February 1988. The Secretariat of the Helsinki Commission has been made aware that the final advice from ICES will not be available until after the mid-term meeting of ACMP in June 1987.

The sections of the BMP Guidelines that ICES is responsible for reviewing include recommendations on the sampling of biota in offshore areas of the Baltic Sea, methods for preparing the samples prior to analysis, and analytical procedures for determining trace metals and certain chlorinated hydrocarbons in these biota. The ACMP noted that these guidelines were different in

certain respects from the guidelines for the Cooperative ICES Monitoring Studies Programme. ICES had also provided advice on appropriate species and methods to use in monitoring temporal trends in contaminant levels in coastal waters, which is not formally a part of the Baltic Monitoring Programme. In addition, ICES has been requested to review the section of the guidelines concerning the monitoring of contaminants in sea water, for which only the measurement of petroleum hydrocarbons is presently a mandatory part of the programme. The monitoring of contaminants in sediments is the subject of a separate request by the Helsinki Commission (cf. Section 3, above), but general information should be provided in June 1987 on whether ICES might recommend the inclusion of sediments in the BMP and, if so, how this monitoring should be conducted. Finally, ICES should amend the reporting formats for contaminants in organisms and sea water, if required.

It was noted that the ICES/SCOR Working Group on the Study of the Pollution of the Baltic had reviewed the relevant sections of the Guidelines at its 1986 meeting and had identified experts to coordinate the detailed review and amendment of existing sections of the Guidelines and to draft any new parts that may be proposed for addition to the Guidelines.

The ACMP stressed that the revised Guidelines should reflect, more than they currently do, the need to link monitoring in the open sea with investigations in the coastal areas in order to detect trends and to produce a basis for realistic input and mass balance estimations.

The ACMP was informed that first drafts of major revisions to the Guidelines will be prepared by early autumn 1986 for review and revision during the autumn and winter. Revised drafts will be further reviewed and presented at the 1987 ICES/SCOR Working Group meeting for consideration and ultimate transmission to the ACMP for final approval.

The ACMP felt that this procedure would be adequate to meet the request of the Helsinki Commission. Two members of ACMP were appointed to provide special assistance in this review procedure, both to facilitate the review and to ensure a further harmonization of the Baltic Monitoring Programme of the Helsinki Commission with the Joint Monitoring Programme of the Oslo and Paris Commissions. Such harmonization, especially in terms of the methods and reporting formats in use for contaminant studies in both areas, would be valuable because only in this way can a comparable (and, if necessary, exchangeable) data base be produced.

4.5 Review of Guidelines for Monitoring Sediments for the Joint Monitoring Programme

The ACMP was informed that the Joint Monitoring Group had requested ICES to prepare a simplified set of guidelines for the monitoring of contaminants in sediments, for use in the Joint Monitoring Programme, as the advice prepared earlier by ACMP (contained in Annex 2 to the 1983 ACMP Report and Annex 2 to the 1984 ACMP Report) had been considered too broad and complex for application in the JMP. In response to this request, the ACMP prepared a streamlined set of guidelines, based on the principles

of the previous documents, which are contained in Section 15, below. In preparing these guidelines, the ACMP wished to point out that more detailed information on monitoring contaminants in sediments will be presented in a future ACMP report on the basis of a full evaluation of the results of three intercalibration exercises on analyses of metals in sediments and the outcome of other relevant work conducted by the Working Group on Marine Sediments in Relation to Pollution.

4.6 Formats for Data on Contaminants in Marine Media

The ACMP took note of the most recent version of the Interim Reporting Format for Contaminants in Fish and Shellfish. No substantive changes had been made to the format itself, but the list of contaminant codes had been expanded to include the individual polychlorinated biphenyl congeners that have been agreed and several descriptions of data fields had been clarified. No further changes in the format were anticipated for the next few years. The ACMP noted that this format accommodated all the requirements of the Oslo and Paris Commissions as well as the Helsinki Commission.

A substantially revised version of the Interim Reporting Format for Contaminants in Sea Water was considered. This format had been revised to permit easier automatic handling of the data, reduce the amount of repetition of certain types of information and to permit the reporting of data on a greatly expanded list of contaminants and also nutrients. This revised format includes a new form, the Sea Water Sampling and Methods Form, on which codes describing the sampling and pretreatment methods and analytical techniques for each contaminant are reported. The Sea Master Form has been rearranged to meet the needs of the Helsinki Commission for closer correlation with the ICES Oceanographic Data Formats. The Sea Water Contaminant Data Form has been revised substantially to permit considerable flexibility in the parameters and contaminants on which data in sea water can be reported. Noting that the concentration units for contaminants and nutrients have been fixed in the list of codes for these substances, the ACMP observed that the units chosen may ultimately to be revised but this should await the outcome of the JMG intercalibration exercise on trace metals in estuarine waters.

It was noted that a reporting format for data on contaminants in sediments will be developed in the near future for review in late 1986 and early 1987. The ACMP looked forward to reviewing this format at its 1987 mid-term meeting.

The ACMP was informed of plans to develop a "blueprint" format for the reporting and exchange of data on oceanographic and environmental parameters. This "blueprint" format will be developed further under the Marine Data Management Working Group.

4.7 Monitoring Based on Studies of Benthic Communities

The ACMP noted that the Benthos Ecology Working Group was in the process of preparing draft guidelines for monitoring dumping grounds and coastal areas receiving pipeline discharges of wastes using studies of benthic communities. The ACMP looked forward to reviewing these guidelines at its 1987 mid-term meeting.

5 THE USE OF BIOLOGICAL EFFECTS TECHNIQUES IN POLLUTION MONITORING PROGRAMMES

5.1 The Potential Use of Pathology in Studies of the Effects of Contaminants

On the topic of the usefulness of pathology in studies of the effects of contaminants on fish and shellfish, the ACMP had available to it the report of a two-day Workshop on the Use of Pathology in Studies of the Effects of Contaminants (Dublin, April 1986) and relevant parts of the 1986 report of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO).

The question of the usefulness of pathology in biological effects studies had been discussed for several years and was considered in detail at a one-day joint meeting of the WGPDMO and the Study Group on Biological Effects Techniques referred to in the 1985 ACMP report.

The ACMP reviewed the available information on this subject. For the European part of the ICES area, the results of an increasing number of studies, investigating links between contamination and fish diseases, are available. However, the conclusions are weak, since, in many cases, the necessary associated chemical analyses were not carried out and relevant information on the possible population-level effects was not available.

This lack of data permits controversy between different hypotheses as to the effects of contaminants on fish health because it allows different interpretations of results, especially in view of the limited understanding of the natural prevalence of diseases in fish populations. Research scientists raise working hypotheses and will, in their work, seek information to test them, whereas advocates of nature conservation groups or industries responsible for waste disposal often will seek proof predominantly in a specific direction.

For the testing of cause-effect hypotheses, it is first necessary to understand normal fish disease incidence. Only then is it worthwhile to move to the next stage, which should be to assess whether or not the disease prevalences can be correlated to gradients in contaminant concentrations.

It also should be stressed that studies of fish diseases <u>versus</u> contamination levels are multifactorial. The understanding of the epidemiology of a fish disease requires not only studies in pathology and contamination, but also in ichthyology, fisheries biology, hydrography, population dynamics of food stocks, etc. Because of the major influence of natural factors on them, some diseases, e.g., infectious diseases with high mortalities, were considered not to be useful for pollution monitoring studies.

It should be recognized, however, that a pathological condition may be the end result of a long sequence of events within tissues and cells. Hence, such a condition lacks sensitivity and is also likely to lack specificity because of the limited ways in which tissues can respond. Such effects can often be reversible once the causative agent is removed, because of the power of regener-

ation of fish tissues. Moreover, as a consequence of the pathogenicity, pathological conditions can be difficult to measure because of differential mortality rates in fish populations.

No pathonomic lesions specifically associated with contaminants have been identified in the North Sea and, consequently, pathology will probably be most useful as an indirect index. It has been shown that lowered environmental quality results in increased disease prevalence in laboratory studies, but because of the strong influence of natural factors on disease levels and the lack of knowledge of the incidence of fish disease, it has not yet been possible to clearly establish links between contamination and disease in wild populations. Absolute levels of fish diseases may be of less significance than trends over a period of time.

A firm data base is required for pathology-pollution studies with particular emphasis on principles of epidemiology, mortality effects and the relationship between prevalence and incidence of infections. The accurate standardization of data from different sources is essential. This has yet to be achieved.

Resources, particularly cost and manpower availability, impose severe constraints on disease study programmes and, although methods employing commercial catches, joint cruises, etc., have been attempted, the preferred approach has been to use cruises specifically designed for fish disease studies and staffed by specialists. There can be advantages, e.g., in terms of reduced slaughter of fish, in using fish survey cruises for fish disease work, provided that such cruises are adequately staffed by fish disease experts. Because of the influence of natural phenomena on fish disease levels and the impracticality of performing frequent extensive disease study cruises, a system is preferred in which the effects of natural variations are reduced as far as possible by standardizing sampling in terms of season, fish species, area, disease studied, etc. Similarly, because disease often occurs at low prevalence levels, extensive sampling of a few conditions in large numbers of fish is preferred to intensive studies of a few fish. Appropriate diseases for study are those easily and accurately diagnosed and which preferably have a known aetiology with low mortality and information available on their natural variation. Knowledge of fish stocks is essential to permit the maintenance of sampling homogeneity in wild fish; is essential to alternatively, relatively static groups or species of fish should be used.

From national reports, it is apparent that sampling should be repeated over a long time scale if seasonal and inter-annual fluctuations, which have been recorded, are not to unduly influence the results. This concept has been used in Dutch surveys according to the following criteria: (a) continuous recording should be carried out for a long period (at least five years), (b) recordings must be selected for high and low condition seasons (for Atlantic waters this means twice a year, early spring and autumn), (c) recordings must be made in a wide area, covering several populations and/or environmental situations, (d) data are to be plotted per disease and per fish species in a geographical grid system (e.g., ICES statistical rectangles), (e) because of the existence of natural variations of prevalences, a

simple wide-scale classification must be used, and (f) a choice of internal and external macroscopically visible diseases must be made to permit standard handling.

The usefulness of experimental work has been presented in several of the national reports. Evidence for Lymphocystis regression in experimentally infected dab was found after 6-7 months. A neoplastic condition in the common cockle could be transmitted by injection of neoplastic cells, but the condition failed to develop within six months of cohabitation between healthy and diseased animals. In other cases, experimental results were negative. Even though virus particles have been found in all samples of hyperplasia and papilloma examined, experiments to transmit hyperplasia/papilloma by cohabitation, rubbing or scarification were negative after three months.

The results of surveys which included disease work were reported from eight countries, five of which concluded by finding no evidence for relating the diseases investigated to contamination, two did not mention any relationship, and only one stated that a possible relationship could be present.

Fin erosion in perch in the Baltic Sea, however, was clearly shown to be associated with the effluent from pulp mills. In addition to fin erosion, Finnish workers reported abnormal liver conditions in the perch. Fin erosion was experimentally induced by holding perch in cages exposed to the effluent from a pulp mill. On the other hand, an eye disease in Baltic herring that was previously thought to be associated with discharges of wastes from titanium dioxide production has now been shown to be caused by an experimental artifact, namely, UV irradiation of the fish cages caused by sunlight.

New approaches in disease studies related to biological effects monitoring, such as immunological studies, were also discussed. The use of lysosomal activity as an indication of immunodepression in dab was reported, and the use of changes in the prevalence of ectoparasites on certain fish was suggested. Liver histopathology may also be a useful parameter.

The ACMP noted that fish should not necessarily be the only species used for exploring indications of biological effects. Tests that utilize other indicator species should also be considered; examples could be physiological studies on invertebrates, scope for growth in mussels, hydroid tests, and studies of top predators including mammals and birds.

The major criteria for choosing an animal for study should be its availability and the types of phenomena or abnormalities associated with it, coupled with a basic understanding of its biology and movements. Sessile or limited range species were considered preferable (e.g., invertebrates, flounder, etc.). It was not regarded as necessary for all scientists to use the same species, but it was considered essential that the approaches and methodology be standardized to permit comparisons of data.

Noting the conclusions of the Workshop on the Use of Pathology in Studies of the Effects of Contaminants, the ACMP drew attention to the following conclusions:

- 1) There is a growing recognition that the problem of linking pollution with disease is much more complex than hitherto believed.
- 2) There is a growing appreciation that even if the link is proven, disease events (abnormalities) cannot always be used as direct indices of pollution, but rather as the basis for general statements on the quality of the environment.
- 3) There is a primary need for extensive data bases on disease prevalences in wild fish species, i.e., readily observable conditions measured annually (two seasons) over a 5-year period and plotted for specific and confined areas, e.g., the ICES statistical grid.
- 4) Specific pollution-related studies should be encouraged in contaminated areas with suitable indicator species for the area(s) concerned.
- 5) The interpretation should be based on stocks rather than solely on geographical areas.
- Internationally agreed and calibrated standard methods should be applied.
- 7) Work should be concentrated on juveniles and adults, since studies on larval forms in general are unlikely to yield useful results.
- 8) Certain results should be followed up in experimental studies.
- Dedicated cruises for disease studies using trained observers are best, followed by combined cruises also using trained observers.

The ACMP noted that, with one exception, all participants in the Workshop were drawn from the disease field. It must be emphasized that if fish studies are to be designed to gauge the link between pollution and disease, then pollution and population experts as well as pathologists must be involved in the planning process and in any subsequent evaluations and interpretations.

The ACMP particularly stressed the need to obtain statistically sound baseline data on disease incidence in the ICES area, recalling that it had made a similar recommendation previously.

5.2 IOC/GEEP Workshop on Biological Effects Techniques

The ACMP was informed about the progress in the plans for the Workshop on Biological Effects Techniques organized by the IOC Group of Experts on the Effects of Pollutants (GEEP), which was intended to be a practical workshop to evaluate a number of biological effects techniques. The workshop was to be held in Oslo for three weeks in August 1986. Attendance at the workshop was by invitation, which aimed at a balance between scientists involved in the various levels of biological organisation (biochemists, cytologists, pathologists, physiologists and population and com-

munity biologists). Several statisticians had also been invited to attend to provide advice on sampling, analysis and modelling. ICES had also been invited to send one or more participants to this workshop. ICES has responded positively to this invitation, and will contribute an expert on molluscan pathology.

The ACMP, in noting the details of the proposed coverage of the workshop, commented that it did not include all the procedures it might have hoped would be tested. Nevertheless, the ACMP welcomed the activity as a valuable start, realized that fully comprehensive coverage was impracticable and noted with satisfaction that ICES was represented at the Workshop by Dr M Auffret and one of the members of ACMP attended the GEEP meeting immediately following the Workshop. It was further agreed that the ACMP should follow closely the outcome of the workshop with a view to ensuring continued involvement by ICES in this field of study.

5.3 Utility of Bioassays using Marine Fish Eggs in Effects Monitoring Studies and the Need for Standardisation

Recently developed strategies for incubation trials using marine fish eggs were presented and discussed. Most of the published information on bioassays is related to the effects of one or a few substances on various ontogenetic stages of fish embryos in terms of concentration and exposure time. A number of sublethal responses have been identified which have ecological significance.

However, it has been questioned to what extent the conventional toxicity tests performed in laboratories are suitable to assess the likely impact of environmental stressors. In an attempt to overcome this problem, the incubation trials concentrated on eggs derived from sea caught females of several stocks and species, assuming that if the exposure of the parental generation to environmental stress is significant it would be possible to demonstrate this at least for those substances which are accumulated in the gonads and passed on to the F_-generation (i.e., PCBs, DDT and degradation products). A relationship between gonad burden and larval viability could repeatedly be demonstrated using sublethal criteria previously identified in conventional exposure tests. However, the data show a large variability, part of which could be attributed to insufficient standardisation of the test procedures.

The ACMP noted that this urgent need for further standardisation and intercalibration of bioassays has been one major reason why the field applicability of biological effects techniques has so far provided unsatisfactory results. Minimizing the experimental background variability through standardisation would certainly help to determine the inherent variability of the test species and improve the data quality when employing bioassays to evaluate the impact of gonad burden on reproductive success in fish populations. The ACMP encouraged the conduct of further work on this topic.

6 FISH DISEASE ISSUES

On the question of fish diseases, the ACMP had available to it the draft report of the 1986 meeting of the Working Group on Pathology and Diseases of Marine Organisms (WGPDMO). This meeting was preceded by a two-day Workshop on the Use of Pathology in Studies of the Effects of Contaminants, referred to in Section 5.1, above.

The national reports on disease studies cover disease events both in wild populations and in mariculture stocks. From the reports, it is evident that in many countries the main effort on disease work is associated with mariculture. The possible contaminant-related diseases are discussed under Section 5.1.

Reports from three countries on impacts of disease agents imported both with live and dead fish have raised considerable concern. Of particular concern is the nematode, previously only encountered in Australian eel, that is now spreading in the European eel populations. The latter seem to have no resistance to it and this could cause a decline in the stocks of European eel.

Another item from the reports worth stressing concerns the results of using vaccines against vibriosis in salmonid farming. In Finland, for example, vibriosis is no longer a problem in the farming of rainbow trout in brackish water, and the amount of antibiotics used in one region has been reduced to 1% of the amount used in 1983, even though the production of fish has doubled. Vibriosis vaccines were also reported to be very efficient in salmonid farming on the east coast of Canada, in contrast to the situation on the west coast, where vibriosis is still an important problem despite vaccination. Avoiding vibriosis in mariculture could also be of importance for wild fish species, as disease outbreaks usually lead to an increase in the virulence of the bacterial strains, and vibriosis is known to occur in a large number of wild fish species. Infectious pancreas necrosis (IPN), another infection known from several fish species, has recently been found in farmed turbot, provoking some mortalities.

In the series of diagnostic leaflets on diseases of marine organisms, ten new leaflets have been published, bringing the total number published to 30. Another ten leaflets are ready for printing and about 20 new titles are under preparation. The report from the Anton Dohrn workshop in 1984, entitled "Methodology of Fish Disease Surveys", has recently been published in the Cooperative Research Report series.

The ACMP noted that mariculture is rapidly developing in many ICES countries and has necessitated new legislation both in connection with mariculture operations and particularly in connection with diseases. The ACMP accordingly encouraged the plans of the WGPDMO to produce a document containing relevant legislation from all member countries in the original language, followed by an appraisal in English.

The possible use of fish parasites in relation to monitoring the effects of contaminants was discussed. At one stage or another in their life cycles, parasites might be more sensitive to contaminants than their hosts and there seems to be sufficient features, such as known appearances and disappearances of particular parasites from fish stocks, modifications to reproductive capacities, etc., to warrant further research in this field.

It was noted that, in many ways, the impact of parasite infections on fish is a neglected field of research. The present knowledge on host-parasite interactions was reviewed and it was agreed that aspects of defense mechanisms, therapy, specificity of the parasite and the role of genetics and phylogeny need further study.

One important issue is the extended use of antibiotics and chemotherapeutics in mariculture. Fish cannot be treated at the individual level, as is practised in warm-blooded animals. The therapeutics have to be administered through the feed or applied through a bath. One of the first disease symptoms in fish culture is that the fish stop eating, indicating that administering medication through the feed inevitably leads to losses to the aquatic environment. In the case of both types of therapy, the solutions used should be dispersed in more open waters for rapid dilution, but this is far too often neglected.

Apparently there is little information on the main problems associated with the use of antibiotics in mariculture. The problems needing further research are:

- The effects of the different drugs on the environment in general,
- The development of drug resistance in bacteria on the farm and in the local environment,
- The transfer of drug resistance to aquatic bacteria of human health significance,
- The accumulation of drugs in sediments under fish farms and the effect on the normal bacterial flora in these sediments;
- The presence of drug residues in farmed fish and local wild fish on the market.

It was noted that the problems associated with medication in aquaculture will be one of the main issues to be considered at the 1987 WGPDMO meeting.

The ACMP took note of this information with interest and supported the work of the WGPDMO, particularly concerning the use of antibiotics in mariculture operations and the environmental effects of these antibiotics. The ACMP agreed that this is an important issue and urged the WGPDMO to provide an explanation of it for discussion by a multidisciplinary audience so that attention can be given to questions relating to, e.g., the assimilative capacity of an area for antibiotics.

7 CONTAMINANT LEVELS AND DISEASES IN MARINE MAMMALS

7.1 Report of the Working Group on Baltic Seals

The 1985 report of the Working Group on Baltic Seals was presented and discussed. The report contains an assessment of Baltic seal populations and trends in these populations. It was concluded that this was a concise and objective evaluation of the subject and that the substance of the report should be included in the record of ACMP's deliberations. The report, in slightly edited form, is therefore presented below in order to provide background to the conclusions drawn.

The Working Group on Baltic Seals had been requested to:

- 1) Consider what changes are likely in the size of the seal populations in the Baltic over the next years.
- Evaluate evidence on the connection between high levels of PCBs, DDT and other pollutants in seals and their reproductive success.
- 3) Consider the possible effects of changes in pollutants in the Baltic on the conclusions under (1).
- 4) Advise on what steps should be taken to preserve the existence of all Baltic seal populations and to improve their habitat.

7.1.1 Current Size of Baltic Seal Stocks

7.1.1.1 Levels of hunting

Approximately 100-150 ringed seals have been shot in the Finnish Gulf of Bothnia each year, a decline from the "few hundred" reported to the previous meeting of the Group in 1983. A few dozen ringed seals are still taken in the Gulf of Finland. Grey seals are completely protected in Finland and the USSR.

All seals are protected from hunting in Sweden, but fishermen are allowed to shoot seals in the immediate vicinity of their nets if the seals appear likely to cause damage. There are no estimates of the numbers of seals killed in this way. In Denmark, all seals are protected. However, fishermen can apply for licenses to protect their nets and approximately 30 harbour seals are shot under these licenses every year.

7.1.1.2 Current status of ringed seals

An aerial survey of ringed seals in the Bothnian Bay had been conducted by Finland in the spring of 1984. Approximately 2000 seals were estimated to be on the ice (Helle, in press); this was substantially less than the estimate of 3000 seals from a survey conducted in 1975. However, without a value for the standard deviation of these estimates and without estimates of day-to-day and year-to-year variations in the proportion of the population

resting on the ice at any one time, it was not possible to conclude whether there had been a real decline in the ringed seal population in this area.

It was noted that Tormosov and Esipenko (in press) had estimated a population of 3700-4000 ringed seals in the Gulf of Finland. Although this was higher than the figure of 3000 previously made available, it was noted that the more recent figure appears to be based on the results of the same survey (conducted in 1982).

7.1.1.3 Current status of grey seals

Studies of the size of the Swedish grey seal population have been continued using local observers who regularly count, from the shore or from boats, the numbers of seals hauled out in their Although such counts will almost certainly underestimate the number of seals in a particular area, they are more effective than aerial surveys and provide a good index of distribution and abundance. In all areas there are wide fluctuations in the number of seals counted; however, in the area south of Aland the largest number of seals is seen in May-June. North of Aland there is peak, but there is some evidence of an increase in numbers clear in September. This coincides with the opinion of old seal hunters there is a northward migration of grey seals in the summer. that In the period 1975-1979, between 500 and 950 seals were counted each year in the area south of Aland, and 130-270 in the northern area. Since 1980, 500-800 animals have been counted in the south and 130-330 in the north.

figures provide no evidence of a change in the size of the Swedish grey seal population. However, there does appear to have been a northerly shift in the distribution. Grey seals are no longer seen hauled out at localities in the south which were used regularly in the 1960s, whereas the number hauled out at some northern sites has increased substantially. However, figures must be interpreted with caution because some new seal sanctuaries have been established recently in northern Sweden; as a result, the seals in these areas are less shy and are more easily counted. They may also spend more time hauled out and the apparent increase in the north may be simply due to a change in behaviour. The combined counts suggest that there are about 1150 animals of adult size in Sweden. This figure would normally be considered as a minimum estimate, but it is possible that some animals have been counted twice - first in the south and later in the north.

It was noted that two pups had been born to the small group of grey seals kept in the grounds of a nuclear power station near Uppsala. These pups had now been released in the southern Baltic.

In Finland, there is a general impression that the number of grey seals seen in summer has increased. However, this could be due to a minor change in distribution rather than a real increase. Up to 500 seals have been counted in the Åland area, and over 150 on the Finnish side of the Gulf of Finland. About half of the Åland population is probably also included in the Swedish counts.

The USSR population of grey seals in the Gulf of Finland and the Gulf of Riga is estimated to be 200-300 animals (Tormosov and Esipenko, in press). Some of these animals were probably also included in the Swedish counts.

The results of these surveys together suggest that the total population of grey seals in the Baltic is approximately 2000. Because of the uncertainties surrounding the individual survey results, this value is not significantly higher than the estimate of 1500 quoted in the previous report of this Working Group.

7.1.1.4 Current status of the harbour seal

Since 1975 there have been increases in the numbers of harbour seals hauled out in the southern part of the Swedish Baltic proper, particularly in the Øland and the Øresund areas. In these areas about 20% of the animals are pups, which suggests that the reproductive rate in this population is now at a normal level for harbour seals. However, the harbour seal is still rare in the Baltic, with a total population of around 200 animals. The establishment of seal sanctuaries in Swedish waters during the period covered by these results may have influenced the behaviour of the seals and made them easier to count.

On the Swedish west coast (outside the Baltic Sea), the population in the north has stabilized, but it is still increasing in the south. About 2500 animals are found on the west coast (Härkönen, 1985).

The harbour seal population, as indicated by direct counts and complaints from fishermen, has increased throughout Denmark. Animals are now being seen in areas, such as the southern Baltic, where they had not been seen for many years.

7.1.2 Recent Changes in Population Parameters

7.1.2.1 Fecundity

7.1.2.1.1 Evidence of recent changes in fecundity

Data on 36 female ringed seals shot in the Bothnian Bay during 1980-1985 showed that 19 % of these animals had uterine occlusions. This was substantially less than the percentage of occlusions found in previous samples, but there were differences in the age structures of the two samples. However, when a correction for this was made, the difference in the percentage of animals with occlusions was still statistically significant. However, the proportion of animals with occlusions appeared to have declined by a similar amount in all the age classes in the 1980-1984 This was unexpected because the development of occlusamples. sions is believed to be irreversible and, therefore, the proportion of animals with occlusions in the older age classes should have remained constant. It was possible that some of the observed difference was due to differential sampling of affected animals in the two periods. In this context, it is relevant that 24% of the 1980-1984 samples were animals less than four years old, whereas only 2% of the animals shot in 1977-1979 were this young. This might indicate an increase in fecundity in the population.

Autopsies carried out on grey and ringed seals found dead along the Swedish coast indicated that very few of these animals had evidence of normal pregnancies (Bergman and Olsson, 1985). Sample sizes were too small to indicate any trends, but observations of relatively young animals that are chronically sick or have recently developed uterine occlusions indicate that problems are still occurring.

7.1.2.1.2 Possible effects of environmental contaminants

Baltic grey and ringed seals appear to be suffering from a disease syndrome. Impairment of reproduction is only one symptom of this, but others are: regional loss of hair and hyperkeratosis; ulceration and perforation of the gut wall at sites of hookworm infestation; renal glomerulopathy; and adrenocortical hyperplasia (Bergman and Olsson, 1985); severe loss of teeth, malformation of the jaw, and loss or deformation of claws and digits (Olsson, pers.comm.). Female grey seals found in Sweden (Bergman and Olsson, 1985) and Finland (Stenman, pers.comm.) also suffer from uterine leiomyomas (benign tumours of the myometrium).

These symptoms are not known to occur in this combination and with such severity in other seal populations. Consequently, it is important to search for evidence of similar disease syndromes in seal populations from other regions than the Baltic, including those in both relatively pristine and contaminated areas.

The Swedish findings suggest that there has been disruption of both the endocrine and immune systems of Baltic seals. Such symptoms are not characteristic of the effects of heavy metals; nor are the levels of heavy metals in the Baltic Sea particularly However, organochlorine compounds in general, and PCBs in high. particular, are known to have effects of this kind on a number of mammalian species. Recent studies on captive harbour seals (Reijnders, pers.comm.), fed either on "clean" mackerel from the North Atlantic or on "contaminated" flatfish from the Wadden Sea (which have higher levels of organochlorines), have shown that significantly fewer pups were born to the group fed on "contaminated" fish. The effect was not on ovulation, but appeared to at the time of embryonic implantation. Circulating levels occur of oestradiol in the non-pregnant group were lower than in pregnant animals. Further tests have to be carried out to see if the levels in the non-pregnant "clean" group were different from those in the "contaminated" group.

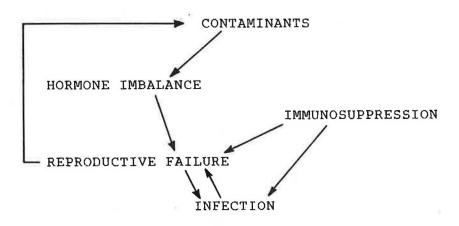
Although seals from the Baltic Sea have higher average levels of organochlorines in their blubber than seals found anywhere else except the Wadden Sea, individual animals with similar levels have been found in the UK. None of these animals, nor those from the Wadden Sea, have shown the gross pathological anomalies observed in the Baltic animals, although the reproductive rate of the Wadden Sea animals has been reduced. However, levels of

organochlorines in fish from the Baltic have been substantially higher than elsewhere. It should be noted that the daily or seasonal intake of organochlorines could well be more critical to an animal's health than the residues accumulated in its tissues.

The usefulness of measuring residue levels in depot tissue, particularly blubber, was discussed. Data from harbour porpoises captured incidentally by Danish fisheries (Clausen and Anderson, 1985) indicated that organochlorine levels in the blubber of young animals increase until puberty; they then remain approximately constant in females but continue to increase in males. This is presumably because breeding females pass some of their young. Similar changes are seen in contaminant burden to Danish harbour seals, although the results are more variable and sample sizes much smaller. These results imply that nonreproducing female seals, such as those with uterine occlusions, also accumulate organochlorines and will therefore have higher levels than animals which are reproducing normally. blubber of adult animals are likely to be highly the variable and difficult to interpret. Levels in animals found dead are also highly variable. The most useful group to study may therefore be animals up to three years old which drown in nets.

Most intercalibration exercises on the measurement of organochlorine residues conducted within ICES have used material derived from fish. Because of its high fat content, seal blubber poses particular problems for the extraction and analysis of residues. A small intercalibration exercise using seal blubber would resolve this anomaly.

It seems most likely that organochlorine contamination is, in some way, responsible for the disease syndrome seen in Baltic seals. PCBs appear to be the most likely cause, but they might be acting synergistically with DDT and effects due to toxaphenes or dioxins cannot be ruled out. However, it is possible that infections and stress due to physical disturbances (see Section 7.1.1.3) could also be involved in the disease complex. The figure below illustrates the processes that might be involved.



7.1.2.1.3 Possible effects of disturbance

There have been suggestions that noise created by icebreakers might interfere directly with reproduction in ringed and grey seals by disrupting mating behaviour. However, any such effect

must be relatively minor because the increase in icebreaker traffic throughout the winter in the Bothnian Bay did not occur until the 1970s, and reproductive failure had already been observed by this date. In addition, a decline in seal numbers has occurred in areas where there is virtually no icebreaker traffic. Nevertheless, the effect of recent increases in icebreaker traffic needs to be investigated.

7.1.2.2 Survival

Three possible sources of additional juvenile mortality for Baltic seals have been identified: (i) desertion of pups due to disturbance, (ii) accidental entanglement in fishing gear, and (iii) the destruction of ringed seal lairs by icebreakers.

With regard to (i), no estimates of desertion rate, and its relation to disturbance, were available. However, it was noted that the creation of Danish seal sanctuaries, free from disturbance during the pupping season, had contributed to the recent increase in the Danish harbour seal population. Concerning (ii), 20 out of 100 grey seals tagged as pups in the Baltic had been recovered drowned in fishing nets within six months of tagging (Almkvist et al., 1980). This was a high rate of incidental mortality; by contrast, less than two percent of grey seals tagged in the UK were recovered in fishing gear (McConnell et al., 1984). Finally, as to (iii), in the light of observations referred to in paragraph 7.1.2.1.3, above, this may be regarded as a minor effect.

7.1.3 Predicted Changes in the Size of Baltic Seal Populations

7.1.3.1 Trends in contaminant levels

Sweden has been monitoring the levels of organochlorines in young herring collected in the same area each year since 1968. there has been a decline in PCB and DDT levels in the Bothnian Bay and the Baltic proper, but levels of PCBs in the Bothnian Sea have not declined (Olsson and Reutergardh, 1982). A decreasing trend is also seen in DDT and PCB levels in the eggs (Uria aalge) from the Baltic proper. A review of of quillemots data from different sources seems to show that the levels of PCBs in the blubber of seals from the Bothnian Bay has also varied in the same way. However, the observations of chronically sick animals and seals with recently developed occlusions indicate that current levels of contaminants may be affecting the seal populations.

7.1.3.2 <u>Trends in seal numbers</u>

No firm prediction about future changes in seal numbers can be made. However, the deliberate killing of grey and ringed seals by fishermen in Sweden and of ringed seals by hunters in Finland was probably a significant mortality factor. A halt to this killing would improve the chances for recovery of the seal populations in these areas. Any recovery of these populations would be slow be-

cause of the high proportion of sterile animals. At present, the distribution of haul out sites and sanctuaries used by grey seals in Sweden appears to be closely linked with the distribution of cod. If, as seems possible, there are changes in the abundance of cod stocks in the future, the distribution of the seals may also change and an early relocation of the sanctuaries would be necessary to maintain protection.

7.1.4 Future Research Requirements

The following research programmes are considered to have high priority:

A continuation of regular national surveys, particularly those for grey seals. Further attempts at international coordination would be valuable.

Annual aerial surveys for ringed seals in the Bothnian Bay over a five- to ten-year period to provide an indication of the variability in the number of animals on the ice.

More experimental work on the effects of contaminants on physiological processes in seals and related species. A search for evidence of the occurrence of any specific effects identified by these experiments in wild populations would also be valuable.

A general pathological survey to investigate the level of incidence of the symptoms of the disease syndrome observed in Baltic seals in other seal populations, particularly those in areas with relatively low environmental contaminant levels. Such a survey should include an investigation of the potential role of infections in the development of the symptoms.

Work to identify the presence of other toxic organic compounds in tissues of seals or their prey from the Baltic Sea.

Investigations of the effects of sampling procedures on estimates of contaminant levels in seals.

Studies of the effects of physical disturbance on the maternal and reproductive behaviour of seals.

7.1.5 Conclusions of the ACMP on the Report of the Working Group on Baltic Seals

The ACMP concurred with main the conclusions of this report, namely, that

1) ICES should coordinate an intercomparison of techniques for the determination of organochlorines in seal blubber. The ACMP noted that this recommendation had been considered by the Marine Chemistry Working Group. The MCWG had expressed the view that the conduct of such an intercalibration, based on the methods presently applied to organochlorine measurements in marine mammals, would not be as valuable as adopting a step-wise approach to methodological improvements. For this reason, the ACMP supported the MCWG proposal to conduct a

critical review of the methodology currently used for marine mammal tissue analyses, to provide information on methodological improvements that can be achieved on the basis of recent research using standard reference materials, and to advocate the development of a high-fat reference material for polychlorinated biphenyls. Notwithstanding, the ACMP regards the early conduct of an intercomparison of procedures for the determination of organochlorines in marine mammal tissues to be essential. It further noted that the number of laboratories reporting data from such measurements is relatively small and this will simplify the conduct of such an exercise.

- 2) National laboratories having access to live or dead seals should be encouraged to examine these samples for the occurrence of disease symptoms similar to those observed previously in Baltic seals. These symptoms are described in Section 7.1.2.1.2, above, and in Bergman and Olsson, 1985. These examinations should be conducted in collaboration with mammalian pathologists.
- 3) It would be advisable, in order to allow time for Baltic seal populations to recover, for all deliberate killing of seals in the Baltic to be discontinued.
- 4) If the killing of Baltic seals continues to be permitted, the practice should be licensed to ensure that such kills are justified and adequate records of the effects of the practice are maintained.
- 5) Existing seal sanctuaries in Sweden, Denmark and Finland should be maintained and recently proposed sanctuaries should be established.
- 6) New seal sanctuaries should be established in the Baltic as the distribution of seals changes in response to alterations in their food supply.

Finally, the ACMP concurred with the view, expressed by the Baltic Seal Working Group, that further evaluations of seal populations should be deferred until additional data on the incidence of disease syndromes in seals from outside the Baltic Sea area become available and after the evaluation of the comparability of data on the analyses of marine mammal tissues has been completed. It was noted that a joint ICES/IOC review of the influence of organochlorines on marine mammals, with particular attention to hormonal and immune defense system responses, was being undertaken and the results of this review should be awaited before reconvening the Baltic Seal Working Group.

The ACMP acknowledged and expressed its appreciation for the excellent work of the authors of the Baltic Seal Working Group Report comprising, J Harwood (Chairman), I L Byrd, B Clausen, E Helle, M Olsson, J Ploebz and P Reijnders.

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7.2 ICES/IOC Review of Contaminants in Marine Mammals and Their Effects

Noting that UNEP and FAO, in the Action Plan for the Conservation, Management and Utilization of Marine Mammals, had requested ICES to cooperate with IOC in the preparation of a review of information on the occurrence of contaminants in the tissues of marine mammals, their effects on the mammals and on deaths or injuries to marine mammals presumed to be caused by contaminants, the ACMP reviewed progress in the implementation of this activity. The ACMP was informed that a group had been constituted consisting of Dr J Harwood (Convener), Dr M Olsson and Dr P Reijnders to consider the biological aspects of this issue. Dr R Addison will participate in this work on behalf of IOC.

In addition, on the initiative of the MCWG, a review of the data available on organic contaminants in marine mammals will be conducted by Dr A Knap and Dr L Reutergårdh during the autumn of 1986 to validate these data and indicate which results should be included in the overall review of contaminant concentrations. The MCWG has also proposed that a special meeting be held in the winter of 1987 to bring together chemists and biologists concerned with the study of contaminants in marine mammals in order to develop an agreed approach to such studies.

The ACMP agreed to the formation of this group to prepare a review on contaminants in marine mammals. The ACMP also wished to stress the urgent need for an assessment of the reliability of organochlorine data from mammalian populations reported to be suffering reproductive failure and increased incidences of lesions. The levels of organochlorines in marine mammals reported from other industrialized areas of the world, having obviously healthy populations, are also important to consider in this review. The influence of sex, age, season and health conditions on organochlorine burdens in seals should be considered.

8 EXCEPTIONAL ALGAL BLOOMS

Based on the report of the 1984 ICES Special Meeting on Causes, Dynamics and Effects of Exceptional Marine Blooms and Related Events, the ACMP recognized in its 1985 report the need for increased basic research on the biology and life cycles of blooming algal species and on the role of organic factors and inorganic nutrients in primary production. Reviewing the 1985 report of the Working Group on Exceptional Algal Blooms (WGEAB), the ACMP noted that the WGEAB also recommends further research into the biology and life histories of bloom organisms, specifically in order to progress further towards circumventing the deleterious effects of blooms on mariculture and shellfisheries.

The ACMP is of the opinion that the WGEAB, in its 1985 report, satisfied its terms of reference to a large extent by taking a pragmatic approach to the problem of exceptional algal blooms and recommending procedures to obtain necessary information to give management advice on how to overcome bloom effects on mariculture.

The ACMP recognized that there also is a pressing need for a better understanding about (1) how environmental factors interact to create situations in which blooms may occur, (2) which environmental factors can trigger specific exceptional blooms under such conditions, (3) which environmental factors contribute to sustaining bloom conditions, and (4) which factors make fish more susceptible to the influence of bloom species.

Knowledge about the physiology and life cycles of bloom organisms and their interaction with environmental factors is essential as a background both for the development of pragmatic approaches to overcoming the effects of blooms on mariculture and for methods to predict (and possibly prevent) bloom incidents.

Accordingly, the ACMP suggested the formation of a Study Group to continue the work initiated by the Special Meeting on Exceptional Algal Blooms. Proposed terms of reference for this Study Group would be to suggest research directed towards increasing the knowledge of the role of physical, chemical and biological factors in creating conditions which initiate and sustain the development of specific blooms. Since specific answers to these terms of reference may depend on the nature of specific bloom organisms, the ACMP considered it essential that there be increased research on the physiology and life cycles of species causing exceptional blooms.

In concluding its discussion of this topic, the ACMP noted the relevance of studies of primary production in general and the importance of obtaining intercomparable data on primary production indices in the ICES area. The ACMP noted that ICES has on several occasions supported the conduct of an intercalibration workshop on the measurement of primary production, but none has yet been held. The ACMP encouraged the conduct of such a workshop as soon as possible.

9 ANALYSIS OF TOXINS

At its 1985 meeting, the ACMP had taken note of the fact that the methods used for assessing concentrations of toxins, derived from blooms of toxic algae and present in shellfish, all use animal assays. It had, however, recognised that there had been some attempts in recent years to develop alternative methods using chemical analysis procedures, and had requested two of its members to report on the situation at the 1986 meeting.

Reports on the development of methods for the analysis of PSP (paralytic shellfish poisoning) and DSP (diarrhetic shellfish poisoning) were available to the meeting and were briefly discussed. Although it was apparent that considerable progress had been made, neither of these procedures was at the stage where it could be widely applied routinely.

Paralytic Shellfish Poisoning (PSP)

The toxin involved is known to comprise several components, most of which are present on every occasion but in varying proportions depending on the particular circumstances. The individual constituents have been isolated and their toxicity in terms of their effect on mice (the normal bioassay species) has been established. A method of analysis, based on high performance liquid chromatography (HPLC), has now been proven feasible. This technique gives good resolution and has adequate sensitivity to allow reasonably reliable quantitative results to be obtained. The overall sensitivity is better than that of the bioassay and reproducibility can, under certain circumstances, be better. Further development is, however, necessary in order to establish whether the correlation with the mouse bioassay can be maintained consistently. This is expected to take at least another year.

Diarrhetic Shellfish Poisoning (DSP)

The ACMP was informed about progress realized in Japan and France on chemical analysis of the Diarrhetic Shellfish Poisoning (DSP) agent in contaminated molluscs. The principles of the method include three steps:

- DSP extraction with acetone from mollusc hepatopancreas and clean-up of the extracts on silica gel and alumina columns eluted with various concentrations of methanol,
- derivatization of the toxic fraction with 9-anthryldiazomethane (ADAN) producing fluorescent esters,
- high performance liquid chromatography of fluorescent esters on reverse phase columns eluted with acetonitrile,
- water fractions and then quantification of the okadaic acid component with an okadaic acid standard.

This method, used by Kumagai and co-workers (publication submitted), has been useful to demonstrate differences between toxins produced by <u>Dinophysis acuminata</u> and <u>D. acuta</u> in Europe, and <u>D. fortri</u> in Japan. In all European contaminated mussels, okadaic acid (OA) has been found to be the major toxin, as compared with the Japanese mussel, in which a methyl derivative of OA is the primary toxin. However, before this method can be used to replace bioassays (mouse test) for monitoring in affected areas, two difficulties have to be overcome: the preparation of a stable fluorescent agent and the production, in sufficient quantities, of pure OA as a standard for quantification.

10 ENVIRONMENTAL IMPACT OF AQUACULTURE

Noting the growing importance of mariculture operations in the ICES area and the increasing amount of attention being given to the environmental impact of mariculture (cf. Section 6, above, on the use of antibiotics in mariculture), the ACMP considered it useful to develop an overview of aquaculture operations on a world-wide basis. A summary of this overview is contained in the remainder of this section.

Aquaculture has recently gained considerable importance in many regions of the world. The introduction of new technologies, the expansion of suitable areas for cultivation, the improvements in feed technology, and the demand for high-quality protein products have opened new opportunities for a rapid expansion of the industry. Aquaculture has become a substantial food production sector, contributing about 8.7 million metric tonnes, or over 10%, of the world fishery in 1979/1980. Finfish and molluscs provided over two-thirds of the production, while the more valuable shrimps contributed less than 1% of the overall yield. Between the years 1979 and 1983, world aquaculture production passed the 10-million tonne mark, with an annual increase in finfish production of over 300,000 tonnes in Asia, 60,000 tonnes in Europe, and 11,000 tonnes in North America.

In many regions, aquaculture has presently been identified as the only growth sector within fisheries. Several predictive investigations estimate an overall aquaculture production of about 25-30 million tonnes by the end of this century, which requires an annual growth rate of over 12%.

Aquaculture in marine and brackish waters has substantial potential for expansion, in both temperate regions and the tropics. Progress in aquaculture development, however, will always be accompanied by a number of problems and constraints that arise with, or through the expansion of, the industry. Aquaculture systems are structured around the use of natural waters and often of natural feeds. As such, they are essentially part of the environment and, consequently, consideration should be given to their wider environmental impact. Modern aquaculture systems in brackish and marine waters have to operate at high efficiency, and maximizing biomass output per unit investment becomes essential in order to compete with other alternative users of the critical resources, i.e., water, land and nutrients. The trend towards intensification will, therefore, continue.

The possibility that aquaculture may affect the environment has largely been overlooked in the past. Aquaculture, like any other industry, has the potential to generate large amounts of contaminants which affect water quality. Environmental and ecological concerns can no longer be ignored and become a risk factor for the industry itself. A recent EIFAC (European Inland Fisheries Advisory Commission) study has evaluated the nature and extent of the problems which are, or may be, caused by the discharge of effluents from land-based systems in freshwater. From this study, it becomes obvious that aquaculture effluents have in most cases changed the levels of certain constituents in the receiving water, but have not necessarily caused pollution. Where problems have occurred, they differed in nature and extent and

depended on the size of the fish farm and the sensitivity of the receiving water to effluent input.

In brackish and coastal waters, aquaculture is primarily conducted in net cages moored at well-protected sites. With the expansion of this industry, overloading of culture units in areas in which cage farming was initially successful has occurred, indicating an urgent need to provide guidelines on the carrying capacity of suitable coastal areas. The number of applications for farm licenses is rapidly increasing in various countries and the criteria employed to issue permits are chosen, in most cases, without sufficient background scientific information.

Recent studies in ICES member countries indicate the overall amounts of nutrients released from salmonid cage farms, providing first insights on the extent of the problem. Most studies have recorded increases in the levels of suspended solids and nutrients (total-P, NH, -N, organic N, C, BOD, COD) and decreases in dissolved oxygen in and around the enclosures.

The release of phosphorus from fish farms depends mainly on the type of food used. Usually, the amount of phosphorus supplied via diets exceeds by far the requirements of the fish. British investigations indicate that about 15.7 kg total phosphorus are released into the environment with each tonne of fish produced. Since economically viable farm sizes vary between 50 and 200 tonnes of annual output, the total phosphorus input of an average farm producing 100 tonnes of fish annually would amount to over 1.5 tonnes total phosphorus per year.

input of organic carbon to the sediments from cage farms occurs in two forms: uneaten food and faecal waste. The amount of waste food will depend on husbandry, but it is generally accepted that 15 to 20% of the total feed is lost as waste. Approximately 25% of the food ultimately ends up as faeces. The amount of carbon in faecal waste can be estimated to be in the range of 30% of that contained in the diet. From these figures, it can be inferred that approximately 50% of the ingested carbon is respired. With regard to nitrogen, on average only 22% of the consumed nitrogen is retained by the fish and about 65% is lost as soluble nitrogenous waste. In addition, soluble nitrogenous waste originates from the mineralisation of organic nitrogen in uneaten food Under practical farming conditions, a salmon farm faeces. with an annual production of 50 tonnes will probably release 20 tonnes of uneaten food (containing 1.5 tonnes of organic nitrogen and 8.8 tonnes of organic carbon), 10.6 tonnes of faecal carbon about 4.0 tonnes of soluble nitrogenous waste, assuming that a feed conversion factor of 2:1 can be achieved.

The environmental impact of net cage farming is greatly influenced by the local conditions, where water retention time and bottom dynamic conditions determine the accumulation or dispersion of suspended solids. Well-protected bays and inlets tend to serve as sediment traps (fjords) and will probably accumulate suspended solids under the cages, resulting in undesirable local effects, whereas erosional areas generally indicate good flushing and consequent dispersion of the wastes throughout larger areas.

Enclosures and cages can have an impact on submerged vegetation through excessive sedimentation of suspended solids. Such areas are often spawning grounds for commercially important species. On the other hand, inshore areas are also important nursery grounds for fry and juveniles of many species and nutrient inputs through aquaculture can be beneficial to the enhancement of production. Therefore, not all the impacts of enclosure structures will necessarily be negative. The attraction of fish to free-floating and anchored objects has been widely reported and utilized through installations such as artificial reefs in order to provide shelter and substrate.

The flow of water through the cages is affected by drag forces exerted by the framework and netting. The reduction in flow is dependent upon a number of variables, including flow rate, cage size and shape, mesh type, degree of fouling and stocking density. Cage structures, if installed at one site in large quantities, can have a considerable impact on local currents, and this has a number of implications regarding the sedimentation of suspended solids, the supply of oxygen and the removal of toxic waste metabolites from the vicinity of the fish. There is also evidence that the materials used may have adverse effects on adjacent sea life and perhaps on the enclosed stocks.

Recently, concern has been expressed about the excessive use of medication in cage farms, through which antibiotics are released into the environment. Nothing is presently known about the transport and degradation of these antibiotics or their possible effect on bacterial resistance in the caged populations or adjacent wild populations.

The role of increased nutrient levels, often associated with intensive cage culture, in promoting proliferation of parasites is not clear; however, eutrophic conditions have been shown to favour increased production of intermediary hosts.

Gaps in understanding of science and technology related to water quality management can be identified in three major areas which are crucial to the future development of aquaculture:

- 1) Water quality criteria of the water resource systems potentially suitable for aquaculture purposes,
- 2) Water quality requirements within farming systems,
- External impact of water quality alterations caused by aquaculture.

Improved knowledge in these areas could help to determine the most appropriate information that governments could, in the future, expect the aquaculture industry to provide in relation to "environmental impact statements". This seems to be of particular importance, because the aquaculture industry itself will be the first to suffer any ill effects of environmental degradation. It would also be useful if strategies could be developed to minimize waste outputs from fish farms while at the same time seeking efficient means to utilize locally enhanced nutrient inputs in a mixture of extensive and intensive culture systems.

Having taken note of this information, the ACMP looked forward to reviewing further details of the environmental impact of the mariculture industry at its 1987 mid-term meeting.

11 INTERCALIBRATION AND QUALITY ASSURANCE ISSUES

11.1 Plans for a New Programme to Optimize the Analysis of Specific Petroleum-Derived Hydrocarbons

The ACMP discussed the deliberations and recommendations of the Marine Chemistry Working Group concerning the analysis of specific petroleum-derived hydrocarbons in marine samples. On the basis of a review of the results of recent intercomparison exercises on the determination of hydrocarbons in biological tissue, the MCWG had concluded that relatively little progress had been made on the analysis of specific hydrocarbons and had recommended that a more systematic approach be taken to resolve the problems of lack of intercomparability of data.

The first step in this programme would involve a check on the calibration of instruments (gas chromatograph/mass spectrometer (GC/MS) and high performance liquid chromatography-ultra-violet fluorescence (HPLC-UVF)) using a series of specific hydrocarbons in solution. Additional steps in this exercise would be decided by the participants on the basis of an analysis of the results of the first step. The ACMP accepted the need for this systematic approach and agreed with the design of its first phase.

In connection with the analysis of specific hydrocarbons, the ACMP noted that the MCWG had established an <u>ad hoc</u> group to work intersessionally on a critical review of methodology curently in use for the analysis of hydrocarbons in all marine matrices. This review will cover the analysis of hydrocarbons in sea water, sediments, biota and samples collected in connection with atmospheric input measurements. The ACMP encouraged the MCWG to carry out this review in as expedient a manner as possible.

11.2 Reports of Intercalibration Exercises on Marine Sediments

11.2.1 Report of the First Intercalibration on Trace Metals in Marine Sediments

The ACMP noted that the draft report on the results of the First ICES Intercalibration Exercise on Trace Metals in Marine Sediments (1/TM/MS) (Coordinator: Dr D. Loring) had been presented at the 1986 meeting of the Working Group on Marine Sediments in Relation to Pollution (WGMS). The intercalibration had utilized three samples of different origin and composition: (a) a carbonate-rich sediment from a French estuary, (b) a Canadian harbour sediment, and (c) "MBSS", a mud sediment sample from the western Baltic Sea. These samples, appropriately checked for their composition and homogeneity, had been distributed to 62 laboratories from which only 40 returned results.

The ACMP felt that the aims of the exercise, which were to compare different extraction/decomposition procedures used widely for the analysis of sediments (leaching by weak acids such as acetic acid and 1N HCl, treatment with aqua regia and dissolution of the alumino-silicate matrix by hydrofluoric acid (HF)) were satisfied. In relation to pre-treatment procedures, the following

observations had been made by the Coordinator, concerning the intra-laboratory and inter-laboratory results from the various dissolution/extraction procedures used in metal determinations:

- 1) The HF plus aqua regia dissolution is the most effective procedure of those tested for removing the total metal concentrations from estuarine and coastal marine sediments for subsequent determination by FAAS and/or GFAAS, or any relevant method such as ICP or DPP. Furthermore, only digestions using HF can be applied to reference materials for quality assurance purposes, because sedimentary and geological reference materials are only certified for the results of total analysis techniques.
- 2) Aqua regia digestion releases significantly <u>less</u> Al, Cd, Cr, Ti, and Zn from the three intercalibration samples than the HF plus aqua regia dissolution. Depending on the sample, the aqua regia digestion also removes significantly less Cu, Fe, Mn, Ni, and Pb.
- 3) The 1N HCl extraction procedure removes significantly larger amounts of Cu, Mn, Pb, and Zn from the three intercalibration samples than the acetic acid treatment, and significantly larger, but sample dependent, amounts of Cd, Cr, Fe and Ni.
- 4) Of the two weak acid treatments tested, the 1N HCl treatment appears to be the one most likely to attack aluminium lattices in the samples studied.
- 5) The analysis of the residues from the HNO₃, HCl, and acetic acid treatments shows that varying amounts of metals remain undissolved, confirming that the aqua regia digestion does not release all the metals from the intercalibration samples.

The ACMP noted that some of the variance associated with the results of the acetic acid leach may be due to inadequate attention to pH control (i.e, inadequate compensation for calcareous material buffering).

The comparability of the results on "total" (HF extraction) concentrations of Al, Fe, Mn and Zn reported by the participants was "acceptable" (below a relative standard deviation of ± 20 %). The relative standard deviations obtained for Cd and Hg were unacceptably high.

One of the reasons potentially explaining poor results, as identified by the Coordinator, was that reference materials had either not been used or had been used improperly.

The ACMP regards the results of this intercalibration as most valuable and has recommended that the report be published in the ICES Cooperative Research Report series.

11.2.2 Other intercalibration exercises

The ACMP was informed about the preliminary results of the intercalibration of analyses of trace metals in marine sediments coordinated by France under the auspices of the JMG. This exercise, dealing with the comparison of results using different digestion methods and with the use of different methods of particle fractionation prior to digestion, was conducted in two phases.

The first phase took place in 1980 with the dispatch of three samples of fine sediments of different types having different trace metal compositions. For the second phase, late in 1983, two samples of differing particle size were sent to the participants, who were requested to use both a strong acid and a weak acid digestion, with the latter corresponding to the procedures used in the Baltic Sediment Intercalibration Exercise.

Twenty-seven laboratories from nine countries participated in the first phase and twenty laboratories from eight countries in the second phase. The preliminary results of this exercise were discussed at the 1986 meeting of the Joint Monitoring Group. The following results were obtained:

- 1) The concentrations measured by the methods giving total metals (e.g., HF digestion, X-ray fluorescence) are always greater than those obtained by the methods using strong acids not combined with HF. However, the concentration differences between the two types of methods vary with the nature of the samples.
- 2) The concentrations obtained by the various methods of digestion by strong acids were very similar; in contrast, the digestion method using 25% v/v acetic acid provided a wider range of values.
- 3) Although the coefficients of variation for Hg and Cd were very high, it was noted that for most of the other elements (Zn, Cu, Pb) the coefficients of variation were always less than ±25%.
- 4) The method of particle sizing does not seem to have any obvious effect on the results.

The ACMP noted that the Coordinator of this exercise, Dr M. Chaussepied, is preparing a more complete interpretation of the results of these two exercises for presentation to the JMG in 1987. The ACMP considered that, from the information given thus far, the results of the JMG intercalibration seemed to be comparable with those of 1/TM/MS. In this context, it was noted that the WGMS intended to conduct an assessment of the results of the Baltic Sediment Intercalibration, 1/TM/MS, and a Canadian marine sediment intercalibration in order to draw more universal conclusions. The ACMP recommends that this review should also take into account the results of the JMG sediment intercalibration referred to above.

11.3 Needs for Other Intercalibration Exercises

The ACMP noted that the Marine Chemistry Working Group would be examining intersessionally the feasibility of extending the pilot intercomparison exercise for trace metals in suspended matter to include all ICES laboratories interested in conducting such measurements. The MCWG would also consider at its next meeting the need for intercomparison exercises for the determination of organomercury in marine organisms and for the measurement of nutrients in sea water. This latter activity is discussed further in Section 19.1, below.

11.4 Needs for Standards and Reference Materials

The ACMP noted that the MCWG had identified the need for a number of standard reference materials for use in relation to studies of contaminants in the marine environment and monitoring programmes.

In terms of reference materials for trace metals, priority was given to the preparation of marine mammal liver and kidney standard reference materials with high levels of cadmium.

For trace organics, the most urgently required reference materials for organochlorine analysis were considered to be a material with a high fat matrix, for use primarily in the analysis of marine mammal tissue, and a material based on a fish muscle or mussel homogenate. Other organic components for which certified concentrations could be usefully provided were identified as:

- chlorobiphenyls at least the ICES primary list
- alpha- and gamma-chlordane
- oxychlordane
- trans-nonachlor
- dieldrin
- alpha- and gamma-HCH
- octachlorostyrene
- heptachlor
- hexachlorobenzene
- pentachlorobenzene
- 2,4-DDT, 2,4-DDD, and 2,4-DDE
- 2,3,6,7-tetrachloronaphthalene
- pyrene
- anthracene
- phenanthrene
- fluorene
- fluoranthene
- chrysene
- benzo[a]pyrene
- benzo[a]anthracene
- 1-methyl phenanthrene
- 2,3-dimethyl naphthalene

In addition, pure standards of at least two polychlorinated camphenes are required.

The ACMP noted that all chlorobiphenyl (CB) congeners referred to in its 1985 report are now available from the EEC Bureau of Community References (BCR), and that some of them are also available

from the National Research Council of Canada. The MCWG will continue to update this list of CBs in relation to investigations of these compounds in the environment. It was noted that the BCR will consider synthesizing additional CBs as necessary.

The ACMP observed that some criticism had been raised concerning the ICES list of CB congeners in terms of problems with separating some of the CBs easily on an average quality SE-54 column and on their relevance to marine studies. As the ACMP had considered the ICES list to be a provisional one, and one that was not based solely on the chromatographic behaviour of the CBs, it was agreed to continue with the present primary list of CBs, namely

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

Nevertheless, the ACMP recommended that three new chlorobiphenyls, namely IUPAC numbers 194, 206 and 209, be added to the secondary list, which comprised IUPAC Nos. 18, 31, 44, 66/95, 110, 149, 187, and 170.

The ACMP noted that US National Oceanic and Atmospheric Administration (NOAA) is currently compiling a looseleaf handbook listing available standards and standard reference materials from all sources for use in the analysis of contaminants in marine samples. Each leaflet provides a full description of the sample, including certified values, and the name and address of the producer together with costs of purchase, where appropriate. On completion of this handbook, NOAA will make it available to ICES and other international organizations concerned with studies of contaminants in the marine environment to assist them in identifying further requirements for these materials.

In terms of standards for nutrients in sea water, the ACMP noted that the MCWG was satisfied that the Sagami nutrient standards fulfilled all their needs in relation to quality assurance practices for nutrient measurements in sea water.

Finally, the ACMP noted that the IOC has established a new Group of Experts on Standards and Reference Materials for Chemicals in the Marine Environment and that ICES will be associated with this Group.

11.5 Good Laboratory Practice

The ACMP discussed the proposals made by the MCWG in relation to the ACMP request for a leaflet on good laboratory practice. It noted that there were mixed views amongst the members of MCWG about the need for such a leaflet in view of the availability of adequate published information on this topic.

The ACMP noted, however, that a leaflet will be prepared on good laboratory practice for the analysis of trace metals in marine samples, consisting of a list of suitable reference papers with a short introductory section. This will be published in the new ICES series of leaflets on "Techniques in Marine Science". For persons interested in information on good laboratory practice for the analysis of trace organic compounds, the MCWG had prepared a list of relevant citations from the scientific literature, which

the ACMP had included in Annex 1 to the 1985 ACMP Report (Coop. Res. Rep. No. 135).

Although the ACMP felt that both of these lists of relevant papers from the literature had been useful contributions in relation to the original request, it concluded that not all analysts were as conscious of the need for good laboratory practice as those who are members of the MCWG. These other analysts clearly needed some general guidance on this subject to complement the list of detailed publications previously provided by the MCWG. This general guidance should address approachs to collecting reliable data through adequate attention to the following points:

- a) the design and conduct of a representative sampling programme,
- b) the selection and use of suitable storage procedures for samples to minimize changes in the analyte concentration and form prior to analysis, and
- c) the adoption of analytical procedures which enable measurement of appropriate accuracy and precision to be made in relation to the aims of the investigation.

The use of reference materials in the development and testing of analytical methods should be stressed and analysts should be encouraged to participate in interlaboratory comparisons to obtain an independent assessment of their analytical capability.

The ACMP decided that such a paper should be prepared by several of its members, working by correspondance, with a view to adopting a final text at its next meeting.

12 FEASIBILITY OF THE CONDUCT OF AN INTERCALIBRATION ON PETROLEUM HYDROCARBONS IN SEA WATER

The ACMP had requested the MCWG to examine the feasibility of conducting an intercalibration for petroleum hydrocarbons in sea water in order to assist the ACMP in responding to a request on this topic from the Oslo and Paris Commissions. The ACMP had further requested the MCWG to examine two proposals for the design of an appropriate intercalibration, one developed by ACMP itself and another provided to MCWG by two Canadian scientists.

The ACMP noted that the MCWG, having reviewed the situation, concluded that such an intercalibration was unnecessary and that monitoring of dissolved/dispersed hydrocarbons could be carried on a reliable and intercomparable basis through the use of the methodology specified in IOC Manuals and Guides No. 13. UV-fluoresence method for the measurement of dissolved/dispersed hydrocarbons described in this document has been well tested evaluated during the Kiel Workshop on the Analysis of Hydrocarbons in Seawater (HELCOM, 1982) and the IOC Workshop on Petroleum Hydrocarbon Measurements held in Bermuda in 1984. Therefore, the application of this method to monitoring within the Oslo Convention area should be straightforward and permit Paris assessments to be made of the incidence and distribution of dissolved/dispersed hydrocarbons. The MCWG had further advised that there exists a more urgent need to pay attention to the improvement of methodology for specific aromatic hydrocarbons through the application of GC-MS and HPLC-UVF techniques rather than to carry out a further intercalibration based upon the UV-fluorescence technique, which provides limited insight into the nature of the substances being monitored.

The ACMP was of the view that, while the development of more selective techniques for the detection and quantification of hydrocarbons of petroleum origin is being pursued, routine monitoring of inshore waters for dissolved/dispersed hydrocarbons sea water can be carried out using the UV-fluorescence method specified in IOC Manuals and Guides No. 13. Evaluation data from the Kiel Workshop (HELCOM, 1982) and a recent IOC Bermuda Workshop has shown that the UV-fluorescence technique provides a sensitive and precise method for petroleum hydrocarbon monitoring in inshore waters. It has been further demonstrated that more accurate estimates of the oil content of samples can be gained if the reference standards used in the application of this technique are closely matched to the types of oil in the samples. Caution must, however, be used in the application of this technique to very low levels since the UV-F signal obtained does not necessarily correspond solely with the presence of petroleum or combustion product hydrocarbons in such samples.

The ACMP concluded that the above advice should be forwarded to the Commissions, as it would imply that no new intercalibration exercise was necessary. Nevertheless, if the Oslo and Paris Commissions still feel it necessary to conduct a further intercalibration of the UV-fluorescence technique for monitoring purposes within the Conventions area, two alternative approaches can be considered. These are:

- 1) To convene an intercalibration workshop along the lines of the Kiel Workshop of 1981 (HELCOM, 1982) and the IOC Bermuda Workshop of 1984. In this approach, representatives of the OSPARCOM Contracting Parties' laboratories could be brought together to carry out a joint evaluation and intercalibration of the UV-fluorescence technique. The most suitable venue for such an exercise, based upon experience with the conduct of similar workshops and resident analytical instrumentation and expertise, is the Institut für Meereskunde, Kiel.
- To conduct a round-robin intercalibration for hydrocarbons in sea water on the basis of the proposal previously made to the MCWG.

An amended form of this proposal is presented below.

PROPOSAL FOR A DISSOLVED/DISPERSED PETROLEUM HYDROCARBON INTER-CALIBRATION

Introduction

The objective of this proposal is to establish the relative accuracy and precision of laboratory procedures for the determination of hydrocarbons in sea water by the UV-fluorescence method. The design of the intercalibration also permits the use of other analytical techniques, if the participants wish to use them, in addition to the UV-fluorescence method.

Experimental Design

The design would comprise the circulation of replicate natural sea water and replicate spiked seawater samples together with a hydrocarbon mixture to be used for calibration purposes. Natural seawater samples would be collected from a relatively homogeneous body of deep water using a sequence of Blumer sampler casts. Each cast could be used to prepare fourteen 1-liter samples of which would be used for internal homogeneity check analyses and for establishing the variance between sequential Blumer bottle The remaining nine samples from each cast would be used samples. to prepare three sets of triplicate samples for distribution to participants. The overall number of casts required would be determined by the number of participants in the experiment, which have to be established beforehand. It is assumed that the cast-to-cast variability can be established from the analysis five samples from each cast retained by the organizer. Equally, the identity of these samples and those sent to participants could be maintained if corrections for inhomogeneities between casts were required to be made following the receipt of results by the coordinator.

Spiked samples, at two levels, would be prepared by spiking individual samples of natural sea water with a known quantity of weathered bunker oil dissolved in hexane. The spiking solution would be prepared by artificially weathering a sample of bunker oil and then dissolving the weathered oil in hexane. The solution would then be filtered or centrifuged to separate the dissolved and insoluble fractions. The insoluble fraction would be dis-

carded, the hexane removed by evaporation, and the remaining material weighed. A known mass of this residue would then be redissolved in hexane to make up the spiking solution. Samples of the spiking solution, together with information on its content (mass) of bunker oil hydrocarbon residue, would be distributed to participants for use as a reference standard in the intercalibration. Fluorescence spectra for the spiking solution would also be provided to the participants to enable them to carry out checks on the validity of the reference standard and the performance of their instruments before proceeding with the analyses of the replicate samples.

Participants would be requested to conduct analyses of the six seawater samples by UV-fluorescence techniques using the spiking solution as a standard. Each participant would then submit the results of these analyses to the coordinator, who would then able to determine analytical precisions at the spike level, spike recovery, and the extent to which the unspiked sea water was subject to contamination during extraction and analysis. The unspiked and spiked seawater samples would be distributed Teflon bottles and the participants would be expected to carry out the extraction procedures within these containers. Once UV-fluorescence measurements had been made by the participant, the extract could be subjected to more detailed analysis by participant using GC or GC/MS techniques, if desired. The coordinator would be responsible for establishing the sample-tosample variance through the analysis of the balance of the samples prepared from each Blumer bottle cast.

The ACMP noted that the procedure described above will evaluate the sample extraction and instrumental analysis techniques on the basis of a relatively stable standard. If there is a desire procedures on the basis of a broad range of aromatic components, including more volatile low-molecular weight hydrocarbons, second phase of the experiment would need to be conducted to include a duplicate set of samples containing a broad-range mixture such as diesel oil. However, in this instance, a great deal more preparative work would be required to ensure the integrity of samples between the time of preparation and their extraction by the participating laboratories. If the experiment is intended be used as a basis for comparing inshore water monitoring results, where the loss of hydrocarbon components due tility is likely to be important, the experiment should comprise two phases, both using a similar approach. In the first phase, procedure described above would be followed using spikes and standards both containing a stable mixture, such as weathered bunker oil. The second phase would follow the same procedure but would use, as a spike and reference standard, a broad-range mixture of hydrocarbons, such as diesel oil.

It should be appreciated that if this latter approach is adopted, some additional time and effort will be required for proving of the sample integrity during storage and shipping. This would provide greater assurance that time delays between the preparation and extraction of the samples would not compromise the validity of the experiment.

Both approaches, the workshop and the round-robin procedures, would involve some outlay of expenses. Both would include the need for ship time, preparative work, such as the acquisition and testing of solvents, the interpretation of results and the preparation of a final report. These costs would be incurred by the coordinator. In the case of the Workshop approach, other costs would be greater because of the need for participant travel and subsistence expenses. In the round-robin approach, these other costs would involve the purchase of Teflon sample containers and shipping costs. On balance, the round-robin approach should be the less expensive of the two. In either case, the actual costs that would need to be borne by the proponent could only be specified once a coordinator had been identified and the details of the procedure agreed to between the coordinator, ICES, and the Oslo and Paris Commissions, if the Commissions wish to proceed through an arrangement with ICES as was the case with the recent intercalibration for trace metals in estuarine waters.

Acknowledgements

The ACMP acknowledges and thanks Dr E.M. Levy of the Bedford Institute of Oceanography, Dartmouth, Canada, for providing the basis of the round-robin intercalibration approach described in this section of the Report.

Reference

HELCOM, 1982. Report of the Workshop on the Analysis of Hydrocarbons in Seawater. Baltic Sea Environment Proceedings No. 6. Baltic Marine Environment Protection Commission, Helsinki. 52 pp.

13 FEASIBILITY OF AN INTERCALIBRATION FOR LINDANE IN BIOTA, SEA WATER AND SEDIMENTS

The ACMP considered the request from the Oslo and Paris Commissions to assess the feasibility of conducting an intercalibration exercise for lindane in marine organisms and sediments. It first reviewed the response to its request to the MCWG to provide relevant advice on this topic. The MCWG believed that it was feasible to carry out intercalibration exercises for lindane (gamma-hexachlorocyclohexane $(\gamma-HCH)$) in sediments, sea water and marine organism tissues, but that, based upon the aims of the JMP, the most appropriate phase for the conduct of an early intercalibration for this contaminant was in sea water. Lindane has a much higher water solubility (\underline{ca} . 10 mg/l) than other organohalogens and a low distribution coefficient (k_d) of 110 compared to PCBs, which generally exceed 10,000 (Marchand \underline{et} \underline{al} ., 1983). Furthermore, the octanol/water coefficient is also lower (3.7) than that for DDT (6.2) or PCBs (>6) (Karickhoff, 1981). All these factors argue that the majority of lindane should be found in the dissolved phase compared to living organic matter or sedimentary material. This is consistent with the notation by Tanabe and Tatsukawa (1983) that the residence time of lindane in surface sea water is approximately two orders of magnitude greater than the residence times of PCBs or DDT. It was further noted that the alpha isomer usually has an abundance equal to or greater than that of lindane in all phases and that the alpha and beta isomers are considered more toxic than lindane, with the alpha isomer being suspected of having carcinogenic properties. Thus, there was some justification for monitoring for chlorinated hydrocarbons to include attention to the family of HCH isomers, for which the additional work would be relatively small, the use of lindane as an indicator of the presence of this group of isomers was useful. Nevertheless, for the reasons given above, the initial phase for attention for lindane should be sea water.

In considering an approach to a lindane intercalibration for all marine phases, the ACMP also considered a paper prepared for the MCWG, some aspects of which are outlined below. In presenting this material, it should be noted that many of these aspects are applicable to quality assurance approaches for other contaminants. Nevertheless, it is presented in the context of lindane since it was specifically prepared in response to the request for advice on a lindane intercalibration.

13.1 An Approach to Intercalibrations for Lindane in Marine Materials

13.1.1 Introduction

There now exists a large body of information on the results of intercalibration exercises for a wide range of pesticides (Smart, 1984, 1985; Storet, 1982), some of which include reference to lindane (Palmork, 1980). The general approaches to this type of exercise are well documented (Horowitz, 1981; ISO, 1981).

Nevertheless, it is believed useful to outline some aspects of the approach to quality assurance intercalibration exercises that need to be considered in relation to the development of further intercalibrations for lindane or other similar determinands.

13.1.2 Approach

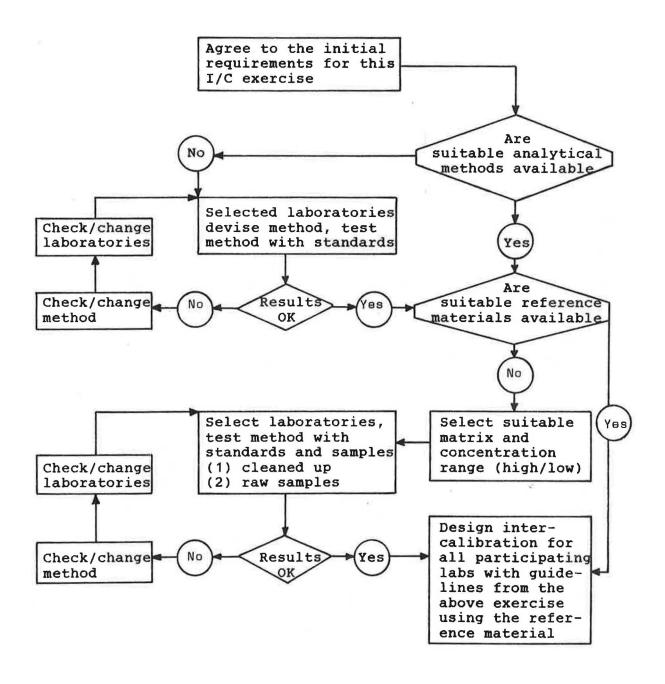
number of previous intercomparison exercises have been less successful than they might have been (Holden, 1980) for one of the following reasons. First, the intitial planning may result in the adoption of a design for an exercise that ambitious. This often follows from a desire to evaluate rapidly a number of different but related aspects of the problems associthe sampling, storage or analytical procedures. An with overly ambitious programme has the result that the work assumed by the participants is substantial and requires greater care in following the coordinator's instructions, which must necessarily be rather detailed. A second related factor can be a lack of coordination and extended deadlines for receipt of results, which further complicated if the work in a single intercalibration is overly detailed and time-consuming. Third, the initial expectations of the ease with which difficulties can be overcome by participants are often unrealistic or are not based upon an adequate understanding of the nature of the problems associated with a particular procedure. Finally, the more complicated and multifaceted the experiment becomes, the less likely that laboratories with limited familiarity with the procedures being compared would willing to be involved or would potentially gain as much from the conduct of the experiment.

Many of these problems have been encountered in previous intercalibrations for a wide variety of contaminants, including metals and organic contaminants in various marine phases. Increasingly, the approach to future intercalibrations is becoming one based upon the adoption of a systematic step-by-step framework within which each particular problem, which hinders the accuracy, precision and intercomparability of determinations, is tackled individually and separately. Figure 1 sets out a strategy for this new approach which identifies the specific sequence of steps necessary to prepare an adequate design for an intercalibration study together with the appropriate critical review stages.

By adopting this strategy, many of the drawbacks associated with earlier approaches can be overcome. In the initial stages of the development of a widespread intercalibration exercise, a small number of key laboratories should be selected based upon their existing expertise with the contaminant and matrix to be This group would spearhead the development of a viable intercalibration for wider participation by tackling some of outstanding problems in a concerted and coordinated manner. This group would thus act as the 'pilot team' for the development intercalibration for the benefit of a wider group of participants. This approach was adopted for the recent intercomparison procedures for the analysis of trace metals in suspended particulate material that was carried out under ICES auspices number of laboratories. This intercomparison has demonstrated that it is now possible to design an intercalibration for the analysis of suspended matter for trace metals among a larger

FIGURE 1

Flow Diagram for an Intercomparison Exercise



group of laboratories having a greater diversity of experience with such analyses. The actual work of the pilot team would be to solve any outstanding problems that would prevent the conduct of a useful intercalibration, as outlined in Figure 1. The team would then proceed to design an intercalibration, or a sequence of intercalibrations, that would facilitate the assessment and improvement of capability among a wider group of laboratories. The emphasis, in any event, would be to design simple one-step intercalibrations, each of which would address a specific problem in the measurement of a particular determinand.

Horowitz (1982) has shown that a group of laboratories working together on a common analytical problem rarely obtains good intercomparability during the initial intercalibrations. improvement in comparability takes several cycles, involving perhaps four exercises, before broad intercomparability is obtained. Thus, in the approach advocated here, the initial impediments to a concerted attempt to improve data comparability are first tackled by a small pilot group before the benefits of this work are extended to a wider audience through the conduct of well-designed and meaningful intercomparisons. The additional benefit is that a number of improvements to analytical methodology will only become apparent during the evaluative stages of a programme in which the feasibility of conducting an intercalibration is being assessed (Tuinstra et al., 1985). These improvements can be applied and evaluated most effectively by the pilot group for the wider benefit of the later participants in the intercalibration. It should be noted that this proposed approach has largely been used in the development and execution of the ICES series of intercalibrations on trace metals in sea water with considerable success.

13.2 Application of this Approach to Lindane

13.2.1 Analytical methods

Although there are a large number of laboratories who are currently analysing for lindane, there should be common agreement on the suitability of these methods, now and for the foreseeable future. Since this compound is usually determined by gas chromatography (GC) at the same time as a number of other organochlorine residues, it is important to select a method which, in general terms, can also be applied to these other components. With these general points in mind, the following specific questions must be addressed.

13.2.2 Availability of suitably pure primary standards

There are a number of suppliers of γ -HCH as a standard material. These should be listed and cross-checked for purity (presence of other isomers in particular).

13.2.3 Written methods for the preparation of standard solutions

No single method will necessarily be right, to the exclusion of others, but it is essential to be able to examine the laboratory's analytical quality control practices and to specify changes where necessary.

13.2.4 Internal standards for quantitation and retention index markers for identification

Capillary column chromatography has become almost a standard tool for quantitative organic trace analysis and it is almost mandatory that at least one internal standard be included for each chromatograph.

There have been a number of internal standards which have been used in organochlorine analysis, However, recently there has been a move towards attempting to adopt some rational approach to this problem. If the internal standard forms part of a homologous series of standards, then it is possible to use them for accurate retention indices measurements to aid identification as well as quantification (Wells, 1985).

13.2.5 Method of determination

Capillary column chromatography with Ni-63 electron capture detection is currently preferred as the method for the analysis of organochlorine residues, including lindane. Therefore, this should be the basic method used in such an intercalibration exercise. The use of autosamplers/integrators/computer-controlled systems may be regarded as optional and their use discussed by the group designing the intercalibration.

13.2.6 Chromatographic conditions

The chromatographic conditions should be carefully tested to determine the optimum conditions for reproducibility and separation from other isomers and possible interfering peaks. This should include the normal instrument check procedures, with particular reference to:

- 1) Injector, detector and initial oven temperature.
- 2) Carrier gas purity and linear velocity.
- 3) Split time, if splitless injector system is used.
- 4) The length, internal diameter, film thickness, and stationary phase of the capillary column.

These conditions should be examined by the participating laboratories using controlled standard solutions issued from a single laboratory. If there are discrepancies in the results, they should be examined by the participating laboratories to identify the causes. This should be completed with a view to improving each laboratory's performance to the required level of accuracy.

13.2.7 Certification of reference materials

There are a number of reference materials available for a wide range of determinands in different matrices (BCR, NBS). However, at present there are none specifically for lindane. Therefore, it will be necessary for the participating laboratories to agree on the matrices and the level of contamination required for the reference material (RM). Since there are a number of agencies who are involved full time in preparing and certifying such RMs, it may be useful to seek their advice and possibly participation at an early stage of any exercise. One such group is the IOC Group of Experts on Standards and Reference Materials with which ICES is a collaborating agency. This collaboration would greatly assist in:

- 1) Evaluating the wider demand and applicability of the selected candidate RMs.
- 2) Assisting in the location and preparation of RMs, including homogeneity and storage testing.
- Seeking financial support for (1) and (2), above, and assisting in certification.
- 4) Obtaining wider credibility for the RMs once the analysis has been completed.
- 5) Developing a central repository as a future source of the RMs for participating and other laboratories.

13.2.8 Selection of the matrix

Two matrix compartments have been proposed for the intercalibration studies for γ -HCH by JMG. These are sediments and biological tissue. Since these matrices differ widely, both in substrate and level of contamination, it would be appropriate for the group to consider them separately. However, this would not require two separate groups for designing the appropriate intercalibration exercises.

The common points which require detailed group discussion are:

- The selection of the matrix and the expected range of contamination. The starting reference material should be obtained as a natural, unspiked sample and the content certified by analysis.
- 2) Sufficient quantities of these materials should be identified, not only to cover the initial intercalibration, but for a longer-term use as RMs.
- 3) Methods of extraction and clean-up, and information on the post-extraction stability and storage of the samples are particularly valuable (Mowrer and Jensen, 1982).

4) Post-extraction treatment/reactions to remove specific interfering compounds should be evaluated where they are required in sample preparation.

The diversity of possible matrices and contaminant levels might initially suggest a need for a number of RMs. However, it should be possible to limit the desired concentration range, depending upon the programme (i.e., survey, baseline monitoring, regulatory control) to two levels, namely high and low. The range of values within these classes should be chosen relative to the data already available from the analysis of natural samples. Some information is included in Tables 1 and 2 as examples.

The sediment matrix could be separated into two classes: (i) coarse grain fraction, with low organic content, possibly associated with a lower concentration of lindane (50-200 ng/kg), and (ii) a fine grain fraction (silt and clay), having a greater organic loading and high lindane concentration (2000 ng/kg).

The high and low brackets in the biological tissue will be very much a function of lipid content. Muscle could be used as a low lipid, low lindane (5-20 μ g/kg) concentration matrix and a marine mammal blubber as the high lipid/lindane matrix (100-500 μ g/kg).

13.3 Acknowledgements

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TABLE 1
Y-HCH IN SEDIMENTS

		Mean values µg/kg	Range µg/kg			
Lake Ontario	1976	3.7 5.0		STORET (1978)		
Firth of Forth (Bell Rock)	1975 1978 1980	0.17 4.30	0.08 - 0.30 0.30 - 7.2 0.07 - 0.29	FFL - DAFS DATA FFL - DAFS DATA FFL - DAFS DATA		
(St Abbs Head)	1975 1978 1980	0.24 0.55	0.04 - 0.34 0.03 - 1.98 0.13 - 0.39	FFL - DAFS DATA FFL - DAFS DATA FFL - DAFS DATA		
North Sea	1981		0.09 - 0.40	FFL - DAFS DATA		

TABLE 2

Y-HCH IN BIOLOGICAL TISSUE

		Wet W	eight	Lipid	Weight	E
		Mean µg/kg	Range µg/kg		Range µg/kg	-
Freshwater						
Lake Ontario	1976		10-36			Freshwater Fish STORET (1976)
River Tweed	1979		2-19 1-5			Trout Liver FFL-DAFS Trout Muscle
River Stour UK	1980	23 216				Dace Muscle FFL-DAFS Dace Liver
Marine						
North Sea/Dutch Wadden Sea	1974	3.2 11.3 3.3 6.4 2.0		0.2 0.29 0.2 0.1 0.08		Mussel Herring O(M)) Plaice O (M))Ten Berg and Herring 3(M))Hillebrand 1974 Plaice 3 (M))
English catch	1970-73		<1-66			Many species Portmann (1979)
Firth of Clyde	1980		4-31 4-11			Herring Liver FFL-DAFS Herring Muscle
Sogndals fjord and Dalsfjord	1982	10 9 1 1	6-16 4-15 1-3 nd-2			Cod (L)) Haddock (L))Skare <u>et al</u> Lemon Sole (L))1985 Flounder (L))

14 FEASIBILITY OF CONDUCTING AN INTERCALIBRATION FOR PCBS IN MARINE SEDIMENTS

The ACMP noted that the MCWG had considered its request to discuss the feasibility of conducting an intercomparison exercise for PCBs in sediments. A proposal for this exercise, based on the protocol drawn up by the MCWG, had been prepared intersessionally for consideration by ACMP and is given below.

14.1 Introduction

The approach outlined below for the conduct of an intercalibration for the measurement of PCBs in marine sediments is based upon the systematic approach for the improvement of organochlorine measurements described previously in Section 13.

14.2 Pre-Implementation Actions

The first step is to select a coordinating laboratory. It must be a laboratory experienced in the analysis of PCBs in environmental matrices and one that has, or can obtain, the resources to follow the intercomparison programme to its conclusion.

Next, it is necessary to determine the PCB congeners that are to be used as calibrants and how the data are to be reported. It is assumed that the congeners that have been accepted or proposed for the ICES list will be used as calibrants. These congeners are IUPAC numbers 18, 28, 31, 44, 52, 66, 95, 101, 110, 118, 138, 149, 153, 170, 180, 187, 194, 206, and 209. It is further assumed that only concentrations of these congeners in any sample are to be reported.

The coordinating laboratory should prepare data reporting forms that explicitly specify each data point to be reported. Also, the coordinating laboratory must determine how many replicates of each analysis are to be performed, and if a standard procedure is to be followed for analysis. If a standard procedure is required, it must be described in detail to the participants. Finally, the criteria for evaluating the level of performance must be determined.

It would be wise for the coordinating laboratory to conduct a mini-intercomparison among its own chemists and technicians to verify that the instructions are clear and that they lead to satisfaction of the objective of the intercomparison.

14.3 Implementation

This intercomparison exercise for PCBs in sediments will be conducted in several stages. The intercomparison itself will consist of three sequential stages designed to evaluate: (1) GC/ECD analysis only; (2) analysis plus extract clean-up; (3) analysis plus clean-up plus extraction of the sample. Each stage is repeated until the desired level of performance is obtained. The coordinating laboratory will prepare/obtain and distribute all solutions, standards, and samples to the participating laboratories.

The coordinating laboratory should prepare calibration solutions at three concentration levels to check linearity over the range of analytes expected. (Concentrations of 10, 30 and 100 pg/ μ l of each analyte are suggested for GC/ECD.) The concentrations of analytes in the solutions will be verified by the coordinating laboratory by comparison with the certified reference material CLB-1, distributed by the National Research Council of Canada.

Stage One of the intercomparison should include the use of the three calibration solutions to determine a response curve, followed by analysis of CLB-1 by each participating laboratory.

Stage Two should comprise analysis, by all the participating laboratories, of a test extract prepared by the coordinating laboratory from a moderately to heavily contaminated sediment.

Stage Three should comprise analysis of the certified reference sediments HS-1 and/or HS-2, distributed by NRC Canada, along with analysis of an uncompromised reference sediment prepared and characterized by the coordinating laboratory.

14.4 Continuing Actions

Each laboratory should periodically analyze both known and uncompromised reference sediments, prepared and distributed by the coordinating laboratory, to verify constancy of performance. Results from these periodic analyses should be reported to the coordinating laboratory, which in turn should prepare reports summarizing the data. Data from intercomparison exercises and from periodic analyses of reference materials should be submitted along with data on environmental samples to sponsoring agencies and data banks.

If this proposal is acceptable to the Oslo and Paris Commissions, ICES could proceed to identify a suitable coordinator. However, it should be understood that certain costs, as yet undetermined, associated with the exercise would need to be borne by the Commissions.

15 GUIDELINES FOR THE USE OF SEDIMENTS AS A MONITORING TOOL FOR STUDIES OF CONTAMINANTS IN THE MARINE ENVIRONMENT

15.1 Introduction

The following is an amplification of earlier advice provided by the ACMP on the use of sediments as a monitoring tool for studies of contaminants in the marine environment. This amplification was requested by the Oslo and Paris Commissions to meet needs specified by the Joint Monitoring Group.

15.2 Sampling Methods

Different problems dictate different approaches and levels of sophistication in monitoring sediments. The ACMP suggests three levels of sampling and analysis appropriate to differing requirements.

15.2.1 First level

The first level is limited to the measurement of total contaminant concentrations in surface sediments. Analysis of bottom grab samples can provide an immediate assessment of the present levels of contamination in an area in relation to the textural and geochemical characteristics of the sediment.

Tightly closing grab samplers are usually adequate for studies of the most recently deposited layer, provided that they are well designed and handled. Normally, only the uppermost layer is used for the studies. Such grab samples do not, however, provide much information on the accumulation of contaminants in the past. In the case of strong biological perturbation of the sediments, the contamination signal of the surficial layer may also be significantly damped. A visual inspection of the sample is often sufficient to indicate the absence of animal disturbance, especially in the case of unambiguously laminated sediments.

Sampling of sediments should be exclusively performed in accumulating areas. Since many contaminants are enriched in the fine particulate fraction of sediments, zones in which muds accumulate are to be preferred. Background information can be provided from topographic maps and current charts. Areas of interest are associated with zones of low hydraulic energy related to weak tidal currents and wave actions. They are normally found at the deepest parts of an area. This background information can be usefully supplemented by topographic mapping using echo-sounding and seismic profiling.

The diversity and varying intensity of physical, chemical and biological conditions in marine areas imposes a need to assess variability in a given area through appropriate sampling. The number of samples required for this purpose can be evaluated by appropriate statistical analysis of the variance within and between samples.

15.2.2 <u>Second level</u>

The second level involves the sampling of cores at selected sites with a box-corer or a large diameter gravity corer. With these samplers, assuming that they are properly deployed, recovered and sub-sampled, the surface is more reliably sampled and it is possible to examine the vertical structure and composition of the sediments.

The depth and intensity of biological mixing can often be qualitatively assessed by visual inspection or by X-radiography of cores. In unmixed sediments, the vertical distribution of the concentrations reveals the evolution of the depositional flux of contaminants in the most recent past and allows one to define a reference level of concentrations in the deepest part of the core, which may represent the natural level in the area in question.

In most areas, 1 cm slices are a reasonable compromise between the desired vertical (historical) resolution, the number of samples to be processed and the amount of material necessary for a variety of different analyses. Smaller slices, down to about 2 mm, are still practicable in areas of low deposition, depending on the intensity of biological mixing.

15.2.3 Third level

The sampling methods at this level are the same as those at the second level, but with the addition of radiochemical (e.g., Pb-210, Th-234, Cs-137, and Pu-239/Pu-240) or other measurements to determine the rate of deposition and the nature and consequences of biological mixing. It is the objective of this work to understand the rate and mechanism of contaminant build-up in the sediment reservoir and eventually to determine contaminant budgets and temporal trends.

15.3 Sampling frequency

The sampling frequency (and vertical resolution) is essentially determined by the rate of deposition, the intensity of biological mixing and the thickness of the layer one can sample. It also depends on the anticipated changes of contaminant fluxes to the sediment with time and on the reproducibility of the analytical methods applied for contaminant determinations. Since high depositional rates in coastal environments are of the order of a few centimeters per decade, the required time interval for repeated sampling of marine sediments in a monitoring programme is usually several years.

15.4 Sample description

A log book should be used during sampling where a visual description of the sample is made. The description should contain the following information:

- textural description,
- homogeneity and indication of bioturbation or stratification,
- colour (Munsell colour chart).

If possible, the sediment cores should be X-rayed before slicing to confirm the information on textural changes and biological mixing.

15.5 Sub-sampling and sample storage

The sub-sampling of sediments should preferably be performed immediately after sampling. Care should be taken to avoid smearing of the sides of extruded cores. Sub-samples for physical and chemical analysis should be stored frozen or freeze-dried.

15.6 Sedimentological and Geochemical Information

For any study of marine sediments in relation to contamination, a basic amount of information is necessary about the deposit and its composition. This information requires the determination of:

- water content
- grain size characteristics
- organic and inorganic carbon content
- Al (or Sc) and Fe (or Mn) content
- the contaminants of concern.

The redox potential should be evaluated at least qualitatively (i.e., whether the surficial sediments are oxic or anoxic and, if oxic, whether there exists a redoxcline within the core).

15.6.1 Grain size distribution

As contaminant levels are usually much higher in finer grained sediments, it is appropriate to determine the fine-grained size fraction and to apply the chemical analysis to that fraction. It is convenient to separate particles at the sand/silt size classification boundary (63 $\mu m)$. The grain size separation may be performed by dry-sieving or wet-sieving using uncontaminated deionized water. In cases where contamination of the coarse fraction is suspected, both fractions should be analysed.

15.7 Chemical analysis

For the analysis of inorganic constituents, the sample should preferably be freeze-dried. Alternatively, the sediments may be dried at 105°C, except for subsequent analysis of volatile substances (e.g., dimethyl mercury). Sub-sampling should be performed on a dry sample previously homogenized in a mortar.

For organic constituents, sub-sampling of wet sediments is recommended. The water content may be determined on a parallel sample. Alternatively, freeze-dried sediments may be used following careful checks on loss of volatile substances and of contamination (e.g., by vacuum pump oil).

For most types of analyses of organic and inorganic constituents, well-documented methods are available. However, for coordinated studies only satisfactorily intercompared methods should be used. Some guidance in relation to the expected reproducibility of those methods is given in reports of recent intercalibration exercises.

16 SEDIMENT QUALITY CRITERIA: NORMALIZATION TECHNIQUES FOR METALS

16.1 Introduction

This section of the report presents a tentative normalization technique for evaluating the concentrations of metallic contaminants in sediments with respect to background or natural levels expected for similar non-contaminated deposits. Its purpose is to determine where anomalous concentrations occur relative to those normally expected in marine sediments under natural conditions.

A wide variety of substances entering the marine system are subjected to various biogeochemical processes and become associated with fine-grained particulate matter in such a way that the behaviour and fate of these substances are determined by particulate dynamics. Thus, preferential accumulation of particleassociative contaminants occurs in zones of fine sediment deposition and a comparison of sediments from various areas must, therefore, take into account the granulometric distribution. Two approaches to normalization have been selected here. The first is purely physical and consists of characterizing the sediment by measuring its content of fine material. The second approach is of a chemical nature and is based on the fact that the small size fraction is usually rich in clay minerals, iron and manganese oxi-hydroxides and organic matter. Chemical parameters representative of these components may thus be used to characterize the small size fraction.

It is strongly suggested that several parameters be used in the evaluation of quality criteria of sediments. The types of information gained by utilizing these various parameters are often complementary and extremely useful, considering the complexity and diversity of situations encountered in the sedimentary environment. Furthermore, the measurements of the parameters selected here are relatively simple and inexpensive.

The interpretation of the data generally requires a comparison between the chemical composition of the sediments from a selected area and background or natural values found in uncontaminated sediments. In this context, the relationships between the concentrations of contaminants and various sedimentary characteristics, such as grain-size distribution and mineralogical composition, are very useful. A step-by-step description of the selected procedure and a short justification of the methodology are given below.

16.2 Sampling Strategy

Ideally, a sampling strategy should be based on a knowledge of the source of contaminants, the transport pathways of suspended matter and the rates of accumulation of sediments in the region of interest. However, existing data are often too limited to define the ideal sampling scheme. Since contaminants concentrate mainly in the fine fraction, sampling priority should be given to areas of mud or organic-rich deposits, which usually correspond to zones of deposition.

The methodology of sampling and analysis should follow the recommendations outlined in Section 15, "Guidelines for the Use of Sediments as a Monitoring Tool for Studies of Contaminants in the Marine Environment." In most cases, samples of the uppermost layer of sediments, collected with a tightly closing grab sampler (level 1 in Section 15), are sufficient to provide information concerning the level of contamination in a given area compared to sediments from uncontaminated locations or reference materials.

However, one of the main advantages of using sediments as monitoring devices is that they often have recorded the historical evolution of the composition of the suspended matter deposited in the area of interest. The degree of contamination may thus be easily estimated by comparison of surface sediments with deeper samples, taken below the biological mixing zone. The concentrations of trace elements in the deeper sediment may represent the natural background level in the area in question and can be defined as a baseline value. This approach requires sampling with a box-corer or a gravity corer (levels 2 and 3 in Section 15). Clearly however, the foregoing statement must be judged in the context of geochemical processes which can also give rise to pronounced gradients in the vertical distribution of contaminants.

16.3 Normalization Techniques

As pointed out previously, the concentrations of contaminants in sediments collected in a given area are strongly dependent on the hydrographic properties controlling the deposition of fine material in that area. It is, therefore, convenient to express these concentrations as a function of the parameters characteristic of the potential capacity of components to accumulate contaminants.

Since contaminants have a marked tendency to accumulate in the small-size fraction of sediments, the use of a physical parameter directly linked to the size distribution of the particles in the sediments has often been proposed. The concentrations of trace elements are, therefore, expressed relative to the weight fraction of the sediment sample smaller than a given size.

The sieving of samples at 63 μm , as recommended in the previous guidelines, is adequate for the initial normalization of the concentrations of contaminants with respect to grain-size. This normalization technique is particularly useful for the comparison of sediments of various textures and origins at different locations the same area. Particle-associative contaminants are normally increasingly concentrated in progressively smaller size fractions sediments. Nevertheless, the use of smaller grain-size separations than the <63 µm recommended for subsequent contaminants is tedious, increases the risk of sample contamination, and is generally unwarranted unless very geochemical studies are required. There is, however, some benefit in assessing the proportion of sedimentary material by mass at

sizes such as <16 μm or <2 μm to provide further information on the grain-size distribution in the sediment sample.

It is obvious that size determination alone is not sufficient characterize satisfactorily the sediment, nor to interpret the trace element content. Since contaminants are mainly associated with the clay minerals, manganese and iron oxi-hydroxides and organic matter which are most abundant in the fine fraction of the sediments, more information can be obtained by measuring the concentrations of elements representative of these components in the samples. An element such as aluminium, a major constituent of clay minerals, may be selected as an indicator of that fraction in areas not significantly influenced by the products of glacial erosion. Aluminium assay by atomic absorption or colorimetric spectrophotometry may be carried out rapidly and with good precision and accuracy. Normalized concentrations of trace elements with respect to aluminium are commonly used to characterize particulate material (see below). Aluminium may be considered as a conservative major element, which is not affected significantly by, for instance, early diagenetic processes.

In addition to the clay minerals, manganese and iron compounds are often present in the fine fraction, where they exhibit exchange properties strongly favouring the incorporation of various trace elements. Manganese and iron are easily analysed by flame atomic absorption and their determination may provide insight into the distribution of contaminants.

Organic matter also plays an important role as scavenger of contaminants and controls, to a large extent, the redox characteristics of the sedimentary environment. Wet chemical oxidation or catalytic combustion methods on carbonate-free samples are well-established chemical determinations of this parameter.

Finally, the carbonate content of sediments is easy to determine and it gives additional information on the geochemical characteristics of the sediments. Under certain circumstances, carbonates can fix contaminants such as cadmium and copper. It can be measured simply by the loss of weight of the sediment after acid leaching or by measuring the volume or pressure of CO₂ evolved during acid leaching.

Normalization of the concentration of trace elements with respect to aluminium (or scandium) has been used widely and reference values on a global scale have been established for trace elements in various environmental compartments: crustal rocks, soils, atmospheric particles, river-borne material, marine clays and marine suspended matter (cf., e.g., Martin and Whitfield, 1983; Buat-Ménard and Chesselet, 1979).

These values can be compared to the normalized values obtained for the sediments of a given area. Large departures from these mean values indicate either contamination of the sediment or local mineralization anomalies.

This normalization also allows the definition of an enrichment factor for a given element with respect to a given compartment. The enrichment factor EF is given by:

$$EF = (X/Al)_{sed}/(X/Al)_{ref}$$

where (X/Al) refers to the ratio of the concentration of element X to that of Al in the sample and (X/Al) could be either a global mean ratio for crustal rock or a typical mean ratio for areas representing natural conditions.

This permits the calculation of element excesses in the sediments sampled, expressed as:

Excess =
$$X_{sed} - [(X/Al)_{ref} \cdot Al_{sed}]$$

When other parameters (Fe, Mn, organic matter and carbonates) are used to characterize the sediment, either alternatively or in addition to Al (Sc), (multiple) regression analysis of the contaminant concentrations with these parameters often yields useful information on the source of contamination and on the mineralogical phase with which the contaminant is associated.

16.4 Analysis of Trace Elements

It is essential to analyse the total content of trace elements in sediments if quality criteria is the goal of the study. The total content of elements can be determined either by non-destructive methods, such as neutron activation, or by a complete digestion of the sediments followed by methods such as atomic absorption spectophotometry or emission spectroscopy.

This complete digestion can only be achieved using HF in combination with HNO, HCl and/or HClO. The use of strong acids without HF leaves an insoluble residue and extracts different amounts of metals from different minerals, which makes normalization difficult. This is especially the case for aluminium, proposed here as a reference element. Total dissolution of samples should be a requirement in this kind of programme. Metals are readily measured, after digestion, at natural concentrations by atomic absorption (flame, flameless or graphite furnace) or by any other relevant method, such as plasma emission spectroscopy. Previous intercomparison studies have shown that these methods can produce satisfactory results when properly used. Laboratories should be encouraged to use standard reference materials and to participate in intercalibration exercises to make sure that their results are in harmony with those from other laboratories.

16.5 <u>References</u>

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17 DETERMINING THE BIOAVAILABILITY OF CONTAMINANTS IN SEDIMENTS

Bioavailability is the extent to which a substance associated with sediments is able to influence biological processes or to become incorporated into living tissues. It is of particular relevance to contaminants in sediments since it may be the most important factor in determining the potential of a contaminant to cause harmful effects on living resources. In the context of international conventions for the prevention of pollution in the marine environment, the assessment of bioavailability may be a necessary step in establishing whether or not a contaminant should be regarded as a potential pollutant.

At present, there is no universally applicable technique measuring the bioavailability of contaminants in sediments. Recent work within the ICES Working Group on Marine Sediments in Relation to Pollution (WGMS) and elsewhere has clearly shown that bioavailability is not only a function of the substance itself, is related to the structure and composition of the sediments and the physical and chemical conditions of the surrounding medium. Clearly, in coastal areas there is extreme spatial and temporal variability in physical, biological and chemical conditions, as well as in the forms in which contaminants are introduced. For these reasons, it would be misleading to suggest that a broadly applicable method for measuring bioavailability is likely to emerge from future research into this topic. What more probable is that a suite of tests involving chemical and biological procedures might be proposed which would allow approximation of bioavailability under a range of site-specific conditions. Despite the need for more detailed studies, guidance may be given on certain aspects of bioavailability assessment which should help in evaluating data from sediment monitoring programmes and in predicting the consequences of dumping contaminated dredged materials.

17.1 Chemical Approaches

The contaminants of greatest concern are generally persistent organohalogen compounds and toxic metals. While the former are primarily of anthropogenic origin, a significant fraction of the content of sediments is of natural origin and associated with naturally-occurring minerals, e.g., silicates. A portion of these metals are tightly bound within the crystal lattices of mineral particles and, under the range of pH and Eh conditions in aquatic environments, they are unreactive and unavailable to biota. (It should be noted that this may not apply on geological time scales.) For this reason, analytical techniques which are sufficiently vigorous to release lattice-bound metals will tend to over-estimate the bioavailable metal content of the sediment. An example is digestion using a mixture of hydrofluoric acid (HF) and aqua regia.

Metals not bound to silicate lattices, or included in spinell-type material, include those attached to exchange sites by weak electrostatic and ion-exchange forces, those co-precipitated with oxides, those contained within carbonate crystal structures, metal sulphides and metals associated with organic matter. Organic matter is also likely to be a major repository of organohalogen compounds in sediments. While all the contaminants in

this group might be considered "potentially" bioavailable, investigations have shown that in some non-lattice matrices, notably contaminants will remain tightly fine (mud) fraction. bound for very long, if not indefinite, time periods. extractions which permit quantification of all non-latquently, tice contaminants might also fail to provide a reliable estimate of the truly bioavailable fraction. The situation is further complicated by the fact that no extraction will release all metals to the same extent irrespective of the matrix structure. Clearly, there is no possibility of using a single chemical extraction to estimate the truly bioavailable fractions of several metals in a range of sediment types.

For these reasons, an approximation of the bioavailable fractions of metals can only be obtained by a series of extractions, using replicate samples of sediment, which simulate the extremes of the pH and Eh regimes likely to occur at the site in question. These might range from oxidizing (hydrogen peroxide extraction) to moderately reducing conditions (hydroxylamine extraction) and to mildly acidic conditions (dilute acid extractions). The fractions released should then be compared to those released by strong acids (aqua regia) or total digestions (HF). Strong acid leaching without HF probably releases more than the bioavailable fraction by releasing tightly-bound constituents. Even using a series of chemical procedures, it is likely that only an approximate indication of true bioavailability can be obtained.

17.2 Biological Approaches

Where it is necessary to determine the true or "actual" bioavailability of metals, and in all assessments of bioavailability for organohalogen compounds, biological tests must be used. Attention should be given to both controlled laboratory tests and confirmatory field exposures, where this is possible. The species and the test conditions should be selected to reflect those from the area where the sediments occur.

At present there is insufficient research experience to specific recommendations on the design of experiments to determine the bioavailability of sediment contaminants; however, points are evident. Availability to organisms may be demonstrated by acute toxicity, chronic toxicity, or by changes in growth rate, behaviour, metabolism or incidence of disease (lethal or sub-lethal effects). Frequently, but not invariably, effects may result from bioaccumulation. Symptoms of bioavailability are most likely to be observed in organisms which live within the sediment, or in close proximity to the sediment surface, and in sedentary as opposed to more mobile species. ever, ingestion of sediment particles which are voided without absorption of contaminants through the gut wall does not constitute bioavailability. Recent studies have shown that, for some sediments, biological effects may be related to the very phases of the sediment rather than to the large-grained material. Consequently, procedures which involve particle size separations followed by separate exposures of the animals to filtered and unfiltered supernatants, as well as to the intact sediment, may give valuable information on relative bioavailabilities and the modes of toxicant interaction with the organism.

17.3 Future Prospects

It will be evident from the above discussion that there can be no simple or inexpensive solution to the measurement of bioavailability in sediments. Considerable research will be necessary before more systematic procedures can be developed. techniques alone are unlikely to provide a satisfactory approach and biological tests cannot be substance-specific unless they are coupled to specialized chemical analyses. However, selective use of chemical and biological methods, reflecting conditions at the sediment site, may provide reasonable assurance of non-bioavailability of sediment contaminants. In the interim period, the use of chemical tests, as outlined above, is strongly encouraged, particularly if they are applied consistently within geographical areas which contain sediments of relatively uniform structure. In the longer term, research which attempts to relate biological responses to analytical data obtained from different extraction procedures, applied to a range of sediment matrices, may provide some possibilities for improving bioavailability estimates by non-biological means.

18 ISSUES RELATED TO SUSPENDED PARTICULATE MATTER

18.1 <u>Measurement of Concentrations of Suspended Particulate</u> <u>Matter in Sea Water</u>

In respect to the measurement of concentrations of suspended particulate matter (SPM) in the marine environment, there currently exist reliable and reproducible procedures for such measurements based on gravimetry. Such gravimetric procedures also have advantage of making available suspended particulate material for subsequent compositional analysis, including the quantification This gravimetric procedure involves the some contaminants. collection of seawater samples with Niskin or Go-Flo bottles, a homogeneous volume of these water samples into a of suitable container and filtration, to completion, through preweighed 0.4 µm Nuclepore filter membranes. Following a washing of the filter membrane with distilled water to remove soluble salts, filter is dried and re-weighed to determine the mass of particulate material removed by the filter. It remains a simple matter to calculate, from this mass and the volume of water filtered to completion, the concentration of suspended particulate material. Nuclepore membranes have advantages in this procedure, since unlike Millipore membranes, they maintain constant weights through numerous washing/drying cycles and maintain a constant effective pore-size over a wide load range. The use of Millipore and similar web-matrix filter membranes, whose effective pore sizes alter as loading increases, is not appropriate for this work and should be avoided.

It should be stressed that such a procedure will provide a reliable and quantitative determination of SPM concentrations over a wide range of concentrations, which can be accommodated by suitable adjustment of the volume of water filtered, provided that the volume chosen results in the mass of SPM retained on the filter being within the 0.5 - 1.5 mg range. The procedure has a high precision, limited predominantly by the weighing uncertainties. Some fast-settling and transient particulate matter will not be included in the material measured by this procedure because the particles involved either constitute a small volumetric concentration in the water or are too ephemeral (e.g., loosely aggregated flocs) to be retained by the latter.

There are other methods for turbidity or SPM measurements that do require the collection of samples. These are generally in <u>situ</u> survey methods that can be ideal for situations required on the spatial or short-term teminformation is only poral distribution of SPM. These methods involve the use (devices generally using optical scattering technephelometers niques) or transmissometers (devices measuring optical opacity or absorption), and their quantitative utility is subject to the adequacy of the associated calibration and standardization prolength of time for which these remain valid. and the Thus, while the ACMP intends to provide specific advice regarding gravimetric procedures for the measurement of SPM concentrations in 1987, if information on other survey techniques is required, the ACMP can initiate the development of such advice.

18.2 Analyses of Trace Metals in SPM

During its 1985 meeting, the ACMP considered the successful outcome of the Intercalibration Study on Analyses of Trace Metals in Suspended Matter (1/TM/SM), in which only a small group of invited laboratories participated. Before proposing an additional intercalibration in this field, which was seen as a prerequisite for studies on a very important environmental issue, the ACMP asked the WGMS and MCWG to advise on whether:

- there is already an adequate basis of agreed sampling procedures (type of filters, mode of filtration, filtration equipment, volumes, etc.) for suspended particulate matter (SPM) to be able to study particulate trace metal concentrations in sea water.
- if not, should these procedures be intercalibrated?

The WGMS had discussed this matter and agreed that a question-naire should be distributed among persons working on measurements of SPM. The questionnaire is intended to collect information on the types of studies presently carried out in different laboratories on problems encountered with regard to SPM sampling and on issues related to the analysis of contaminants therein. In addition, it was decided that a document should be prepared intersessionally which reviews different sampling strategies and collection methods for SPM that appear to work well.

The discussion of this matter in the MCWG focussed mainly on the feasibility of conducting an extended version of the Intercalibration Exercise on Trace Metals in SPM. Further discussion on this question will take place intersessionally.

The ACMP encouraged both Working Groups to carry out these activities as expediently as possible.

19 ISSUES RELATED TO THE MEASUREMENT OF NUTRIENTS

19.1 Intercalibration of Nutrient Measurements

The ACMP noted that the MCWG had discussed extensively the need for a nutrient intercalibration exercise. The MCWG had agreed that exercises based on preserved sea water samples would not be useful, but that it was difficult and costly to hold intercalibration workshops or inter-ship exercises using freshly collected sea water samples. It was accepted, however, that whenever a joint exercise, e.g., the Joint International Multi-ship Investigation of Patchiness in the Baltic Sea (PEX), was conducted, such a comparison should be carried out when research vessels were operating in the same area at the same time. The ACMP noted that the MCWG intended to review the status of nutrient intercomparability on the basis of previous nutrient intercalibrations. The ACMP stressed that this review should include an evaluation of experiences gained during the PEX experiment, in consultation with the ICES Hydrographer. The outcome of this review should be used to determine both whether there is a need to conduct further comprehensive or cooperative studies of the comparability of nutrient measurements or whether analytical modifications to currently used methods need to be made. The ACMP recommended that any conclusions drawn from this study should be discussed in the Hydrography Committee so that the needs, experience, and advice of the hydrographers can be taken into account.

19.2 Review of Nutrient Measurements in Relation to Trend Monitoring

The ACMP noted that the MCWG proposed to review the measurement of nutrients in sea water by ICES laboratories following the ACMP request to produce guidelines on the monitoring of temporal trends of nutrients in sea water. This review would not only assist in the identification of areas where such trend studies might be considered, but it could also be useful to identify gaps in the collection of nutrient data in relation to monitoring studies.

As for Section 19.1, above, the ACMP requested that this review of nutrient measurements be carried out in collaboration with the appropriate working groups of the Hydrography Committee and the ICES Hydrographer.

19.3 <u>Turbidity Effects on the Determination of Nutrients by Autoanalyzers</u>

The ACMP noted the results of an investigation of the effects of turbidity on the measurement of nutrients (nitrate, nitrite, phosphate and silicate) in seawater. Two species of phytoplankton were used to provide samples with a defined turbidity. At a concentration of 20 mg/m³ chlorophyll-a, the highest value normally measured in a "bloom" situation, a slight turbidity effect was observed. It was concluded that in most situations phytoplankton would not be a major source of turbidity. It was estimated that high turbidities were only observed in one percent of nutrient

data from recent measurements, mainly in near-bottom samples from the northern Kattegat, although ten percent of the data obtained during the months of March and April show high turbidity due to the presence of diatoms. Normally, it was not necessary to take turbidity into account, however, appropriate corrections should be made for very turbid samples. It was pointed out that the autoanalyser used for this study is unique (see Doc. C.M.1984/C:19). A report of a similar investigation by the Finnish Institute of Marine Research, using Technicon and AKEA autoanalysers, was also discussed. The results of this work indicated that the turbidity should always be measured when nutrient concentrations are low.

The problems encountered in analysing turbid samples can be avoided by filtration, centrifugation, or dilution of the sample. Synchronous analysis of turbidity and the sample could be used to correct for the effects of turbidity, but this approach would be difficult for most laboratories to apply on a routine basis. A simple approach is to analyse a suitable reference for each sample.

It is recommended that when phosphate, nitrite, or nitrate (when using a cadmium coil) are being analysed, turbidity should also be measured and taken into account. In order to obtain accurate data, it is also necessary to take salt effects into account, especially in the analysis of nitrite/nitrate, silicate and ammonium. The salt effect can cause both optical and chemical interferences. It was pointed out that the cell design plays an important part in refractive index effects.

The ACMP accepted the recommendation from MCWG on the need for turbidity measurements in the analysis of nutrients by autoanalysers.

19.4 Analysis of Total Nitrogen

The ACMP noted the discussions of the MCWG on the comparison of a new method for the analysis of total nitrogen in sea water, using a high temperature catalytic oxidation procedure, with the method currently in use by marine chemists, i.e., persulphate oxidation. Concentrations of total nitrogen by this new technique were found to be significantly higher than those obtained by the persulphate method. It was suggested that the difference was due to the inability of persulphate to break down the high polymer organic matter in sea water. In this context, a need has been identified for information on which organic compounds could serve as suitable models for use in testing the oxidative capacity of both methods. It was noted that the MCWG will discuss this matter again at its next meeting, following a review of the oxidative capacity of the wet digestion method.

The ACMP noted that problems are also encountered in the analysis of total phosphorus, particularly organically bound phosphorus, and requested the MCWG to pay commensurate attention to this matter.

19.5 Nutrient Data Holdings at the ICES Secretariat

The ACMP took note of two activities relevant to the compilation of nutrient data for the North Sea area which are currently underway at the ICES Secretariat. These are related to the overall reorganisation of the historical, regional data holdings and the hydrochemistry data set obtained during the annual International Young Fish Survey, respectively.

With regard to the reorganisation of the data bank, an important priority has been to ascertain gaps in the data holdings by comparing the data that have already been submitted to ICES with the information contained in inventories, specifically ROSCOP (Report of Observations, Samples Collected by Oceanographic Programmes). ROSCOP shows that in the last five years, there have been approximately 12 cruises each year in the North Sea during which nutridata have been collected; this compares unfavourably with ent corresponding activities in the Baltic Sea by a factor of 3 - 4. ROSCOP also shows a considerable decrease in activity in recent years. As a result of the reorganisation so far, most of the data collected by Denmark, Sweden, the Federal Republic of Germany, and the United Kingdom (one institute) are relatively complete and readily accessible. Nutrient data have never been submitted from Norway, Belgium or the Netherlands. It is understood that is mainly the result of the poor data banking procedures at some institutes, which suggests that this situation is unlikely to change in the near future.

With regard to the data collected during the International Young Fish Surveys, following a Council Resolution endorsed in nutrient data were collected at only two stations during the period 1976-1983. Following a reminder in 1983, and a revision of station coverage, four ships collected nutrient data at 231 stations during the February 1984 survey. These data have now all been submitted and are undergoing appraisal with regard to their overall quality and suitability as water mass tracers and for trend analysis purposes. In 1985 and 1986, only three of the eight ships participating in the survey collected nutrient data. As a result, the coverage of stations is not as complete as it could be, with large gaps in most coastal regions, especially in the eastern North Sea, including the Skagerrak, Kattegat and the Norwegian coast. It is known, however, that other data exist for this period and these will go some way to filling at least one of these gaps.

20 OVERVIEWS OF CONTAMINANTS IN THE MARINE ENVIRONMENT

20.1 General

The ACMP continued its task of reviewing current knowledge about selected contaminants in the marine environment on the basis of overviews prepared by Working Groups. The ACMP took note that several of these overviews were in the course of preparation but only one was in a form which could be utilised directly by ACMP. This concerned polycyclic aromatic hydrocarbons (PAHs) and the completed text, as amended by ACMP, is contained in Section 20.1, below. The main conclusions arising from this overview are that PAHs are unlikely to pose an acute toxic hazard to marine organisms. The main cause for concern stems from the potential effects of PAHs on human health as a consequence of their accumulation in marine organisms and their carcinogenic and mutagenic properties. There may be similar reasons for concern with respect to top predators.

The ACMP further noted that the MCWG had discussed an investigation of diphenyl sulphone in the Baltic Sea. Concentrations of this compound have been found to be ten times higher than that of any other PAH. The presence of this compound, which represented a degraded hydrocarbon and which was much less degradable than its parent compound, was considered a matter which justified additional research from the point of view of toxicity to biota, particularly in the surface microlayer.

In considering priorities for action on overviews which were either in progress or for which a need had been demonstrated, the ACMP recalled that it had assigned a high priority to an overview on organosilicon compounds. In view of the recent decisions taken by the Oslo and Paris Commissions, the recommendations London Dumping Convention Scientific Group and the fact that GESAMP was about to publish a review on the subject, it was that no further need existed for an overview on this subject. However, the ACMP reconfirmed its opinion that overviews on phenols and lindane in the marine environment would be useful and welcomed the plans of the MCWG to prepare overviews on arsenic, chromium, copper, nickel and surface active agents and to update the overview on mercury with special emphasis on organo-mercury compounds. The ACMP requested that it be kept informed of progress in this work.

20.2 Polycyclic Aromatic Hydrocarbons in the Marine Environment: An Overview

20.2.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds based on structures of three or more fused aromatic rings. Many isomers exist, particularly for the larger PAHs. These may differ both in the arrangement of the aromatic rings and in the position of alkyl side-chains, where these are present. The aromatic rings may also be modified by the substitution of nitrogen, sulphur or oxygen atoms for ring carbons to form heterocyclic compounds.

PAHs of environmental concern are those with molecular weights up to that of coronene ($C_{24}H_{12}$, MW 300.36).

PAHs are of interest primarily because of the association between substances containing PAH and the occurrence of cancer in humans. The acute toxicity of aromatic hydrocarbons decreases as the number of fused rings increases, so although one- and two-ring aromatic hydrocarbons are quite acutely toxic to marine animals, it is unlikely that PAHs will commonly present problems of acute toxicity in the marine environment. PAH are, however, of major toxicological concern regarding chronic mutagenic and carcinogenic effects (Uthe, 1979).

20.2.2 Production and Discharges

PAHs are formed by pyrolytic reactions occurring at both relatively high and low temperatures. Complex organic molecules are broken down to lower molecular weight fragments, many of them free radicals, which recombine to form stable PAHs. Combustion of organic fuels at relatively high pyrolysis temperatures leads to the formation of mainly non-alkylated PAHs, whereas the formation of crude oil from organic material, which occurs at relatively low temperatures (generally below 150°C) (Blumer, 1976), leads to a predominance of alkylated PAHs with two to four rings (Mackie et al., 1980).

Biosynthesis of PAHs

Evidence for direct biosynthesis of PAHs by bacteria and plants is contradictory, particularly for PAHs with more than four fused rings. Reported rates of biosynthesis are all very low, and it is unlikely that this could represent a significant input of PAHs to the marine environment. Any production of PAHs by complete biosynthesis would be expected to follow particular pathways, and give rise to very simple mixtures of only a few specific PAHs (Blumer, 1976).

Certain PAHs, perylene and retene (1-methyl-7-isopropyl phenanthrene), have been found at high concentrations in sub-surface sediments. Orr and Grady (1967) and Aizenshtat (1973) observed increasing perylene concentrations with depth in reducing marine sediments of the Santa Barbara basin and Saanich Inlet, respectively, and ascribed this to the production of perylene in situ. Perylene is thought to result from the chemical reduction in anoxic sediments of extended quinone pigments and related comsynthesized by terrestrial fungi and insects, though the occurrence of perylene in Namibian Shelf sediments raises the question of a possible marine precursor (Wakeham et al., 1979). Sediments in this area are thought to receive very little terrigenous material by comparison with the large input of marinederived organic matter resulting from the high productivity in the overlying Bengeula current upwelling area (Chester et al., 1972; Morris and Calvert, 1977; Gagosian and Farrington, 1978). Retene is believed to be the product of the dehydrogenation of abietic acid, a major component of pine rosin.

Whilst they may be important locally, these processes probably do not contribute significantly to the environmental burden of PAH.

PAHs from petroleum

Crude oil contains about 1-3% PAH by weight, although catalytic cracking processes lead to higher concentrations in some products. Crude oil is rich in low molecular weight PAHs, the concentrations of different ring systems being 2>>3>>4>5 (Mackie et al., 1980). Used lubricating oils can contain high concentrations of PAH and their disposal into sewer systems ultimately constitutes a PAH input to the marine environment.

PAHs from combustion

The quantity of PAH formed during combustion is inversely related to the combustion efficiency. Combustion-derived PAHs, which are largely non-akylated, probably represent the greatest PAH input to the environment as a whole. They are generally associated with airborne particulate matter, and the long range transport of these particulates has been suggested as the reason for the uniform low background of PAHs in sediments remote from obvious sources (Uthe, 1979; Neff, 1979; Jensen, 1983, 1984).

PAHs from industrial wastes

Some industrial processes contribute large quantities of PAHs locally to the marine environment, especially if effluents are released directly to the sea. Coking plants produce coal tar which contains large amounts of PAHs, and emissions from the coke ovens contain a large number of PAHs, 60 having been identified in one study (Lao et al., 1975). Creosote, a coal tar distillate, is rich in PAHs, and the residue of this distillation, coal tar pitch, may contain up to 50% PAHs. Creosote is mainly used as a wood preservative and coal tar pitch is used in the manufacture of protective coatings, including road surfaces (Uthe, 1979).

Soderberg electrodes are made from anthracite, coke tar, pitch and anthracene oil. They are used in aluminium (and other) smelting operations, and are burned continuously whilst smelting is in progress. PAHs are released with fumes generated from the electrodes and, where wet gas scrubber systems are used, are also present in the scrubber effluents (Palmork et al., 1973). A study in the Saudafjord, in western Norway, of PAHs derived from waste effluents from a ferro alloy smelter identified up to 34 individual PAHs (Bjorseth et al., 1979).

PAH inputs

Estimates of the inputs of total PAHs and of the carcinogen benzo[a]pyrene alone to the aquatic environment have been derived by Neff (1979). These estimates are based on the NAS (1975) figures for petroleum input and, therefore, include inputs from operational shipping losses. His table of estimates is reproduced below.

INPUTS	OF	TOTAL	PAHS	AND	BEN	NZO[A]P	YRENE	ŢO	THE	ENVIRONMENT
			(Uni	.ts a	are	tonnes	year	')		

Sources	Total PAHs*	Benzo[a]pyrene
Biosynthesis	2,700	25
Petroleum	170,000	20-30
Domestic and industrial wastes	4,400	29
Surface land run-off	2,940	118
Fallout and rainout	50,000	500
	230,040	697

^{*}The figures for total PAHs include naphthalenes.

Although the data base on which these estimates are made is far from complete, it is believed that the order of magnitude of the estimates is correct, and that they represent a reasonable picture of the relative contributions from different sources to the inputs of PAHs (Neff, 1979). The major contributions to the total PAH input are from petroleum spillage (74%) and from fallout and rainout (22%), whereas the corresponding figures for benzo[a]-pyrene are 3.6% and 72%, respectively. This reflects the composition of crude oil and many petroleum products in which the lower PAH are much more abundant than those of higher molecular weight.

The use of creosoted pilings for docks, wharves, etc., may represent an important localized source of PAHs (Zitko, 1975; Dunn and Stich, 1976), as the PAH content of creosote can be very high and, therefore, may have a large effect in areas of heavy use, such as some coastal areas. It does not, however, contribute significantly to the total input of PAHs to the aquatic environment.

20.2.3 Distribution and Levels in Marine Compartments

Before discussing levels of hydrocarbons found in the environment, it is necessary to mention the difficulties associated with the analysis of PAHs, in order to explain the caution needed when comparing results obtained by different laboratories and methods.

The formation of PAHs by processes other than biosynthesis yields complex mixtures of compounds. Most analyses, therefore, require the separation of this complex PAH fraction from the sample matrix as the first stage of the analysis. Isolation of PAH is usually achieved by saponification and solvent extraction, followed by partitioning and/or column chromatography to yield a PAH fraction (Uthe, 1979). If the aim of the analysis is to quantify a specific PAH (usually benzo[a]pyrene), UV absorption or fluorescence techniques are then applied. If, as is now more common, it is intended to identify and quantify a large number of PAHs, then capillary gas chromatography or capillary gas chromatography/mass spectrometry are the methods of choice. PAH metabolites are usually polar oxygenated compounds not amenable to gas chromatography, and analysis of these compounds is usually carried out by high-pressure liquid chromatography (HPLC) (Lee,

Novotny and Bartle, 1981). The use of HPLC with fluorescence detection is also becoming more common in the analysis of complex PAH mixtures, though high resolution columns are normally not used because of the more sophisticated pumping systems required, and because of the long analysis times necessary.

Two remarks need to be made at this point:

- 1) Although laboratories using exactly the same method can produce reasonable agreement on PAH concentrations (Haenni, 1978), the use of different methods and techniques generally produces very poor comparability of results (e.g., Hilpert et al., 1978; Law and Portmann, 1982; Farrington et al., 1985; Uthe et al., 1985).
- 2) Intercomparability of analytical results can be improved by the use of certified standard reference materials to prove the worth of analytical methods when applied to real samples and matrices. Currently no samples are available containing certified levels of PAHs in marine waters, sediments or biota, and a major improvement in intercomparability seems unlikely until this situation is rectified, or until standard methodology can be adopted.

PAHs in water

The solubility of PAHs in sea water is low, and generally decreases with increasing molecular weight. The presence of dissolved or colloidal organic material may enhance their solubility, but PAHs are usually associated with particulate material and are removed by sedimentation and, therefore, seawater concentrations of PAHs are very low. Concentrations of PAHs in marine surface microlayers may be an order of magnitude higher than those of the underlying bulk water (Hardy, 1982).

PAHs in sediments

There is general agreement that the majority of PAHs in recent sediments are combustion derived, transported to the sediment following fallout or rainout of combustion-derived aerial particulates. Analysis of dated sediment cores has shown an increase in the concentrations of PAHs over the last 125 years, whilst the distribution of alkylated and parent PAHs has remained similar. These results reflect an increasing source between 1850 and 1900 (Hites et al., 1977) and are consistent with the rise in the use of fossil fuels over this period, rather than with the records of forest fires which have been suggested as an alternative source (Blumer and Youngblood, 1975).

PAHs are transported to the sediment adsorbed onto particulate material, which may be of inorganic or organic (e.g., zooplankton faecal pellets) (Prahl and Carpenter, 1979) origin. Once deposited in sediments, PAHs are less prone to oxidation (particularly in anoxic sediments) and more persistent, and may accumulate to high concentrations (Neff, 1979). In addition, the main process of degradation of sedimentary PAHs, microbial degradation, is usually slow in the marine environment, and may be very slow indeed in reducing sediments or where water temperatures are low.

Total PAH concentrations in sediments close to an industrial source, a ferro-alloy smelter discharging 3-4 tonnes of PAHs annually into a fjord in western Norway, were up to 99 μ g g⁻¹ dry weight (34 PAHs) (Bjorseth et al., 1979).

Reported concentrations of benzo[a]pyrene determined in marine sediments show wide variations (see Table 3). The highest levels generally occur adjacent to regions of high population or intense industrial activity, though small amounts are detected in remote regions. In a study carried out in British Columbia around a sewage treatment plant outfall, a sharp concentration gradient towards the outfall was observed (Dunn and Stich, 1976), with concentrations of benzo[a]pyrene ranging from 0.4 to 121 $\,\mu g$ g dry weight.

PAHs in biota

Marine biota, in particular those living in and on the sediments, readily accumulate PAHs into their lipid pools as a result of the hydrophobic and lipophilic nature of PAHs. The sites of accumulation of [9-14] C]-phenanthrene, used as a model PAH, have been lation of [9 shown to vary between different species of fish, with higher concentrations occurring in fatty tissues (e.g., Solbakken and Palmork, 1980). The rates of elimination also vary greatly (Solbakken and Palmork, 1980, 1981). Metabolism of PAHs is carried out by aryl hydrocarbon hydroxylase (AHH), an inducible mixedfunction oxidase enzyme system found in teleosts and higher animals and at lower levels in some invertebrates. Induction of AHH occurs during exposure to various PAHs, including benzo-[a]pyrene. The primary function of this system is to render poorly water-soluble lipophilic materials more water-soluble so that they can be excreted (Neff, 1979).

Analyses of tissue samples from fish and shellfish have generally focussed on benzo[a]pyrene, and few data are available for total PAH levels. Baseline levels of benzo[a]pyrene in fish muscle and shellfish are low, and there is no evidence that severe contamination by benzo[a]pyrene (and by inference PAHs in general) is widespread. Sewage effluents and industrial and refinery discharges which contain oil, and the operation of docks, oil terminals, transhipment facilities, all of which involve the spillage of oil, may be expected to increase PAH levels in local biota. Higher levels of PAH have also been found in shellfish associated with creosoted wharf pilings or stored in pounds constructed from (Dunn and Stich, 1976; Dunn and Fee, 1979). creosoted timbers Concentrations of benzo[a]pyrene in the tail meat of lobsters stored in such pounds for three months rose from 0.4-0.9 to 7.4-218 ng g $^{-1}$ wet weight, with a maximum concentration in digestive gland (hepatopancreas, an edible organ) of 2300 ng g $^{-1}$ wet weight (Dunn and Fee, 1979) and 544 ng g $^{-1}$ wet weight (Uthe et al., 1984).

Baseline levels of benzo[a]pyrene in mussels in Southern California were estimated to be less than 0.5 μg g wet weight (Dunn and Young, 1976). Higher concentrations (0.5 to 2.3 μg g) were associated with areas of human activity, and a sample of mussels taken off pilings contained 8.2 μg g . A study of PAHs in mussels from around the coast of Scotland (Mackie at al., 1980)

showed a correlation between high PAH concentrations and proximity to urban or industrial centres (Table 4). High levels of 4-ring PAHs found in mussels from a remote site were tentatively ascribed to runoff from a recently asphalted loch-side road. Total PAH levels (25 PAHs including naphthalenes) in oyster (Crassostrea virginica) from the Gulf of Mexico ranged from 2120-9160 ng g wet weight (Bravo et al., 1978).

20.2.4 General Toxicology

PAHs, particularly those of higher molecular weight and larger number of rings, do not seem to be acutely lethal to fish, probably because of their extremely low aqueous solubilities (Neff, 1979). The concentrations of PAHs that are acutely toxic to aquatic animals are several orders of magnitude higher than concentrations found in the most heavily polluted marine waters, and no acute toxicity problems of a widespread nature should be encountered (Uthe, 1979).

Chronic exposure to low concentrations of PAH, whether in water, sediment, or food, can produce sublethal effects in aquatic organisms. These effects can occur at much lower concentrations than those which cause acute toxicity, but generally they are still much higher than concentrations encountered in all but the most contaminated environments.

Different species of organisms vary substantially in sensitivity to PAH-induced carcinogenesis. Many aquatic organisms possess the mixed-function oxidase enzyme system necessary for the metabolic activation of PAHs, and some at least produce the active metabolites necessary for carcinogenesis. Tumerous growths have been identified in the tissues of natural populations of marine invertebrates and fish, although in most cases the causative agent is unknown. PAHs have not been unequivocally identified as the causative agent in any increase in incidence of cancer in any natural population of aquatic organisms (Neff, 1979).

20.2.5 Implications and Public Health Aspects

The major concern over PAHs is with respect to their effects on human health, because of their chronic carcinogenic and mutagenic activity. In general, materials containing high levels are associated with human cancers. An increased incidence of cancer in humans has been reported in individuals exposed to tobacco and combustion smoke, motor vehicle exhausts, coal tar, creosote and certain foodstuffs (Uthe, 1979). High levels of carcinogenic PAHs in fish or shellfish consumed by humans could give rise to an increased risk of cancer, and to prevent this it may be necessary to limit consumption of such foods. In Iceland, the uneven distribution of stomach cancer was shown to be linked the consumption of smoked trout and smoked mutton, the incidence being highest in the areas of highest consumption (Dungal, 1961; Uthe, 1979). Benzo[a]pyrene concentrations in these smoked foods were only 1-3 μg g wet weight, but much higher levels of other PAHs were also found. This makes the question of control much more difficult. It would be easy to set control limits based on concentrations of a single compound, although problems of methodology and comparability would still need to be solved; controls specifying 20 or 50 compounds would be much more difficult to implement. The existence of synergistic effects further complicates the picture, as some compounds not in themselves carcinogenic may promote the activity of some carcinogenic PAHs.

Where the concentrations of PAHs in the edible portions of fish or shellfish are so high that a diet study indicates an unacceptable risk to human health, then action may need to be taken. This would probably be limited to a small area around a local input, and may take the form of depuration prior to sale. If this proved not to be possible, then the closure of these fishery areas may be necessary to prevent damage to human health.

Acknowledgements

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20.2.6 References

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Table 1 Concentrations of benzo[a]pyrene in marine sediments from various locations (µg g dry weight). (Mostly from Neff, 1979).

Source	Concentration	Reference		
Bay of St. Malo, France		Mallet <u>et al</u> ., 1963		
Pissot Fours-a-Chawe Bassin	0.16 1.32 0.17			
Bay of Naples, Italy	0.001-3.00	Boucart and Mallet, 1965		
Southern Beaufort Sea	<0.001-0.02	Wong <u>et</u> <u>al</u> ., 1976		
Polynesian atolls	<0.001-0.007	Niaussat <u>et al</u> ., 1975		
Villefranche Bay, France	trace - 1.5	Lalou, 1963		

Footnote:

The data provided above were derived using similar analytical methods. They do, however, span a time-frame of at least thirteen years and were produced by different workers. They are unlikely to be strictly comparable and the figures should certainly not be regarded as absolute. They should be regarded simply as the range of values which might be encountered under the influence of local and distant scales of input.

Table 4 A comparison of concentrations of 3- to 5-ring PAHs in mussels from clean and urban/industrial sites around the Scottish coast (from Mackie et al., 1980) (ng g wet weight).

The second secon					and the same of th		
a) <u>Clean</u>	site	<u>s</u>					
Station	P	C ₁ P	Py	Fl	BA/BP	B[a]P	Total
1	30	6	3	2	1	1	43
2	16	8	6	27	45	13	115
3	9	49	8	13	25	6	110
4	11	38	10	6	14	13	92
5	7	4	2	5	3	1	22
6	15	9	6	10	8	5	53*
7	18	12	161	201	514	255	1,161
14	33	18	78	85	47	12	273
27	17	19	13	31	13	6	99

High values believed to result from run-off from a recently asphalted road.

b)	Urban and	Indust	rial Si	.tes			
Sta	tion E	C ₁ P	Ру	Fl	BA/BE	B[a]P	Total
8	42	19	158	198	363	236	1,016
9	8	4	7	. 11	4	2	36
10	32	31	9	12	31	22	137
11	147	214	283	269	627	329	1,869
12	12	: 6	3	6	14	13	54
13	621	197	540	476	710	137	2,681
15	22	18	75	92	110	29	346
16	335	5	280	438	130	40	1,228
17	8		5	7	5	22	110
18	9		16	26	28	15	101
19	43	12	46	49	32	9	191
20	30	94	7	8	10	5	154
21	4	22	8	12	25	13	84
22	123	150	63	76	127	78	617
23	15		29	35	30	9	125
24	10		154	94	168	55	486
25	7	3	16	11	34	35	106
26	28	20	25	32	24	18	147

phenanthrene

⁻ methyl phenanthrenes/anthracenes

⁻ pyrene

⁻ fluoranthene

BA/BP - benzanthracenes/phenanthrenes B[a]P - benzo[a]pyrene

21 MEASUREMENTS OF NET INPUTS OF CONTAMINANTS TO THE SEA THROUGH RIVERS

The ACMP recalled the history of the development of ICES advice to the Paris Commission on the topic of the input of contaminants to the marine environment via rivers. In its 1984 Report, the ACMP had provided advice on several approaches to the measurement of net discharges of contaminants from rivers. This advice followed earlier advice, contained in the 1982 ACMP Report, on strategies and techniques for the measurement of gross riverine discharges. The ACMP noted with satisfaction that the advice provided in 1982 forms the basis for a pilot programme to monitor gross inputs from rivers coordinated by the Technical Working Group (TWG) of the Paris Commission.

In a recent dialogue with the Paris Commission and its technical groups, it was reported that the advice next required by the Paris Commission is in relation to techniques for measuring net fluxes at estuarine and nearshore boundaries, whereas the ACMP has thus far only provided advice related to such measurements at the continental shelf break. Althought ICES offered to develop new advice on the specific question of net flux measurements at suitable inshore boundaries, the Commission has indicated that this issue is now considered to be of low priority and might be deferred until a greater body of information has been obtained on gross riverine discharges of contaminants through the TWG's pilot programme.

Despite this response, and the subsequent deletion of this item from the 1987 ICES work programme requested by the Commissions, the ACMP felt that there was justification for keeping the subject under review by the Marine Chemistry Working Group. It agreed that the MCWG, particularly its chemical oceanography and trace metal sub-groups, should be encouraged to continue to study this problem as an item of lower priority in its programme of activities. In this context, predominant attention should be paid to methods of assessing net fluxes across inshore, rather than continental shelf, boundaries.

The ACMP took note of the comments of the Marine Chemistry Working Group regarding procedures for gross riverine flux measurements and approaches to net flux measurements contained in the 1982 and 1984 ACMP Reports, respectively. The ACMP concurred with the view that rivers are not the only source of material to the nearshore marine environment, but noted that earlier advice on gross inputs pertained specifically and exclusively to river flux measurements, as requested by the Paris Commission. The ACMP was pleased to see an interest by the MCWG in refining the details of gross riverine flux measurements so as to provide a more comprehensive basis for such measurements and encouraged the MCWG to keep the suggested approaches to the estimation of net riverine flux under review with the aim of developing further advice when it is requested.

22 POLLUTION-RELATED STUDIES IN THE BALTIC SEA

22.1 <u>Multi-Ship Investigation of Patchiness in the Baltic Sea</u> (PEX)

The ACMP was informed about the execution and outcome of the Joint International Multi-Ship Investigation of Patchiness in the Baltic Sea (PEX) which took place in April - May 1986 under the coordination of Dr B.I. Dybern. The investigation was conducted in the central part of the Baltic Proper; fourteen ships from six countries around the Baltic Sea participated. Obligatory parameters measured in this investigation included: (1) physics: temperature, salinity, Secchi depth, currents and meteorological conditions, (2) chemistry: oxygen, phosphate, nitrate and nitrite, and, for special purposes, alkalinity and pH, and biology: chlorophyll, phytoplankton, mesozooplankton and primary production. In addition, several ships measured other parameters, e.g., light, microstructure, silicate, total phosphorus, fluorescence and fish distribution. Interpretation of satellite images and remote sensing by airplane will complete the picture.

The area under investigation was divided into two grids, a larger grid (eddy grid) with a distance between stations of 4 nautical miles, and a smaller grid (slope grid) with a distance between stations of 2 nautical miles; the smaller grid was situated inside the larger grid. In this way, different spatial scales were covered. The grids were divided into 6 transects, each with 11 stations; a number of ships made measurements along the transects, simultaneously taking parallel stations so that each grid was covered in one day. The grids were covered with a network of 13 current meter stations, and some ships also studied currents by means of drifters. Inside the slope grid, there were also two fixed stations where four anchored ships carried out measurements.

The data available to date show clear patchiness systems and complex current patterns. The ACMP was informed that two of the intercalibrations carried out did not give consistent results, so correction factors calculated according to other methods may have to be used on some of the data. The data will be compiled and preliminarily worked up by the ICES data centre. After the draft results have been distributed to all participants, a Workshop will be arranged to discuss the overall evaluation of the data and the preparation of the final report.

The Study Group on Patchiness Investigations in the Baltic will continue its work in order to facilitate the evaluation of the data and the preparation of the final report.

The ACMP took note of this information on PEX and congratulated the people involved in the exercise. It considered the results to be of very great interest and endorsed the further work on the compilation and interpretation of the data.

22.2 Sediment Studies

The ACMP was informed that, having completed the report on the results of the Baltic Sediment Intercalibration Exercise, the ICES/SCOR Working Group on the Study of the Pollution of the Baltic, through its Sub-Group on Sediment Studies, is now carrying this work further to be able to respond to a request by the Helsinki Commission. This request is for the preparation of a specific assessment on contaminants in Baltic sediments, for which two relevant activities are now being conducted.

The first activity involves the preparation of maps of sedimentation areas in the Baltic Sea. Maps of the depositional areas in the Gulfs of Finland and Bothnia and the northern Baltic proper will be prepared by Dr L Niemistö, the Coordinator of the Sub-Group, while maps for most of the remaining parts of the Baltic Sea will be prepared by Dr B Larsen.

The second activity involves the preparation of a critical review of existing data on contaminants in sediments in the Baltic Sea. The results of recent relevant studies will be collated and evaluated so that an assessment of the level of contamination of Baltic sediments may be made. Recommendations as to whether contaminants in sediments should be monitored as part of the Baltic Monitoring Programme will also be developed on the basis of this critical review.

The ACMP took note of this information and expressed its support for these activities.

22.3 Other Pollution-Related Studies in the Baltic Sea

The ACMP was informed that the ICES/SCOR Working Group had continued its review of the results of coastal monitoring studies. As a result of this review, it was agreed that coastal monitoring programmes must be carefully planned to meet their objectives, balancing the need to monitor many different compartments broad range of determinands to be able to interpret any observed changes against the problems of trying to run an overly complicated monitoring programme at the local level. It was noted that it is very important to know and understand the ecosystem from the biological standpoint so that any effects of discharges on the ecosystem can be determined; this is specific to an area, but clearly biological monitoring must be carried out in the context of much broader studies, including physical and chemical monitoring, so that the biological data can be interpreted. Moreover, the conditions in the Baltic Sea as a whole can have an influence local ecosystems, so that local conditions cannot be considered in isolation from general conditions in the Sea as a whole.

In addition to coastal zone monitoring, monitoring along sections from the coast to the open Baltic Sea has been encouraged by the Working Group. Results of some of these studies have shown that, in some areas at least, there is very little mixing from the coast to the open sea, but along the coast there are large mixing processes. Questions were raised concerning the transport and exchange of substances in archipelago areas, as the situation in these areas is very different from that in the open sea.

23 INTERNATIONAL CONFERENCE ON THE NORTH SEA

The ACMP took note of the preparations for the second International North Sea Conference, which will be held in London in 1987. A Scientific and Technical Working Group (STWG) has been established to prepare the background scientific document for this Conference. This document will update the information in the North Sea Quality Status Report that had been prepared for the Bremen Conference (November 1984). This new Quality Status Report will also attempt to identify trends in the condition of the North Sea.

part of the preparation of the Quality Status Report, an Oceanography Sub-Group was established to review recent information on the physical oceanography of the North Sea and provide an appropriate overview. The report of this Sub-Group highlighted the recent efforts in obtaining an appreciation of the variability of the North Sea circulation by means of numerical models. These models confirmed the conclusions reached from earlier ad hoc current measurements and tracer studies that the circulation of the area varied appreciably on all time scales from days to years. Because of this variability, a detailed understanding of the natural factors influencing the water quality of the North Sea was very dependent on the further development of these models, which in turn are very dependent on the correct parameterization of relevant physical, chemical and biological processes. As a result, the Sub-Group proposed that a necessary next stop towards predictability of North Sea water quality is extensive and collaborative modelling studies backed by widespread and coordinated observational programmes.

The ACMP noted that, in addition to assisting in the development of the report of the Oceanography Sub-Group and the Quality Status Report, ICES anticipates contributing the results of the 1985 Baseline Study of Contaminants in Fish and Shellfish to the preparations for this Conference.

24 REGIONAL ASSESSMENTS

24.1 Skagerrak-Kattegat Area

In reviewing the report "Assessment of the Environmental Conditions in the Skagerrak and Kattegat", submitted by the Working Group on Pollution-Related Studies in the Skagerrak and Kattegat, the ACMP concluded that the report is very informative and useful. The ACMP, however, considered that the report would benefit from further elaboration and editorial improvements. In particular, the ACMP agreed that problems related to eutrophication in the Skagerrak and Kattegat, as well as sedimentation in the transition zone between the Skagerrak and Kattegat, should be described in greater detail and that other editorial improvements should be made. The ACMP looked forward to reviewing this amended report at its 1987 mid-term meeting.

24.2 Irish Sea Status Report

The ACMP reviewed a first draft of an Irish Sea Status Report prepared in the UK and agreed that the report was pitched at about the right level of scientific detail and straightforward explanation to be of considerable value as a management tool for the area. The ACMP was also pleased to note that the contributors to the report had also found it to be a worthwhile exercise.

The ACMP noted that, following the expected completion of this draft in the autumn of 1986, it was intended to convert the report into a full international study through the incorporation of a promised major contribution from Ireland and inputs from relevant ICES working groups and the ACMP. The ACMP expressed its willingness to participate in this exercise and looked forward to reviewing the next draft of this document.

The ACMP agreed with the suggestion of the authors of the report that, ideally, the status report should have paid equal attention to radioactive contaminants (and relevant processes) in the area. Noting that the UK monitoring management group system precludes this, the ACMP agreed that ICES should contribute to an expansion of the report in its present form.

25 THE PRINCIPLES OF ACMP ASSESSMENTS AND THE ASSIMILATIVE CAPACITY CONCEPT

25.1 Introduction

For some years, the ACMP has been operating to a set of principles which, whilst not tacitly stated or recorded as its underlying policy, have been more or less clearly understood by the members. The ACMP considers that it would be useful if principles were now documented, as they provide a backdrop against which future advice should be considered. The ACMP noted, deciding to undertake this task, that there are currently two extreme approaches to controlling the entry of substances to the marine environment. These are, on the one hand, the ultra-conservative approach that demands avoidance of inputs under all circumstances and, on the other hand, the approach that allows almost any input provided it is within certain, often loosely described, constraints as to rate and quantity. The ACMP regards these two approaches as potentially devisive in an era of cooperative pollution control action. It hopes that the following clarification of its basic principles will serve to show that it pursuing a balanced approach between these extremes, which recognises realities, but ensures that adequate environmental protection, as well as human health protection, is achieved.

The ACMP notes that, even at the most basic level of existence, human society produces wastes and these wastes will have to be disposed of somewhere or destroyed in an environmentally acceptable manner. The adoption of extreme policies lacking scientific foundation may force the use of other options which are not those offering the least detriment to human health or the environment. The ACMP, therefore, considers it to be important that decisions be well thought out and the implications fully considered before action is taken. This should include all steps, from the decision to adopt a new practice, through to the disposal of the product and any waste arisings. At present this rarely occurs; as the following explanation of ACMP principles outlines, it always should.

25.2 The Case for Assimilative Capacity

There are a number of frameworks or conventions whose objectives are the prevention and/or reduction of "marine pollution" that have adopted a definition of "pollution" which involves some deleterious consequence of a practice. Several have adopted definitions of pollution based upon the GESAMP model which defines pollution in the following manner: "Pollution means the introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water, and reduction of amenities." Amended forms of this definition have been incorporated into the texts of guidelines of Conventions such as the Paris Convention for the Prevention of Marine Pollution from Land-Based Sources (1974), the Convention on the Protection of the Marine Environment of the Baltic Sea Area (1974), the Convention for the

Protection of the Mediterranean Sea Against Pollution (1976), and the Law of the Sea Convention (1982). All of these Conventions have as goals, inter alia, the protection of the marine environment from pollution. Implicit in these definitions of pollution is that controlled input of wastes to the marine environment can occur without causing harm to living resources or changes that would be unacceptable to society. It therefore follows that the environment has an assimilative capacity for all substances. There is, therefore, a concentration range which can be permitted, although for some contaminants the amount which could be discharged might be so small as to rule out the option.

It is further implicit that the instruments referred to accept de facto the existence of an "assimilative capacity" as covering the range of conditions between the uncontaminated situation and that in which contamination becomes deleterious. Exactly constitutes a deleterious effect depends very largely on what society is prepared to accept. As this is likely to vary according to each society's aims, abilities to appreciate the consequences of a given action, and its perception of what is acceptable, it is clear that the boundary between contamination and concentrations that cause pollution may change. It is equally that an individual society's perception of acceptability obvious will also change, since this is related to both the state of current knowledge and the society's desire to improve that knowledge. Moreover, any definition that contains language of the form "likely to result" rather than "to result" (as in the GESAMP definition), will, in principle, make the defined assimilative capacity somewhat lower.

The above is a generic argument for the implied existence of an assimilative environmental capacity based upon the aims objectives of current international legislation. From a wholly technical view, the existence of such a capacity can be demon-"drop in the bucket" strated by the analogy. This goes as follows: it is clear that a single milliliter of a saturated solution of mercuric chloride dropped into the surface waters of the North Atlantic would not cause any significant deleterious effects. Acceptance of this argument implies that the ocean has a finite capacity to absorb wastes without harmful effects and that can, in principle, be quantified. In practice, the scientific community may be able to define effects in quantifiable terms as measurable concentration, or statistically significant changes in hazards to human health, animal or plant communities, mortality, enzyme function, etc. It may also be able to advise on the probable impact of a particular type of effect, the cost ensuring that the effect does not occur, and the cost of the detriment if it does occur. Such advice will be possible for range of foreseeable effects and options and can be elaborated on by the provision of estimates of precision and accuracy. Cost the sense used here is not necessarily purely a monetary matter but, irrespective of how cost is defined, acceptability cannot be determined solely by the scientific community. Thus, while scientists can advise on whether or not a particular scientifically measurable effect is deleterious, only society as a whole can decide whether the effect is acceptable or not.

Whether the concept of assimilative capacity is approached from a technical or a societal standpoint, the conclusion reached is

that there exists a range of contamination levels that do not cause, or are not likely to cause, unacceptable deleterious effects. The assimilative capacity concept has considerable appeal to environmental managers and bodies faced with the regulation of activities that involve potential detriment to society. The same arguments can be pursued in relation to all sectors of the environment, viz., air, land, fresh and marine waters. Indeed, it is important that they are extended to all environments, in order to take into account interactions between environmental sectors and to develop a holistic view of the consequences of disposal.

The problem the marine scientific community faces is that of attempting to define marine assimilative capacity for practical purposes. This latter question has already been addressed by GESAMP Working Group No. 23 (GESAMP, 1986). Nevertheless, the ACMP has pursued an independent approach in the belief that if different routes lead to similar conclusions, they are mutually supportive. Furthermore, a set of principles has been elaborated by the International Commission on Radiological Protection (ICRP, 1977), which have an important bearing on this subject. The ACMP considers that these principles can be applied to the regulation of any of man's activities which potentially impact upon the environment or human health. These principles are as follows:

- 1) Justification. No practice should be adopted unless there exist clear net benefits to society, i.e., the overall benefits outweigh the overall detriments to the society affected. Justification applies to an entire practice (e.g., investment in the production of a new agricultural pesticide) rather than to individual components of that practice, such as the disposal of any waste products.
- 2) Compliance with exposure limits. Limits of exposure to products, their raw materials and associated wastes by both employees in relevant industries and members of the public are established and observed.
- 3) Optimization. Exposures to the substances concerned should be kept as low as reasonably achievable, taking technical, social and economic factors into account. Thus, exposures should be reduced by technical means, or through the use of alternative options for the handling and disposal of products and wastes, so that the overall exposures resulting from the activity or sub-activity are as low as economically and socially justifiable. The application of this principle requires complex balancing of scientific, economic and political factors, but in many cases these balances can be somewhat simplified.

25.3 Justification

One of the great difficulties faced in recent years has been the fact that many substances were produced simply because a market was identified. The overall benefits and disbenefits of the entire practice (i.e., the production process, the wastes produced, and the use of the product and its eventual disposal) have only rarely been considered in a comprehensive manner and hardly ever in an international context. Even when justification

has been applied, the boundaries and time scales considered were often too narrowly defined. This has resulted in, for example, the problems encountered with plastic wastes and with persistent compounds such as DDT and PCBs following their escape from the site of use. In short, the justification principle, as described above, has not been applied.

Provided the justification principle has been demonstrably observed, the decision makers have simply to resolve the question of where to site the development. In such a situation, opposition may still exist, but will be of the NIMBY variety (Not In My Backyard). The solution to such arguments is to demonstrate that principles 2 and 3 can be complied with, i.e., exposure limits will not only be met, but will be kept as low as reasonably achievable.

Further criticisms may still arise from those who consider that particular natural species will not be adequately protected. These can only be countered if societal goals have been clearly defined and accepted. This highlights the importance of environmental objectives first having been clearly defined by society as a whole, before the scientist is expected to define exposure limits. If the goals are constantly and unpredictably changing, realistic exposure limits cannot be set. Changes in objectives should only be introduced as part of an iterative reassessment process which, from time to time, includes a reconsideration of the objectives included in the environmental protection policy.

25.4 Exposure Limits

The second of these principles, compliance with exposure limits, has direct relevance to the application of assimilative capacity. In radiological protection it is accepted that there are levels of radiation exposure, below the exposure limits, that may be deemed acceptable. In the application of the assimilative capacity concept, it would equally be accepted that there are levels of corresponding dose (or effect) that do not cause direct detrimental effects to man and other organisms or interference with other legitimate activities. In the case of radiological protection, at levels of exposure below those specified as exposure limits, the third principle, that of optimization, comes into play. The application of this principle to the control of pollution by non-radioactive materials is discussed later in this document.

Determination of the assimilative capacity for a particular marine environment, as defined above, depends upon two major considerations. The first of these is technical; this pertains to the means of determining under what conditions detrimental effects upon man or marine organisms, or interference with other legitimate uses of the sea, will occur. In order to define and utilize the concept of assimilative capacity, it is necessary to be able to determine at what level of concentration of a contaminant such effects occur. To this end, in some instances, it may be possible to use pessimistic assumptions about such levels and conditions and utilize some portion of the available capacity based on these assumptions. If this is not permitted or possible, the necessary data will have to be generated by testing. The second major factor pertains to society's perception of what

constitutes a detrimental effect and, thus, what is acceptable. This clearly lies in the sphere of social and political science.

25.5 Practical Difficulties

Just as society's view of unacceptable deleterious effects is likely to change with time, so does the actual state of the environment. Consequently, assimilative capacity must be regarded as a dynamic concept. As such, it is not only highly case-dependent, i.e., site-specific, but is liable to change in the light of social aims and perceptions, or even in the light of expanding knowledge. It is therefore essential that compliance with defined limits be monitored closely, not simply to ensure that predictions were correct, but also to ensure that the basis of the assessments as to what was at risk were correct and did not change.

The fact that the environment undergoes natural changes and fluctuations, and is seldom divisible into neat self-contained compartments, can create practical difficulties in applying the concept of assimilative capacity. When an environment, which is in dynamic equilibrium, is subjected to anthropogenic disturbit will react but, provided the disturbance is within the assimilative capacity, the change will either be undetectable within the acceptable range. However, because the environment is in itself subject to natural changes, when a change is detected, or may not be in response to the anthropogenic disturbmay ance. One must also cater for the fact that change may be very gradual and on a day-to-day, or even year-to-year, basis may be undetectable, unless or until change progresses to the where it is obvious. At the other end of the scale, the environment is capable of recovery from negative types of fluctuations, whether these be due to natural causes or disturbances due to man's activities. Marine flora and fauna, like any other living organisms, are subject to a variety of natural stresses and all eventually die. Some additional stress or even premature death of some individuals would not normally be regarded as unacceptable, provided there was no danger to the population as a whole.

Short-term transgressions of acceptability may be tolerated if long-term standards are observed. In this context especially, the "recovery time" of a disturbed environment must be considered in relation to assimilative capacity.

A second practical difficulty occurs in defining the physical boundary of the environment to be affected. For example, heated water discharges, e.g., from an electricity generating plant, could adversely affect a species coming into direct contact with these discharges. That effect will rapidly become undetectable, through dilution and dispersion, farther away from the discharge as near-normal temperatures are attained. Discharge limits will be influenced by the size of the mixing zone, in which effects are accepted, and the boundaries of the area to be protected. For example, in defining spatial boundaries, is the limit to be drawn in convenient geographical terms, e.g., a bay, or should it be extended to include a nearby area populated by a particularly sensitive group of organisms.

It should be recognised that in the marine environment, physical processes occur which will always lead to dilution and dispersion of the waste concerned. These processes will vary in strength according to the site. In practice, they may be so slow that the site is regarded as non-dispersive. This may lead to the assimilative capacity of that site being more readily exceeded and the near-field effects being more easily detected. Far-field effects will still occur, but they will be limited by a decreased potential for reaching harmful concentrations.

The real assimilative capacity of the environment will largely be determined by its capacity to degrade the contaminant concerned or to bind and remove it in an acceptable form. In this context, dilution is obviously a valid component of the equations for nonpersistent substances. Dilution may also be valid for persistent substances, such as the heavy metals, provided it can be shown that unacceptable concentrations will not be built up over appropriate temporal and spatial scales. If this is not possible, the assimilative capacity may be apparent rather than real, especially if, in order to meet the requirements, dilution has to be assumed over oceanic rather than local spatial scales. In this respect, the guiding principle should be to ensure that any changes in the marine environment are either reversible or do not compromise the preservation of environmental options for future societies.

These practical difficulties argue for caution in defining assimilative capacity, and in setting discharge limits. The need for careful monitoring and regular reassessment will also be obvious. On the other hand, what is regarded as short- or long-term may be stretched considerably. Society may accept a drastic decrease in environmental quality if the benefits (jobs, public health, etc.) are great and obvious. It may be most ready to do so if the system has a potential for fast recovery, but, if the benefits are great enough, the standards applied may be lowered so as to accept some degree of long-term change and extend the defined assimilative capacity.

25.6 Conceptual Difficulties

Some scientists fear that an evaluation of assimilative capacity based upon some procedure for establishing deleterious effects will be taken as a license to use the environmental capacity for waste disposal and increased use of marine resources. They therefore resist making evaluations of this kind. It may be argued that, if the assimilative capacity is carefully defined in wholly scientific terms (based obviously upon some guidance from the political and social science sphere as to the nature of the framework within which it is to be applied), perhaps by expunging term 'acceptable' and substituting for it some scientifically-defined standard for environmental disturbance, then it becomes a straightforward scientific task to determine the assimilative capacity, even if the latter involves some degree of conservatism or pessimism to allow for uncertainties. If no attempt is made at assessments, development may nevertheless proand the consequences may be both unpredicted and unchecked. Use of the best available treatment technology for effluent treatment is no guarantee of safety in all situations or for all

sectors of the environment. What is important, therefore, is to remove, by careful analysis and logical argument, the direct conceptual link made by some between a license to pollute, on the one hand, and the sensible and controlled use of the capacity of the environment to assimilate wastes, on the other. The use of optimisation procedures is essential to this process.

25.7 Optimisation

No matter what the assimilative capacity of a given marine system is calculated to be, or whether it is based upon realistic or pessimistic (conservative) assumptions, it is important that, before all or part of the capacity is utilised, optimisation, between the detrimental effects of a practice and the benefit likely to follow from its adoption, is undertaken. The purpose of optimisation is to reduce, to all reasonable extents, the actual effects that might ensue from a practice. In doing so, we can at this stage be either highly selective or very severe in what we consider to be undesirable effects. For example, if there exists a perception that maintenance of the environment in a pristine state is a desirable thing, we can treat contamination per se as 'effects' in the context of optimissomething negative. Thus, ation may be far broader than those which would be regarded as detrimental by most members of society. This is entirely consistent with the broader range of disciplinary factors considered in the optimisation process, such as social, economic and even political factors. Perception can, therefore, assume a greater importance than would be the case in a wholly technical consideration.

The purpose of optimisation is to seek the course of action which presents the best practical environmental option (BPEO) or, as it is sometimes expressed, that which presents the least detriment in relation to the benefits gained. For example, in considering the best option for waste disposal, at an initial level this would involve comparing the ocean disposal option with others (e.g., land burial, destruction, re-cycling, etc.) on as realistic and holistic (i.e., environmentally comprehensive) a basis as possible to select the option that, overall, offers the least disturbance, or the least chance of detriment, taking technical, social and economic factors into account. Having optimised the avenue for waste disposal, optimisation should again be used to select the actual method of disposal or disposal conditions, such that disturbance is minimised. At this second level, technical, social and economic factors should again be taken into consider-Not to couple a comprehensively based system of optimisation to the application of the assimilative capacity concept would seem to be little short of folly. Only when optimisation is incorporated into the use of the assimilative capacity concept can it be ensured that the least detrimental option is identified.

25.8 Other comments and the need for caution

There is a very real risk that decision makers will take the easy route and seek to avoid at least the first level of optimisation, with the consequence that wastes will be disposed of to that sector of the environment where the effects will be least obvious to public at large and/or the assimilative capacity concept is most well developed. In practice, for coastal developments often be the marine environment. Ideally, therefore, until general acceptance of the optimisation principle has been achievin respect of non-radiological applications, there is a case for avoiding the use of assimilative capacity in management Certainly, assessment of marine assimilative capacity decisions. should not be undertaken except on the clear understanding it is a component of an holistic management procedure embracing all sectors of the environment and employing optimisation.

In practice, inputs have already taken place and are continuing. Pressure for new inputs may also be so high that full application of optimisation may not be possible. Under these circumstances, it is obviously better to assess assimilative capacity than to allow a polluting discharge to continue unchanged or development to take place unrestricted. Some guidance as to how this can be achieved was provided in an earlier ACMP report on Standards and Environmental Criteria (ACMP, 1981). This will be thoroughly revised and updated in the 1987 ACMP report. Further development of the principles of assessing assimilative capacity, including a review of recent literature, will be included in the 1988 report.

25.9 Conclusions

The ACMP advocates the adoption of the principle of optimisation as outlined in this document. Acceptance of this principle is a valuable prerequisite to the sensible application of the assimilative capacity concept. Not to accept these two aspects of environmental management in combination will prejudice the adoption of a balanced and objective approach to environmental and human health protection.

The ACMP further recognizes the value of multilateral and international arrangements for the implementation of both the principle of optimisation and the concept of assimilative capacity in respect to marine, and other, environments. It, therefore, advocates that, wherever possible, relevant international bodies and agreements be used as a means of promulgating holistic approaches to environmental and waste management.

25.10 Future activities of the ACMP

The ACMP fully appreciates that the cumulative consequences of multiple practices need to be taken into consideration in the application of the assimilative capacity concept. It also recognises the need to ensure that, whatever course of action is adopted, the options available to future generations should not be prejudiced. In this context, the ACMP wishes to emphasize that the guiding principle in the utilization of a defined assimilative capacity is always to minimize the adverse effects of

individual and cumulative practices by limiting the input to the lowest practicable level (social, economic and technical factors taken into account). It also considers that careful environmental monitoring provides an additional safeguard in the use of this concept and must be conducted. The results of monitoring should be thoroughly assessed and fed back into a reassessment of the situation, along with any appropriate new knowledge, with a view to redefining discharge limits and/or modifying the monitoring programme as necessary. The ACMP plans to develop this concept further in the light of these latter objectives.

ANNEX 1

GUIDELINES FOR TEMPORAL TREND ANALYSIS OF DATA ON CONTAMINANTS IN FISH

These statistical guidelines have been developed to fulfill the need for routine reporting of contaminant concentrations in fish tissue for temporal trend monitoring purposes. Because of the large number of CMP/JMP data sets, the analysis must satisfy two conflicting objectives: it must proceed quickly with little human intervention, and yet must have the facility to draw attention to anomalies/irregularities in the data/analysis.

The principle of the analysis is that concentration is related to one or more covariables. Before measuring trends or comparing contaminant levels in different areas, concentrations are adjusted for the effect of the covariables, and expressed relative to selected values of the covariables which are the same for all time periods, areas, etc. (cf. C.M.1985/E:10, Annex 4).

In practice, the experience of members of the $\[\underline{ad} \]$ Hoc Group of Statisticians assisting WGMPNA on Trend Monitoring Issues has been that when the covariables are mutually correlated (e.g., as with length, weight, age), a single covariable may be essentially as effective as all of the covariables acting together. For concentrations of metals in muscle, length has usually been found to be the most effective single variable. Also, experience has indicated that the relationship between log concentration (y) and length (x_1) is linear, and that the resulting error structure is Normal with constant variance. This proposed analysis provides a check that these assumptions are met.

The method of analysis follows the guidelines given in Annex 4 to C.M.1985/E:10. The series of models are as follows:

Model 1:
$$E[y] = \mu_t + b_t x_1$$

which has a different intercept and different regression coefficient in each year t.

Model 2:
$$E[y] = \mu_t + bx_1$$

which has a different intercept in each year, but the same regression coefficient.

Model 3:
$$E[y] = \mu + bx_1$$

which has the same intercept and regression coefficient in each year.

Model 4:
$$E[y] = a_0 + a_1t + bx_1$$

which has the same regression coefficient in each year, and a linear trend in the intercepts. This series of models are compared using the principle of reduction in the residual sum of squares, i.e., as the number of parameters in the model de-

creases, the residual sum of squares (RSS) will increase. The simpler model is rejected in favor of the more complex model if the increase is significantly large. For example, to compare model 1 (complex) with model 2 (simple), calculate

$$\frac{[(RSS_2 - RSS_1)/(df_2 - df_1)]}{[RSS_1/df_1]}$$

and accept model 1 if this is significantly large compared to an F distribution with $(df_2 - df_1)$ and df_1 degrees of freedom.

The analysis is designed in the expectation that model 2 will be appropriate. The output from the analysis includes the adjusted mean log concentrations calculated at a selected value of \mathbf{x}_1 .

An equation of the same form can be applied for the other model comparisons by inserting the appropriate RSS's and df's, except in the case of the test for a linear trend, where model 3 is tested against model 2 and model 4 as follows:

$$\frac{[(RSS_3 - RSS_4)/(df_3 - df_4)]}{[RSS_2/df_2]}$$

which has an F-distribution with $(df_3 - df_4)$ and (df_2) degrees of freedom.

The rest of the analysis has been designed to ensure

- a) that there are no problems within the data, and
- b) that model 2 is, in fact, appropriate.

To satisfy criterion (b), model 2 is compared with two additional models:

Model 5:
$$E[y] = \mu_t + b_{t1}x_1 + b_{t2}x_2 + ... + b_{tp}x_p$$

which has different intercepts and regression coefficients in each year, and all available covariates included.

Model 6:
$$E[y] = \mu_t$$

which has year effects, but no covariates (i.e., the mean log concentration in each year).

A test of model 2 against model 5 establishes whether there is significant information in the additional (p-1) covariates which has not been exploited. A test of model 2 against model 6 establishes whether x_1 itself contains no useful information. In either case, the output from model 2 would usually be reported, but qualified by an appropriate comment.

Analysis

The analysis has been built around procedures in the statistical package SPSS-X. (SPSS Inc., Suite 3300, 444 N. Michigan Ave., Chicago, Illinois 60611, USA.)

The first stage is to fit model 1 and for each year to look closely at the residuals (the difference between the observed and predicted values of y). This stage is very important. It establishes that the assumptions about linearity and about the error structure are correct, and that there are no irregularities in the data. The residuals are plotted first against x₁ and secondly against a coded sex variable.

Figures 1 and 2 show satisfactory plots. In Figure 1, the residuals are spread evenly about zero, and there is no discernable dependence of the residuals on length. For Figure 2, the residuals for each sex code are spread around zero, and are not displaced relative to each other.

Figures 3 to 7 show examples of residual plots which suggest that there are problems with either the data or the model.

In Figure 3, the spread of residuals increases with increasing length. This suggests that some transformation other than logarithmic might be appropriate. If no changes are made, the estimated adjusted log concentrations are all right, but the analysis of variance will only provide approximate guidelines as to which model should be chosen. The results should be qualified to the effect that the variance and mean value are related.

In Figure 4, the residuals for each sex code are displaced, implying that sex may need to be included in the model. If this plot is seen for other years, then model 1 needs to be re-run with sex included as a factor. If the residual sum of squares is significantly reduced, then sex should be included in all subsequent models.

In Figure 5, there is evidence that the linear relationship between y and x_1 is not appropriate. The data for this year may include some very large or very small fish which are outside the range for which the model has previously been found to be linear. If this is the case, or if there is evidence of non-linearity in other plots, the analysis should be discontinued. The user should obtain help, or simply report that the model is not linear.

The plot in Figure 6 suggests some outlying points, i.e., points which do not seem to belong to the rest of the data. The data source should then be checked and, if found wrong, the corrections should be made and the model re-run. If the data are correct and the "outliers" are less than 2.5 standard deviations away from zero, they should be left in. If they are more than 2.5 standard deviations away, they should be excluded and a comment made to that effect in the report.

In Figure 7 there is evidence of a more extreme form of outlier. Its residual is not large, but it is clearly not in agreement with the rest of the data. Again, the data source should be checked and, if correct, the model should be re-run with the

point excluded to determine how much the fitted line changes. The fitted line should be checked against those from the other years. If all the evidence is against the validity of this point, it should be excluded and a comment made in the report to that effect.

If the residual plots are satisfactory, the analysis should be continued. If the residual sum of squares for model 2 is significantly greater than that for model 1, the data should be examined more closely. It may be that an outlier as in Figure 7 is present, or there may be imbalance in the distribution of \mathbf{x}_1 from year to year. If the latter is the case, the analysis should be continued using model 2, but an appropriate comment should be made in the report.

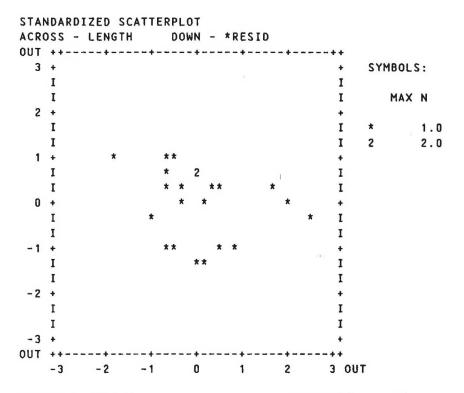
If there is no imbalance in the data, model 1 should be used and the analysis should continue as shown in Example 2 in Doc. C.M. 1985/E:10, Annex 4.

Also, the residual standard deviations in each year should be checked. They should be similar. If they are not, a check for outliers should again be made. If the residual sum of squares for model 2 is not significantly greater than that for model 1, the adjusted mean log concentrations can be reported together with 95% pair-wise significance bands (Nicholson, 1985). These have an advantage over standard errors and 95% confidence limits in that they can be used for testing between the adjusted means: if the bands overlap, then the means are not pair-wise significantly different. If they do not overlap, then the means will necessarily be significantly different only if the numbers of observations in those means are equal. This simple graphical display is only an aid to interpretation. The results of the tests of model 2 against model 3 and the tests for linear trend should also be reported.

Finally, the results of the tests of model 2 against the new models 5 and 6 should be checked. If the residual sum of squares for model 2 is significantly greater than that for model 5, then a comment to that effect should be made. Also, the percentage increase in the residual standard deviation, which may be small, should be quoted. However, it may be necessary that an alternative model be developed. If the residual sum of squares for model 2 is not significantly greater than that for model 6, then a comment to this effect should be made. In both cases, the results from model 2 should be reported.

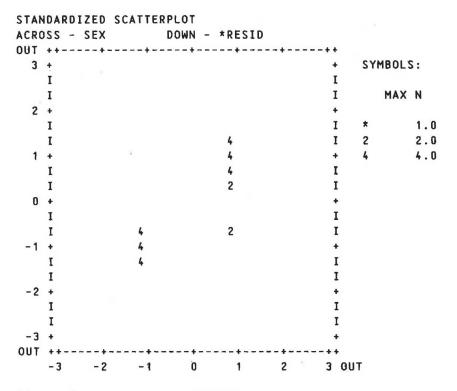
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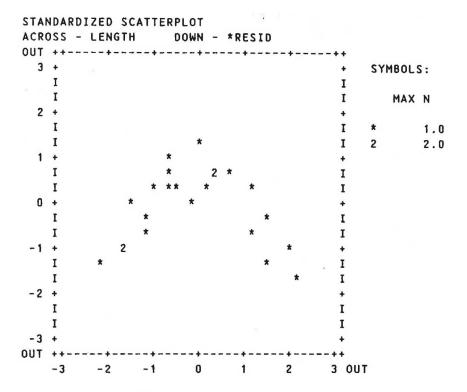
Nicholson, M.D. 1985. The treatment of time-effects in the stat istical analysis of contaminant monitoring data. Doc. ICES C.M. 1985/E:31.

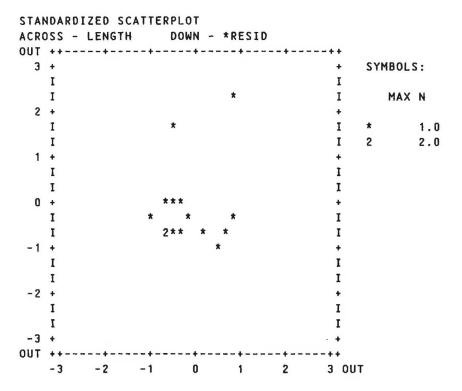


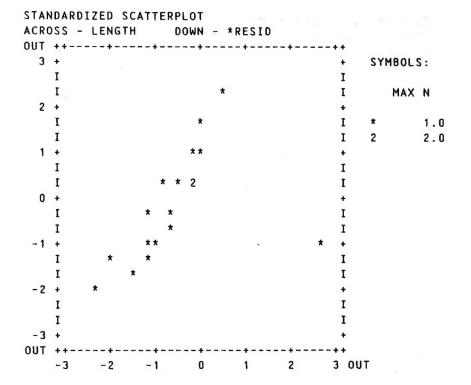
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EXAMPLE OF THE REVISED PROCEDURE FOR THE ROUTINE ANALYSIS OF DATA ON CONTAMINANTS IN FISH FOR PURPOSES OF TREND MONITORING

Introduction

The following report provides an example of the procedure for the analysis of contaminant trends in fish, as described above. The example concerns a trend analysis of mercury in muscle tissue of flounder caught off the Belgian Coast (JMG area code JO1; ICES statistical rectangle 31F2).

Results/Analysis

Notes (i) - (x) refer to results summary attached.

Using length as the single covariate and ln-mercury concentration as the dependent variable, Model 1 was fitted for each year 1978 to 1984 (i). Inspection of the residuals plots (residuals versus length and residuals versus sex - not shown here) did not show any serious irregularities in the data.

Models 2 to 4 were fitted (ii), and the models compared.

The residual sum of squares for Model 2 is not significantly greater than that for Model 1 (iii), therefore, the adjusted mean contaminant levels <u>versus</u> time are reported, together with their pair-wise 95% significance bands (iv).

Comparison of Model 3 <u>versus</u> Model 2 (v) showed that there are significant differences in the adjusted concentration levels between years. Comparison of Model 3 <u>versus</u> Models 2 and 4 (vi) and Model 4 <u>versus</u> Model 2 (vii) showed that these differences cannot be described by a linear trend.

In Model 5, length, weight, age and sex (as a factor variable) are the covariates. The residual sum of squares for this model is significantly lower than that for Model 2 (viii). Therefore, it is concluded that length alone is not sufficient to describe all features of the data and that the addition of other covariates to the models should be explored. The residual standard deviation for Model 2, however, shows only an 11.5% increase over that of the more complex Model 5 (ix).

In Model 6, ln-mercury concentration is fitted against years without including any other covariates. The residual sum of squares for this model is significantly larger than that for Model 2 (x), so it was concluded that the length covariate is appropriate, i.e., the biological variable length does provide significant information about the data.

Figure 8 shows the results for the adjusted mean concentrations using length alone as a covariate (data from table, (iv)). In addition, adjusted mean concentration values calculated from Model 5, which includes all the covariates (length, weight, age and sex), have been plotted for comparison. Both sets of values are calculated for an average fish of length 300 mm, assuming in the latter case variable values equal to the sample average values (weight 377 g; age 3.45 years, and further assuming a half male half female population).

RESULTS OF TREND ANALYSIS FOR

: Flounder Species ICES area code : 31F2

Contaminant : Hg (mg/kg wet weight)
Tissue type : muscle
For years : 1978 to 1984, where there are data for 7 years

Covariant $X_1^{-1} - X_p^{-1} : length$ covariant $X_1^{-1} - X_p^{-1} : length$, weight, age, sex[1..2]

Results from Model 1 and 5 (by years):

	[Model 1	(X ₁)	Mode	1 5 (x ₁ -x _p)
	Year	df	RSS	st	df	RSS	st
	1978	18	3.86	0.463	15	3.14	0.458
	1979	18	5.17	0.536	15	4.56	0.552
(i)	1980	17	2.13	0.354	14	0.546	0.198
	1981	18	5.92	0.573	15	5.09	0.583
	1982	26	14.60	0.749	23	8.30	0.601
	1983	23	5.54	0.491	20	4.99	0.500
	1984	18	3.25	0.425	15	1.92	0.358
	sums	138	40.47	0.542	117	28.54	0.494

Results for Models 2, 3, 4 and 6:

			Models 2-	Model 6 (year)			
(ii)	Model 2 3 4	df 144 150 149	RSS 43.72 49.38 49.19	st 0.551 0.574 0.575	df 145	RSS 58.80	st 0.637

Model comparisons:

Model	vs	Model		F-value	1-p	s/ns	comment
2 (X ₁ , yrs[1t]) 3 (X ₁) 3 (X ₁) 4 (years, X ₁) 2 (X ₁ , yrs[1t])	vs 1 vs 2 vs 2 vs 2 vs 5	(X ₁ by years) (X ₁ , yrs[1t]) and 4 * (X ₁ , yrs[1t]) (X ₁ to X _p by years) (X ₁ , yrs[1t])	: : : : :	1.85 3.10 0.632 3.60 2.30	43.4	ns s ns s	1 2 3 4 5

The % increase in residual std. dev. for Model 2 over Model 5 = 11.5 % (ix)

Comments to tests of significance:

- No significant differences exist in the slopes of linear relationships between contaminants and biological variable(s) between years. (iii)
- Contaminant levels adjusted for biological effects differ between years - Refer to plot of adjusted mean log concentrations <u>versus</u> time. (v)
- 3.) No evidence of a linear trend. (vi)
- 4.) (vii)
- 5.) Model 5 (with covariates X_1 to X_p by years) is better than Model 2 (with X_1 and years[1..t]). (viii)
- 6.) The covariate X_1 is necessary. (x)

Abbreviations:

```
RSS - Residual sum of squares

df - Degrees of freedom

st - Residual standard deviation = \sqrt{(RSS/df)}

SB - Pairwise 95% significance bands = \bar{X} \pm (1.96st_2)/\sqrt{2n}

where st_2 - st for Model 2

n - number of observations in a year

X_n[1..n] - Covariable expressed as a factor

s/ns - significant/not significant
```

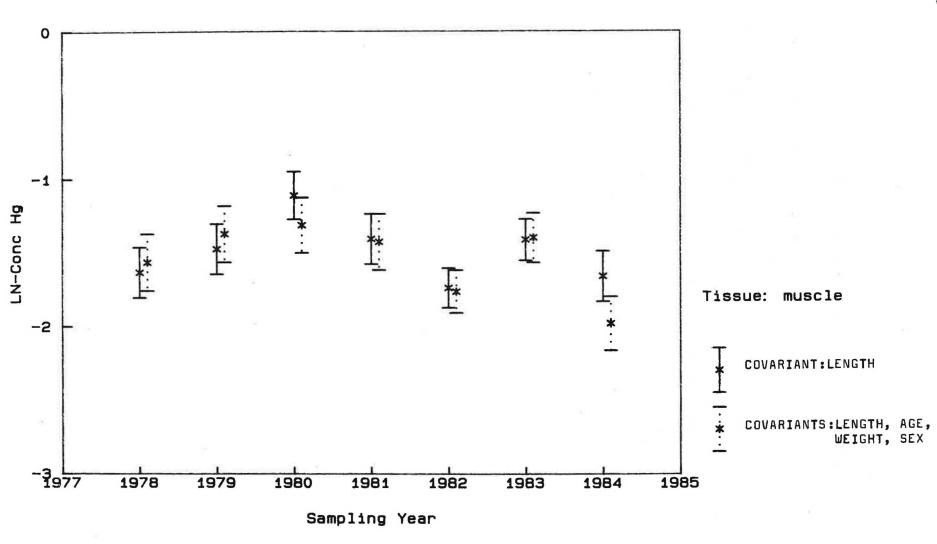
Model 3 is tested jointly against Models 2 and 4

Data summary

Adjusted mean contaminant levels <u>versus</u> time (see plot)

	===== :	=== ln ===	=======	======	== e ^X ==:	
			5B			5B
Year	mean	lower	upper	mean	lower	upper
1978	-1.634	-1.805	-1.463	0.195	0.165	0.231
1979	-1.475	-1.646	-1.304	0.229	0.193	0.271
1980	-1.112	-1.287	-0.937	0.329	0.276	0.392
1981	-1.409	-1.579	-1.238	0.244	0.206	0.290
1982	-1.742	-1.886	-1.598	0.175	0.152	0.202
1983	-1.415	-1.567	-1.262	0.243	0.209	0.283
1984	-1.662	-1.833	-1.491	0.190	0.160	0.225
	1978 1979 1980 1981 1982 1983	Year mean 1978 -1.634 1979 -1.475 1980 -1.112 1981 -1.409 1982 -1.742 1983 -1.415	Year mean lower 1978 -1.634 -1.805 1979 -1.475 -1.646 1980 -1.112 -1.287 1981 -1.409 -1.579 1982 -1.742 -1.886 1983 -1.415 -1.567	Year mean lower upper 1978 -1.634 -1.805 -1.463 1979 -1.475 -1.646 -1.304 1980 -1.112 -1.287 -0.937 1981 -1.409 -1.579 -1.238 1982 -1.742 -1.886 -1.598 1983 -1.415 -1.567 -1.262	SB Year mean lower upper mean 1978 -1.634 -1.805 -1.463 0.195 1979 -1.475 -1.646 -1.304 0.229 1980 -1.112 -1.287 -0.937 0.329 1981 -1.409 -1.579 -1.238 0.244 1982 -1.742 -1.886 -1.598 0.175 1983 -1.415 -1.567 -1.262 0.243	SB Year mean lower upper mean lower 1978 -1.634 -1.805 -1.463 0.195 0.165 1979 -1.475 -1.646 -1.304 0.229 0.193 1980 -1.112 -1.287 -0.937 0.329 0.276 1981 -1.409 -1.579 -1.238 0.244 0.206 1982 -1.742 -1.886 -1.598 0.175 0.152 1983 -1.415 -1.567 -1.262 0.243 0.209

Note: adjusted mean contaminant concentrations for an 'average' fish, of length 300 mm.



Area: 31F2

FIGURE 8: ADJUSTED MEAN CONCENTRATIONS (and SB's) VS. TIME

Species: Flounder

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

-0-0-0-

