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REPORT OF THE ICES ADVISORY COMMITTEE ON MARINE POLLUTION, 1984

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International Council for the Exploration of the Sea Palægade 2-4, 1261 Copenhagen K DENMARK 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 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 Gorups (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 Advisory Committee on Marine Pollution.

The Advisory Committee on Marine Pollution consists of a number of scientists acting - when they meet as a committee - 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 are not national representatives. The 1984 membership of the Committee is found on page 1.

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REPORT OF THE ADVISORY COMMITTEE ON MARINE POLLUTION, 1984

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EXECUTIVE SUMMARY

In 1984 the ACMP decided to preface its detailed Report with an executive summary which would provide a brief review of the current status of work for the Regulatory Commissions, separate from the body of the Report. The work requested from ICES by the Commissions consists of some items which might be completed within a year and others which involve continuing work or at least require a longer time-table. Any annual work programme is thus a mix of items, some carried over from the previous year and others which are new. The ACMP Reports are correspondingly a mix of progress reports and completed accounts, the latter often amplified in detailed technical annexes.

Work Requests from the Oslo and Paris Commissions

During 1984, the ACMP addressed fourteen items at the request of the Oslo and Paris Commissions. Brief details of the progress made are given in Section 2 of the Report, following Section 1 on the functions of the ACMP. These details are given under the topic headings assigned by the Commissions. For the benefit of the reader who does not wish to study the detailed report, a brief elaboration of the main topics is given below under the three headings: General Monitoring Issues, Specific Problems, and Continuing Responsibilities.

General Monitoring Issues

One important aim of monitoring is to detect possible trends in contaminant concentrations over time and in this context fears have been raised that the use of different statistical techniques for analysing the data could produce conflicting results. A group of statisticians examined this matter in relation to contaminants in marine organisms and, while they proposed further investigations to overcome remaining problems, they have been able to allay the general fears about purely statistical aspects. However, it was emphasised that the fish samples to be analysed should be drawn from the same stock and that advice on this should be sought from fisheries management experts. Even within a stock, a number of biological factors were identified on which further information and knowledge are required. No changes to the guidelines already laid down by ICES for trend monitoring are recommended at the present time.

A second major monitoring issue concerns the detection of biological effects of marine pollution. It is widely recognised that an understanding of biological effects is essential for a complete assessment of the significance of chemical measurements, and ICES has been examining a range of techniques, including macrobenthos population monitoring, bioassays using oyster larvae, observations of various pathological conditions in fish, and a range of methods to determine biochemical and physiological changes in organisms exposed to contaminants. A number of these approaches can now be confidently recommended for site-specific application, but the definition of techniques for more general routine monitoring still requires further study.

The success of monitoring exercises by different laboratories depends on the validity of the comparison of their results, and intercalibration exercises are essential to establish this. ICES has carried out work in this field for over a decade and has recently conducted a new intercalibration exercise on the measurement of trace metals in sea water. This included a filtration component which showed that contamination of samples during filtration is generally minor, given appropriate precautions, and a number of filtration procedures which produce uncontaminated filtrates was identified. Guidelines are being prepared on the appropriate methods for sampling, pre-treatment and storage of sea water for heavy metal analysis.

Petroleum hydrocarbons have also been studied and an exercise on the analysis of hydrocarbons in biological tissues has been successfully concluded, as well as an intercomparison of determinations of polycyclic aromatic hydrocarbons (PAHs) in biological tissues. Full reports on these exercises are in preparation and there will be a recommendation for the inclusion of PAH determinations in tissues in the 1985 baseline study. Assessing the comparability of measurements of petroleum hydrocarbons in sea water is made difficult by the problem of preparing and storing solutions containing these compounds for use in an intercomparison exercise. However, a procedure has now been devised and an assessment of its feasibility is expected to be made in the near future.

Concerning the determination of PCBs in biological tissue, there is at present considerable interlaboratory variance in analytical results and the Commissions are concerned to resolve these uncertainties. The ACMP examined the aims of various exercises and noted that different aims involved different analytical requirements. Thus, the detection of broad-scale distributions and temporal trends in environmental levels, especially in biota, need not necessarily involve detailed individual congener analysis and either packed column or capillary column techniques may be used, although the latter are strongly recommended. If the need is simply to detect the response, in terms of environmental concentrations, of measures to restrict inputs, it is now possible to advise on the extent to which this can be done by individual laborato-Until intercomparability among laboratories has improved, it is ries. not possible to do these studies on a generally cooperative basis, although some bi- or tri-lateral comparisons may be possible. Of additional and perhaps more important interest, however, is the fact that the various congeners of PCBs do not all suffer the same fate in the environment, nor are they likely to have the same impact in toxicological terms. Thus, in order to be able either to study the fate of individual chlorinated biphenyl compounds, or to assess the toxicological importance of the most prevalent or persistent congeners, individual congener analyses are required. Until the problems involved in such analyses are resolved, it will not be possible to advise on how these requirements can be met. This is expected to take at least a further three years.

On the use of sediments in monitoring contaminants in the marine environment, the ACMP has now added to its earlier guidelines by providing advice on sub-sampling, storage, pre-treatment and analysis of sediments. The ACMP noted the importance of understanding the availability of contaminants in sediments to benthic organisms and that this required a knowledge of the mechanisms of uptake by different benthic species from interstitial water, organic particles and mineral or amorphous materials. At present, a purely geochemical approach using various leaching procedures to determine, for example, the maximum amounts of potentially available metals is applied. The relationship between such results and the truly bioavailable fraction is not known. In an attempt to answer this question, a detailed report on the problems of bio-availability is being prepared and this will be relevant to a wide field, including the availability of organochlorines in dumped dredge spoils.

Specific Problems

Five of the items put to ACMP are discussed under this heading. One important matter was the problem of unusual plankton blooms. It was noted that much of the evidence on the role of nutrient enrichment in this context was either inadequate or contradictory, and that information on fluxes rather than only concentrations of nutrients was important. The appropriate ICES Working Group will produce a comprehensive overview of the subject, and the Proceedings of the Special Scientific Meeting on Causes, Dynamics and Effects of Exceptional Marine Blooms and Related Events in October 1984 will provide relevant information.

Another important matter concerned the atmospheric input of contaminants to the sea. ICES has previously reported on this, giving estimates of the inputs of metals and organochlorines to several sea areas and confirming that the atmosphere could be a significant source of some substances. There still remain significant problems, however, in determining the flux at the sea surface and in assessing the importance of the atmosphere as compared with the other routes of input. Work on this problem is continuing both within ICES and by GESAMP.

The ACMP also examined evidence on the effects of disposal of waste from the titanium dioxide industry on the marine environment. The ACMP recognised that investigations of these effects were underway in several countries and that a full assessment should await the availability of these data. However, it also recognised that since these investigations could continue for some years, an interim assessment was required and it addressed itself to this on the basis of the information before it. It was noted that all the constituents of the wastes are natural inorganic materials and that, once the large discharge concentrations have been dispersed, the effect should be no more adverse than that from a natural river. The laboratory tests of sublethal effects of TiO2 wastes were reviewed, and various assumptions were made on the distribution of the waste in different circumstances, including dumping and land-based discharges. It was concluded that TiO₂ wastes would have an impact when disposed of in the sea on both water quality and biota, but that the impact would be local and not likely to affect fish stocks or population levels. In none of the areas for which data were available (Humber Estuary, Bothnian Bay, German Bight) was there evidence that the area affected was increasing.

On a fourth topic, the "special care" method of capping contaminated dredged spoils, the ACMP had completed its examination of the procedures and agreed that capping as a special care measure was feasible, but it was emphasised that further information was required on a number of aspects such as the permanence of the cap and the extent of leakage. Finally, on the question of determining the net riverine input of contaminants to the shelf, the ACMP provided information on the development of estimates of this input and a description of three approaches to carrying out these estimates.

Continuing Responsibilities

Two items are reported under this heading. First, ICES in cooperation with the Joint Monitoring Group (JMG) is developing an ADPcompatible reporting and exchange format for environmental quality data. A reporting format for data on contaminants in fish and shellfish has been prepared and accepted for use in the JMP, starting in 1984. An interim reporting format for contaminants in sea water has been prepared for interim (2-3 year) use and a more comprehensive format for sea water data is under development. In addition, a preliminary draft interim reporting format for contaminants in sediments has been prepared and is under review.

The second continuing responsibility is to keep under review and report back on any new contaminants that may be of interest to the JMG. In this session, overviews were prepared on furans and dioxins, alkyl-tin compounds, polychlorinated terphenyls, and zinc, and these are included in the Report.

Work Requests from the Helsinki Commission

During the 1984 session, the ACMP addressed four specific requests from the Baltic Marine Environment Protection Commission (Helsinki Commission). Further details of progress on these items are given in Section 3 of the Report.

The first of these requests required ICES to develop reporting formats on contaminants in sea water and in sediments. These reporting formats are at present progressing well and the work is expected to be completed in 1985.

The second request concerned reporting the results of an intercalibration exercise on the analysis of marine sediments in the Baltic Sea. This exercise has been completed successfully, showing a relatively good performance with respect to most of the substances included. The report is in preparation and should be available for general circulation by mid-1985.

ICES was also asked to continue the work on estimating changes in the seal populations in the Baltic Sea, and to assess their condition in relation to pollution. On the basis of the Working Group's report, it was concluded that the available evidence did not permit any firm conclusions on the association between contaminants and the reproductive success of seals in the Baltic Sea. A number of recommendations were made for further research and monitoring, and it was noted that an adequate survey of Baltic seal populations requires a coordinated international survey. A status report on the work is provided.

Finally, in response to the request for a phytoplankton species code list, a document is being finalised, and will be submitted to the Helsinki Commission before the end of 1984.

1. INTRODUCTION

1.1 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 reports of which it considers and on which it may call for carrying out specific activities. At its 1984 mid-term meeting, the ACMP considered, <u>inter alia</u>, the most recent reports of the following Working Groups:

Marine Chemistry Working Group (MCWG)

Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA)

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

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

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

Working Group on Baltic Seals.

1.2 The ACMP Report is structured in terms of the Committee's overall deliberations on pollution matters, but specific features relevant to the various Commissions' requests are drawn out into an Executive Summary which is at the beginning of the Report, and are further itemised in Sections 2 and 3, where the individual work items from each Commission are listed and related to relevant sections of the main text.

2. PROGRESS IN THE WORK REQUESTED BY THE OSLO AND PARIS COMMISSIONS FOR 1984

A summary of the progress in the 1984 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:

 to provide further reports on aspects of trend monitoring, including modifications to the sampling guidelines for this monitoring;

> Work on this subject is continuing. No changes in the currently recommended sampling guidelines for this type of monitoring are proposed, although the guidelines are being kept under review. See Section 4.5 of the report;

 (ii) to report on the experience gained by laboratories within the ICES framework on biological effects studies and on their relevance to monitoring;

Work on the application of biological effects monitoring techniques is still in progress. Steps have been taken to extend the experience available and to review the suitability of available techniques for cooperative monitoring purposes. See Section 5 of the report.

(iii) to finalise work on the identification of appropriate sampling methodologies to determine the input of contaminants to the marine environment via rivers, with particular reference to net inputs;

The determination of net riverine inputs of contaminants, or net fluxes, applies to the estimation of the component of the gross input or flux that survives estuarine and continental shelf removal processes and succeeds in passing to the deep ocean basins. While the determination of net inputs is a complicated process, it depends in the first instance upon reliable estimates of the gross river inputs of contaminants. Thus, the development of estimates of gross riverine inputs of contaminants according to the methodology provided in the 1982 ACMP Report (Annex 6, Coop. Res. Rep. No. 120 (1983)) is encouraged. Information concerning the development of estimates of net riverine fluxes of contaminants and a description of three approaches to carrying out these estimates are given in Annex 1 of the present Report.

 (iv) to report the outcome of the ICES fifth-round intercalibration exercise in sea water, concerning in particular methods of sampling and pre-treatment;

This intercalibration proved to be remarkably successful and, as a result, it is possible to recommend a limited scale baseline study of trace metals in sea water. Some laboratories which may take part in this study have yet to prove their ability and a mechanism for achieving this is proposed. See Section 6.2 of the report. (v) to report on progress made in studies of sediments and pollution, in particular on the outcome of the first and second steps of the pilot studies;

> In continuation of the guidelines for the use of sediments in contaminant monitoring programmes contained in the 1983 ACMP Report ("The Potential Role of Sediments in Pollution Monitoring", Annex 2, Coop. Res. Rep. No. 124 (1983)), guidelines are given in Annex 2 of the present Report for sampling, subsampling, storage, pre-treatment and analysis of sediments.

> Summaries of progress reports on the Pilot Sediment Study in the Skagerrak and the Pilot Sediment Study in the German Bight are contained in Annex 3 of this Report.

(vi) to report on progress towards the feasibility of starting an intercalibration exercise on the measurement of hydrocarbons in sea water;

The difficulties of preparing and storing solutions containing petroleum hydrocarbons have hampered the design and conduct of an intercalibration for assessing the comparability of petroleum hydrocarbon determinations in sea water made by different laboratories. However, a procedure for such an intercalibration has been devised that will be evaluated in 1985 and a clear statement of its feasibility should be available in the next ACMP Report.

(vii) to produce a method for the calculation of the concentration of PCBs in marine environmental samples;

Information is given on the status of the development of new techniques for the analysis of PCBs. A solution to the outstanding problems in the ultimate application of these new techniques can be expected within three years; in the meantime, clarification of the Commissions' needs on this subject is sought. See Section 6.4 of the report.

(viii) to examine, in cooperation with JMG, the automatic processing of marine pollution monitoring data and to prepare an ADP-compatible data reporting and exchange format;

The initial handling of 1983 JMP data for the Commissions is expected to be completed on schedule and draft reporting formats for data on contaminants in sea water and sediments have been developed. See Section 4.7 of the report.

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

From the information available to ICES, it is apparent that wastes from the production of titanium dioxide will have an effect on the marine environment on a scale larger than was previously considered likely. Under present conditions, however, no really serious effects may be expected on fisheries. See Section 8 of the report and Annex 10. (x) to provide a summary and evaluation of the "special care" methods of capping contaminated dredged spoil dumping sites;

This subject was handled in the 1983 ACMP Report in paragraphs 99-100 and Annex 7 (Coop. Res. Rep. No. 124 (1983)). Based on a review paper ("Information on Capping of Contaminated Dredged Materials" in Annex 7 of the above-mentioned Report), current activities related to studies of the use and effectiveness of capping techniques carried out in Japan, the United States and certain European nations were noted. The ACMP agreed that capping, as a special care measure was technically feasible, but that further studies are required. Such studies should be designed to assess (1) how the capping materials stay in place with time, and especially following major storms or unusual hydrographic events; (2) leakage of contaminants from solid wastes through the capping materials; and (3) various sediment types as the most effective capping materials.

 (xi) to review knowledge of the input of contaminants from the atmosphere to the sea, and to define the problems of assessing pollution from this source;

This subject was not discussed at the 1984 session, but a report is expected to be completed for the 1985 ACMP meeting.

(xii) 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;

This issue was the subject of the Special Meeting on "The Causes, Dynamics and Effects of Exceptional Marine Blooms and Related Events" (4-5 October 1984, Copenhagen); the report of this meeting (Document ICES, C.M.1984/E:42) summarises the information presently available on this topic. See Section 9 of the ACMP report.

(xiii) to keep under review the question of any new contaminants that may be relevant to the interests of JMG and to report back;

Overview reports on furans and dioxins (Annex 4), certain organo-metals (Annex 5), polychlorinated terphenyls (PCTs) (Annex 6) and zinc (Annex 7) are presented in this report. While it is apparent that organo-tin compounds cause problems in some areas of the marine environment, the other substances considered do not appear to cause marine environmental problems, although some additional limited-scale investigations are desirable for furans, dioxins and PCTs.

(xiv) to assess the importance of the bioavailability of organohalogen compounds in dredged spoils dumped in the Oslo Convention area;

Work on this is underway and a report is expected at the 1985 mid-term ACMP meeting. In the meantime, paragraph 7.3 of the report is relevant.

3. PROGRESS IN THE WORK REQUESTED BY THE HELSINKI COMMISSION

The ACMP took note of the current requests from the Baltic Marine Environment Protection Commission (Helsinki Commission) and the present status in this work, as follows:

(i) to develop reporting formats on contaminants in sea water and in sediments;

These reporting formats are presently under development and are expected to be completed by mid-1985, see paragraphs 4.7.3 and 4.7.4 of the report.

(ii) to report on the results of an intercalibration of sediment analyses;

The report on this intercalibration exercise is in preparation and is expected to be available for general circulation by mid-1985. See paragraphs 6.3.1 and 6.3.2 of the report.

(iii) to continue the work on changes in the size of the seal populations in the Baltic Sea, and to assess their condition in relation to pollution;

It is clear that there are several causes of the decline in Baltic seal populations. Further work is required to establish whether <u>prima facie</u> evidence exists for a connection between reproductive failure and body burdens of contaminants. A detailed report of the information presently available is contained in Annex 8. See also Section 12.

(iv) to prepare a phytoplankton species code list;

This was an earlier request from the Helsinki Commission. A code list for Baltic phytoplankton species according to the RUBIN system has been completed and will be forwarded to the Helsinki Commission in autumn 1984.

In addition to the items referred to above, a number of other sections of the report are of particular relevance to the Helsinki Commission, and attention is drawn to Sections 11 and 12 and paragraphs 6.3.1, 6.3.2, 7.4.3, 8.7, 9.4 and 9.5 of the report.

4. MONITORING ISSUES

4.1 1982 Cooperative ICES Monitoring Studies Report

- 4.1.1 The ACMP noted the draft report on the results of the Cooperative ICES Monitoring Studies Programme for 1982. This report contained the results submitted on analyses of contaminants in fish and shellfish for the Protection of Human Health (Objective 1 of the monitoring programme) and on Monitoring of Fish and Shellfish for Time Trend Analysis of Contaminant Concentrations (Objective 3). In reviewing the results submitted for the protection of human health, the ACMP noted that a significant proportion of the data submitted were not consistent with the guidelines. In particular, many samples of fish contained either fewer than or more than the specified number of 25 fish, while several samples of molluscs did not adhere to the specified number of 50 molluscs, and at least some of the samples may not have been taken in the pre-spawning period as required. While it was realised that much of this non-conformity may result from the fact that 1982 was the first year utilising these new guidelines in the Cooperative ICES Monitoring Studies Programme, the ACMP agreed that it was important to adhere as closely as possible to the guidelines. They had been developed as a result of eight years of experience and detailed discussion at Working Group level with a view to promoting a greater comparability and consequently a greater possibility to interpret the results. A failure to follow them will decrease the overall value of the monitoring programme. To emphasise the criteria which must be observed, the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA) has requested that a check list be developed which will highlight the critical parameters on sample collection and sample preparation; this check list should also request information on the month of spawning of the stocks which are sampled.
- 4.1.2 Accordingly, in terms of the section of the report containing data on contaminants relevant to the protection of human health, the ACMP agreed that the body of the report and the main set of tables should include only data which conform with the sampling guidelines. Other data which have been reported should be included in an Annex. As had been recommended by the WGMPNA, a deviation in the number of specimens in the sample by ± 10% from the recommended number would be considered acceptable in determining compliance.
- 4.1.3 The section of the report concerned with trend monitoring contained the raw data which had been submitted, but no trend analysis could be conducted on the basis of data from only one year. Therefore, these data will not be included in the 1982 report, but will be retained for analysis when sufficient similar data become available.

4.2 The 1985 Baseline Study on Contaminants in Fish and Shellfish

4.2.1 The ACMP noted that the plans for the conduct of this study were well advanced and that an outline of proposed national contributions had been discussed by the WGMPNA and the ICES/SCOR Working Group on the Study of the Pollution of the Baltic. Following these discussions, pledges of further support had been received from a number of countries. It is now apparent that most of the Baltic Sea area and the northern European sector of the North Atlantic will be adequately sampled. A summary of the full contributions proposed, as of September 1984, is contained in Annex 9, along with details of the procedure to be followed in the collection, pre-treatment, preservation, storage and analyses of samples, and the reporting of results.

4.2.2 The ACMP noted with approval that the Marine Chemistry Working Group (MCWG) had concluded, on the basis of the most recent intercalibration exercise on analyses of metals in biota (7/TM/BT) (see Section 6.1), that most laboratories would be likely to report reliable results for most metals (with lead and arsenic as possible exceptions) and that measures were well in hand to allow analytical quality control to be assured throughout the exercise. To this end, sample materials will be available for analysis before and after the conduct of analysis of the fish and shellfish samples for the Baseline Study. It was also noted that, although the intercalibration status in relation to organochlorine compounds was less satisfactory (see Section 6.4), the inclusion of analyses for these residues in the Baseline Survey was considered acceptable subject to the proviso that the laboratories involved attempt to collect data from relatively broad geographical areas and ensure overlapping coverage of adjacent areas. The storage of some samples or sub-samples could be useful to permit analysis at a later time, after the analytical problems have been solved.

4.3 Proposals for a Baseline Study of Trace Metals in Sea Water

4.3.1 The ACMP noted that the possibility and practicability of including measurements of trace metals in sea water within the baseline survey programme had been discussed by the MCWG at its 1984 meeting. An ad hoc group, which met during the 1983 Statutory Meeting, had concluded that the inclusion of metals in coastal zone baseline studies was unjustified if it caused significant re-direction of resources from basic marine geochemical and ecological research. However, a need for some assessment of the nature of spatial variations in trace metal levels in shelf waters, particularly near to coasts, was perceived within the regulatory Commissions, and the MCWG agreed to adopt a pragmatic, if simplistic, approach to satisfy this need. As a result, the MCWG had devised ways of conducting suitable baseline surveys for trace metals in sea water of regional areas of the North Atlantic. While laboratories existed with capability (demonstrated within various ICES quality assurance exercises) in all aspects relevant to trace metal measurements (sampling, sample filtration, storage, pre-concentration and analysis), they were small in number. A further group of laboratories had demonstrated adequate analytical capability for the conduct of baseline surveys, but their sampling, sample filtration and storage procedures had not been assessed. Since it is unreasonable to expect the small number of wholly-qualified laboratories to undertake all necessary baseline survey measurements, and since there is inadequate time before the conduct of the 1985 Baseline Survey of Contaminants in Fish and Shellfish to allow a further intercomparison exercise to be designed and conducted, a suitable mechanism had to be devised to maintain quality assurance for baseline survey data. The MCWG, therefore, had specified the type of ancillary measurements that would need to be made coincident with a trace metal baseline survey to enable the baseline data to be reliably interpreted. It had further proposed the establishment of a number of "reference" or "intercalibration" stations, one of which would need to be occupied during the course of an individual laboratory survey programme. One specific

station and four general areas were identified at which temporallyinvariant vertical distributions of metals and nutrients would exist for reference purposes. The locations of the few European stations, and the likely extent of stability of metal distributions in the deeper parts of these stations, still need to be specified in collaboration with members of the Hydrography Committee or its Working Groups. A suitable station off the United States shelf is Ocean Station 'S' off Bermuda, for which there are adequate hydrographic (time-series) data and reliable vertical trace metal profiles. It is recommended that at least one of these reference stations be occupied and that samples be collected and analysed for trace metals, nutrients, suspended particulate matter, and hydrographic variables by each laboratory as an integral part of its own baseline survey.

- 4.3.2 The ACMP noted that these proposals are described in ICES document C.M.1984/E:39. The MCWG has agreed to provide descriptions of suitable sampling, filtration and measurement procedures to enable laboratories to improve or develop their capability for metal determinations in sea water.
- 4.3.3 The ACMP agreed that the acquisition of broad spatial coverage of coastal (shelf) areas for data on trace metals in sea water should, if accompanied by the ancillary measurements referred to above, provide at least some measure of the range and gradients in metallic contaminant concentrations in the ICES region.

4.4 Conclusions on the Baseline Survey Programme

4.4.1 The ACMP concluded that, on the basis of the information provided by the national representatives, it seemed likely that a substantial effort will be mounted by a number of countries for the 1985 Baseline Study of Contaminants in Fish and Shellfish. This should lead to the production of a Baseline Study report containing data on the concentrations of contaminants in fish and shellfish which are more comparable than those obtained previously and which relate to a larger and more comprehensively sampled area than has previously been possible. The report on the results of this study should be available in 1987. The ACMP noted that it was also possible that the first results of the Baseline Study of Trace Metals in Sea Water will become available in 1986.

4.5 Trend Monitoring of Contaminant Concentrations in Biota

- 4.5.1 It was noted that an informal meeting had taken place in winter 1984 in Halifax, N.S., of a group of statisticians from Canada, Denmark and the United Kingdom to discuss trend monitoring issues. The WGMPNA had received an oral report of this meeting; the full report provided by the Convenor of the meeting, Dr. J Uthe, was discussed by ACMP.
- 4.5.2 The statisticians had addressed a number of outstanding problems and a full-scale statistical analysis of the data set under discussion was proposed as an approach to overcoming the remaining problems related to statistical techniques. The main problem in sampling relates to the spatial and temporal definition of the stock to be studied from a contamination perspective. The stock in this respect might well differ from a fisheries management definition of stock. Discussion of the treatment of samples by pooling did not result in a decision one

way or the other, but there are circumstances in which pooling can be utilized in a statistically sound manner. Each case in which pooling is to be used must, however, be justified on the basis of the analysis of individual fish within the pool. A number of biological issues that need further elucidation were identified:

- choice and number of variables (body length is used for convenience);
- unit and scales of measurement (e.g., a single unit error in age measurement can have severe effects on the results);
- extent of intra-stock genetic variability;
- choice of tissues or organ (need for physiological/biochemical information);
- longevity of species (short-lived animals appear most suitable).
- 4.5.3 In examining the data sets available, the group had been faced in one instance with clear but opposite trends in two species from the same area; such results cannot be interpreted without a deeper knowledge of the environmental and biological factors controlling the uptake and release of contaminants in those species. The group defined three categories of applications of trend monitoring: to local "hot spots", to regions or fishing grounds, or to wider areas; the first of these three is the most amenable to study at present. Further statistical analysis of the data sets, especially that on cod, was proposed.
- 4.5.4 On the basis of the oral report, WGMPNA had recommended that the group should be enabled to meet again late in 1984 or early in 1985 to continue their work on statistical methods and to review the first two years of trend monitoring data from the Cooperative ICES Monitoring Studies Programme with a view to advising on the tabulation and analysis of the data and to carry out a preliminary analysis of the 1982/ 1983 data. The group should report back to the WGMPNA and Dr. Uthe was suggested as a coordinator for the meeting. The ACMP endorsed this recommendation.
- 4.5.5 It was noted that the statisticians were not recommending any changes to the current guidelines for trend monitoring. While these guidelines could be considered interim in nature, it would be valuable to continue to collect data within these guidelines.
- 4.5.6 The ACMP noted that the statisticians' group was making encouraging progress in the purely statistical aspects, but was coming up against limitations due to a lack of sufficient physiological information on the passage of contaminants through biota and the factors controlling this. For this reason, all future meetings on this topic should include physiologists and biochemists involved in this type of work. It was decided that, on the basis of his report to the Halifax meeting, Dr. Uthe should be asked to prepare a non-technical statement of the current capabilities of the statisticians on trend monitoring, identifying as far as possible the limitations on their further advance.
- 4.5.7 Recognising that further advances in the development of trend monitoring techniques depend not only on additional work on statistical aspects, but also on the provision of information on the biological sources of variance in contaminant levels in fish tissues, the ACMP

concluded that to make further progress:

- (a) the restrictions on progress in trend monitoring must be identified, especially with respect to biological factors, and as part of this work, (i) a review should be made of current knowledge of the physiological factors governing the uptake, distribution between organs and release of contaminants in species relevant to the monitoring programme; and (ii) the key physiological and ecological questions must be identified for which answers are required in order to provide an adequate understanding of biological sources of variability in contaminant levels;
- (b) the statistical aspects of trend analysis methodology must continue to be developed, including, if necessary, changes to the sampling procedures to be used.

These points will be drawn to the attention of the appropriate Working Group. In the meantime, the ACMP recommended that the existing guidelines for the sampling and analysis of fish and shellfish for purposes of time-trend assessment of contaminant concentrations should continue to be followed.

4.6 Use of Seaweeds in Contaminant Monitoring

- 4.6.1 At the request of ACMP, the WGMPNA had considered the use of seaweeds as indicator organisms, and reviewed a paper which compared the use of mussels and <u>Fucus spp</u>. This suggested that the choice of indicator organism depends on the metal to be monitored, with <u>Fucus</u> giving a clearer indication of variations in copper and zinc, while mussels were better indicators of lead distribution. In the discussion, the ACMP noted that <u>Fucus spp</u>. and <u>Ascophyllum spp</u>. were being used to monitor heavy metal concentrations in some Norwegian fjords, and higher plants (<u>Zostera</u>) with root systems were being studied in Denmark in connection with sediment contamination. The ACMP also noted a number of topics that need further clarification before any decision can be made on whether to include seaweeds in programmes for monitoring pollution. These include:
 - the ageing of seaweed tissues;
 - the use of annuals or perennials;
 - the use of less differentiated rock-living algae to measure water concentration versus the use of higher plants (Zostera) with rooting systems to study sediment contamination;
 - the relevance of radiobiological studies and monitoring programmes to model the response of algae to stable element analogues.

The ACMP noted that the WGMPNA has sought further papers on the use of seaweeds as indicators and has taken steps to ensure that the points raised by ACMP will be considered by the Working Group at its next meeting. It is hoped that a statement on this question will be provided within three to four years.

4.7 Automated Handling of ICES and JMP Monitoring Data

4.7.1 The ACMP had before it the May 1984 version of the Interim Reporting

Format for Contaminants in Fish and Shellfish. This represented the final draft of the Format, which has been in development for two years in connection with the reporting of data for the Cooperative ICES Monitoring Studies Programme as well as for the Joint Monitoring Programme of the Oslo and Paris Commissions and the Baltic Monitoring Programme of the Helsinki Commission. This new version of the Format contained only minor changes, such as the addition of a field to report the detection limit of the contaminants measured, and the request that the species of the organisms reported be coded according to the RUBIN eightletter species code. Also, this version of the Format contained the full details of the guidelines to be followed for sample collection, preparation and analysis of fish and shellfish in the conduct of the Cooperative ICES Monitoring Studies Programme, which were agreed in April 1982. In addition to this paper form for the reporting of data on contaminants in fish and shellfish, full specifications for the reporting of data on magnetic tape are available through the ICES Secretariat.

- 4.7.2 The ACMP was informed that the software development for the utilisation of this format and the accessioning of data in the ICES computer are now nearly complete. A data base system according to the Scientific Information Retrieval (SIR) system has been developed.
- 4.7.3 The ACMP took note of the Draft Interim Reporting Format for Contaminants in Sea Water, which had been drafted on the basis of the present requirements of the Joint Monitoring Programme of the Oslo and Paris Commissions. Accordingly, this Format is mainly intended to report data on mercury and cadmium concentrations in sea water. However, it can equally well be used for the reporting of data on petroleum hydrocarbons in sea water in the context of the Baltic Monitoring Programme of the Helsinki Commission. Further work will be carried out on the development of this Format so that it can accommodate the reporting of data on a full suite of trace metals, as well as other substances, in sea water.
- 4.7.4 Finally, the ACMP took note of a Preliminary Draft Interim Reporting Format for Contaminants in Sediments, which has been drafted on the basis of the requirements of the pilot sediment part of the Joint Monitoring Programme of the Oslo and Paris Commissions. This Format has also been developed for a wider application and thus allows for the reporting of data on other contaminants in sediments as well as for data on the concentrations of other metals and components of sediments which are important in the interpretation of data on contaminants. This Reporting Format is still in the developmental stages, and should be finished by mid-1985.
- 4.7.5 The ACMP concluded that the progress in the automated handling of contaminant data by the ICES Secretariat was satisfactory. It was noted that the processing of the 1983 data from the Joint Monitoring Programme of the Oslo and Paris Commissions should be completed on schedule and that progress is being made towards the completion of interim reporting formats for contaminants in sea water and sediments, to add to that for fish and shellfish.

5. BIOLOGICAL EFFECTS STUDIES

5.1 Review of Techniques

- 5.1.1 The ACMP noted that the WGMPNA has continued its examination of biological effects monitoring techniques, considering first their practicability (e.g., ease of application, cost effectiveness, requirement for equipment and trained personnel, and interpretability of the results) and, second, their uses with the strategy for biological effects monitoring adopted by ACMP in 1982 (Annex 3 to Coop. Res. Rep. No. 120 (1983)). The main aims of this review were to encourage more widespread experimental application of techniques developed in particular laboratories, and to identify techniques that might be suitable for inclusion in a cooperative biological effects monitoring study.
- 5.1.2 Macrobenthos population monitoring techniques were recognised as being among the most commonly used methods in ICES member countries for biological monitoring, but they are expensive in terms of ship-time, manpower and expertise. These techniques are most useful for examining spatial variations when monitoring on transects away from point sources, e.g., dumping sites. Considerable gaps remain in our knowledge of the natural and temporal fluctuations in macrobenthos communities, which makes discrimination between natural and anthropogenically-induced changes difficult. In this context, a need was identified for a better understanding of the factors controlling natural fluctuations, and also of the significance of the changes observed in relation to the wider marine environment and to fisheries. To advance this subject, a number of questions were posed to the Benthos Methodics Working Group about the relationships between benthos and fish populations, and about the procedures for detecting changes in the benthos, and separating natural from man-induced changes.
- 5.1.3 A bio-assay method based on oyster embryo development was also discussed. This is a simple and inexpensive technique requiring little expertise except in the management of oysters and the induction of their spawning. It was considered that this technique was best applied to the quantification phase of biological effects monitoring rather than to the identification of "hot spots" of pollution, since other factors affecting water quality have a considerable impact on the results. In particular, it has been noted that in some areas subject to algal blooms, the effects on the oyster larvae are greater than would be expected purely from what is known about the levels of contaminants present.
- 5.1.4 Biochemical and physiological methods, including the adenylate energy charge (AEC) technique and several other enzyme-based methods, were considered. These techniques are relatively sophisticated, requiring specially trained personnel and, although they are all becoming more widely used, it was not felt that it would be appropriate to recommend their incorporation in cooperative programmes at this stage. However, many of these techniques could prove useful in particular for the identification phase of biological effects studies. This was especially true of a technique which identified the incidence of micronuclei in fish red blood cells, which is a result of chromosomal damage. Such techniques may in the future provide a method for the rapid routine screening of water quality, though the cause-and-effect relationships are not well understood at present.

5.1.5 Some approaches are of more relevance for laboratory or <u>in situ</u> monitoring of effluent quality rather than for general use in the marine environment. One such technique makes use of the development and growth of mussels, including shell growth, valve movements and byssal thread formation. Another is the rotatory flow technique, which depends on a behavioural response in fish as an assay of water quality. Although the sensitivity of these techniques may be such as to preclude their use for environmental monitoring, they have great potential for monitoring effluent quality.

5.2 Workshop on Biological Effects Monitoring Techniques

5.2.1 The ACMP recalled that, on the basis of a recommendation of the WGMPNA, the Council had resolved (C.Res.1983/2:27) that a Workshop on Biological Effects Monitoring Techniques should be held in May 1984 to demonstrate and evaluate methods which might be used as a biological effects component of the 1985 Baseline Studies on Contaminants. The Federal Republic of Germany had agreed to host this Workshop, with a sea component on board the research vessel "Anton Dohrn" and a land-based component at the Biological Station on Helgoland. Information concerning the Workshop and the criteria for the selection of techniques to be demonstrated was circulated to potential participants on several occasions. Unfortunately, owing to an inadequate reponse, the Workshop had to be postponed. Taking note of this information, the ACMP agreed that the rescheduling of this Workshop should be considered in discussions at the 1984 Statutory Meeting concerning the overall enhancement of the work on biological effects monitoring conducted by ICES.

5.3 Results of the Workshop on Methods in Fish Disease Surveys

- 5.3.1 The ACMP received a report on the Workshop on Methods in Fish Disease Surveys, which was held on 3-12 January 1984 on the research vessel "Anton Dohrn" (Federal Republic of Germany). The aims of the Workshop were to consider methods for conducting fish disease surveys, to intercompare details of diagnosis and sampling, and to agree on standardised sampling procedures. One further aim was to bring together scientists involved in fish disease surveys to encourage coordination of future work in order to ensure satisfactory geographical coverage in the ICES area and avoid unneccessary overlap in areas which are investigated by more than one nation.
- 5.3.2 The Workshop, which was co-chaired by Dr. E Egidius (Norway) and Dr. V. Dethlefsen (Federal Republic of Germany), was attended by twelve scientists from ten ICES member countries (Belgium, Denmark, Federal Republic of Germany, Finland, France, Netherlands, Norway, Sweden, United Kingdom and USA). The cruise started in the German Bight, and covered the Dogger Bank, British coastal waters, the central North Sea, and Danish coastal waters before returning to the German Bight.
- 5.3.3 The Workshop was divided into a practical component, in which participants had the opportunity to test different methods of sampling and diagnosis, and a discussion component, in which eleven contributed papers were presented and extensively discussed. During the experimental work, the Workshop identified a variety of methodological shortcomings in current fish disease surveys. Major sources of variance were detected in sampling (fishing gear, fishing methods), sub-sampling and, particularly, in the frequency of sampling. To keep within a varia-

bility of $\pm 20\%$ in prevalence of diseases of dab in the German Bight, it was calculated that up to six 30-minute hauls had to be performed (depending on the disease prevalence and the number of fish). The presence of marked seasonal cycles of prevalences of disease of marine organisms, which are different for different diseases and areas, has to be established to characterise the magnitude of this variability. Since repeated sampling is often impossible, fish disease studies have to be long-term investigations.

- 5.3.4 During the experimental phase of the Workshop, it was established that the diagnosis of external lesions created few difficulties, and there was a good uniformity in the classification of the externally visible phenomena. Since internal lesions and parasites are often not searched. for, the importance of the inclusion of these diseases also was stressed.
- 5.3.5 Difficulties were found in the detection of the early stages of lymphocystis and in the distinction between healed, healing and acute ulceration of dab. Classification systems were developed to indicate the intensity of disease symptoms and the severity of parasitism. Special attention was given to the standardisation of the sampling effort and the intensity of investigation. The value of check lists that include all diseases and parasites that have to be searched for, and which also require the recording of the absence of phenomena, was emphasised.
- 5.3.6 The possibilities for the inclusion of fish disease studies in routine fish stock assessment work, the training of personnel, the use of computer facilities, the selection of indicator species or indicator diseases, the planning and preparation of disease studies, and the reporting and evaluation of results were further major points in the discussion.
- 5.3.7 The participants in the Workshop agreed that the exercise had been very useful and felt that the results obtained will provide a better basis for future cooperative studies of fish diseases.
- 5.3.8 The ACMP felt that the Workshop had considerably enhanced the prospects of cooperative studies on fish diseases and had increased the likelihood of the participants producing comparable data in their future studies. The ACMP expressed its appreciation to the coordinators of and participants in the Workshop.

5.4 Fish Diseases in Relation to Pollution and Effects Monitoring

- 5.4.1 The ACMP took note of the activities concerning fish diseases in relation to pollution in the WGMPNA and the Working Group on the Pathology and Diseases of Marine Organisms (WGPDMO). To achieve optimum effort on this subject, a Joint Meeting of the two Working Groups is envisaged to discuss:
 - 1. The role of environmental among other factors in fish disease etiology, including possible relationships between contaminant body burdens and disease.
 - 1.1 The types of diseases most likely to be environmentally influenced.
 - 1.2 The types of environmental factors most likely to be relevant.

- 1.3 Other environmental variables that would be useful to support epidemiological studies.
- 2. Methodology including statistics in evaluating the relationship between pollution and disease.
- 3. The types of diseases most likely to be feasible for inclusion in a monitoring programme.
- 4. Outcome of epidemiological studies to date, particularly on disease "hot spots" and study of disease maps.
- 5. Suggestions for further work.
- 5.4.2 The ACMP encouraged the WGPDMO to use the results of its epidemiological studies to prepare a map of the occurrence and prevalence of fish diseases in the ICES area. At the Joint Meeting, areas of "disease hot spots" could be checked to determine whether they correlate with areas of known "pollution hot spots".
- 5.4.3 The ACMP considered that the measures proposed above should lead to the generation of more information on the occurrence and prevalence of fish diseases and a better understanding of the relationship between the incidence of fish diseases and anthropogenic activities, including the discharge or dumping of wastes into the sea.

5.5 Biological Effects Component to the 1985 Baseline Study

5.5.1 The ACMP was informed that the WGMPNA had considered that it would be valuable to include a biological effects monitoring component in the 1985 Baseline Study. Despite the postponement of the Workshop to identify techniques suitable for use in a biological component of the Baseline Study on Contaminants in the Marine Environment (see Section 5.2, above), the ACMP recommended that ICES member countries should apply their own most favoured techniques over much wider areas than at present and especially in areas subject to chemical baseline studies, with the aim of gathering data on biological variability however induced (natural or anthropogenic) over a wide area, and of assessing the use and sensitivity of the techniques. In addition, it was considered that the 1985 Baseline Study would provide an excellent opportunity to collect information on the incidence and prevalence of fish diseases over a wide area and, in particular, to gather data on fish diseases in the context of the contaminant monitoring studies. Accordingly, the ACMP requested the WGPDMO to provide advice on the best approach to this work.

5.6 Conclusions on Biological Effects Monitoring

5.6.1 In concluding its consideration of this item, the ACMP noted that a wide range of approaches to biological effects monitoring were available, involving biochemistry, physiology, pathology, population structure, bioassay, and including experimental techniques in the laboratory and in the field. It recognised that many of these approaches are already in use on a national basis, although usually on specific sites and often within an experimental context. It accepted that much of the work is still in a developmental phase and that more research and evaluation are required before concrete guidelines can be given for widespread application of these techniques in the context of international cooperative programmes. However, the ACMP considered that significant advances were being made. It noted that the WGMPNA would continue its evaluation of techniques; it welcomed the activities of the WGPDMO in the context of pathology; it warmly endorsed the proposal to include biological effects component in the 1985 baseline study; and it considered that it would be useful to hold a workshop to demonstrate the most relevant techniques at some time in the future.

6. INTERCALIBRATION EXERCISES AND ANALYTICAL ISSUES

6.1 Trace Metals in Biological Tissues

- 6.1.1 The ACMP noted that the first phase of the Seventh Intercalibration Exercise for Trace Metals in Biological Tissues (7/TM/BT) has now been completed, and that a full evaluation of the results will be presented at the 1984 Statutory Meeting. At the time of the Marine Chemistry Working Group meeting, 41 out of a total of 57 laboratories which had received samples had returned the results of their analyses to the Coordinator, Dr. S Berman. A preliminary evaluation of the results showed that the capability for copper, zinc and mercury determinations is good, but considerable discrepancies occur for the analysis of lead and arsenic at low concentrations. On the basis of the results of 7/TM/BT, Dr. Berman will ask participants with the best methods to document their procedures for the preparation of leaflets to be published in the new ICES series "Techniques in Marine Chemistry".
- 6.1.2 The ACMP was informed that planning for the second phase of 7/TM/BT is well in hand. A series of uncompromised samples (i.e., samples containing known but undisclosed concentrations of contaminants) is being prepared for distribution prior to the 1985 Baseline Survey. Participants in the Baseline Survey Programme will be asked to analyse these materials, at the beginning and at the end of their baseline work, for Cu, Zn, As, Cd, Hg and Pb. The results of these analyses will be used to evaluate the baseline data by the MCWG prior to review by the WGMPNA. It was noted that Dr. Berman has agreed to assist, by correspondence, laboratories that have experienced difficulties in the first phase of 7/TM/BT in order to help them improve their analytical capabilities.
- 6.1.3 Noting this information, the ACMP agreed that progrees was rapidly being achieved toward the establishment of appropriate quality assurance procedures for use in the 1985 Baseline Study and other programmes.
- 6.2 Trace Metals in Sea Water
- 6.2.1 The ACMP noted that the results of two components of the Fifth Round Intercalibration for Trace Metals in Sea Water (5/TM/SW) had been presented during the 1983 Statutory Meeting and discussed by the MCWG. The results of the filtration component (Doc. ICES, C.M. 1983/E:18) revealed that the contamination of samples by filtration is generally minor when normal precautions are taken and that a number of different filtration procedures produce uncontaminated filtrates. There was generally good agreement between the results produced by the eight filtration systems that were compared. All systems were capable of giving, and generally gave, contamination-free filtrates for copper, nickel, cobalt and manganese and, with two exceptions, for cadmium and iron at concentrations that would be encountered in coastal waters. All the systems also appeared capable of giving reasonable results for zinc and lead at the somewhat elevated levels encountered in this experiment. No one system seemed to stand out as being better than the others for any of the elements measured.
- 6.2.2 With the results of this experiment complete, all significant aspects of sampling, filtration, sample storage, pre-concentration and analysis have been investigated through various intercalibration exercises and suitable procedures for the conduct of baseline studies of trace metals

in sea water (dissolved phase or "total dissolvable") can be recommended. It was noted that the coordinators of this series of intercalibrations will prepare descriptions of the appropriate techniques for publication by ICES, probably in 1985.

- 6.2.3 The ACMP was informed that the analytical intercalibration component of 5/TM/SW, coordinated by Dr. S Berman (Doc. ICES, C.M. 1983/E:24), showed better agreement in sea water analysis for trace metals than previous intercalibrations. Two-thirds of all laboratories reporting quantitative results for cadmium, copper, manganese and nickel agreed on mean concentrations for these metals with relative standard deviations varying from 19 to 30 per cent. This is a notable performance. The precision was somewhat worse for zinc, with two-thirds of the laboratories yielding a mean with a 38% relative standard deviation. This may be a reflection of the contamination problems which affect the analysis for zinc at trace levels. The two problem elements of the seven were lead and iron. Two-thirds of the laboratories recorded a mean for lead with a relative standard deviation of 55%. This, nonetheless, represented an improvement in the analysis for this metal. Only a few values were reported for iron, whose mean had a relative standard deviation of 57%.
- 6.2.4 The ACMP concluded, on the results of this intercalibration exercise, that a substantial number of laboratories in ICES member countries have the capability of reliably analysing filtered sea water for a number of metals. It is worth recording that the samples used were derived from a nearshore location (ca. 25 km offshore), but had metal levels comparable with those in open ocean waters. It should be noted that, although the water mass sampled was not of estuarine origin, it was not atypical of many coastal waters. Convictions that nearshore levels of trace metals are always substantially higher than levels in offshore waters are clearly erroneous. The care and analytical sensitivity and precision required for open-ocean measurements are, therefore, required for the conduct of coastal zone baseline and research studies.
- 6.2.5 The mercury intercalibration component of the experiment has been repeated by Drs. D Cossa and P Coureau using water samples collected in the St Lawrence River estuary. The results of this experiment were briefly discussed during the 1984 MCWG meeting but were not formally reviewed. It was noted that a report on the results of this experiment will be presented at the 1984 Statutory Meeting.
- 6.2.6 The ACMP noted that reports on the results of the various components of 5/TM/SW are expected to be published in the ICES Cooperative Research Report series in 1985.
- 6.2.7 The ACMP concluded that, with the completion of recent intercalibration exercises on the measurement of trace metals in sea water, it is now possible to describe techniques for the determination of dissolved metals in coastal waters for the conduct of the 1985 Baseline Survey and other programmes. Appropriate quality assurance procedures for the 1985 Baseline Survey are being developed and they should complete the methodological proving stages for the measurement of dissolved trace metals in sea water. Attention is now turning to the development and testing of procedures for the determination of metals associated with suspended particulate matter in coastal waters.

6.3 Metals in Sediments

- 6.3.1 The ACMP noted that the first part of the Intercalibration Exercise on the Analysis of Baltic Sea Sediments had reached the final stage. Following approval of a draft version by the Joint Meeting of the Working Group on Marine Sediments in Relation to Pollution and the Marine Chemistry Working Group in February and by the ICES/SCOR Working Group on the Study of the Pollution of the Baltic in April 1984, the preliminary report was sent to the 28 participating laboratories from fifteen ICES countries for review. The results of this exercise indicated a relatively good performance on the analysis of most of the metals included (Zn, Cu, Pb, Mn, Fe, Ni, Al, Co), as measured in both samples distributed, the Arkona Basin sediment sample and the Mecklenburg Bight sample. However, the deviations found in the values reported for mercury, cadmium and chromium were not acceptable. The approach of using a simple and quick leaching method to obtain an idea of the "maximum potential bioavailable fractions" of metals was considered pragmatic and sensible. Most of the lead, cadmium and zinc present in the samples could be leached by 1N HCL. Medium amounts (40 - 60%) became available for copper, nickel and cobalt. For primarily lattice-bound metals, e.g., aluminium, iron, chromium, only between 5% and 30% were leached.
- 6.3.2 It was reported that the second part of this exercise will consist of the analysis of trace metals in sliced cores and dating using radiochemical techniques. It was expected that an overall report on the results of both parts of the exercise would be published in the Cooperative Research Report series in due course.
- 6.3.3 The ACMP also noted that samples for the ICES First Intercalibration Exercise on Trace Metals in Marine Sediments (1/TM/MS) have already been distributed. This intercalibration, participation in which is ICES-wide, will investigate the results and interlaboratory comparability obtained when applying four different suggested reference methods, comprising leaching by weak acids (acetic acid, 1N HCl) and strong acids, including a "total" dissolution procedure.
- 6.3.4 The ACMP was informed that the Second JMG Intercalibration Exercise on Marine Sediments, 1983, dealing primarily with the relationship between particle size and the content of different determinands including trace metals, has been finalised. It is hoped that a report will be available at the JMG Meeting in 1985.
- 6.3.5 Noting that the results and conclusions of the various intercalibration exercises for trace metals in marine sediments will be available by 1985, the ACMP considered that they will provide a basis for the conduct of cooperative baseline measurement programmes. Cooperative studies of PCBs in marine sediments will have to await the development and proving of suitable analytical techniques for PCB congeners. These techniques will be tested initially on marine biological samples.

6.4 Organochlorines

6.4.1 The ACMP was informed of the results of the Fifth Intercomparison Exercise on the Determination of Organochlorine Residues in Fish Oil (5/OC/BT). Out of 30 participating laboratories, over one-half had attempted to identify fully four chlorobiphenyls, as requested. The interlaboratory coefficients of variation, though large, were equivalent

to those associated with the measurement of PCBs using Aroclor 1254. From the exercise, it can be concluded that the correct identification of individual chlorobiphenyls and the full recovery of each added chlorobiphenyl remain a problem. An interim study has been conducted since the conclusion of this intercomparison exercise to examine and clarify some of the problems identified. The results of this study are expected to be available in 1985.

- 6.4.2 After several intercalibrations of PCB analyses in biological tissues have been conducted, the overall interlaboratory comparability is still poor although there has been some improvement. The major errors contributing to the interlaboratory variance are probably systematic and these should be identified and corrected before another intercalibration is conducted. The ACMP was informed that some laboratories in EEC member countries are studying such errors and a report is expected in mid-1984 which will be made available to the MCWG. Interlaboratory variability in general presents less of a problem and it is certainly possible for some laboratories to determine trends in time and space using their own data.
- 6.4.3 The analytical situation for other chlorinated hydrocarbons is considered to be similar to that for PCBs and this should be kept in mind when planning monitoring studies. It is recognised that the most suitable technique for the analysis of chlorinated hydrocarbons is that using capillary columns. Accordingly, laboratories which are still using packed column methods should only continue to do so for as long as they are unable to obtain equipment capable of using capillary column techniques. It must be emphasised that the use of packed columns for the analysis of PCBs can only be expected to yield useful results if the concentrations found are well above the level of detection. Provided that the concentrations measured are high, it may be possible for the laboratory to compare its results obtained with packed columns with those it may generate using capillary columns, when it eventually makes that change. However, this comparison will only be possible to make if quantification continues to be carried out on the basis of a technical formulation and a thorough check of comparability of the results obtained by both techniques on the same samples is conducted by that laboratory to confirm the most appropriate congener peaks to be used in multi-peak summation.
- 6.4.4 It should be noted, however, that the general trend as capillary columns are adopted is to identify and quantify only selected individual PCB congeners. At present, there are two problems preventing wide-scale adoption of these procedures, namely, the lack of ready availability of pure congeners of PCB and the lack of general agreement on the congeners on which attention should be focussed. Adequate supplies of congeners are not available at present. Those which are available are expensive, and in some cases of doubtful purity, but steps are being taken to rectify these deficiencies.
- 6.4.5 Assuming that these problems are solved and that the change in approaches to PCB quantification from formulations to specific individual congeners takes place, no comparison will be possible between these data and those which have been generated using packed columns and/or formulations as standards.
- 6.4.6 The ACMP was informed that the present analytical problems do not permit the conduct of an intercomparison study for individual chlorinated

hydrocarbons in sea water. In the case of sediment analysis, it was noted that reference materials are available from Canada, and these might prove useful for future quality assurance activities.

- 6.4.7 The ACMP noted the importance attached by both the WGMPNA and the Oslo and Paris Commissions to the need to resolve uncertainties in the analysis of PCBs. The ACMP concluded that there are several reasons for analysing PCBs and that the analytical technique used should be chosen according to the aim of the study, as outlined in the next two paragraphs.
- 6.4.8 In the simplest sense it is, as noted above, already possible for <u>a</u> <u>single laboratory</u> to detect spatial distributions and temporal trends in environmental levels of PCBs, especially in biota. Such analyses need not always involve detailed individual congener analyses using capillary columns, and either packed or capillary column techniques may be used, subject to the proviso in the previous paragraphs. Consequently, if the need is simply to detect the response, in environmental concentration terms, of measures to restrict inputs, it is now possible to advise on methods of analysis which can be used. However, until the intercomparability among laboratories is improved, these studies cannot be conducted on a cooperative basis.
- 6.4.9 More important, however, is that the various congeners of PCBs do not all suffer the same fate in the environment, nor are they likely to have the same impact in toxicological terms. Thus, in order to be able either to study the fate of individual chlorinated biphenyl compounds, or to assess the toxicological importance of the most prevalent or persistent congeners, individual congener analyses are required. Until the problems involved in such analyses are resolved, it will not be possible to advise on how these requirements can be met. This is expected to take at least a further three years.
- 6.4.10 The ACMP is not at the present time able to answer further the questions posed by the Oslo and Paris Commissions as to what method of analysis of PCBs can be recommended. However, in view of the complexities of the problem indicated above and the differing state of the art depending on the problems to be addressed using the two techniques, the ACMP would welcome further clarification from the Commissions as to their requirements; for example, (a) is the interest primarily in spatial or temporal trends and, if the latter, over what period, (b) is the interest only in highly contaminated areas, (c) is the interest in those congeners which are most persistent or those which have the greatest toxicological significance?

6.5 Hydrocarbons

6.5.1 The ACMP was informed that the Second Intercomparison Exercise on the Determination of Petroleum Hydrocarbons in Biological Tissues (2/HC/BT) has been successfully concluded, as well as the Intercomparison Exercise on the Determination of Polycyclic Aromatic Hydrocarbons (PAH) in Biological Tissues (3/HC/BT). For the first of these two exercises, which is a joint ICES/IOC activity, results have been reported using three different methods: (1) UV fluorescence, (2) gas chromatography, and (3) gas chromatography/mass spectrometry, and data are being analysed on the basis of each class of methods. For the second exercise, participants were asked to determine ten specified PAH compounds and any others as appropriate. The full reports of these exercises are expected to be available in 1985.

- 6.5.2 It is expected that the current intercalibration for PAHs in tissue will provide sufficient information to warrant a recommendation for the inclusion of the determination of PAHs in tissues in the 1985 Baseline Study on Contaminants in Fish and Shellfish.
- 6.5.3 Concerning the analysis of petroleum hydrocarbons in sea water, it was recognised that the determination by the ultra-violet fluorescence technique (UVF), which was successfully intercalibrated at the Kiel Workshop of 1981, provides acceptable results for screening and might be considered acceptable for inclusion in the Baseline Study Programme. However, the composition of the fluorescent material must be known if an assessment of the pollution status in a given area is needed, or if sources are to be determined. Accordingly, if UVF is used as the screening method for the Baseline Study, it should be checked occasionally for individual PAHs when readings are low (<1 µg/1) and more frequently if readings are high. The UVF screening procedure can also be applied to sediments, but the correlation between UVF readings and the determination of individual compounds must be checked even more frequently before firm conclusions about the extent and nature of contamination can be drawn. The increased availability of suitable reference materials should facilitate greater progress in this field.
- 6.5.4 It was noted that instruments are now available which allow virtually continuous measurement of petroleum hydrocarbons in sea water using the UVF technique. These instruments have adequate sensitivity for use in shelf waters, but are not yet sufficiently sensitive to measure the lower concentrations in open ocean areas.
- 6.5.5 Concerning the feasibility of conducting a round-robin intercalibration (i.e., an exercise in which samples are sent out to participants for analysis in their own laboratories) on the analysis of petroleum hydrocarbons in sea water, the ACMP noted that the difficulties of preparing and storing solutions containing petroleum hydrocarbon residues have thus far hampered the design and conduct of round-robin intercalibrations to assess the comparability of determinations in sea water made by different laboratories. The ACMP was informed that a mechanism for the conduct of an intercalibration exercise on petroleum hydrocarbons in sea water would be considered at the 1985 MCWG meeting and the feasibility of conducting such an exercise will be determined. If this type of exercise proves to be impractical or uneconomic, the MCWG will have to develop other quality assurance procedures.
- 6.5.6 The ACMP considered that the inclusion of total hydrocarbon measurements in the 1985 Baseline Study was a welcome advance. While the ACMP was interested in being able to make other recommendations for work on hydrocarbons, it concluded that until the current round of intercalibration exercises is completed, it will not be possible to assess what cooperative work will be practicable. In this context, it was noted that the MCWG is devoting special attention to the early completion of the work.

7. STUDIES OF CONTAMINANTS IN SEDIMENTS

- 7.1 It was noted that a computer programme in FORTRAN is now available for the implementation of the "Decision Tree Method for Selecting Monitoring Sites for Investigations on the Contamination of Sediments by Metals". This Decision Tree is contained in "The Potential Role of Sediments in Pollution Monitoring", Annex 2 of the 1983 ACMP Report (Coop. Res. Rep. No. 124 (1983)). For ordinary field application, estimates instead of exact numbers will be acceptable for some of the main criteria, such as biological mixing rate, grain size and deposition rate.
- 7.2 The ACMP reviewed the recommendations of the Working Group on Marine Sediments in Relation to Pollution (WGMS) on methods for sampling, sub-sampling, storage, pre-treatment and analysis of sediments. The description of these methods is intended as a supplement to the information contained in "The Potential Role of Sediments in Pollution Monitoring", from the 1983 ACMP Report. In the methods for sampling, preference was given to box corers instead of grabs when sampling in mud areas. A wet sieving method using a plastic 63 µm net was recommended. The drying methods applied, storage conditions (containers, temperature) and sub-sampling tools should be selected according to the class of contaminant to be investigated and the aim of the study. The description of these methods is attached as Annex 2 to this Report.
- 7.3 One objective of studies of contaminants in sediments is to develop an understanding of the availability of the substances to benthic organisms so as to be able to predict the impact of contamination levels on such organisms. This very complex question is closely connected with the methods of uptake by the different organisms, e.g., from interstitial waters, from organic particles, or from mineral or amorphous material. Other factors must be considered in this context, including the energetics of the organisms, which determine the amount of sediment processed to extract the necessary food. Due to the still limited knowledge of these factors at present it is only possible to adopt a purely geochemical approach; to this end, selected leaching procedures are used to estimate the maximum amount of potential biologically available metals. For the 1985 meeting of the WGMS, a more detailed background report has been commissioned on the state of the art on bioavailability.

7.4 Reports on the Pilot Sediment Studies

7.4.1 The Skagerrak Study

A progress report on the Pilot Sediment Study in the Skagerrak, giving the results of studies of the characteristics, distribution and transport of suspended matter in that area, was presented at the 1984 WGMS meeting. This report was based on cooperative work between laboratories from three countries. From the amount and chemical composition of the suspended matter, and salinity, temperature, turbidity and chlorophyll-<u>a</u> measurements carried out on several transects through the Skagerrak, five different water masses could be distinguished. The results of the investigations showed again the unique character of the study area, which seems to act as a trap for particulate matter originating from three sources - the North Sea, the Baltic Sea and the surrounding land areas. Based on these preliminary results, a bottom sediment sampling programme will be developed. A summary of this progress report is given in Annex 3.

7.4.2 The German Bight Study

This pilot study is being carried out in an area of the German Bight where active mud deposition is occurring. This mud area has been found to be a sink for contaminants, which are present in increasing concentrations in the more recent sediment layers. The objective of the study is to estimate the quantities of fine-grained material that are deposited annually in the German Bight so that the accumulation of contaminants can be assessed. A summary of the progress in this study is contained in Annex 3.

7.4.3 The Baltic Sea Study

The ACMP noted that the ICES/SCOR Working Group on the Study of the Pollution of the Baltic recommended that the Pilot Study on Pollutants in the Baltic Sediments (cf. C.Res. 1982/4:9) be carried out in 1985, with sampling conducted in particular in the Gulf of Bothnia, the Åland Sea, the Gulf of Finland, the Gotland Sea, the southern Baltic Proper including the Gdańsk Deep, the Kiel Bight, and the Belt Sea and the Kattegat. The ACMP urged ICES member countries bordering the Baltic Sea to support this programme, in particular through granting permission to sample sediments in their economic zones.

8. EFFECTS OF WASTES FROM THE TITANIUM DIOXIDE INDUSTRY

- 8.1 The ACMP continued its assessment of the effects of wastes from the titanium dioxide industry on the marine environment and began by considering a number of documents made available via the ICES Secretariat and members. These included a paper from Finland on the results of long-term studies of the effects of wastes from the titanium dioxide industry; a critique (prepared by a consultant under contract to the TiO₂ pigment industry in the USA) of data originally presented by Dethlefsen and Watermann (Paper No. 8, ICES Special Meeting on Diseases of Commercially Important Fish and Shellfish, 1980) on the possible association between increased disease incidence in dab and the dumping of wastes from the production of titanium dioxide; and an assessment of the effects of wastes from the TiO2 industry which had been presented by Greenpeace International to the Technical Working Group of the Paris Commission at its 11th session (1984). In addition, the ACMP had before it an assessment document prepared by the Norwegian Institute for Water Research (NIVA) under contract to the Oslo and Paris Commissions and, although this had not been formally distributed to ICES, it was taken into consideration.
- 8.2 The ACMP recognised that investigations of the effects of wastes from the TiO₂ industry discharged or dumped into marine areas were still underway in several countries, including the important medium-term series of observations being undertaken by the Federal Republic of Germany on disease incidence in fish. While it was reiterated that a full assessment should await the results of these investigations, the ACMP also recognised that the process of collecting observations in one form or another may continue for many years. Since most members considered that enough data were available to allow a reasonable interim evaluation of the impact of wastes from the TiO₂ industry, it was agreed that a statement on the current position should be made.
- 8.3 An examination of the constituents of the waste revealed that, although the concentrations of metal ions and acid differ according to, for example, the process used and the extent of pre-treatment given, all the constituents are inorganic. No synthetic organic compounds are involved; the waste is essentially inorganic in character and almost all the metals are derived from the raw natural minerals illmenite or rutile, from which the majority of the titanium has been extracted by means of powerful acid leaching processes. It was pointed out that acid leaching of minerals occurs as a natural process; thus, although in the industrial situation the process is accelerated, the waste will bear a qualitative resemblance to the products of natural weathering. It was emphasised in drawing this analogy that the concentrations of metal ions and acid in the waste are extraordinarily large. Consequently, some of the ions, at least on initial discharge, may be in an unusually active form relative to those produced in natural weathering processes. Nevertheless, after large-scale dilution and some time in the marine environment, the products of neutralisation, hydrolysation, oxidation and precipitation will, in both their chemical nature and concentration, be similar to those naturally discharged by major rivers.

Although on initial discharge their impact will be different and may be substantial, after large-scale dispersion (e.g., over basin-wide scales) their impact is clearly no more adverse than that caused by the discharge of natural weathering products from rivers. The problem, therefore, is to define the distance scales over which these wastes might have significant impact between these obvious extremes.

- 8.4 A review of demonstrated effects from laboratory tests on wastes from TiO2 production suggests that the lowest concentration at which sublethal effects are just detectable is at a dilution of 1 part waste in 45 000 parts of sea water. Given that laboratory tests are of necessity carried out with a restricted range of organisms, it can be argued on the one hand that there may be species among those not studied which could be more susceptible and that a 10-fold safety factor should be applied to reduce the risk of adverse effects occurring in the marine environment. On the other hand, it can be argued that laboratory tests are conducted in an artificial situation such that the test organisms are exposed far more continuously and directly to the waste under conditions which are worse than they would experience in the sea for the lowest detectable effect concentration. Thus, for a waste containing essentially natural constituents, it can be argued that no safety factor need be applied to the lowest detectable effect concentration.
- 8.5 Both arguments were taken into account by the ACMP in applying the available data to make theoretical calculations of whether effects would be likely to occur in the marine environment. The example chosen was the North Sea and numerical details of these calculations and the assumptions on which they are based are set out in Annex 10 and include "worst case" situations. From the calculations, it is clear that some effects must occur. It is important therefore to consider whether effects have in practice been detected, over what scale, and whether the situation is deteriorating, improving or remaining stable. The latter will depend upon whether the various removal processes are in balance with the rates of input. The acidity is unlikely to be detectable over large distances due to the rapid buffering which will take place on mixing with sea water. The iron, and with it most of the metals present in solution or suspension, will be precipitated or coprecipitated, and eventually settle to the sea bed. Taking the North Sea, which receives more waste from TiO_2 production than any other sea area (5 countries dispose of waste to the North Sea), the input of iron via TiO2 waste is about the same as the aggregate amount discharged via the rivers Rhine, Elbe, Schelde, Thames and Humber. For the other metals, the input via wastes from TiO2 production is smaller than that from the rivers, with the possible exception of manganese. The impact of both the iron and other metals will therefore be small unless they settle rapidly and permanently in the immediate vicinity of the disposal area, as might occur if the disposal area is quiescent, in which case locally there may be a substantial detectable effect on sediment metal concentrations and biota.
- 8.6 A review of the information available on the areas where disposal of waste from the titanium dioxide industry takes place confirms that effects are detectable. In the Humber Estuary, the waste is discharged via pipelines terminating close to the estuary bank. The waste has a visual impact, staining the shoreline, affecting benthos and possibly affecting pelagic biota which may attempt to colonise the area alongside the effluent discharge points. There is little evidence of elevated concentrations of metals in either biota or sediments beyond the range of detectable pH differences in the water. The intertidal flats

0.5 km from the outfalls are of considerable importance as feeding grounds for sea birds of a wide variety of species, suggesting that even if the benthos is affected the size of area so affected is not large. The pH differences were earlier reported to be confined to a narrow plume within a few 100 m up and downstream of the outfalls. Recent surveys show that pH differences can be detected over a wider area. Nevertheless, the scale of detectable effects on both water quality and benthos is small, $2 - 5 \text{ km}^2$ at most, and the impact on the estuary as a whole is minimal. It should be noted that the Humber Estuary carries a very high natural suspended load (up to 20 000 mg/l and typically > 100 mg/l) and is subject to unusually strong tidal currents. Consequently, the contribution of the effluent to the standing stock of suspended solids and iron in the Humber Estuary is relatively small.

- 8.7 It is clear that the Finnish discharge into the Baltic Sea also has an effect on biota and water over a larger area than that impacted in the Humber. This can be attributed to the particular conditions of the Baltic Sea, i.e., lower salinity and no tidal and less current mixing and dispersion. However, contrary to earlier fears, the data indicate that no increase in the size of the area affected has occurred in recent years and there is some evidence of a decrease.
- 8.8 In the German Bight, observations in recent years show that, as was originally reported, no decrease in pH can be detected except transiently in surface waters. However, the area is not normally very highly stratified and, as the theoretical calculations suggest, excess suspended iron can be detected throughout the water column in the dumping area. Details of biological effects were not available to ACMP although it was understood they have been clearly established.
- 8.9 No information was available on the impact of the disposal of wastes from TiO₂ production to other areas (e.g., off the Netherlands and Belgium), but on the basis of the above data it may be expected that effects do occur and are detectable.
- 8.10 The foregoing review led ACMP to conclude the following:
 - (1) On the basis of laboratory tests and even the most optimistic assumptions about dilution, the disposal of TiO₂ wastes into the marine environment will have some impact on both water quality and biota.
 - (2) Because the waste is composed entirely of inorganic materials, it can be regarded as equivalent to the products of a greatly enhanced weathering process; the marine environment as a whole must have a capacity to absorb the waste without problems arising over large areas. The metal ion inputs (except iron and perhaps manganese) are small in overall terms relative to the inputs from natural river runoff.
 - (3) There will, however, be local impacts of TiO₂ wastes in the vicinity of discharges in areas in which disposal takes place.
- (4) Examination of the detailed information available to ACMP confirms that effects have indeed been detected in all areas examined, including the German Bight where earlier observations had suggested that effects were undetectable. It would appear on the basis of the present evidence that in no case are the areas over which effects are detectable increasing in size.
- (5) Under present conditions, no really serious effects may be expected on fisheries at the stock or population level.
- (6) Because after dilution the products are essentially the same as those entering via rivers, on the basis of our present knowledge it seems unlikely that any of the constituents of TiO₂ wastes will exert an effect beyond the area of initial impact, although the scale of that area will vary according to the local conditions.
- 8.11 An important remaining question is whether disposal at sea is the best environmental option in any given case. This can only be decided by an assessment of the impact of alternative methods of disposal or treatment and the relative values that may be put upon the local impact in the sea, compared with the overall impact of other methods of disposal on the land or freshwater environment. Such assessments are for the country concerned and perhaps its immediate neighbours. They are not matters on which the ACMP is qualified to advise. The ACMP does, however, consider them highly relevant to the decision-making process of whether or not it is desirable to reduce the impact which wastes from TiO₂ production have on the marine environment by diversion to other waste disposal options.

9. EXCEPTIONAL PLANKTON BLOOMS

- 9.1 The ACMP noted that the WGMPNA, at its 1984 meeting, had held an extensive discussion on primary production and nutrients on the basis of review papers on nutrient distribution and trends in the North Sea, nutrient enrichment and primary production in the North Sea, and the use of phytoplankton measurements in monitoring trends in nutrient enrichment. Reports on recent events of low dissolved oxygen in Danish coastal bottom waters and a report on the results of the intercalibration exercise on primary production methods held at the Second Biological Intercalibration Workshop (Rønne, Denmark, August 1982) were also considered.
- 9.2 The ACMP was informed that the Working Group considered that much of the evidence presented on the possible role of nutrient enrichment in increasing primary production and inducing exceptional bloom events was either inadequate or contradictory. In particular, it was noted that frequently measurements were made of nutrient concentrations rather than fluxes, although the latter would be more relevant to changes in production, and that measurements are rarely made in the period before major bloom events. Nevertheless, there is sufficient evidence of the existence of relationships between enrichment and primary production increases in some areas, especially in inshore enclosed waters, to merit deeper study. Accordingly, it was noted that the Working Group will continue these deliberations at its next meeting with the aim of producing a comprehensive overview on the subject. In the meantime, it was considered premature to include nutrient studies in the Baseline Study on contaminants in the marine environment.
- 9.3 The ACMP noted that the Working Group had also pointed out that inorganic nitrogen and phosphorous are by no means only "nutrient" factors involved in primary production, that dinoflagellate blooms could occur in waters depleted of the traditional nutrients and that other factors including natural chelating agents, trace metals, vitamins and other growth factors could all have important roles. The ACMP endorsed this view. While instances were given of possible associations between increased bloom incidence and extentions of the spring bloom in the Kattegat area with increased inorganic nitrogen and phosphorous inputs, the role of cycling in the sea water with sediments as a source was stressed. It was pointed out that organic nitrogen (as urea, purines, pyrimidines and other dissolved organic forms) probably constituted larger sources of nitrogen in some seasons and that the role of bacteria in recycling nitrogen through this route was very important. Iron, as a stimulating factor, and manganese, as an inhibiting one, were also important. A discussion on the role of large anthropogenic inputs of iron (e.g., in TiO2 waste disposal) concluded that the anthropogenic flux was very much lower than the natural flux, and that the iron introduced in this form was very rapidly oxidised to insoluble hydroxides. Attention was drawn to an empirical model based on ten years of research in the Bay of Sendai, Japan, which included not only nutrient and hydrographical (including stratification) parameters, but also iron, manganese and sediment factors.
- 9.4. Turning to the Baltic Sea, the ACMP noted that the ICES/SCOR Working Group on the Study of the Pollution of the Baltic had agreed that there were many unanswered questions on the influence of land-based discharges of nutrients on conditions in the open Baltic. At present time, it is not possible to state what effects will result from a decrease in

land-based discharges of nitrogen or phosphorus. These questions are of great economic importance, given the costs associated with reducing point source discharges of these nutrients. Other matters brought up included (1) the effect of the two large periods of stagnation*) that have occurred during this century on the eutrophication situation in the open Baltic, (2) whether phosphorus discharged via a river can be transported directly to the open sea without becoming involved in biological processes, precipitated to the bottom sediments and then released from there, (3) the relationship between phosphorus and nitrogen and their relation to eutrophication, and (4) the role of various hydrographic factors in terms of eutrophication.

9.5 This Working Group had discussed the possible eutrophication of certain open sea areas, and concluded that the critical factors had not been established. Changes in hydrographic conditions, increases or other changes in the input of nutrients, changes in the concentration ratios of major nutrients such as nitrogen and phosphorus, and natural biological variability all appear to be relevant. The role of nitrogen and phosphorus must be more clearly understood; their circulation in the Baltic ecosystem for example is entirely different, as there is a self-regulating mechanism for nitrogen so that it can reach steady-state again, but this does not exist for phosphorus. Phosphate has been shown to increase with increasing salinity, and phosphate is also released from the sediments during anoxic conditions in fairly large quantities. The role of sediments in nutrient cycling needs additional study and the transport of nutrients from the coast to the open sea must also be studied. In addition, natural biological variations that are not related to pollution must be established so that other changes may be properly interpreted.

9.6 The ACMP discussed the continuing confusion generated by the use of the term "bloom" to refer to such events as the spring bloom, "red tides" and other natural or anthropogenically stimulated events. Many "red tides" were perfectly natural events; on the other hand, some extreme outbursts of growth show no effect at the sea surface. In reality, it is difficult to draw any satisfactory boundary between different degrees of increases in phytoplankton production. In making proposals for the Special Meeting to be held in 1984, the ACMP had used the term "Exceptional Marine Blooms" to try to make a distinction between the outbursts occurring in spring and autumn, and other blooms; "exceptional" in this case is synonymous with "noticeable". One characteristic of these blooms may be that their production is not channelled into useful secondary production, but is used locally with such results as extreme primary biomass production and/or production of micro-organisms resulting in red water, or of other deleterious (though often "natural") results such as toxicity or reduction in the oxygen concentration in the water.

^{*)}During periods of stagnation in the Baltic Sea, oxygen concentrations in the bottom waters decrease to very low levels, resulting in anoxic conditions in certain areas, especially in the central Baltic. Anoxic conditions cause the release of precipitated phosphate from the bottom sediments.

- 9.7 At its October 1984 meeting, the ACMP took note of the outcome of the Special Meeting on the Causes, Dynamics and Effects of Exceptional Marine Blooms and Related Events, held in Copenhagen on 4-5 October 1984. The report of this meeting is contained in ICES Document C.M. 1984/E:42; this report will be considered in detail by the ACMP at its mid-term 1985 meeting.
- 9.8 The ACMP noted that, as a result of the recommendations of the Special Meeting, ICES had decided to set up a Working Group on Exceptional Algal Blooms. This Working Group will meet in April 1985 with the following terms of reference:
 - (a) to establish means of collecting and exchanging information on the incidence of problems due to exceptional blooms on mariculture operations and on bivalve fisheries;
 - (b) to consider means of improving the predictability of bloom events in time and space scales relevant to fish and shellfish farmers, including analysis of weather patterns in relation to bloom incidence;
 - (c) to consider proposals for research on management techniques for overcoming the effects of exceptional blooms; and
 - (d) to prepare advice for ICES member countries on the principles of site selection in mariculture, and on monitoring, predicting and managing bloom events for fish and shellfish farmers and fishermen.
- 9.9 In conclusion, the ACMP agreed that it will review in detail the report from the Special Meeting at its 1985 mid-term meeting. In addition, the WGMPNA will commence an overview of the role of anthropogenic nutrient enrichment in primary production and exceptional blooms on the basis of which future work would be planned and the ICES/SCOR Working Group will review the results of national programmes studying eutrophication in the Baltic Sea area and the results of studies of nutrient distributions from the coast to the open sea.

10. REGIONAL ASSESSMENTS ON THE STATE OF THE MARINE ENVIRONMENT

- 10.1 The ACMP briefly reviewed progress in the development of assessments on the state of the marine environment on a regional basis. It noted that the WGMPNA was actively following this up, and that the Working Group expects that the first assessments on the mid-Atlantic Shelf Area off the USA, on the Skagerrak-Kattegat area, and on the area off the east coast of Scotland will be available in early 1985. The ACMP emphasised the importance of following as closely as possible the guidelines laid down for these assessments (published in Annex 3 to the 1983 ACMP Report (Coop. Res. Rep. No. 124)). It noted finally that this project was still in the developmental stage and that further recommendations would be made after an examination of the first assessments has been carried out.
- 10.2 The ACMP also took note of the progress in the first periodic assessment of the Baltic Sea area, which is being carried out under the Helsinki Commission.

11. POLLUTION-RELATED STUDIES IN THE BALTIC SEA

11.1 Patchiness Studies

- 11.1.1 The ACMP noted that the 1984 meeting of the ICES/SCOR Working Group on the Study of the Pollution of the Baltic was preceded by a oneday meeting of the Study Group on Patchiness in the Baltic Sea. The deliberations of the Study Group, as approved by the ICES/SCOR Working Group, are summarised below. It was reaffirmed that the three major aims of the studies of patchiness were:
 - (1) To compile statistics on the occurrence of patchiness so that it may be described and mapped in the Baltic Sea;
 - (2) To gain an understanding of the mechanisms and processes for the generation and dissipation of patchiness; and
 - (3) To determine the significance of patchiness in relation to the "ecosystem" of the Baltic Sea (including fish), and in relation to pollution, pollution monitoring and effects of and on fisheries.

In order to make progress in meeting these aims, it was recommended that

- a multi-ship Joint International Study of Heterogeneity/Patchiness in the distribution of physical, chemical and biological properties should be carried out in the Baltic Sea during three to four weeks in April (-May) 1986 in the general area of BOSEX, and
- (ii) to facilitate this Joint International Study, a pilot study should be carried out in the same general area in April (-May) 1985 to test out methods and the general plan for the programme.

ICES member countries bordering the Baltic Sea were urged to support this programme.

11.1.2 The parameters to be investigated during the patchiness study were agreed upon as follows:

physical parameters

obligatory:	temperature, salinity, currents, meteorology influencing patchiness;
voluntary:	light measurements, turbidity, particle counting drifters, current crosses;

chemical parameters

- <u>obligatory</u>: oxygen, total phosphorus, phosphate, nitrate, nitrite, ammonium, silicate;
- voluntary: total nitrogen, particulate phosphorus, urea, amino acids, nitrous oxide, pH, alkalinity, dissolved organic carbon, trace metals, pesticides;

biological parameters

obligatory:	chlorophyll-a, phytoplankton biomass, zoo-
	plankton biomass, bacteria counting, fish, larvae, primary production;

voluntary: bottom fauna, other chlorophylls than chlorophyll-a, estimates of grazing.

11.2 A mechanism for preparing summaries of appropriate methods to be used has been established. The ICES/SCOR Working Group agreed with the structure of the experiment, with transects, a central point, and several polygons. In addition to the development of detailed plans for the conduct of the joint multiship patchiness study, agreements will be made on the forms for reporting data, for data exchange, analysis and compilation of data, as well as for publication of results. The Study Group will meet in October 1984 and before the pilot study in 1985 to consider further detailed planning for the joint study and its follow-up.

11.3 Sediment Studies

11.3.1 An intercalibration exercise on the analysis of Baltic sediments is being carried out in two steps. The first part of the exercise has been completed while the second part is still under way. (See also paragraphs 6.3.1 and 6.3.2, above.) The ACMP supported the recommendation by the ICES/SCOR Working Group that the report on the results of the intercalibration exercise on the analysis of Baltic Sea sediments should be published in the Cooperative Research Report series. Progress on the Pilot Study on Pollutants in the Baltic Sea Sediments is referred to in paragraph 7.4.3, above.

11.4 The Baltic Component of the 1985 Baseline Study of Contaminants in Biota

- 11.4.1 The ACMP noted with satisfaction that all countries around the Baltic Sea have indicated that they will participate in the Baseline Study. The ICES/SCOR Working Group had designated contact persons in all Baltic Sea countries to assist in any questions raised as to the conduct of the Baseline Study. The ACMP recalled that the Helsinki Commission had endorsed the conduct of the Baseline Study in the Baltic Sea.
- 11.5 Second International Baltic Year
- 11.5.1 The ICES/SCOR Working Group on the Study of the Pollution of the Baltic Sea had recommended that, in view of the major studies that will be carried out in the Baltic Sea - the Pilot Sediment Study, the Baseline Study of Contaminants in Biota, the Joint International Study of Heterogeneity/Patchiness - during 1985 and 1986, a Second International Baltic Year should be designated for the period 1985-1986; countries around the Baltic Sea and relevant International Organisations are encouraged to make every effort to support and take part in marine environmental studies during this IBY-2. The ACMP supported this proposal.

11.6 Biogeochemical Cycling, Inputs and Budgets

11.6.1 The results of intersessional work on these topics had been presented

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at the meeting of the ICES/SCOR Working Group. The Working Group had drawn attention to the fact that different input figures are quoted from different sources and emphasised the need for developing a scientific basis for measuring inputs.

- 11.6.2 The Working Group had concluded that the knowledge of the concentrations of a number of trace metals in the sediments, and perhaps to a certain extent the flux of these metals to the sediments, is in a reasonably good state of agreement and that values from different sources of data appear to be consistent. In terms of trends and fluxes, however, more work is needed on how much is entering and leaving the overall system. These studies emphasise the importance of the various types of boundary layers. For example, the coastal zone does not have any effect on the passage of certain metals through to the open sea; for other metals, however, the coastal zone is an area of precipitation.
- 11.6.3 Further work on trace metal budgets as well as some work on budgets for petroleum hydrocarbons and DDT and PCBs in the Baltic Sea will be carried out intersessionally.

11.7 Scientific Aspects of Marine Pollution Monitoring

- 11.7.1 Considering the scientific basis for marine pollution monitoring in the Baltic Sea, it was agreed that studies are important of the conditions in the coastal zone, including inputs from the coast and rivers and the connection between the coastal zone and the open sea in terms of what substances are mainly transported to the open sea and what substances are mainly retained in the coastal zone. Two general types of coastal zone studies were identified: (1) small, local programmes concentrated in the near-shore area along a length of coastline, and (2) sections studied from the coast to the open sea. Papers giving the results of studies based on each of these types of monitoring will be discussed at the next Working Group meeting.
- 11.7.2 Another item considered under this topic concerned the optimal frequency for carrying out monitoring in the Baltic Sea. An attempt will be made to compare the results obtained using a low monitoring frequency at a certain station with those for a higher frequency of monitoring at the same station.
- 11.8 Biological Effects Studies
- 11.8.1 The ACMP noted that there had been difficulties in starting joint work on biological effects studies in the Baltic Sea. However, examples of biological effects of pollution had been referred to and discussed, including certain fish diseases, the problems arising from discharges of wastes from a TiO₂ industry into the Bothnian Sea, as well as changes in the littoral ecosystem. It was noted that there were several possible explanations for the recent changes observed in <u>Fucus</u> communities in the Baltic Sea, including hydrographic changes, pollution, light factors, and competition. In concluding its discussion of biological effects studies, the Working Group had agreed to continue to follow the work of other groups on this subject without taking specific action at present.

11.9 Eutrophication, Inputs and Blooms

11.9.1 The ACMP noted that the ICES/SCOR Working Group had discussed this topic. A summary of the discussion is contained in paragraphs 9.4 and 9.5, above.

12. BALTIC SEALS

- 12.1 The ACMP considered the Report of the Working Group on Baltic Seals which had met in 1983 in order to
 - (i) consider what changes are likely in the size of seal populations in the Baltic over the next years;
 - (ii) evaluate evidence on the connection between high levels of PCBs, DDT and other pollutants in seals and their reproductive success;
 - (iii) consider the possible effects of changes in pollutants, in the Baltic on the conclusions under (i);
 - (iv) assess the effects of environmental disturbance on seals in the Baltic;
 - (v) advise on what steps should be taken to preserve the existence of all Baltic seal populations and to improve their habitat.
- 12.2 The Working Group had considered all points of its agenda and had provided a summary of the information presently available for each topic. The available information was not sufficient, however, to permit the Working Group to make any firm conclusions on the association between high levels of PCBs, DDT and other contaminants in seals and their reproductive success, nor to consider the possible effects of changes in the concentrations of contaminants in the Baltic Sea on the reproductive success of Baltic seals. Accordingly, a series of recommendations were made on additional research which should be conducted to elucidate this and other questions which remain open in connection with the full assessment of the present status of the populations of seals in the Baltic Sea and the prediction of future trends in these populations.
- 12.3 The ACMP noted that the Marine Mammals Committee had reviewed the report of this Working Group during the 1983 Statutory Meeting and had endorsed the Working Group recommendations for conservation and research. The Marine Mammals Committee had noted that the implementation of these recommendations and the continuation of the existing research programmes on Baltic seals were the minimum actions necessary for the protection of grey and ringed seals in that area. The Marine Mammals Committee had further considered that more research was needed on the way in which pollutants are sequestered in and released from the tissues of marine mammals, and how this affects reproduction. Careful monitoring of the proportion of one-year-old animals in the populations could provide essential information on changes in recruitment. The Committee had noted that Baltic seal populations could only be surveyed adequately by a coordinated international programme. It was also recognised that recent changes in the reproductive capacity of the Baltic seal populations were part of a wider problem of the protection of the marine environment with relevance not only to the Baltic but also to all of the world's oceans. Based on the recommendations of the Marine Mammals Committee as well as of the ACMP, the Council had recommended that the Working Group on Baltic Seals be broadened geographically and also scientifically to include experts on the physiological effects of contaminants. This Working Group will next meet early in 1985 to examine

the physiological effects of contaminants and other perturbations (e.g., fishing, ice-breaking activities) on seals and their populations, with particular reference to the Baltic Sea.

12.4 The ACMP endorsed the conclusions of the Marine Mammals Committee, as well as the recommendations for conservation and for research which had been carried up from the Working Group Report. The ACMP further recommended that, in the continuation of this work, other seal populations should be examined to determine whether <u>prima facie</u> evidence exists for a connection between reproductive failure and body burdens of contaminants. Noting the value of the information contained in the Working Group Report, the ACMP agreed to annex this report to the ACMP Report. It is attached as Annex 8.

13. POLLUTION-RELATED STUDIES IN THE SKAGERRAK-KATTEGAT AREA

- 13.1 The ACMP considered progress in the work carried out by the Working Group on Pollution-Related Studies in the Skagerrak and Kattegat. It was noted that information on on-going research activities in the Skagerrak and Kattegat area has been collected. When finalised, this will constitute a valuable catalogue of laboratories, researchers and projects in Denmark, Norway and Sweden related to the area.
- 13.2 A major project of this Working Group has been to prepare an assessment of the environmental problems in the area. This is being done in accordance with the ICES Guidelines for Assessments (published as Annex 3 to the 1983 ACMP Report (Coop. Res. Rep. No. 124)). Drafts of the various chapters of the assessment were reviewed at the 1984 Working Group meeting. It was reported that the authors of the assessment had experienced difficulties in keeping their chapters within the lengths recommended by the guidelines. Given that the Skagerrak-Kattegat area is a transition area between the North Sea and the Baltic Sea with entirely different hydrographic and biological conditions from each other, the descriptions of these conditions are necessarily complex but nonetheless must be made so that the assessment itself will be understandable. The ACMP noted that this assessment is expected to be completed in the spring of 1985 and looked forward to reviewing it at its 1985 mid-term meeting.
- 13.3 The ACMP noted that a third item to be covered by this Working Group, based on its compilation of information on research projects in the Skagerrak-Kattegat area and on the conclusions of the assessment document, will be the development of proposals for future research and international cooperation in that area.

14. REVIEWS OF MARINE CONTAMINANTS

14.1 As requested by the Commissions, the ACMP continued its work of reviewing current knowledge of selected contaminants on the basis of a series of overview papers prepared for it by the Working Groups and their members. Overviews representing the agreed views to ACMP on four subjects are annexed to this report, and summarised below.

Furans and dioxins

14.2 The overview on polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) (contained in Annex 4) provides information on the structure of these compounds, their sources, methods of analysis, occurrence in the environment, and toxicity. Some of the PCDD isomers are among the most toxic chemicals known. These substances are now nearly ubiquitous in terrestrial and aquatic ecosystems, but problems have mainly been associated with inland waters.

Organo-metal compounds

14.3 There has been considerable interest in the effects of organo-metal compounds on marine biota, following reports by French scientists of serious adverse effects on oysters of tri-butyl tin (TBT) compounds used in anti-fouling paints on boats and concerns about alkyl-lead compounds. Various reports on this subject were discussed. Based on these reports, a summary overview was prepared on the information available and the ecological problems caused by TBT compounds and alkyl-lead compounds in the marine environment. This concentrates on the effects of TBT and can be found in Annex 5. It is apparent from this overview that problems with oysters and other molluscan shellfish may be encountered where there are large numbers of boats close to areas of molluscan shellfish cultivation. The impact of these problems on commercial-scale production can be extremely serious. Effects may also occur with other species, especially at the larval stage of their life-history, but the significance of any such effects has not yet been established. A short review of information on alkyl-lead compounds is also included; the main conclusion is that, in view of the scale of production of these substances, there is a remarkable lack of information on their impact on the marine environment and this should be rectified.

Polychlorinated terphenyls

14.4 The overview paper on polychlorinated terphenyls (PCTs) describes the nature, properties and applications of PCTs. It then discusses the incidence of PCTs in marine organisms and the toxicological effects of these compounds. The toxicity evaluations referred to deal with the effects of PCTs at concentrations considerably in excess of those found in the natural environment. The ACMP pointed out that research should be directed at confirming whether the postulated similarities in behaviour and distribution of PCTs and PCBs are indeed correct. The review concludes that, while no major additional effort on PCTs is justified and wide-scale monitoring is not necessary, some further work in the areas known to be contaminated would be desirable to establish whether levels of PCTs always parallel those of PCBs. Zinc

14.5 An overview paper on zinc in the marine environment is attached as Annex 7. It includes information on the speciation and concentrations of zinc in the marine environment, sources, transport and distribution, including in marine animals, and concludes with an assessment of the toxicological implications, for both marine biota and man, of the levels of zinc in the various marine compartments.

Oxidation products of fossil fuel hydrocarbons

- 14.6 In addition to the above-mentioned review papers, an overview paper on auto- and photo-oxidation of fossil fuel hydrocarbons by K Tjessem and K H Palmork was considered. It described the nature of such oxidation products and discussed both the analytical problems presented in quantifying original hydrocarbon mixtures and oxidation products and assessing their respective toxicological effects. In particular, the paper discussed previous drawbacks and new approaches to the measurement of the more polar, hydrophilic compounds and stressed the need for greater care in assessing the toxicology of poorly defined mixtures of hydrocarbons and degradation products. Much of the initial hydrocarbon mixture may be rapidly converted, by oxidation, to products having different (enhanced) toxicity and not amenable to recovery by commonly employed extraction and analytical procedures. These products may also have very different biodegradabilities from those of the original compounds. Photo-oxidation may occur under irradiation by both ultra-violet and visible light. This should be taken into consideration when undertaking the analysis of stored samples. There is a need for further development and application of extraction and analysis techniques for the determination of oxidation products, in concert with the standard techniques for hydrocarbon analysis.
- 14.7 During the discussion of this topic, it was stressed that initial degradation of hydrocarbons in the environment might be expected to occur by way of a number of processes, such as microbial degradation, auto- and photo-oxidation and vapourization. The rate-limiting process is likely to differ according to the form of the hydrocarbons and ambient environmental conditions. It was also pointed out that many photo-oxidation products with enhanced toxicity seemed so unstable that they cannot be recovered unchanged by normal extraction and isolation procedures. The products recovered have both different composition and toxicity relative to the photo-oxidized material.

15.1 The ACMP discussed the sources and effects of releases of oil at low concentrations into the sea, distinguishing between diffuse and point sources. It considered that the impact of surface slicks and possible long-term effects of low concentrations of petroleum hydrocarbons required further examination, and arranged for a paper to be prepared for its next meeting that would form the basis for discussion.

ANNEX 1

ESTIMATION OF RIVER COMPOSITION AND RIVERINE INFLUXES OF CHEMICALS TO THE MARINE ENVIRONMENT

1. Specification of River Composition for Marine Influx Assessment Purposes

Current knowledge of the discharge fluxes* of chemical substances from rivers is rather poor. In fact, it is fair to say that more is currently known about the processes controlling the marine transport and fate of many contaminants than is known about their rates of influx to the ocean itself. This situation arises largely because of the paucity of trace compositional measurements in rivers rather than a lack of basic knowledge as to the rates of river discharge, hydrologic conditions, or major riverine compositional features. The accumulated literature on the concentrations of trace constituents in rivers leaves the strong impression that the sampling and analysis of river water should be far less complicated and difficult than for sea water. However, recent measurements of river composition made by laboratories having good sampling and analytical capability, largely developed for application to sea water, reveal that the concentrations of many trace contaminants in rivers are of the same order of magnitude as their corresponding concentrations in sea water. A large part of the literature on river composition is outdated about 1976. It is suspected that the revolution that has occurred in the approach to, and the accuracy and precision of, marine trace metal measurements during the last decade has yet to occur in the freshwater analysis field. Thus, it is imperative that river compositional measurements be made with the rigorous attention to quality control and intercomparability that has now become accepted and applied to measurements of trace constituents in sea water. It should be stressed that the marine community's interests are in having data available from a large number of major rivers of both pristine and anthropogenically-influenced types. Thus, the range of concentrations to be covered by river measurements is likely to be large and extend down, in most cases, to levels typical of those in marine waters. While it is appreciated that many freshwater compositional measurements are made for regulatory purposes, in which the interest is at relatively high concentrations of contaminants, it is essential that an appreciation of the natural and anthropogenically-augmented levels of such contaminants be obtained for long-term management and scientific purposes. Furthermore, it is no longer adequate to to acquire bulk measurements of concentration. It is increasingly necessary, wherever possible, to differentiate between, and separately determine, the dissolved and particulate concentrations of contaminants and to obtain ancillary information in order to facilitate the interpretation of concentration measurements and the calculation of constituent river discharge fluxes to the ocean.

^{*}The term 'flux' as used in this paper implies transport in units of mass/ time. By convention, in physics, flux is defined in units of mass/area/ time. Thus, 'flux' as used here is really a spatial integral, over a twodimensional section, of a conventionally-defined flux.

These realisations have stimulated considerable interest in improving our knowledge of river discharge fluxes of trace chemical constituents, especially environmental contaminants. The Intergovernmental Oceanographic Commission's Group of Experts on Methods, Standards and Intercalibration (GEMSI) has proposed field activities in regional sea areas to study the trace chemical composition of rivers and the United Nations Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) has established a Working Group to examine land to sea transport of contaminants, particularly with regard to the determination of gross and net river constituent fluxes into the ocean.

While there exist a variety of compositional data for world rivers, particularly in relation to major ionic constituents and turbidity, there has been a tendency for the collection of compositional data, largely for human health, agricultural or environmental management purposes, to be restricted to major ions, particulate organic matter, individual trace contaminants and hybrid components such as hardness. The marine community is in considerable need of reliable estimates of the river discharge fluxes of trace organic and inorganic contaminants, in both dissolved and particulate form, as well as organic matter and suspended particulate matter from as wide a variety of large rivers as possible. Thus, the riverine analyses most useful to the marine community are those which are as specific as possible for individual constituents (e.g., individual metals, specific organic compounds) in dissolved and particulate forms near to the mouths (but in the freshwater regime) of major rivers. These measurements need to be made at locations for which there exist sufficient hydrological data to enable a broad picture of the fluvial discharge/marine influx of these components to be obtained. Interpretation of the contaminant measurements would be further simplified by the concomitant determination of major riverine characteristics such as pH, alkalinity, dissolved organic carbon, particulate organic carbon, particulate aluminium and suspended particulate matter concentrations.

An improved understanding of gross river discharge fluxes of contaminants would permit better comparison with the rates of introduction of contaminants through other avenues of release and disposal, such as dumping and direct discharge. Valuable information might also be provided as to the consequences of terrigenous anthropogenic activites in respect to compositional differences between rivers, although clearly purely natural variability would need to be accounted for.

This note is intended as a plea to agencies responsible for hydrologic, environmental and geochemical measurements in rivers to be as specific as possible with regard to the individual constituents that are determined. The most important aspect of these measurements is that they be as accurate and precise as possible and, at the least, undertaken with the degrees of care and sensitivity required for marine geochemical and environmental studies. It is recommended that appropriate quality assurance be maintained through the conduct of intercalibrations and the use of reference materials. In this connection, it is anticipated that a riverine reference material will become available by 1985 (S S Berman, National Research Council, Canada, private communication). Furthermore, it would be most useful if chemical constituents were determined at stations or sections for which there exist concomitant hydrological and major compositional measurements. This would provide a basis for interpretation of contaminant measurements in rivers and, ultimately, of assessing the discharge rates of individual contaminants to the ocean.

2. <u>Some Approaches to the Estimation of Net Influxes of Chemicals to the</u> Marine Environment from Rivers

ICES has, on several occasions, been requested by the Oslo and Paris Commissions to provide advice on procedures for determining the influxes of contaminants to the ocean from rivers. Advice on methods of assessing the gross discharges of contaminants from rivers was provided through the Advisory Committee on Marine Pollution in 1982 (ICES, 1983). However, apart from outlining some of the difficulties associated with their estimation, no advice was provided on procedures for assessing the net fluxes of riverborne contaminants. In this context, the term 'gross flux'* applies to the total discharge of a constituent by rivers and the term 'net flux'* applies to the component of the gross flux that survives estuarine and continental shelf removal processes and succeeds in passing into the deep ocean basins. This note draws on previous informal discussions within the ICES community and on the subject of approaches to the estimation of net influxes from land to sea in discussions in other fora, such as the Intergovernmental Oceanographic Commission's Group of Experts on Methods, Standards and Intercalibration (GEMSI) and GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Pollution) Working Group 23 on Land to Sea Transport of Pollutants.

It has been assumed that net fluxes apply to the transport of material across the boundary between the continental shelf environment and the pelagic ocean basins. Thus, the processes that are responsible for the removal of material in the coastal zone are those occurring both in estuaries and on continental shelves. However, the extent to which these processes modify river discharge fluxes is likely to vary from extreme for minor river runoff into large, slowly flushed, shelf regions to small in the case of major rivers having external estuaries on narrow continental shelves such as in the case of the Amazon. This argument is based upon the premise that the longer the residence time of water on the shelf, the greater is the time for removal to occur. There are also varieties of continental shelf environments that will have a pronounced effect on the nature and extent of coastal zone removal. Rivers discharging into constrained marginal seas having limited exchange with offshore shelf waters, such as the Baltic Sea and the Gulf of St. Lawrence, are likely to have smaller net discharges into the deep ocean than similar rivers discharging directly into narrow, well-flushed shelf areas. It is this very heterogeneity of conditions that makes the estimation of net riverine influxes so difficult. Simplifications can be made to obtain crude estimates of the relationships between gross and net riverine fluxes for particular types of environments such as has been done for the Gulf of St. Lawrence (Bewers and Yeats, 1977) and the Baltic Sea (Brügmann, 1984), but it will be necessary to obtain estimates for other types of coastal/shelf areas and river sizes. None of these approaches will, however, serve any purpose in the absence of reliable estimates of gross river flux of contaminants and sufficient insight to be able to scale such discharges to different hydrological and geological regimes. Therefore, it is absolutely essential that early attention be given to improving our knowledge of gross river fluxes.

^{*}The term 'flux' as used in this paper implies transport of units of mass/ time. By convention, in physics, flux is defined in units of mass/area/ time. Thus, 'flux' as used here is really a spatial integral, over a twodimensional section, of a conventionally-defined flux.

During the last decade there has been accelerated interest in the study of estuaries, and it is now possible to gain some idea of the extent of removal processes and the difference between gross and net riverine fluxes for a variety of estuarine types. However, the number of constituents for which such information is available is somewhat limited and has not changed substantially since the assessment of the subject during the SCOR River Inputs to Ocean Systems (RIOS) Workshop in 1979 (UNEP and UNESCO, 1981). Furthermore, in defining net influxes as those pertaining to transport across the shelf/deep ocean boundary, processes of removal on the continental shelves, beyond the estuarine regions, are also involved in the modification of gross riverine fluxes and are, for some constituents, likely to be as important as, or more important than, processes in estuaries.

In its simplest form, the problem of relating gross and net river fluxes of chemical constituents can be expressed in the following way. The global coastal zone has a number of influxes and effluxes which can be assumed to be in quasi steady-state over reasonably long periods of time for constituents that have not had their fluxes systematically, or episodically, augmented by natural or anthropogenic processes. (This does not imply that it may be assumed that any particular coastal zone regime is in internal steady state.) The influxes to the coastal zone comprise gross river discharge, sea water inflow, atmospheric deposition and release from estuarine and shelf sediments through remobilisation processes. Effluxes from the zone comprise mixed water outflow, sedimentation and any volatilization or aerosol ejection to the atmosphere. There are thus seven fluxes involved in the mass balance and it would be necessary to quantify any six of these to derive the seventh. This is likely to be an intractable problem, even if some of the fluxes can be neglected on the basis of an assumption that they are insignificant relative to others. A gross assumption might be made that the difference between gross and net riverine fluxes is largely accounted for by net sediment accumulation within the coastal zone, but, in view of the heterogeneity of sediment deposition and composition, the mass balance would still be an extremely difficult equation to solve. It would, however, be worth while to attempt to quantify the fluxes of certain constituents by direct measurements in areas that are amenable to identification of the carrier water flows. In this respect, it would be more justifiable to give greater attention to marginal seas having well-defined hydrographic regimes, within which it might be possible to make direct measurements and comparisons between constituent fluxes. The recent improvement in the accuracy, precision and, above all, intercomparability, of the methods for determining certain contaminants (e.g., trace metals) would certainly justify renewed attention to marginal sea areas such as the Baltic Sea, the Gulf of St. Lawrence and the Mediterranean Sea, for which the major hydrographical fluxes have been defined. The type of model developed by Bethoux (1980) for water transports in the Mediterranean is very suitable for these purposes and justifies evaluation as a means of estimating chemical constituent fluxes in that sea. It may well be that the hydrographic understanding for these, and other similar, areas is qualified by uncertainties, but this should, in no way, be used as an excuse for not attempting preliminary estimation of the influxes and effluxes of contaminants taking due account of the uncertainties involved.

An alternative approach to the problem might be to examine salinity/contaminant and nutrient/contaminant relationships on continental shelves in an attempt to characterise the major variability within the coastal zone so that the relationships between contaminant concentrations and hydrographic features can be determined. This would then provide a basis for estimating net fluxes in terms of the hydrographic understanding of particular shelf regions and the broad-scale exchanges of water between the deep ocean and continental shelf areas. It is worth noting that coverage of the distributions of trace contaminants in the global coastal zone is not very extensive, especially when the likely heterogeneity of conditions is considered. In this respect, it should be remembered that while assumptions of steady-state conditions can often be made for the deep ocean, such conditions are unlikely to be general properties of continental shelf regions. Heterogeneities in shelf waters are both spatial and temporal and, in consequence, studies of shelf waters need to be much more intensive than those in the deep ocean. It is perhaps time for greater attention to be paid to the study of trace contaminants in shelf areas in relation to the effort devoted to the collection of high-quality chemical data from the deep ocean and localised studies of estuaries. It must, however, be stressed that the precisions and accuracies required for the inshore work are similar to those required for investigations in the deep ocean. With such new data it might be possible to construct some models for typical coastal zone types with which to at least estimate the magnitudes of net contaminant fluxes. The type of work undertaken by Kremling (1983) is an example of the kinds of study that would be useful in this connection. Similarly, extensions of the type of study carried out by Bruland and Franks (1983), with greater emphasis on the relationships between chemical substances and salinity and nutrients in continental shelf waters, would also be valuable.

Another method for the estimation of net fluxes which has received considerable attention in recent years is the global mass-balance approach. This procedure is necessarily rather crude and subject to a great deal of criticism because of the uncertainties involved in constructing such budgets. However, the approach does provide a means of assessing the reasonableness of results obtained from other methods of calculating net fluxes. It also provides a check on the overall geochemical consistency of such fluxes. For crude estimates of the net river flux to the pelagic ocean, the mass-balance equation can be reduced to three major terms: the gross river influx, the atmospheric depositional flux and the pelagic sedimentation flux. It is implicit in this approach, however, that a steady-state balance is assumed. This is unlikely to be an acceptable assumption for a wide variety of artificial organic compounds which have accelerated rates of dissemination in recent years or which degrade during transport within the ocean. Even for some of the inorganic contaminants, such as lead and cadmium, an assumption of steady-state is either untenable or questionable. The accumulation of additional gross river flux information would assist in determining whether elements like cadmium have significantly augmented fluxes caused by anthropogenic activity. Such increased dissemination, relative to the natural fluxes of the elements, should show up as systematic variability in riverine concentrations when the geological and hydrologic characteristics of individual drainage basins are taken into account.

In the view of the ACMP, all these three approaches are valid for the increased understanding of geochemical cycles and net riverine fluxes to the ocean. The suitability of each approach will vary with the particular region of the coastal/shelf environment being dealt with. However, at this juncture, no one approach holds superior promise to another and each should continue to be used in the solution of this problem.

In this discussion, particular emphasis has been placed upon the processes of contaminant removal on continental shelves in order to counterbalance the disproportionate attention devoted to the study of estuaries. Sedimentation outside the deep ocean basins does not all occur within estuaries. Removal of contaminants from dissolved and particulate phases in the coastal zone water column occurs both within estuaries and beyond them, on the continental shelf. While considerable attention has been paid to processes and massbalances in estuaries, comparatively little attention has been devoted to the quantification of removal outside estuaries, which also has the effect of reducing the 'net' or residual fluxes of contaminants to the ocean from terrigenous sources. This is particularly critical for contaminants that are removed from the water column by association with accumulating sediment particles but which may subsequently be remobilised by regenerative and diagenetic processes. Such remobilisation is probably of greater significance in regions of slowly-accumulating sediments (i.e., low sedimentation rates) as exist in large areas of the continental shelf.

Conditions in continental shelf waters should vary from those dominated by estuarine mixing, at the inshore end, to those dominated by deep oceanic biological processes, at the offshore end. The extent to which these differing regimes control the removal of land-derived materials needs to be defined, but it must be stressed that this is likely to be extremely difficult given the great heterogeneity of conditions in such regions.

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References

- Bewers, J M and Yeats, P A, 1977. Oceanic residence times of trace metals, Nature 268, 595-598.
- Bethoux, J-P, 1980. Mean water fluxes across sections in the Mediterranean Sea, evaluated on the basis of water and salt budgets and of observed salinities. Oceanologica Acta 3, 79-88.
- Bruland, K W and Franks, R P, 1983. Mn, Ni, Cu, Zn, and Cd in the western North Atlantic, <u>In</u> Trace Metals in Sea water (C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton, and E.D. Goldberg, Eds.). Plenum Press, New York, pp. 395-414.
- Brügmann, L., in press. Influence of coastal zone processes on mass balances for trace metals in the Baltic Sea. <u>In</u> Proceedings of the Symposium on Contaminant Fluxes through the Coastal Zone. Kullenberg, G. (Ed.). P.-V., Réun. Cons. Int. Explor. Mer, 186.
- ICES, 1983. Report of the ICES Advisory Committee on Marine Pollution, 1982. Coop. Res. Rep. No. 120, pp. 60-72.
- Kremling, K, 1983. Trace metal fronts in European shelf waters. Nature 303, 225-227.
- UNEP and UNESCO, 1981. River Inputs to Ocean Systems: Proceedings of a review workshop held at FAO Headquarters, Rome, Italy, from 26 to 30 March 1979. Published jointly by the United Nations Environment Programme and the United Nations Educational, Scientific and Cultural Organization, 384 pp.

Other relevant literature

- Nriagu, J O, 1980. Global cadmium cycle. <u>In</u> Cadmium in the Environment, Part I: Ecological Cycling (J O Nriagu, Ed.) John Wiley and Sons, New York, pp. 1-12.
- Simpson, W R, 1981. A critical review of cadmium in the marine environment. Progress in Oceanography 10, 1-70.
- Trefry, J H and Presley, B J, 1976. Heavy metal transport from the Mississippi River to the Gulf of Mexico. <u>In</u> Marine Pollutant Transfer (H L Windom and R A Duce, Eds.), Lexington Books, Lexington, Mass. pp. 39-76.
- Yeats, P A and Bewers, J M, 1983. Discharge of metals from the St. Lawrence River. Canadian Journal of Earth Sciences 19, 982-992.

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ANNEX 2

METHODS FOR SAMPLING AND ANALYSIS IN STUDIES OF CONTAMINANTS IN SEDIMENTS

A. METHODS FOR PHYSICAL SAMPLING AND ANALYSIS OF SEDIMENTS IN THE CONTEXT OF POLLUTION MONITORING

This Annex includes brief descriptions of and reference to the preferred methods of sampling and analysis of sediments. There is nothing new in these methods as they have all been published in the scientific literature. A problem is the great extent of this literature, so this simply provides a selective guide to equipment and methods.

1. Sampling Equipment

It is most important to obtain samples of the sea bed carefully, knowing the characteristics of the sampler and the biases it may introduce. A range of sampling devices may be used, depending on the nature of the investigation and the type of sediments involved. Repeated surface sampling for the assessment of spatial and temporal trends is most readily achieved using a Day-, or Van Veen-type of grab. However, it must be noted that most grabs do not recover the surface sediments and fauna intact. Nevertheless, in general surveys, grabs do provide an acceptable means for the rapid sampling of surface material. For detailed study at and below the sediment-water interface, where it is essential that the interface be recovered intact, a box corer is preferred. This may be a Reineck-, or Kastenlot-type device allowing sampling over a 0.20 - 10 metre depth range. Diver-operated corers are also useful alternatives.

The various designs of corers are detailed in Bouma (1969), in particular the Van Veen-grab, Jonasson-Olausson, Kasten and Reineck box corers. Newer samplers which are also suitable are the Soutar and IOS multi-purpose (Morris & Peters, 1981) corers which produce cores about 15 cm square. The advantage of the IOS corer is that it does not have to be laid on its side to be opened as is the case with the original Kasten corer. Box corers smaller and less unwieldy than the Reineck are also in use (e.g., Kanneworff and Nicolaisen's (1973) HAPS sampler in Denmark, the short (20 cm long) 30 cm x 20 cm Tennant box corer at MAFF Lowestoft). The advantage of these various box or square corers is that the cores can be sub-sampled by inserting several 5 cm diameter core tubes into them, and they provide high-quality surface samples.

The sub-samples can then be used for different purposes, e.g., chemical analysis for metals, analysis for organics, splitting for description, sampling for grain size and water content. In all core and grab operations, a slow approach of the sampler to the bed should be ensured. The risk of a significant "bow wave" is greatest with grabs and the use of a corer is recommended in most cases. In general, the wider the corer the better, though even the $2\frac{1}{2}$ inch gravity corer, carefully used in soft sediments, such as the muddy sediments in the Baltic Sea, can yield satisfactory results (Niemistö, 1974).

2. Sampling Strategy

Prior to sampling, the area should be surveyed by echosounder, at the least. A better survey would be obtained using a high-frequency seismic reflection profiler (3.5 kHz system) as well, preferably with side-scan sonar. This allows identification both of regions of thicker sediment, where sampling may yield sequences with rapid accumulation, and of areas of outcrop of older sediments. Sediments with a high organic content often contain gas bubbles which give rise to sampling difficulties, but these areas can be identified

on reflection profiles. Where sampling for the spatial extent of contamination is intended, a gridded or statistically random sampling pattern is needed. Evaluation of the results of successive surveys requires that one is able to assess the variance associated with a single survey. In the case of shallow areas affected by waves and tides, this may be considerable. Thus, an initial survey, with several cores at each point and repeat occupations of each point, is necessary to determine the variance between samples at a point and between re-occupations of the same point (navigation and station-keeping uncertainties) as well as between points. If a box corer is used, the variance within a single box core can also be evaluated. In more tranquil environments, such as fjords, the reproducibility at a point is generally very good. The results of the statistical exercise will indicate the degree of change that is necessary before one can be sure that change has occurred. For a spatial survey, specially chosen points in mud-holes will not always fall in the grid. However, for surveys where time-trends are to be monitored at a few selected points they may be ideal. A statistical assessment of variance within and between samples must be made for the contaminant(s) of interest as these are not always well correlated with lithological variables.

3. Sample Description

The attached form indicates the principal properties of samples that should be noted. These parameters are estimated on board ship. For colour, the Munsell or Geographical Society of America colour charts should be used. The sample form is accompanied by a core description form. If insufficient sample is available to be split or for an X-radiograph to be taken, a rudimentary description can often be made by observing the core through the clear plastic core liner or as the core is extruded for sampling. It is most important to look for evidence of burrowing or sediment lamination. In addition, variations of sediment size, colour, lithology and shell content should also be noted. An X-radiograph is generally very helpful in assessing the degree of biological mixing. Both circular and split cores may be radiographed in liners. For box cores, a 3 cm thick slab may be taken in a clear plastic box inserted into the core. This may be X-rayed on board or returned to the laboratory. Methods are detailed in Bouma (1969).

4. Mater Content

The water content must be measured because it permits the relationship between measurements of sedimentation rate (mm year⁻¹) and mass accumulation rate (kg m⁻² year⁻¹) to be derived. The different parameters in use by soil mechanics are listed on the attached sheet. The two most important parameters are the moisture (or water) content and the dry density. In many cases an average salinity of 35.0 may be assumed for pore water, but where the sediment has a very high water content (e.g., > 90% in some Baltic Sea samples), the pore water should be squeezed and its salinity determined. Samples for water content may be taken in a wide-mouthed 5 cm³ syringe (i.e., the mouth is the same width as the plunger). The syringe tube is then capped off and dipped in wax to prevent any evaporative loss of moisture. This provides a sample of accurately known volume which may then be weighed wet, dried and reweighed.

5. Sub-sampling and Storage (for Physical Purposes)

The most critical sampling operations are related to the avoidance of chemical contamination. Here, procedures are indicated simply for geological/sedimentological assessment. It is impossible to give hard and fast rules concerning the thickness scales for sampling. This will be determined by the layering present in the samples and the sediment accumulation rate. In general, layers of ~ 1 cm thickness prove sufficient. The best method of sampling cores of soft sediment is to extrude the core upwards and slice off layers using a non-contaminating cutter (e.g., stainless steel for organic analysis purposes) and container. A screw-drive to the extruder with known pitch of screw allows very thin layers to be taken if required. For circular cores, a 1 cm deep box of diameter 1 cm less than the core can be pushed over the extruded core and then sliced off. The smeared zone around the outside of the core is thus excluded. If cores are to be split, a wire, knife or sheet of glass or a presplit liner is preferable to the use of an electro-osmotic knife (Chmelik, 1967). The latter causes pore-water migration and samples produced in this way should not be used for chemistry or water content.

6. Grain-size Analysis

The ACMP recognises only one essential grain-size parameter, the precentage of fine material given as $\% < 63 \ \mu\text{m}$. Of course, if the contaminant of concern is in another size fraction, that fraction also must be determined. Other parameters in common use are the $\% > 2 \ \text{mm}$ (gravel) and the $\% < 2 \ \mu\text{m}$ (clay). The total $\% < 63 \ \mu\text{m}$ is silt plus clay, often referred to as mud. Because no chemical pre-treatments are permitted on samples for chemical analysis, no chemical dispersants are allowed prior to size analysis either. The sand/mud separation should be made by wet sieving on a 63 μm sieve made of Nytex[®] or other material that does not contaminate the resultant sample with the analytes of interest. The mud fraction may be forced through the sieve using distilled de-ionized water, collected and dried at 50°C.

Other grain-size fractions may be obtained by wet sieving (for gravel) or pipette (for clay). If the sample contains gravel, the gravel should be removed before wet sieving since gravel may damage the sieve. Details of these procedures are given by Folk (1980).

B. METHODS FOR SAMPLING, STORAGE AND DRYING OF SEDIMENTS PRIOR TO CONTAMINANT ANALYSIS AND FOR DETERMINING ORGANIC CARBON AND CARBONATE

1. Sampling and Storage of Sediments for Contaminant Analysis

- 1.1 <u>Sampling</u>: Samples should be collected by a box corer with a minimum size 15 x 15 cm. When sub-sampling, the core material should be taken from the mid-part of the core to avoid "edge effects". A phenomenon has been identified whereby surface material may "contaminate" the lowest sample in the core during coring, and it would be advisable to discard the bottom 2-5 cm.
- 1.2 <u>Storage</u>: If it is required that the internal structure of a core sample be preserved, the core should be stored intact, vertical, at 4°C.

Prior to analysis, it will be necessary to sub-divide the core at sea or in the laboratory, and preferred materials for sampling and storage apparatus, and storage conditions are given in the appended table. Any grab samples will necessarily be sub-sampled at sea. In most cases, it is advisable that extraction and handling of pore water samples from cores be carried out in a nitrogen atmosphere.

TABLE

Determinand	Sampling tool	Storage container	Temperature of storage
Metals (other than Hg)	Plastic (or stainless steel)	Plastic	- 20 ⁰ C for long storage 4 ⁰ C short term
Organic contaminants	Metal	Glass or metal	–20 [°] C
Mercury	Plastic (or stainless steel)	Plastic	-20 ⁰ C
Organic carbon	Metal or plastic	Glass or metal	-20 [°] C
Carbonate	Metal or plastic	Glass, metal or plastic	4°c

1.3 Sub-sampling for Trace Metal Analysis

The sub-sample for trace metal analysis should be split into several sub-samples: one for dry weight determination, one for trace metal determinations, one for sequential leaching, etc. This is best achieved by taking aliquots from the muddy suspension obtained after wet sieving. The suspension should be stirred vigorously to ensure that the particulates are evenly distributed through the liquid and aliquots of the suspension should be drawn off using a syringe (Eagle <u>et al.</u>, 1978).

If the sample is not wet sieved, it is sufficient to stir the wet sediment to homogenize it and remove a known volume using an openended syringe. In this case, the sediment must be thoroughly mixed with any water which may be present; it is not acceptable for any supernatant water to be present.

When freeze-dried sediment is to be sub-sampled, it should be split using a standard procedure for sub-sampling powder (see <u>e.g.</u>, Allen, 1975).

1.4 Sub-sampling for Trace Organic Analysis

The sub-sample from the box core taken for trace organic analysis should be stratified for depth intervals, if desired, and each portion should be placed in a separate non-contaminating container for storage. Aliquots should be taken from each depth interval for dry weight determination and total organic carbon analysis, with recognition of the risk of inhomogeneity. Sediment samples for trace organic analysis are often extracted "wet" by use of the proper organic solvent or solvent systems. Freeze-drying of sediments prior to extraction has been successfully practiced, but care must be taken to avoid contamination by vacuum oil.

2. Methods for Drying Sediments

Most of the analytical measurements made on sediment samples are, for reasons of comparability, reported with respect to dry weight. Determination of dry weight by the traditional oven-drying method has in recent years been supplemented and partially superseded by freeze-drying, a procedure which has become increasingly popular with the ready availability of commercially made machines. Equally successful freeze-drying can however also be achieved at a fraction of the cost using simple laboratory apparatus and a vacuum pump.

Oven drying at 105°C is suitable for the determination of the water content of the sediment, but is not suitable for chemical analysis because of the potential loss of volatile elements and the possible change in mineral structures. Therefore, determination of dry weight should be carried out on an aliquot of the sample, as stated in Sections 1.3 and 1.4, above.

For metal determinations, drying between 60-80°C is considered to be suitable for retaining the volatile metals, such as mercury, and keeping the structure of the clay minerals intact.

For total metal determinations, however, the drying should be preceded by washing in distilled de-ionized water to remove soluble sea salts.

If this washing procedure has not been carried out, it should be noted that the weight produced after drying is the weight of solids plus salt. Salt correction procedures (for density calculations) are given on page 7.

3. Determination of Organic Carbon and Carbonates in the Sediment

3.1 Determination of organic carbon

The methods currently most used follow different principles:

- (a) Combustion in a furnace. The organic matter is estimated by weighing it after combustion in a muffle furnace. The temperature of the combustion can vary from one sample to another between 450 and 500°C.
- (b) Wet oxidation. The organic matter is oxidized by potassium dichromate in sulphuric acid, followed by back titration with iron sulphate and ammonia.
- (c) Measurement of total carbon with specific instruments (LECO, BECKMANN, OCEANOGRAPHY INTERNATIONAL, etc.). The sample undergoes a total combustion by use of a catalyst in a flow of oxygen and the CO₂ measured.

Several authors have used these different methods on the same samples. It seems that the results provided are very well correlated with each other. Combustion gives higher values and even higher ones when the temperature is raised. On the other hand, the carbon analysers give lower values, but more specific for carbon than the two other methods. In fact, oxidation by dichromate is sensitive to reducing agents and combustion measures volatile salts, hydration water, etc.

Nevertheless, the decarbonation is a critical phase in the measurement by the analysers of total carbon and it should certainly be carried out very carefully.

Under these conditions, it is difficult to recommend one of the methods, since they very much depend on the nature of the sediment. To a certain extent, the choice of method is secondary to that of the necessity of calibrating each one of them.

3.2 Determination of carbonates

The determination of carbonates is generally carried out by measuring the CO_2 released by hydrochloric acid (2 or 4 mole ℓ). In the most simple cases, this measure is by weight or volume (Bernard calcimeter). The analysers of total carbon mentioned above can, of course, provide this value by determining the difference between an untreated sample and a decarbonated sample.

Moreover, the carbonates can be estimated by calcination at 1 050°C, after determination of the organic matter. This method has the same advantages (e.g., simplicity) and disadvantages as for organic carbon; it is not very specific and it depends very much on the temperature chosen and on the way this is regulated in the furnace.

It does not seem that this parameter causes any problems and it has therefore not been specifically investigated. Furthermore, it can be pointed out that the magnesium carbonates are more resistant to HCl attack than calcium carbonates, which could indicate that the duration of the attack could be increased. SALT CORRECTIONS AND FORMULAE FOR BED DENSITY AND WATER CONTENT

Determinations

Known volume of sample = V cm³ Weight, mud wet = x g Dry it for 24 hours at $105^{\circ}C$ Weight, mud dry = y g (x-y) = weight of water = (wt of sea water - wt of salt) = (W_{sw} - W_s) Salinity S = (W_s/W_{sw}) (if not determined, assume S = 0.035) Weight dry mud less salt Y = (y - Sx)/(1-S)

Derivations

Wet bulk density = $\frac{x}{v}$ g cm ⁻³
Dry density = $\frac{Y}{V}$ g cm ⁻³
Water content % = $\frac{(x-y)}{y}$ • 100
Fluid content % $= \left[\frac{(x-y)}{(1-S)}\right]/Y = \frac{(x-y)}{(y-Sx)} \cdot 100$
Porosity (voids vol/V) $P = \frac{(V-Y/\rho)}{V}s^{2}$
Voids ratio (voids vol/solid vol) $\varepsilon = \frac{(V-Y/\rho_s)}{Y/\rho_s} = (\frac{V\rho}{Y} - 1)$
$P = \epsilon/(1+\epsilon)$

Notes:

The density of the solids $\rho_{\rm s}$ may be measured or, for approximate answers, assumed to be 2.65 g cm^{-3}.

It is easier at a practical level to work in c.g.s. units of cm³ and grams. Densities may then be converted to S.I. Kg m⁻³ if required.

Where water content is high the salinity of interstitial water should be determined.

Reference:

Noorany, I., in press. Phase relations in Marine Soils. Proc. Am. Soc. Civil Engineers, J. Soil Mech. & Found. Division.

REFERENCES

- 1. Allen, T., 1975. Particle Size Measurement. Chapman and Hall, London.
- 2. Bouma, A.H. 1969. Methods for the study of sedimentary structures. Wiley-Interscience, New York, 458 pp.
- 3. Chmelik, F.B., 1967. Electro-Osmotic core cutting. Mar. Geol., 5:321-325.
- 4. Eagle, R.A., Norton, M.G., Nunny, R.S. and Rolfe, M.S., 1978. The Field Assessment of Effects of Dumping Wastes at Sea: 2. Methods. Fish. Res. Tech. Rep., MAFF Direct. Fish. Res., Lowestoft, 47, 24 pp.
- 5. Folk, R.L., 1980. Petrology of Sedimentary Rocks. Hemphill Publishing Co., Austin, Texas, 182 pp.
- 6. Kanneworff, E. and Nicolaisen, W., 1973. The "HAPS", a frame supported bottom sampler. Ophelia 10:119-128.
- Morris, R.J. and Peters, R.D., 1981. The IOS multi-purpose gravity corer. Inst. Oceanographic Sciences (U.K.), Report 124, 7 pp, 10 figs (unpublished manuscript).
- 8. Niemistö, L., 1974. A gravity corer for soft sediments. Merentutkimuslait. julk./Havforskningsinst. skr. No. 238:33-38.
- 9. Rey, L. (Ed.), 1966. Advances in Freeze-Drying. Herman, 115 Boulevard Saint-Germain, Paris VI.
- Van Loon, J.C., Radziuk, N., Lichwa, J., Fernandez, F., and Kerber, J. Metal Speciation using atomic absorption spectroscopy. Atomic Absorption Newsletter, Vol. 16, No. 4:79-82.

SAMPLE DESCRIPTION FORM	INSTITUTE:
Cruise No/ Core No	Sub-core No Sample depth cm Equipment core length cm
Position	Date & time Observer
mm GRAIN SIZE dom. rare rare	DESCRIPTION: colour (Munsell/GSA colour chart) smell, H ₂ S
20 STONES	
GRAVEL (ey) coarse fine 2 -	SURFACE brown oxidised cm black _ grey _ no colour difference fluid layer cm disturbed _ mounds _ sessile organisms ripples height cm length cm
SAND (sandy) coarse	SEDIMENT firm medium soft fluid layers sketch overleaf STRUCTURE
0.2 - medium	PELLETS size cm
fine 0.06- SILT (silty)	TUBES organism: live live notes
2μ - CLAY (clayey) MUD (muddy)	SHELLS organism(s): live position random in layers at cmlive
APPROX. % OC	PLANTREM organisms: live
SORTING: good medium medium mixed	BIOTA type:
NOTES: sample OK 🗖	? doubtful



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ANNEX 3

PROGRESS REPORTS ON THE PILOT SEDIMENT STUDY IN THE SKAGERRAK AND THE PILOT SEDIMENT STUDY IN THE GERMAN BIGHT

1. Pilot Sediment Study in the Skagerrak

The aim of the Pilot Study in the Skagerrak is to obtain an understanding of the sediment transport and the transport and distribution of suspended matter in the Skagerrak area, to distinguish water masses according to their particle characteristics, to locate areas with a high rate of sedimentation, and to determine whether some of these areas would be appropriate for studying contaminants in sediments.

In terms of the surface water circulation in the Skagerrak, currents are directed north along the Danish coast (Jutland Current) and form a large counterclockwise gyre, entraining water from the outflowing Baltic Current and from the coastal areas of Denmark and Sweden. Surface waters are then directed along the Norwegian coast as the Norwegian Coastal Current. The surface circulation pattern and the distribution of suspended matter in the Skagerrak suggest that particulate matter and associated pollutants may be transported into the Skagerrak chiefly from the English Channel and the Belgian-Dutch-German and English coastal areas, and secondly also from the Baltic Sea, and that the Skagerrak may be regarded as a sink for these materials. Additionally, run-off along the Swedish and Norwegian coasts may contribute sediments and pollutants, although a considerable fraction of particulate matter is trapped in Norwegian fjords.

On the basis of measurements of temperature and salinity in the Skagerrak in June 1982, five water masses could be distinguished. The surface water in the eastern Skagerrak and eastern Kattegat has a low salinity and a high temperature. Horizontally it merges with Skagerrak surface water, which forms a layer of up to 50 m thickness. Near the Danish coast and further west, the salinity of the surface water is 33 to 34 units and the temperature between 8° C and 13° C, which is water that flows into the Skagerrak from the central and southern North Sea. Below 100 m in the Skagerrak, there is water of very uniform salinity and temperature. Along the southern flank of the Skagerrak, water was present with a salinity of about 35.2 units and a temperature of 6.5 to 7°C. This water mass is regarded as inflow from the Atlantic.

Measurements of turbidity showed that the highest turbidity occurred in the surface waters of all areas, while the lowest was found in deep waters. The total concentration of suspended matter was highest in the eastern Skagerrak and eastern Kattegat, lower in the Skagerrak surface water and lower still in the Skagerrak deep waters and Atlantic waters. The percentages of organic material were in about the same range in all surface waters (52% to 62%) and lower in the deep water (23% to 26%). The median diameter of suspended particles in the surface water is small in the eastern Skagerrak-Kattegat waters and in the waters from the central and southern North Sea and relatively large in the Skagerrak deep water. This corresponds to a reverse trend in concentration and turbidity: eastern Skagerrak-Kattegat water has a high turbidity and a high concentration of fine-grained suspended matter, while the Skagerrak deep water (and Atlantic water) have a low turbidity and a low concentration of coarser suspended matter. Skagerrak surface water is in an intermediate position; it has an intermediate turbidity and an intermediate concentration of suspended matter of intermediate size.

Measurements of chlorophyll-<u>a</u> in the near-surface waters were made to obtain an indication of the productivity at the time of sampling. Chlorophyll-<u>a</u> concentrations varied between $0.21 \mu g/l$ and $10.0 \mu g/l$, with the lowest concentrations in water below the euphotic zone (>40 m depth) and the highest concentrations occurring at 18 m depth at a station on the transect between Denmark and Sweden. Generally, the sub-surface samples (2m to 20 m) showed a higher chlorophyl content than the surface samples. The results of the plankton counts showed that the highest numbers of plankton cells occurred in the eastern Kattegat-Skagerrak area; this may be related to the supply of nutrients transported in freshwater runn-off.

The major elements in the suspended matter collected in the Skagerrak were analysed to obtain information on the major particulate components in suspension, to correlate these components with characteristic water masses, and to study the distribution and pathways of various elements in suspension. Analyses were carried out for Al, Fe, Mn, Si, Ti, P, K, Ca and Mg. Aluminium is considered to be present exclusively in detrital silicate material. The concentrations of particulate aluminium in the Skagerrak varied greatly in the surface water, with the lowest concentration appearing toward the North Sea and the highest concentration close to the Danish coast. The general picture shows diminishing concentrations away from the coastlines. An overview of the transport of aluminium in the surface water shows that aluminosilicates are transported with the Jutland Current to the eastern Skagerrak, following the general current pattern, turning south in the inner Skagerrak and following the Norwegian coast. Iron is present in aluminosilicates and oxide/hydroxide particles, and a certain fraction is tied up in organic matter. The concentrations of iron decrease with increasing distance from the coast. Manganese is a trace constituent in most detrital silicates. The highest concentrations of manganese were found in waters below 250 m in the Skagerrak. Particulate phosphorus is an important constituent in organic material, particularly in living plankton. Phosphorus also occurs in inorganic detrital matter in apatite and iron phosphate. The surface particulate matter in the Skagerrak shows low values in phosphorus. In contrast with the other major elements, phosphorus concentrations are generally higher in the near-surface waters than in the near-bottom waters. Information was also obtained on the major elements silicon, titanium, potassium, magnesium and calcium. Additionally, data were obtained on the concentrations of Cd, Co, Cu, Ni, Pb and In in suspended matter and in the dissolved phase, and on the ratios of these elements to iron in the various surface water masses.

This part of the study has mainly dealt with suspended particulate matter, its characteristics, distribution and transport. In addition, some work has been done on trace metal concentrations in bottom sediments. This work has indicated that the western Skagerrak is not a suitable area for monitoring trace metals in bottom sediments because the sedimentation rate there is very low. Studies will be carried out in the eastern Skagerrak to determine whether it would be a better area.

2. Pilot Sediment Study in the German Bight

This Pilot Study is being carried out in an area of the German Bight where active mud deposition is occurring (sedimentation rate about 70 cm/100 years) despite tidal currents of 60 cm/sec., which would normally prevent the deposition of fine-grained material in suspension. This mud area has been found to be a sink for contaminants, which are present in increasing concentrations in the more recent sediment layers. The objective of the study is to gain more insigt into the quantities of fine-grained material that are being deposited annually in the German Bight so that the accumulation of contaminants associated with the mud can be estimated, and to gain more insight into the deposition mechanism.

Most of the cores obtained from the study area consisted entirely of mud alternating with layers containing fine sand and mollusc shells. However, cores collected in the western part of the area consisted entirely of sand. The mud deposit shows layers with fine sand, admixtures of mollusc shells and erosion surfaces which cut off the layering in the deposit below. The sandy layers are of varying thickness, from 4 cm down to 1 mm. The shells, which often occur at the base of sand layers, are washed in from other areas, probably nearby shallow coastal areas and tidal flats. There is very little regularity in the sand layering and every core shows a different sequence of fine sand and mud layers. Sandy layers could thus not be correlated in the different cores. The erosion surfaces indicate that not only is the mud deposition often interrupted by deposition of sand, but that former deposits have been removed.

Two anchor stations were occupied in the mud deposition area to measure current velocity and direction, suspended matter concentration and salinity during a tidal period of 25 hours. While the near-surface measurements showed no relation between current velocity and current direction and the concentration of suspended matter, a much more consistent relation was found near the bottom between tidal phase, suspended matter concentration, current velocity and salinity. The current velocities were much higher during floodtide than during the subsequent ebb, with the latter often low enough to permit some settling of suspended matter. Accordingly, these preliminary measurements suggest that more suspended matter moves in on the flood than moves out on the ebb, resulting in a gradual accumulation of mud.

Information was also provided on the concentrations of several heavy metals in sediments of the German Bight. Concentrations of lead in the surface sediments were high, at 190 ppm. Analysis of dated cores reveals that elevated levels occurred already in around the year 1850, when lead concentrations around 80 ppm are found, in comparison with a background lead concentration of 20 ppm. Sediments near the coast contain high concentrations of mercury and cadmium; in offshore sediments, mercury and cadmium were found in concentrations near background, while lead and zinc concentrations were twice their background levels. It was also pointed out that some offshore sediments in erosion areas contain high concentrations of certain trace metals. Phosphate concentrations in the German Bight sediments fluctuate a great deal, while sulphate concentrations are more regular and appear to be related to the sedimentation rate. If this relationship between sulphate concentrations and sedimentation rate can be proved, then it may not be necessary to date all cores using radioisotopes.

ANNEX 4

POLYCHLORINATED DIBENZO-P-DIOXINS

AND

POLYCHLORINATED DIBENZOFURANS

Structure

Polychlorinated dibenzo-p-dioxins (PCDDs) are a group of planar aromatic compounds formed by the substitution of one to eight chlorine atoms in positions 1, 2, 3, 4, 6, 7, 8 and 9 of the dibenzo-p-dioxin molecule. The general formula is shown below.



There are 75 and 135 structurally possible PCDD and PCDF congeners, respectively. Polychlorinated dibenzofurans (PCDFs) are homologous with PCDDs, the dibenzo-dioxin nucleus being replaced with a dibenzofuran molecule, as illustrated above.

Sources

The most clearly defined chemical sources of PCDDs and PCDFs are the chlorophenols (CPs) and their derivatives which are in use in the wood industry, herbicide formulations and pest control products. The best known CP derivatives are 2,4-dichlorophenoxy acetic acid (2,4-D) and 2,4,5-trichlorophenoxy acetic acid (2,4-D) and 2,4,5-trichlorophenoxy acetic acid (2,4,5-T). 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) has been the most intensively investigated PCDD isomer. This dioxin is formed during the industrial preparation of chlorophenols, intermediates in the production of chlorinated phenoxy-acetic acids. It is the product of a side reaction during the alkaline hydrolysis of 1,2,4,5-tetrachlorobenzene if the temperature is allowed to rise above 180° C. This impurity can be carried through into products which are manufactured from 2,4,5-trichlorophenol including the herbidicide, 2,4,5-trichlorophenoxy acid, (2,4,5-T) and the germicide, hexachlorophene (2,2-methylene bis-(3,4,5-trichlorophenol)).

The combustion of organic materials is another source of PCDDs in the environment. They have been detected in a wide range of combustion processes, including the burning of fossil fuels, wood and cigarattes. PCDD and PCDF homologues have been detected in fly ash from industrial and municipal incinerators. Chemical dumps are now regarded as point sources of local contamination. PCDFs and PCDDs have been found to be contaminants of polychlorinated biphenyl (PCB) formulations. The tetra- and penta-CDF isomers have been identified in PCBs in concentrations of 1-10 mg/kg (Rappe et al., 1981).
The uncontrolled burning of halogenated organic chemicals such as chlorophenols and PCBs is also a source of PCDDs and PCDFs. It has been noted that PCDDs seem to form from the combustion of trichlorophenols and lower chlorinated benzenes, while PCBs, when burned in a particular temperature range, transform to PCDFs with essentially no PCDD formation (Josephson, 1983; Hutzinger <u>et al.</u>, 1982). It has been determined (Hutzinger <u>et al.</u>, 1982) that at temperatures between 550° and 650°C between 0.5% and 2.8% of the total PCB concentration was converted into PCDFs. Above 700°C no net formation was observed.

Analysis

The analysis of PCDDs and PCDFs is complex and procedures used in laboratories vary considerably (Baker, 1981). Their determination can be separated into two parts: the extraction - clean-up phase and the quantitation - confirmation phase. Depending on the sample matrix, a variety of different extraction and clean-up steps can be used. Methodology for the extraction of these contaminants has involved the treatment of the sample with acid, base or organic solvents followed by partitioning the extract with an organic phase. This is followed by column chromotography. The determination can be completed using capillary column electron capture gas chromatography and identity confirmation and quantitation finalised using gas chromatography coupled with mass spectrometry, both low and high resolution modes being used. Their analysis is not simple and other contaminants, such as chloromethoxybiphenyls, have been recognised as potential interferences in the determination of chlorinated dibenzo-p-dioxins (Phillipson and Puma, 1980).

The limits of detection of the analytical methods used currently are 1 μ g/kg PCDD in chemical products and 1 ng/kg TCDD in environmental samples. PCDDs can be assayed by the following bioanalytical techniques: radioimmunoassay, aryl hydrocarbon hydroxylase induction assay and cytosol receptor assay. These are developmental methods and lack the homologue and isomer specificity and sensitivity that have been achieved with the chemical methodology.

Properties

Features of this group of compounds include a relative inertness to acids, bases, oxidation, reduction and heat with increased halogen content. Increased chemical and environmental stability and lipophilicity are also associated with increased halogen content.

PCDDs are a cause of concern mainly because some of the isomers, in particular, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), are among the most toxic substances known. Other isomers are less toxic; the most toxic isomers are those that are substituted in the 2,3,7 and 8 positions with at least one hydrogen remaining on the dioxin nucleus. The toxicity is progressively decreased by moving one or more chlorines to peri positions (1,4,6 og 9), and/or by having fewer or more positions substituted.

Occurrence

Residues of PCDDs and PCDFs have been reported to be present in environmental and biological matrices including fish, birds' eggs, bird and other animal tissues. General studies of the ambient levels of PCDDs in foodstuffs are not available. Residues have been found in animal feeds and in samples of beef fat, fish, chicken livers, gelatin and milk. The levels reported vary considerably and reflect the degree of exposure (Anon.). There are a number of different routes by which these compounds enter the environment, the relative significance of any one pathway being unproven. The accumulation potential of higher chlorinated PCDDs is relatively large and parallels the pattern observed with other persistent chlorinated hydrocarbons, including PCBs and DDT.

The presence of these residues in biological samples can result from: (1) accumulation within aquatic systems in a manner similar to that of PCBs and DDT; (2) accidental spillages; (3) use of treated wood products or by-products in agriculture; (4) use of contaminated products in the food industry and the use of treated wood wastes in the pulp industry; (5) PCDD-containing herbicides; (6) pyrolytic formation in food during the cooking process.

PCDDs are relatively insoluble in water (0.2 μ g/1) and tend to be rapidly and strongly adsorbed to most soils. The sinks in the aquatic ecosystem are the sediments and particulate matter. TCDD can enter water at low levels and is readily bioaccumulated in a variety of aquatic organisms (algae, snails, daphnids and fish). Fish do not biomagnify it to any great extent through the dietary vector and there is little biomagnification in mammals (Annon.). It is slowly catabolised and is considered persistent, having a half-life of 1-2 years in biologically active soils and sediments. It is slowly photodegraded in water but not in soil. It is not translocated or accumulated by plants (Ramel, 1977; Hutzinger, 1982). Several monitoring studies for TCDD in aquatic organisms have been conducted. TCDD was reported to be present in fish and crustacean samples from Vietnam, taken from an area heavily exposed to 2,4,5-T. Concentrations of 70 to 814 ng/kg were found in fish from rivers in the interior of Vietnam and 18 to 79 ng/kg in fish and shellfish along the seacoast of South Vietnam (Bovay and Young, 1980; Cattabeni et al., 1978).

Levels of TCDD between 20 and 480 ng/kg have been recorded for fish flesh from a number of sources (Arkansas River, Lake Ontario). Of 46 fish samples from the Great Lakes, TCDD was detected in 45, in concentrations between 2 and 162 ng/kg. It was not detected in water samples (Anon.). Concentrations of 4 to 30 ng/kg TCDD were found in eel. Smelt and catfish had the next highest concentrations in general. These species are relatively high in fat content and this is thought to explain the relatively high TCDD content. PCBs were also found in these samples in concentrations ranging from 1.16 to 8.78 mg/kg /Anon.). Table 1 shows that PCDDs and PCDFs in addition to 2,3,7,8-TCDD have been found in biological samples. Earlier attempts to identify PCDFs in the environment were unsuccessful due to the lack of sensitivity of the analytical techniques and the lack of selective contaminant enrichment procedures. The 2,3,7,8-tetra- and 2,3,4,7,8-penta-CDFs have now been identified in environmental samples (Rappe et al., 1981). Fat from the snapping turtle (Chelyda serpentina) from the Hudson River (U.S.A.) and the grey seal (Halichoerus grypus) from the Gulf of Bothnia (Haparanda, Sweden) was found to contain 3 µg/mg and 0,04 µg/kg PCDFs, respectively, with the penta-, hexa- and hepta-CDF isomers being the major predominant isomers identified. The major source of PCDFs in these samples was attributed to direct contamination by PCBs; the turtle fat contained 750 mg PCBs/kg and the seal fat PCB concentration was 100 mg/kg (Rappe et al., 1981). PCDDs and PCDFs have also been identified and quantified in salmon from Umeälven, Sweden (Reutergårdh, pers. comm.). Concentrations up to 19 ng/kg PCDDs and 53 ng/kg PCDFs were determined, the main isomers present being hexa- and octa-CDDs and penta-CDFs.

Effects

With regard to the toxicity of PCDDs, there is a million-fold spread in the dosage level required to kill laboratory animals. The guinea pig is the most sensitive species and LD50 values of 300 000, 0.6 and 73 µg/kg b.w. (body weight) have been reported for di-, tetra- and hexa-isomers, respectively (Long, 1979; Payne, 1982). Other species are less sensitive; LD₅₀ values for TCDD of 284 µg/kg b.w. for mice and 3 mg/kg b.w. for hamsters have been recorded. TCDD in water or food is toxic to fish. Data for fish suggest an LD50 within the mammalian and avian range. Lethal doses of 700, 600 and 5.4 µg TCDD/kg b.w. have been estimated for guppies (Poecilia reticulus), rainbow trout (Salmo gairdneri) and coho salmon (Oncorhynchus kiscutch), respectively. The acute and chronic oral toxicity of chlorinated dibenzofurans to salmonid fish has been investigated (Zitko and Choi, 1973). A median mortality of 120 ± 30 days was found amongst juvenile Atlantic salmon (Salmo salar) fed dry fish food containing di., tri., tetra, and octa-CDF isomers. Only the octa-isomers were subsequently detected in the fish tissue. 2,8-dichlorodibenzofuran was found to have a low acute toxicity to immature brook trout (Salvelinus fontinalis), even at a concentration as high as 122 mg/kg (Zitko et al., 1973). This was attributed to poor absorption of this compound. It appears that the bioaccumulation of PCDFs is somewhat isomer specific (Hutzinger et al., 1982).

The effects of TCDD on the fish (pike, rainbow trout) life cycle (eggs, yolk sac fry and juveniles) have been investigated (Hutzinger <u>et al.</u>, 1982). In water, TCDD (1 ng/l) resulted in developmental and growth retardation of eggs after an exposure of 96 hours. Skeletal malformations were found in a large percentage of fry which survived exposure to TCDD.

Some understanding of TCDD toxicity has been achieved by a study of its effects on biochemical processes. It has been found to induce the activity of a number of mammalian enzyme systems, including hepatic microsomal mono-oxygenases, aryl hydrocarbon hydrolase (a mixed-function oxidase), δ -amino levulinic acid synthetase and glutathionine-S-transferase.

PCDDs are now suspected to be ubiquitous contaminants in terrestrial and aquatic ecosystems. Contamination problems have been associated with inland waters rather than with the marine environment. The main source of this input is from chlorophenols and related compounds, and as there are regulations concerning permitted levels of TCDD, this input into the environment can be controlled.

Conclusions

Information on the presence of both PCDDs and PCDFs in the marine environment is sparse and it is not entirely clear whether this is due to the absence of these substances in that environment or the very limited number of analyses actually conducted. There is, however, some evidence that the former is correct, although there have been some recent reports that PCDDs and PCDFs are detectable in many higher predators. Nevertheless, since the major sources of PCDDs and PCDFs are as impurities in substances used in the terrestrial environment and, given their tendency to be strongly adsorbed on soil particles, the main problems must occur in the land environment. Therefore, there seems little likelihood of major toxicological problems arising in the marine environment. For these reasons, there does not seem to be any justification in widespread sampling and analysis for these substances in a marine context, although a limited account of further work on higher predators may be worth-while from a trend assessment point of view.

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References

Anon., Polychlorinated Dibenzo-dioxins

- Criteria for their Effect on Man and his Environment, NRCC No. 18574. 251 pp.
- Limitations to the Current Analytical Techniques, NRCC No. 18576. Associated Committee on Scientific Criteria for Environmental Quality. 172 pp.
- Baker, P G, 1981. Determination of Polychlorinated Dibenzo-p-dioxins. Anal. Proc. <u>18</u>(11), 478-480.
- Bovay, R W and Young, A L, 1980. The Science of 2,4,5-T and Associated Phenoxy Herbicides. J. Wiley & Sons. 455 pp.
- Cattabeni, F, Cavallero, A and Galli, G (Eds.), 1978. Dioxin : Toxicological and Chemical Aspects. SP Medical & Scientific Books. Spectrum Publications Inc. (J. Wiley & Sons Ltd.). 219 pp.
- Hutzinger, O, Frei, R W, Merian, E and Pocchiari, F, 1982. Chlorinated Dioxins and Related Compounds Impact on the Environment. Pergammon Press. 651 pp.
- Josephson, J, 1983. Chlorinated Dioxins and Furans in the Environment. Environ. Sci. Technol. <u>17</u>, 124A-128A.
- Long, M L, 1979. Comparative Toxicology of Various Chlorinated Dioxins as Related to Chemical Structure. CIPAC Proceedings Symposium Papers (Ed. W R Bontoyan) 1, pp. 141-169.
- Payne, K, 1982. Chemistry and Toxicology of Polychlorodibenzo-p-dioxins. Chem. Ind. <u>10</u>, 298-330.
- Phillipson, D W and Puma, B J, 1980. Identification of chlorinated methoxybiphenyls as contaminants in fish and as potential interferences in the determination of chlorinated dibenzo-p-dioxins. Anal. Chem. <u>52</u>, 2328-2332.
- Ramel, C (Ed.), 1977. Chlorinated Phenoxy Acids and their Dioxins. Ecol. Bull (Stockholm) 27. 299 pp.
- Rappe, C, Buser, H R, Stalling, D L, Smith, L M and Dougherty, R C, 1981. Identification of Polychlorinated Dibenzofurans in Environmental Samples. Nature 292, 524-526.

Reutergårdh, L. Personal Communication.

- Zitko, V and Choi, P M K, 1973. Oral Toxicity of Chlorinated Dibenzofurans to Juvenile Atlantic Salmon. Bull. Environ. Contam. Toxicol. <u>10</u>, 265-271.
- Zitko, V, Wildish, D J, Hutzinger, O and Choi, P M K, 1973. Acute and Chronic Oral Toxicity of Chlorinated Dibenzofurans to Salmonid Fishes. Environ. Health Perspectives, 187-189.

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TABLE 1

PCDD and PCDF Content of Environmental Samples

	Herring Saginar	g Gull ¹ v Bay	Carp ¹ R. Niagara	Carp ¹ R. Niagara
	ng	/kg	ng/kg	ng/kg
2,3,7,8 - T ₄ CDD	70	160	417	53
other $-T_{\mu}CDD$				
- P ₅ CDD				
- H ₆ CDD	88	20	36	24
- H CDD				
- 0 ₈ CDD	19	28	158	19
2,3,7,8 - T ₄ CDF	15	16	5	6
2,3,4,7,8- P ₅ CDF	26	48	80	66
1,3,4,8,9- P ₅ CDF				
other $-P_5^{CDF}$	2	22	2	9
- H ₆ CDF	49	59	203	135
- H ₇ CDF	17	18	304	44
- 0 ₈ CDF	3	5	388	6

¹ Data of D. Stalling, U.S. Fish and Wildlife Service, Columbia, Missouri, NRCC Report No. 18574, p. 35.

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ANNEX 5

ORGANIC COMPOUNDS OF TIN AND LEAD

Introduction

The world-wide production of organo-metallic compounds is increasing; in particular, large quantities of alkyl tin and alkyl lead compounds are produced, respectively, because of their toxic properties and physico-chemical properties. Certain of the derivatives of tributyl tin (TBT) are deliberately dispersed in the marine environment in the course of their use for limiting the development of undesirable species; others reach coastal waters through inputs or atmospheric fallout (alkyl leads used as anti-knock agents). In spite of the dangers presented by these substances to living organisms, their fate in the environment and their effects on living resources are not well understood.

The first indications of undesirable effects on exploitable living resources as a result of the presence of organo-metallic compounds were encountered with organo-tin compounds used as the toxic agents in anti-fouling paints intended for use on the hulls of marine craft.

ORGANO-TIN COMPOUNDS

Production and Use

The use of organo-tin compounds varies according to their chemical and toxic properties. The low toxicity of mono- and di-alkyl tin compounds to mammals allows their use for thermal and photo-chemical stabilisation of PVC (6 500 t/yr in western Europe alone). Dimethyl tin as the chloride is used as a colouring agent in stained glass, producing a surface film of SnO_2 . Dibutyl-tin as the di-laurate, di-acetate or di-(2-ethylhexoate) is used as a catalyst in polyurethane fabrications and for vulcanising silicone rubbers.

The biocidal properties of the trialkyl derivatives of tin (R_3SnX) account for about one-third of the total production of organo-tin compounds and they are used in a variety of applications:

- fungicides for the protection of timber and crops (tributyl and triphenyl tin compounds;
- disinfectants (benzoate and tributyl tin compounds);
- molluscicides (tributyl tin compounds) for the eradication of bilharziosis in tropical areas;
- toxic agents in marine anti-fouling paints (tributyl, triphenyl and methacrylate compounds with TBT).

Physico-chemical Properties

With the exception of dicyclopentanedienyl tin, where the tin is present in the Sn^{2+} form, organo-tin compounds are normally found with tin in the Sn^{4+} form and have the general formula $\operatorname{R}_x \operatorname{SnX}_{(4-x)}$.

There are in fact a series of alkyl-tin compounds with values of x equal to 1, 2, 3 or 4.

Trialkyl tin compounds can be degraded through successive dealkylation steps by hydrolysis, photolysis or biodegradation; the stability of the di- and mono-substituted derivatives is lower than that of the tri- and tetra-derivatives. All degradation routes lead to the formation of tin oxide as the end product.

Dealkylation by alkaline hydrolysis is slow - less than 10% after 5 weeks. In the environment UV photolysis represents the fastest route of transformation of organo-tin compounds. In aqueous solution and under UV irradiation, the T¹₂ of tributyl tin oxide (TBTO) is estimated to be about 18 days, but it can be less in the presence of activating substances such as acetone. Both the dealkylation of alkyl tin compounds and the similar process for aryl tin compounds can be brought about biologically through the activity of microorganisms in soils or of adapted strains; Barug and Vonk (1980) obtained a 50% degradation of TBTO to monobutyl tin in 8 days using a <u>Pseudomonas</u> culture in an aerobic medium.

Methods of Analysis

Preliminary derivatisation of alkyl tin to the hydride form or other alkyl forms (butyl, n-pentyl or methyl) is often necessary. The methods of detection most often used are: atomic absorption spectrophotometry, flame photometry, flame ionisation detection, mass spectrometry and anodic stripping volammetry.

Detection by atomic Absorption

Hodge <u>et al.</u> (1979) derived hydrides from methyl and butyl tin before separation and quantification. The hydrides were broken down in a quartz tube fitted to an atomic absorption instrument. The detection level achieved by this method was of the order of ng l^{-1} calculated on the basis of the alkyl tin chloride concentration. Chau <u>et al.</u> (1982) used a preconcentration step before quantification. Methyl tin compounds were extracted from water by benzene and tropolone. Butylation was achieved using the Grignard reaction with BuMgCl, and the butyl derivatives were separated by gas chromatography. Their atomisation followed in a silica furnace in an atomic absorption apparatus. The detection limit achieved was about $0.04 \text{ µg } l^{-1}$.

For marine organisms and sediment samples, where the levels of butyl tin compounds are higher than $0.03 \ \mu g \ g^{-1}$, selective extraction can be achieved by the following method. The sample is first treated with acetic acid and the various butyl tin compounds are extracted in a solvent such as hexane. Mono- and di-butyl tin are also extracted by the organic phase but can be removed respectively by back-extraction into an acidic or alkaline medium, leaving only the tributyl derivative in the organic phase. Quantification is achieved using electrothermal atomisation in a graphite tube furnace.

Flame Photometric Detection

Maquire <u>et al.</u> (1981) transformed various butyl tin compounds in water to their n-pentyl derivatives using n-PeMgBr and separated them using gas chromatography; the quantification step was conducted using a modified flame photometric technique. The detection limit was about 0.1 $\mu g l^{-1}$.

A similar system was used by Braman <u>et al.</u> (1979) for methyl tin compounds after their conversion to the hydride form using $NaBH_{l_1}$.

Detection by Flame Ionisation or Mass Spectometry

Meinema et al. (1978) used gas chromatography with flame ionisation detection after preconcentration. Butyl tin compounds were extracted from the aqueous phase using an organic solvent (benzene) after complexation using tropolone, and were transformed to butyl methyl tin by reaction with MeMgBr.

The same method of preconcentration and separation was used by these analysts in a method in which they utilised mass spectrometry as the detection system. The level of detection of this method was about 0.03 μ g l⁻¹.

Anodic Stripping Voltammetry

Preconcentration steps would be needed before electrochemical techniques could be used for alkyl tin compounds in sea water. A detection limit of about 40 $\mu g \ l^{-1}$ seems likely by such methods.

Levels Present in the Environment

The levels of organo-tin compounds found in the environment are not well known due largely to the difficulties involved in their analysis. In Lake Michigan water, Hodge <u>et al.</u> (1979) found concentrations of alkyl tin compounds of the order of dibutyl tin 10 to 6 600 ng ℓ^{-1} , butyl tin 22 to 1 220 ng ℓ^{-1} , dimethyl tin 10 to 63 ng ℓ^{-1} , methyl tin 6 to 18 ng ℓ^{-1} and, in San Diego Bay, dimethyl tin 15 to 45 ng ℓ^{-1} and methyl tin 2 to 8 ng ℓ^{-1} .

In coastal waters of the Essex Coast (UK), Waldock et al. (1983) found concentrations of TBT varying between 0.43 $\mu g l^{-1}$ in the Crouch estuary and > 2 $\mu g l^{-1}$ in areas where boats were moored in high density (marinas); in the same areas, the levels of TBT in oysters were between >0.23 and 11.4 $\mu g g^{-1}$ dry weight (both sets of concentrations expressed as TBTO).

Role of the Alkyl Chain

The number of carbon atoms in the alkyl chain determines the toxic properties in relation to different classes of living organisms. The trialkyl tin series of compounds gives rise to several different types of biocides:

insecticides	R = methyl
rodenticides	R = ethyl
fungicides/bactericides	R = propyl
molluscicides	R = butyl

In animals, the iso-substituents are more toxicologically active than the normal isomers and toxicity increases in the inverse order of the number of carbon atoms in the alkyl chain: butyl < propyl < ethyl < methyl. For micro-organisms (fungi and bacteria), toxicity increases with increasing number of carbon atoms.

Effects on Aquatic Organisms

The available data relate mainly to the trialkyl compounds of tin, particularly TBT as the oxide or fluoride, which is employed in the control of vectors of tropical illnesses such as bilharziosis and in marine anti-fouling paints.

The data collected in Table 1 indicate the high toxicity of these compounds to aquatic organisms, especially the larvae of molluscs, the development of which is inhibited by concentrations of the order of 1 μ g ℓ^{-1} or less.

Bioaccumulation

Studies on terrestrial mammals show that TBTO is accumulated preferentially in the kidney, liver and lipids and is rapidly excreted as inorganic tin (Mouse T_2^1 29 days).

For aquatic organisms, Ward et al. (1981) found an accumulation factor of 2 600 in the fish <u>Cyprinodon variegatus</u> exposed for 58 days to concentrations of TBTO between 0.96 and 2.07 μ g l⁻¹. In molluscs the accumulation factor seems to be of the same order: Waldock et al. (1983) found concentration factors of 1 000 to 1 500 for <u>Ostrea edulis</u> after 21-22 days exposure and 2 000 to 6 000 for <u>Crassostrea gigas</u> (exposure concentrations were ca. 0.15 and 1.25 μ g l⁻¹).

Impact on Commercial Fisheries

Since 1975 perturbations in the exploitation of stocks of oysters of the <u>Crassostrea gigas</u> species have been noticed in France and the United Kingdom. These were detected especially in areas situated close to marinas or boat moorings. Recently these perturbations have been attributed to the presence of low concentrations in the water of TBT released by anti-fouling paints. The perturbations noted were:

- a reduction in larval survival with a resulting decrease in the reproduction of the stocks;
- a decrease in shell length growth, in many cases accompanied by an increase in shell thickness, and a decrease in shell cavity volume;
- the appearance of abnormalities in shell deposition characterised by numerous chambers filled with a gelatinous substance.

The Arcachon Basin is one of the two main areas of France in which the oyster <u>Crassostrea gigas</u> is produced where it reproduces naturally. Prior to 1977 spatfall (settlement of larvae) had been excellent, but between 1977 and 1979 no spatfall occurred. The earlier success demonstrated that:

- the water and climatic conditions were suitable;
- the parent stock were not composed of sterile hybrids;
- the larvae released between 1977 and 1979 developed normally if taken into the laboratory but if left in the Basin to settle naturally died after about 8 days.

Toxicity tests in France confirmed that TBT is highly toxic to oyster larvae; 0.1 μ g/l inhibits the development of larvae (His and Robert, 1980). These results were confirmed by similar work conducted in the United Kingdom (Thain and Waldock, Pers. Comm.). An evaluation of the amount of TBT present in the anti-fouling paint on the 15 000 boats which are present in the Arcachon Basin in the summer season allowed an estimate to be made of the order of magnitude of the concentration of TBT present in the water. This was found to exceed the toxic level for oysters.

Effects on the growth of oysters by TBT have been demonstrated in the natural environment in both France and the United Kingdom. Oysters growing close to sources of TBT were found to have shells which were reduced in length but increased in thickness to such an extent that they become ball-shaped. If these same oysters were placed in waters well away from sources of TBT, their growth returned to normal. In one particular area in France (Boyardville), where the oyster beds lie downstream of a 300 boat marina, the effect on shell growth was found to decrease steadily with increasing distance from the marina. Laboratory experiments in the United Kingdom have shown that the shell growth of young oysters (C. gigas) was reduced by exposure to as little as 0.15 μ g l^{-1} TBT. During 56 days of exposure to higher concentrations of TBT, 1.6 μ g l^{-1} , the oysters did not grow at all. The addition of sediment to the system did not further adversely affect the young oysters; indeed oysters exposed to sediment without any TBT present achieved a better growth rate than the oysters used as controls. These results have been confirmed by field trials using oysters from the same stock but laid in various locations. Those laid in clear or muddy water sites with few boats present grew well, whereas those laid at either clean or muddy water sites which had boats present in large numbers, grew badly and became ball-shaped. TBT was found to be present in all deformed oysters, but was not found in any of the oysters which grew well and normally, i.e., those from sites with no boats.

It is therefore clearly demonstrable that the introduction of TBT into the water from anti-fouling paints used on boats moored near to oyster beds has an adverse effect on the shell-growth of oysters.

After the first detection of problems with oyster growth in 1973 in the Arcachon Basin, the extent of shell deposition anomolies rapidly became much more serious in the succeeding years. By 1975 they had seriously affected the commercial quality of the oysters.

The abnormalities, which were found in oysters throughout the whole of the Arcachon Basin area and in some parts of the Marennes-Oleron region, are characterised by the formation of chambers filled with a gelatinous substance. This substance has been identified as a natural protein similar to the calcification protein of bivalves but lacking certain amino acids necessary to link with calcium ions (lysine, serine, etc.).

Experiments conduced simultaneously on stocks of oysters held in the Marennes-Oleron area and in the laboratory in tanks contaminated by paints containing TBT have shown that:

- abnormalities in shell growth appear at the same time in the contaminated tanks as in those parts of the natural environment where TBT is used;
- concentrations of TBT of the order of microgrammes per litre in the water give rise to substantially elevated levels of total tin in oyster tissues;
- the appearance of abnormalities is not linked to the level of tin in the tissues but to the presence of TBT in the water at the time of shell deposition.

The Effect of Controls

The use of organo-tin compounds in anti-fouling paints for use on most craft of less than 25 m was forbidden in France for two years (from 19 January 1982 to 24 September 1984, and the ban has recently been extended for a further two years). The prohibition has had detectable effects on production in shellfish growing areas, particularly in the Arcachon Basin, where:

- the production of spat was excellent in 1982 and enormous in 1983;
- the incidence of abnormal growth in oysters has been considerably reduced;

- the development of chambers in the shell has decreased. In 1983 no anomalies were detectable until May and in 1982 the anomalies developed more slowly and to a lesser extent than in 1980 and 1981. Furthermore in 1982, and even more so in 1983, fewer oysters were found with shell chamber abnormalities than in either 1980 or 1981;
- there is also some evidence to suggest that other species, such as eels, periwinkles, shore crabs and small flatfish, were more abundant in 1983 than in 1980 or 1981.

ALKYL LEAD COMPOUNDS

Production and Use

The annual production of alkyl lead compounds world-wide is greater than 500 000 tonnes; most of the production is as lead tetra-methyl and lead tetra-ethyl. Approximately 37 000 tonnes of that produced is likely to reach the marine environment through atmospheric and telluric inputs. Marine transport (80% of that produced) gives rise to accidental inputs: Trinidad (1981), Cape Town (1966) and the Adriatic (1974). Most of the organo-lead compounds produced are used as anti-knock agents in petrol.

Methods of Analysis

Alkyl lead compounds can be analysed by either atomic absorption spectrophotometry or gas chromatography.

Atomic absorption

Sirota and Uthe (1977) used AAS for the analysis of tissue samples following extraction of the organo-lead compounds by benzene and EDTA. The detection limit was about 1 $\mu g g^{-1}$. De Jonge <u>et al.</u> (1983) obtained a detection limit of 0.02 $\mu g l^{-1}$ for water samples using dithizone as a complexing agent and extraction in chloroform.

Gas Chromatography

Gas chromatography makes analysis of the individual organo-lead compounds easier as it provides a simple method of separating the different organic forms. Quantification can be achieved using either an atomic absorption spectrophotometer or a mass spectrometer as the detector.

Charlou <u>et al.</u> (1982) analysed sea water for the following organo-lead compounds: tetra-methyl, trimethyl ethyl, dimethyl diethyl, methyl triethyl and tetra-ethyl. n-Hexan was used as the extraction solvent.

A detection limit of about 0.07 $\mu g l^{-1}$ has been obtained by Chau <u>et al</u>. (1980) for tetra-alkyl lead compounds using a technique similar to that of Charlou <u>et al</u>. According to Noden (1977), the detection limit achievable using gass chromatography/mass spectroscopy is in the range 4 to 8 $\mu g l^{-1}$ for tetra-alkyl compounds. Forsyth and Marshall (1983) used an electron capture detector for the analysis of alkyl lead compounds after complexation with dithizone with extraction in a benzene-hexane mixture.

Toxicity to Living Organisms and Fate in the Marine Environment

The toxicity of alkyl lead compounds to marine organisms is high (Table 2). Generally the ethyl derivatives are more toxic than their methyl homologues and their toxicity decreases with decreasing numbers of alkyl chains. Lethal concentrations for marine organisms are generally less than 1 mg l^{-1}

and crustaceans appear to be particularly sensitive to tetra-alkyl lead (96 h LC₅₀ for <u>Crangon crangon</u> 0.02 mg l^{-1}). Few data are available on the toxicity of organo-lead compounds to larval stages of marine organisms. There is little or no information available on the effects of organo-lead compounds on living organisms in the natural marine environment.

In aqueous media, alkyl lead compounds can be degraded by UV photolysis giving a solid residue consisting of mixed hydrocerussite Pb $CO_3 \cdot Pb (OH)_2$ and laurionite Pb $(OH)_2 \cdot Pb Cl_2$ (Charlou <u>et al</u>. 1982). Complete dealky-lation is very slow and needs several months of irradiation.

There is only scant information on the levels of organo-lead compounds in marine sediments and organisms. Sirota and Uthe (1977) found alkyl lead in various fish and crustacean tissues at levels of between 0.01 and 0.16 mg kg⁻¹, corresponding to 9 to 8.0% of the total lead present. Forsyth and Marshall (1983) indicated organo-lead levels of around 1 to 4 mg kg^{-1} in herring eggs.

CONCLUSIONS

It is apparent from the work conducted in both France and the United Kingdom that the introduction into the marine environment of compounds containing tributyl-tin has lead to undesirable side effects on the shell growth and marketability of Pacific oysters (Crassostrea gigas). These effects have seriously damaged oyster culture operations in areas close to large numbers of pleasure craft. There is an increasing amount of evidence to suggest that other species of oysters, e.g., Crassostrea angulata and Ostrea edulis, may be affected in similar or different ways and that other molluscan shellfish may also be affected by low concentrations of TBT in the natural environment. The high toxicity of TBT to flatfish larvae suggests that recruitment of these species may also be affected. Further work is obviously required before these suggestions can be confirmed. A number of other organo-tin compounds are used in different forms of anti-fouling preparations, e.g., those containing tri-phenyl tin on nets used for fish cages, and in other ways which may lead to their release to the marine environment, for example, in agricultural fungicides. It is, therefore, strongly recommended that further work on the effects of organo-tin compounds includes work on compounds other than TBT.

Much less is known about the effects of alkyl lead compounds in the marine environment. However, as the foregoing brief review indicates, they do have similarities to organo-tin compounds and they may reach the marine environment in large quantities and, despite possible reduction in use, are likely to do so for some years to come. It is, therefore, suggested that further efforts be made to investigate the presence and effects of alkyl lead compounds in the marine environment.

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REFERENCES

Organo-tin compounds

- Alabaster, J S, 1969. Survival of fish in 164 herbicides, insecticides, fungicides, wetting agents and miscellaneous substances. Inst. Pest. Control, <u>11</u>, 29-35.
- Aldridge, W N, 1976. The influence of organo-tin compounds on mitochondrial functions in organo-tin compounds, new chemistry and applications. Ed. Zuckerman, J J. Washington : American Chemical Society. pp. 186-196.
- Alzieu, Cl., Heral, M, Thibaud, Y, Dardignac, M J, and Feuillet, M, 1981, (1982). Influence des peintures antisalissures à base d'organostanniques sur la calcification de la coquille de l'huitre <u>Crassostrea</u> <u>gigas</u>. Rev. Trav. Inst. Peches marit., <u>45</u> (2).
- Ambrogi, R, Saroglia, M G, and Scarano, G, 1982. Water treatment for fouling prevention - residual toxicity of an organo-tin compound towards marine organisms. IX Annual Aquatic Toxicity Workshop, Edmonton, Alberta, Canada, 2-5 November 1982.
- Barug, D and Vonk, J W, 1980. Studies on the degradation of TBTO in soil. Pestic. Sci. <u>11</u>, 77-82.
- Braman, R S and Tompkins, M A, 1979. Separation and determination of nanogram amounts of inorganic tin and methyltin compounds in the environment. Anal. Chem., <u>51</u> (1), 12-19.
- Chau, Y J, Wong, P T S, and Bengert, G A, 1982. Determination of Methyltin IV species in water by gas chromatography/atomic absorption spectrophotometry. Anal. Chem. <u>54</u>, 246-249.
- Chliamovitch, Y P and Kuhn, C, 1977. Behavioural haematological and histological studies on acute toxicity of bis-(tri-n-butyl tin) oxide on <u>Salmo gairdneri</u> Richardson and <u>Tilapia rendalli</u> Boulenger. J. Fish. Biol., 10, 575-585.
- Heral, M, Alzieu, Cl., Caux, O, Razet, D, and Garnier, J, 1983. Effects des sels organiques de tributylétain sur l'huitre adulte <u>Crassostrea</u> <u>gigas</u>. European Marine Biology Symposium, Oslo, 14-20 August 1983.
- His, E and Robert, R, 1980. Action d'un sel organo-metallique, l'acetate de tributyle-étain sur les oeufs et larves D de <u>Crassostrea</u> gigas (Thurnberg). ICES Doc. C.M.1980/F:27.
- Hodge, V F, Seidel, S L, and Goldberg, E D, 1979. Determination of tin (IV) and organotin compounds in natural waters, coastal sediments and macroalgae by atomic absorption spectrometry. Anal. Chem., <u>51</u> (8), 1256-1259.

Linden, E, Svanberg, O, and Sundström, G, 1979. Chemosphere 11, 843.

Maguire, R J and Huneault, H, 1981. Determination of butyltin species in water by gas chromatography with flame photometric detection. J. Chromatography, 209, 458-462. Mazaev, V T, Igumnov, A S, and Tsai, V N, 1977. Comparative hygienic toxicology assessment of alkyl oxides. Gigiena i Sanitariya, <u>4</u>, 14-18.

- Meinema, H A, Burger-Wiersma, T, Versluis de Hann, G, and Gevers, E C, 1978. Determination of trace amounts of butyltin compounds. Environmental Sci. and Tech. 12 (3), 288-293.
- Polster, M and Halacka, K, 1971. Beitrag zu hygenisch toxikologischen problematik einiger antimikrobiell gebrauchter organozinnverbin-dungen. Erakrungsforschung, <u>16</u>, 527-535.
- Slesinger, A E and Dressler, I, 1978. The environmental chemistry of three organotin chemicals. Pers. Comm.
- Thain, J E, 1983. The acute toxicity of bis-TBTO to the adults and larvae of some marine organisms. ICES Doc. C.M.1983/E:13.
- Thain, J E and Waldock, M J, 1983. The effect of suspended sediment and bis-TBTO on the growth of <u>Crassostrea</u> gigas spat. ICES Doc. C.M.1983/ E:10.
- Waldock, M J, Thain, J E, and Miller, D, 1983. The accumulation and depuration of bis-TBTO in oysters: a comparison between the Pacific oyster (<u>Crassostrea gigas</u>) and the European flat oyster (<u>Ostrea edulis</u>). ICES Doc. C.M.1983/E:52.
- Ward, G S, Cramm, G C, Parrish, P R, Trachman, H, Slesinger, A, 1981. Bioaccumulation and chronic toxicity of TBTO: Tests with salt water fish. Aquatic Toxicology and Hazard Assessment, 4th Conference. pp. 183-200.

Organo-lead Compounds

- Charlou, J L, Martin, G, Chaussepied, M, and Houieux, A, 1980. Approche de la toxicité des organo plombs étude de l'inactivation bactérienne par mesures d'atp. Prog. Wat. Tech. 12 (4), 501-512.
- Chau, Y K, Wong, P T S, and Goulden, P D, 1980. A sensitive technique for the analysis of tetraalkyl-lead compounds. pp. 77-81. <u>In</u>: Branica, M and Konrad, Z, eds. Lead in the Marine Environment. Proceedings of the International Experts Discussion on Lead Occurrence, Fate and Pollution in the Marine Environment, Rovinj, Yugoslavia, 18-22 October 1977. Pergamon Press Oxford.
- Forsyth, D S and Marshall, W D, 1983. The determination of alkyl lead salts in water and whole eggs by capillary column gas chromatography with electron capture detection. Anal. Chem. 49 (11), 2132-2137.
- Harrison, G F, 1980. The Cavtat Incident. pp. 305-317. <u>In</u>: Branica, M and Konrad, Z, eds. Lead in the Marine Environment. Proceedings of the International Experts Discussion on Lead Occurrence, Fate and Pollution in the Marine Environment, Rovinj, Yugoslavia, 18-22 October 1977. Pergamon Press Oxford.
- De Jonge, W R A, Van Mol, W E, and Adams, F C, 1983. Determination of trialkyl lead compounds in water by extraction and graphite furnace atomic absorption spectrometry. Anal. Chem. <u>55</u>, 1050-1054.

- Maddock, B G and Taylor, D, 1980. The acute toxicity and bioaccumulation of some lead alkyl compounds in marine animals. pp. 233-261. <u>In</u>: Branica, M and Konrad, Z, eds. Lead in the Marine Environment. Proceedings of the International Experts Discussion on Lead Occurrence, Fate and Pollution in the Marine Environment, Rovinj, Yugoslavia, 18-22 October 1977. Pergamon Press Oxford.
- Marchetti, R, 1978. Acute toxicity of alkyl leads to some marine organisms. Mar. Poll. Bull., <u>49</u>, 206-207.
- McKim, J M, Benoit, D A, Biesinger, K E, Brungs, W A, and Siefert, R E, 1975. Effects of pollution on freshwater fish. H. Wat. Poll. Cont. Fed. <u>47</u>, 1711.
- Sirota, G R and Uthe, J F, 1977. Determinations of tetra-alkyl lead compounds in biological materials. Anal. Chem. <u>49</u>, 823-825.
- Turnbull, H, Demann, J G, and Weston, R F, 1954. Toxicity of various refinery materials to freshwater fish. Ind. Eng. Chem. 46, 324.

TABLE 1. Toxicity of tributyl tin to aquatic organisms_

Species	Toxicity (µg l ⁻¹)						Reference
Phytoplankton Tetraselmis suesica Skeletonema costatum	Alg Alg	ista ista	tiqu tiqu	ue 5 ue	560 1	- 1 000 - 18	Thain, 1983 Thain, 1983
Zooplankton Brachionus plicatilis Tisbe furcata Nitocra spinipes	TC TC TC	50 50 (I)	24 24	h h		76 86 2	Ambrogi <u>et al</u> ., 1982 Ambrogi <u>et al</u> ., 1982 Linden <u>et al</u> ., 1979
Crustacea Artemia salina Crangon crangon	LC	50	24	h	1	270	Ambrogi <u>et al</u> ., 1982
adults	LC	50	48 96	h h		73 41	Thain, 1983 Thain, 1983
larvae	LC	50	48 96	h h		6.5 1.5	Thain, 1983 Thain, 1983
Carcinus maenas larvae	LC	50	48 96	h h		110 10	Thain, 1983 Thain, 1983
Molluscs <i>Ostrea edulis</i> adults	LC	50	48	h	>	300	Thain, 1983
Crassostrea gigas adults	LC	50	48 96	h h	1	800 290	Thain, 1983 Thain, 1983
larvae	LC LC	100 50	35 48	d b		0.5 1.6	Heral <u>et al</u> ., 1983 Thain, 1983
	inh dev	ibit: elopr	ion	of t		0.1	His and Robert, 1980
Mytilus edulis adults	LC	50	48 96	h h		300 38	Thain, 1983 Thain, 1983
larvae	LC	50	48	h		2.3	Thain, 1983
Fish Agonus cataphractus	LC	50	48 96	h h		26 16	Thain, 1983 Thain, 1983
Solea solea adults	LC	50	48 96	h h		88 36	Thain, 1983 Thain, 1983
larvae	LC	50	48 96	h h		8.5 2.1	Thain, 1983 Thain, 1983
Dicentrarchus labrax	LC	50	96	h		73	Ambrogi <u>et al</u> ., 1982
Cyprinodon variegatus	LC	50	21	d		0.96	Ward et al., 1981
Salmo gairdneri	LC	50	24 48	h h		28 21	Alabaster, 1969 Alabaster, 1969
	los	s of	rhe	eotaz	cis	11.7	Chliamovitch and Kuhn, 1977

TABLE 2. The	e toxicity of a	alkyl	lead	com	pounds to	o aquatio	c organisms	
Species	Toxic	ity	(mg/	<u>1)</u>	Reference			
ALGAE								
Phaeodacty1 (СН ₃)ц (С ₂ H ₅)ц (СН ₃) ₃ (С ₂ H ₅) ₃	lum tricornutu Pb Pb PbCl PbCl PbCl	n EC 50 EC 50 EC 50 EC 50	6 6 6	h h h	1.3 0.1 0.8 0.1		Maddock and Taylor, Maddock and Taylor, Maddock and Taylor, Maddock and Taylor,	1977 1977 1977 1977
Dunaliella (СН ₃)4 (С ₂ Н5)4	<i>tertiolecta</i> Pb Pb	EC 50 EC 50	48 48	h h	1.65 0.15		Marchetti, 1978 Marchetti, 1978	
MOLLUSCS								
Mytilus edu (CH3)4 (C2H5)4 (CH3)3 (C2H5)3	<i>lis</i> Pb PbCl PbCl	LC 50 LC 50 LC 50 LC 50	96 96 96 96	h h h	0.27 0.10 0.59 1.10		Maddock and Taylor, Maddock and Taylor, Maddock and Taylor, Maddock and Taylor,	1980 1980 1980 1980
CRUSTACEA								
Crangon cra (CH ₃)4 (C ₂ H ₅)4 (CH ₃) ₃ (C ₂ H ₅) ₃	nngon Pb Pb PbCl PbCl	LC 50 LC 50 LC 50 LC 50	96 96 96 96	h h h	0.11 0.02 8.8 5.8		Maddock and Taylor, Maddock and Taylor, Maddock and Taylor, Maddock and Taylor,	1980 1980 1980 1980
Artemia sal (СН3)4 (С ₂ Н5)4	lina Pb Pb	LC 50 LC 50	48 48	h h	0.25 0.085		Marchetti, 1978 Marchetti, 1978	
FISH								
Morone labr	Pax (larvae)		1.0	1	0.1			

(Сн ₃)4 (С ₂ н ₅)4	Pb Pb	LC 5	50 50	48 48	h h	0.1 0.065	Marchetti, 1978 Marchetti, 1978
Lepomis ma	crochirus						
(C _{2H5})4	Pb	LC 5	50	24	h	2.0	Turnbull et al., 1954
		LC 5	50	48	h	1.4	
Pleuronect	es platessa						
(CH ₃)4	Pb	LC 5	50	96	h	0.05	Maddock and Taylor, 1980
(C2H5)4	Pb	LC 5	50	96	h	0.23	Maddock and Taylor, 1980
(CH3)3	PbCl	LC 5	50	96	h	24.6	Maddock and Taylor, 1980
(C _{2H5})4	PbCl	LC 5	50	96	h	1.7	Maddock and Taylor, 1980
(CH3)2	PbC12	LC 5	50	96	h	300	Maddock and Taylor, 1980
(CH2H5)2	PbCl ₂	LC 5	50	96	h	75	Maddock and Taylor, 1980
Salmo gaire	dneri						
(C ₂ H ₅) ₄	Pb	LC 5	50	96	h	0.14	Brown, 1968
Salmo gaire	dneri (adults)						
(C ₂ H ₅) _Ц	Pb	LC 5	50	96	h	0.16	Brown, 1968
Salmo iride	eus						
(CH ₂))	Pb	LC 5	50	96	h	32	Harrison, 1980
$(C_2H_5)_{\mu}$	РЪ	LC 5	50	96	h	9	Harrison, 1980

ANNEX 6

POLYCHLORINATED TERPHENYLS

Introduction

Polychlorinated terphenyls (PCTs) are chemical compounds which consist of three connected benzene rings in which one or more of the 14 hydrogen atoms are substituted by chlorine atoms. Terphenyls may be regarded as diphenyl benzenes, and there are three possible isomers, <u>ortho-</u>, <u>meta-</u>, and <u>para-</u> terphenyl. The properties of commercial PCT products are very much like those of highly chlorinated PCBs. They are heat stable, non-flammable yellow resins with densities more than 1.5. PCTs resist aggressive and corrosive chemicals, such as alkalies and strong acids, and are insoluble in water but soluble in various organic solvents and oils (Jamieson, 1977).

Production

PCTs are produced by a controlled chlorination of the hydrocarbon. During chlorination a mixture of different chlorinated terphenyls will be formed. Commercial terphenyl is usually a mixture of o-, m-, and p-terphenyl.

PCT products are mostly marketed with a chlorine content of 32%, 42%, or 60%. These figures correspond to a mean chlorine content of 3, 5, and 9 chlorine atoms, respectively. PCT products also contain small amounts of PCBs. Values around 0.5% are often quoted, but up to 10% can be found (Jamieson, 1977).

PCTs have been produced under different trade names. In the United States, the Monsanto Chemical Co. produced PCTs, the major product being "Aroclor 5460", which contains 60% chlorine (Brinkman and De Kok, 1980). The total production of PCTs during 1959-1972 was about 50 000 metric tonnes. The production was voluntarily stopped in 1972 (Kopp, 1976). In France, PCTs were produced under the trade name "Electrophenyl T-60". In 1976, 1977, and 1978, respectively 587, 685, and 600 metric tonnes were produced (Gunther, 1981). Production in France ceased in 1980. Production has also taken place in the Federal Republic of Germany and Italy (e.g., "Clophen Harz (W)" and "Cloresil A", "Cloresil B" and "Cloresil 100"). Production was discontinued in 1974 in the Federal Republic of Germany and in 1975 in Italy (Brinkman and de Kok, 1980). In Japan, production ("Kanechlor-C") started in 1955. The total production from 1955 to 1972 was about 2 730 metric tonnes (Tatsukawa, 1976). No information is available concerning continued production.

The most important use of PCT is in waxes (trade name "Rigidax", among others) for the investment casting industry, which produces metal parts of high precision for aircraft, nuclear installations, and jewellery.

Environmental Aspects of PCTs

Although the production of PCTs has been relatively limited until now, PCT residues have been detected in many environmental samples. As highly chlorinated aromatics, PCTs might be expected to have a high resistance to biodegradation and photodegradation. Limited information is available concerning environmental pathways of PCTs, but it has been assumed that they resemble those of PCBs (Zitko et al., 1972).

PCTs are biologically stable, lipophilic substances which are capable of being accumulated in living organisms and through food chains. Renberg et al.

(1981) found in the Baltic Sea area 2.8 to 17.2 mg/kg in white-tailed eagles (<u>Haliaëtus albicilla</u>), 0.5 to 1.0 mg/kg in grey seals (<u>Halichoerus grypus</u>), 0.08 mg/kg in eels (<u>Anguilla anguilla</u>). In laboratory experiments with cod (<u>Gadus morhua</u>), PCTs were found in all tissues analysed (Addison <u>et al.</u>, 1972). The liver was the organ with the highest concentration (up to 32 mg/kg). Seventy days after exposure considerable amounts of PCTs remained in the tissues.

Freudenthal and Greve (1973) detected the presence of PCTs in samples of oysters and eel from the Netherlands. In Japan, PCT pollution of the aquatic environment is far lower than that of PCB. Most investigations of fish and water fowl showed no detectable levels of PCTs. Close to Tokyo Bay at Tama River, a mean PCT concentration in several fish species of 2.5 μ g/kg was found (Doguchi, 1977). PCTs have been detected in sea birds such as the herring gull (Larus argentatus) and black-headed gull (Larus ridibundus) (Zitko et al., 1972; Falandysz, 1980).

The toxicological properties of PCTs have not been extensively investigated. In general, the toxicity is considered to be equivalent to that of PCBs, the long-term toxicity being most important. Yap <u>et al.</u> (1971) studied the sensitivity of fish ATPases to PCTs and found a 30% to 40% inhibition of Na⁺-K⁺ ATPase. Reproductive effects of PCBs have been found in several species of aquatic organisms; seals, flounders, sea lions, herring gulls, harbour porpoises, and Atlantic cod (Jensen and Jørgensen, 1983). The reproductive effect of PCTs has only been investigated in a few laboratory experiments with chickens, without showing a significant effect on hatchability (Cecil <u>et al.</u>, 1974; Lillie <u>et al.</u>, 1974).

Implications and Public Health Aspects

Very often PCTs have been detected in paper products. In a survey of 445 samples of food packaging materials in Canada, PCTs were detected in all samples (more than 10 mg/kg in 4% of the samples). The transfer of PCTs into foodstuffs was minimal (Villeneuve <u>et al.</u>, 1973). Earlier, the use of PCTs in sealants for concrete stave silos caused PCT contamination of feed and cow milk in the United States (Fries and Marrow, 1973). In Canada, Foodstuffs contained 0.01 to 0.05 mg/kg PCT (Villeneuve <u>et al.</u>, 1973). In Japanese food-stuffs, PCTs were only detected in vegetable products, including seaweed, but not in marine animal products, among others. The estimated human daily intake was about 0.05 μ g PCT (Doguchi, 1977).

PCT residues in human tissues (blood, liver, fat, milk) have been detected in Japan, the Netherlands, and in the United States (Jensen and Jørgensen, 1983). In spite of decreasing industrial usage of PCTs and negligible residues in foods in Japan, higher levels of PCTs in blood were found compared to PCBs (Doguchi and Fukano, 1975; Watanabe <u>et al</u>., 1980).

In a study lasting two years, Funako and Doguchi (1977) found that the PCT level in blood from the same donors was almost constant, from which they concluded that PCTs have a very long biological half-life in humans. In Japan, the levels of PCTs in human milk were 1/60 of those of PCBs in the same samples (Minagawa et al., 1974). It also appears that the amount of PCTs transported into children via their mother's milk is less than in the case of PCBs (Watanabe et al., 1980).

In animal experiments, PCTs seem to be less acutely toxic than most PCBs, possibly due to lower solubility and absorption in the body (Fishbein, 1974).

Animals exposed to PCTs in their daily diet may gain less body weight than control animals, as has been shown for mice and rats (Shirai <u>et al.</u>, 1978; Norback and Allen, 1972), but not for hens (Lillie <u>et al.</u>, 1974). Rhesus monkeys given 5 000 mg/kg PCT in the diet lost hair and showed subcutanous edema, among other effects (Allen and Norback, 1973).

PCTs may cause a dose-dependent increase in relative liver weight and a proliferation of the endoplasmic reticulum. This has been demonstrated in rats (Norback and Allen, 1972; Sosa-Lucero <u>et al.</u>, 1973) and monkeys (Allen and Norback, 1973).

High doses of PCTs have been demonstrated to stimulate the hepatic microsomal drug metabolising enzyme system in laboratory animals and <u>in vitro</u> systems. Compounds that modify the activity of this enzyme system may consequently alter the toxicity of other environmental or industrial chemicals and disturb the metabolism of endogenous substances such as fatty acids and hormones. Elevated levels of cytochrome P-450, aniline hydroxylase, aminopyrine Ndemethylase, esterases, and nitroreductase and depressed levels of glucose-6-phosphatase and aromatic hydrolase have been reported (Norback and Allen, 1972; Bitman <u>et al.</u>, 1972; Sosa-Lucero <u>et al.</u>, 1973; Cecil <u>et al.</u>, 1975; Toftgård <u>et al.</u>, 1980).

Allen and Norback (1973) investigated the carcinogenicity of PCTs to monkeys and found indications of an eventual neoplastic transformation of the gastric mucosa. Shirai et al. (1978) treated male ICR mice with 250 and 500 mg/kg PCT in the diet for 24 weeks. The animals were sacrificed after 40 weeks. The PCT-exposed mice had a significantly higher incidence of nodular hyperplasma of the liver. The high dose group also had a significantly higher incidence of hepatocellular carcinomas.

In spite of an apparently decreasing industrial usage of PCTs and the tighter regulations in international bodies such as the European Communities and the Paris and the Helsinki Conventions, it should be noticed that PCTs have temporarily been permitted for use in some investment casting waxes in the European Communities.

In view of the control measures already applied (Jensen and Jørgensen, 1983), inputs to the marine environment can be expected to decline. PCTs are similar to PCBs and are likely to follow similar physico-chemical rules, although given their reduced scale of production they are unlikely to present the same scale of problem. Monitoring for PCTs is not, therefore, necessary. Nevertheless, it is important that some further investigations be conducted. In particular, it is desirable that some attempt be made to establish whether the concentrations of PCTs found in biota are always parallel to but at a lower level than the concentrations of PCBs found in the same tissues. If this can be confirmed as a general applicable rule, it is unlikely to be necessary to monitor for PCTs as such, although some analyses of samples found to contain unusually high levels of PCBs may still be considered desirable.

Acknowledgement

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References

- Addison, R F, Fletcher, F L, Ray, S, and Doane, J, 1972. Analysis of a chlorinated terphenyl (Aroclor 5460) and its deposition in tissues of cod (<u>Gadus morhua</u>). Bull. Environ. Contam. Toxicol., <u>8</u>, 52-60.
- Allen, S R and Norback, P H, 1973. Polychlorinated biphenyl and triphenylinduced gastric mucosal hyperplasia in primates. Science, <u>179</u>, 498-499.
- Bitman, J, Cecil, H C, and Harris, S S, 1972. Biological effects of polychlorinated biphenyls in rats and quail. Environ. Health Perspect, <u>1</u>, 145-149.
- Brinkman, V A and De Kok, A, 1980. Production, properties and usage. In: R D Kimbrough (Ed.) Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins, and Related Products. Elsevier/North-Holland Biomedical Press, Amsterdam.
- Cecil, H C, Bitman, J, Lillie, R J, and Verret, J, 1974. Embryotoxic and teratogenic effects in unhatched fertile eggs from hens fed polychlorinated biphenyls (PCBs). Bull. Environ. Contam. Toxicol., <u>11</u>, 489-495.
- Cecil, H C, Harris, S S, and Bitman, J, 1975. Effect of polychlorinated biphenyls and terphenyls and polybrominated biphenyls on pentobarbital sleeping times of Japanese quail. Arch. Environ. Contam. Toxicol., <u>3</u>, 183-192.
- Doguchi, M., 1977. Polychlorinated terphenyls as an environmental pollution in Japan. Ecotoxicol. Environ. Safety, <u>1</u>, 239-248.
- Doguchi, M and Fukano, S, 1975. Residue levels of polychlorinated terphenyls, polychlorinated biphenyls and DDT in human blood. Bull. Environ. Contam. Toxicol., 13, 57-63.
- Falandysz, J, 1980. Chlorinated hydrocarbons in gulls from the Baltic South Coast. Mar. Pollut. Bull., <u>11</u>, 75-80.
- Fishbein, L, 1974. Toxicity of chlorinated biphenyls. Ann. Rev. Pharmacol., <u>14</u>, 139-156.
- Freudentahl, J and Greve, P A, 1973. Polychlorinated terphenyls in the environment. Bull. Environ. Contam. Toxicol., 10, 108-111.
- Fries, G F and Marrow, G S, 1973. Polychlorinated terphenyls as potential contaminants of animal products. J. Assoc. Offic. Anal. Chem., <u>56</u>, 1002-1007.
- Fukano, S and Doguchi, M, 1977. PCT, PCB and pesticide residues in human fat and blood. Bull. Environ. Contam. Toxicol., <u>17</u>, 613-617.
- Gunther, B, 1981. EPA, Personal Communication, March.
- Jamieson, J W S, 1977. Polychlorinated terphenyls in the environment. Environmental Protection Service, Ottawa.

Kopp, T (Ed.), 1976. PCBs in the United States. Industrial Use and Environmental Distribution. Task I. U.S. Environmental Protection Agency, Washington, D.C.

- Lillie, R J, Cecil, H C, Bitman, J, and Fries, G F, 1974. Differences in response of caged white leghorn layers to various polychlorinated biphenyls (PCBs) in the diet. Poultry Sci., <u>53</u>, 726-732.
- Minagawa, K, Takigawa, Y, Sakai, H, and Sasagawa, I, 1974. Polychlorinated terphenyls in human fat and mothers' milk (in Japanese). Nippon Eiseigaku Zasshi, 28, 543-547. Cit.: C.A.82 (1975)11876j.
- Norback, D H and Allen, J R, 1972. Chlorinated triphenyl-induced extensions of the hepatic endoplasmic reticulum. Proc. Soc. Exp. Biol. Med., <u>139</u>, 1127-1131.
- Norback, D H and Allen, J R, 1972. Chlorinated aromatic hydrocarbon-induced modifications of the hepatic endoplasmic reticulum:concentric membrane arrays. Environ. Health Perspec., <u>1</u>, 137-143.
- Renberg, L, Sundström, G, and Reutergårdh, L, 1981. Polychlorinated Terphenyls (PCT) in Swedish White-tailed Eagles and in grey seals. A Preliminary Study. Chemisphere, <u>6</u>, 477-482.
- Shirai, T, Miyata, Y, Nakanishi, K, Murasaki, G, and Ito, N, 1978. Hepatocarcinogenicity of polychlorinated terphenyl (PCT) in ICR Mice and its enhancement by hexachlorobenzene (HCB). Cancer Lett., <u>4</u>, 271-275.
- Sosa-Lucero, J C, De la Iglesia, F A, and Thomas, G H, 1973. Distribution of a Polychlorinated Terphenyl (PCT) (Aroclor 5460) in Rat Tissues and Effect on Hepatic Microsomal Mixed Function Oxidases. Bull. Environ. Contam. Toxicol., <u>10</u>, 248-256.
- Tatsukawa, R, 1976. PCB pollution of the Japanese environment. In: K Higuchi (Ed.), PCB Poisoning and Pollution, Kodanska/Academic Press, 147 pp.
- Toftgård, R, Nilsen, O G, and Glanmann, H, 1980. Polychlorinated Terphenyls and Mixed Types Inducers of Rat Liver Microsomal Cytochrome P-450. In: J A Gustafsson et al. (Eds.), Biochemistry, Biophysic and Regulation of Cytochrome P-450, Elsevier/North Holland Biomedical Press, Amsterdam.
- Villeneuve, D C, Reynolds, L M, Thomas, G H, and Phillips, W E J, 1973. Polychlorinated biphenyls and polychlorinated terphenyls in Canadian food packaging materials. J. Assoc. Offic. Anal. Chem. <u>56</u>, 999-1001.
- Watanebe, I, Yakushiji, T, and Kunita, N, 1980. Distribution differences between polychlorinated terphenyls and polychlorinated biphenyls in human tissues. Bull. Environ. Contam. Toxicol., 25, 810-815.
- Yap, H H, Desaiah, D, Cutkomp, L K, and Koch, R B, 1971. Sensitivity of fish ATPases to polychlorinated biphenyls. Nature, <u>233</u>, 61-62.
- Zitko, V, Hutzinger, O, Jamieson, W D, and Choi, P M K, 1972. Polychlorinated terphenyls in the environment. Bull. Environ. Contam. Toxicol. <u>7</u>, 200-201.
- Zitko, V, Hutzinger, O, and Chio, P M K, 1972. Contamination of the Bay of Fundy - Gulf of Maine area with polychlorinated biphenyls, polychlorinated terphenyls, chlorinated dibenzodioxins and dibenzofurans. Environ. Health Perspec., 1, 47-50.

ANNEX 7

ZINC IN THE MARINE ENVIRONMENT - An Overview

PART 1 - GEOCHEMICAL ASPECTS

Speciation and Concentrations

Several studies have been conducted on the thermodynamically stable speciation of dissolved zinc in both river water and sea water. Depending on the choice of parameters and stability constants in the various models, quantitatively different results are obtained. However, the models generally agree quite well in a qualitative sense. In low alkalinity river water, Zn^{2^+} is dominant with only a few percent or less of various OH⁻, $CO_3^{2^-}$ and $SO_4^{2^-}$ complexes. If humics or other organics are included, they also contribute only a few percent or less to the zinc speciation. At high alkalinity, OH⁻ and $CO_3^{2^-}$ complexes become more important. Sea water is dominated by Zn^{2^+} , and $ZnCl^+$ with lesser contributions from other Cl⁻ and OH⁻ complexes. It seems likely that some organic complexes of zinc also occur in sea water, but little is known of their nature or concentration.

Particulate zinc in rivers consists of a detrital crystalline fraction augmented by zinc either adsorbed or otherwise loosely attached to the mineral grains or associated with particulate organic matter. There is little evidence for changes in the adsorption behaviour of zinc upon entering the marine environment. Some desorption from riverborne particulates or diagenetic release from estuarine sediments might be expected, but has yet not been conclusively proven. Within the marine environment, additional particulate zinc is generated by the extensive incorporation of zinc in the biota.

Concentrations of zinc in coastal sediments generally reflect the zinc content of the terrestrial source rocks. In deep-sea clays, the zinc content is elevated by a factor of 2-3 over that of the source rocks, with higher concentrations in Pacific than Atlantic clays. These clays show less enrichment with zinc than they do for Mn, Co, Cu or Ni. On the other hand, biogenic sediments, particularly silicious oozes, have relatively high levels of zinc.

Because of the extreme contamination problems inherent in the collection and analysis of natural waters for zinc, it is very difficult to make reliable estimates of zinc concentrations in the various environmental reservoirs. The following table of zinc levels in the marine environment was generated using only recent data collected and analysed by the best techniques. Nevertheless, concentrations near the tops of the concentration ranges reported probably mostly reflect contamination. The zinc levels measured in rain and snow, even in remote arctic regions, indicate, on the basis of Zn/Al or Zn/Cl ratios, enrichment of zinc compared to levels in terrigenous particles or sea water. Although these ratios appear to have increased in recent years, even pre-industrial samples show elevated ratios.

Concentration Range Phase Comments River μg l⁻¹ dissolved 1 10 - 400 particulate 100 µg g μg l⁻¹ -1 Rain/snow 0.1 µg l^{−1} Coastal sea water 0.01 -1 (dissolved) 0.005 - 0.6 μ g l⁻¹ Increases with depth Deap sea water covaries with Si (dissolved) -150 μg g Coastal marine sediments 50 (fine fractions) Deep sea sediments $\mu g g_{-1}^{-1}$ higher in Pacific - 300 clays 100

50

Transport and Distribution

biogenic

Zinc is injected into the ocean through dissolved and particulate river input and atmospheric deposition. Most (>90%) of the river discharge of suspended particulate matter is deposited in coastal zone sediments. Since the zinc content of river particulates is generally significantly higher than that in these sediments, one or more processes must be occurring that fractionate the zinc such that the material transported offshore is enriched relative to the material deposited in coastal sediments. This could occur by chemical transformation of the particulate zinc (either in the water column or the sediment) or simply by size fractionation of the particles.

– 150 µg g

The distribution of zinc in the deep ocean is controlled by biological activity and physical mixing and circulation of water masses. Surface water concentrations are depleted as a result of biological uptake. The concentrations increase with depth to a maximum between the thermocline and mid-depth in a manner very similar to silicate. It would appear that zinc is regenerated from biogenic debris in direct proportion to the more refractory biogenic components such as silicate and carbonate exoskeletons. As a result, the distribution of zinc in the upper water column is controlled by biological cycling. In the deep water, zinc concentrations will be influenced by residual dissolution of biogenic debris, but will reflect more strongly the mixing of water masses. In the Pacific Ocean, the distribution of zinc can be related to that of silicate by the equation:

 $Zn (nM) = 0.0535 Si (\mu M) + 0.02 nM, r = .996.$

In the Atlantic Ocean, a qualitatively similar dependence on silicate continues, but the observed Zn/Si ratios are higher and increase from the Sargasso Sea northward. This progression probably reflects greater inputs of zinc to the North Atlantic from river and atmospheric sources.

Removal of metals like zinc from sea water should occur by one or both of two processes: biological uptake and sedimentation of biogenic debris, and/or scavenging of metals by slowly sinking particles. Dissolved zinc distributions indicate that the first process is more important for zinc because extensive scavenging should result in deviations from the observed Zn/Si relationships. The enrichment of zinc compared to most other trace metals in biogenic sediments also points to the importance of deposition of biological debris in the removal of zinc from sea water.

Fluxes Through the Marine Environment

The box model shown in the accompanying diagram is an attempt to estimate the fluxes of zinc through the marine environment under reasonably natural (i.e., unpolluted) conditions. The concentrations used in the model for the input fluxes are generally taken from the lower end of the concentration ranges listed in the table.



The importance of the particulate river input, even at the low zinc content of particles (120 μ g g⁻¹) chosen here, is immediately evident. Even after allowing for nearshore sedimentation, the residual particulate flux contributes 85% of the total input to the deep sea. With the concentration chosen here, inputs and outputs are approximately in balance. The residence time calculated from these fluxes is approximately 1 400 yrs. If only dissolved river inputs are considered, the residence time would be about 10 000 yrs.

Anthropogenic activities have increased the dissolved zinc concentration in several rivers to 10 µg l⁻¹ or so and particulate zinc to about 300 µg g⁻¹. Some apparently reliable reports of zinc in rivers would indicate even higher levels in some isolated instances. A conservative estimate of the anthropogenic contribution to marine atmospheric deposition would be 6 x 10¹⁰ g · yr⁻¹. These anthropogenic sources could increase the total input by as much as 0.5 to 1 x 10¹² g · yr⁻¹ (i.e., 25% to 50% of the natural flux). The majority of the anthropogenic flux is in particulate river discharge and a considerable part of this will be deposited in estuarine and nearshore sediments. This is reflected in elevated zinc levels in coastal sediments in many areas.

PART 2 - BIOLOGICAL ASPECTS

Concentrations of Zinc in Marine Animals and Plants

There have been many compilations of zinc concentrations found in marine organisms, see, e.g., the U.S. National Marine Fisheries Service (National Academy of Sciences, 1979) or the UK Ministry of Agriculture, Fisheries and Food (Murray and Portmann, 1984). The main findings are outlined below.

Zinc is easily detectable in most marine organisms. In most marine organisms used for human food purposes, the concentration in the edible muscle tissue ranges from 3-30 $\mu g g^{-1}$ wet weight. Most finfish appear to be able to regulate the content of zinc in their muscle tissue. However, the amount found in the liver can vary markedly depending on recent exposure to unusual zinc concentrations in either food or water. Food, in fact, is the most important route of uptake of zinc by fish, especially in relation to the component of zinc which is accumulated by the body on more than a short-term basis (Pentreath 1973, 1976; Willis and Sunda, 1984). Molluscs, especially oysters, appear to accumulate zinc at a level related to the exposure concentration and do not appear to be particularly able to regulate the maximum concentration. As a consequence, oyster are typically found to contain concentrations of the order of several hundred $\mu g g^{-1}$, but it is not unusual to find concentrations of up to 1 000 or 2 000 $\mu g g^{-1}$ in oysters from estuaries contaminated by rivers draining metalliferous mineral catchments or receiving mine-water discharges.

Marine macroalgae also appear to accumulate zinc according to the level of exposure experienced in water, and are also poor regulators. Fucus vesiculosis, for example, was reported to contain 20 times more zinc in a zinc-enriched estuarine environment than in other areas (Young, 1975). Bioconcentration factors, based on laboratory experiments, have been reported to range from 3 300 to 16 600 for Fucus spp. (Guthnecht, 1965; and Young, 1975, respectively). Laminaria digitata was found to exhibit somewhat lower concentration factors, ranging from 550 to 2 900, with the lower figure applying to the highest exposure concentration in water (Bryan, 1969).

Toxicity to Marine Organisms

Zinc is an extremely common contaminant in both municipal and industrial effluents and considerable attention has been paid to the effects of zinc on marine organisms. Invertebrates appear to be more sensitive than fish species and, as a consequence, more work has been done with non-fish species. The available data for fish species suggest that the tests were carried out at somewhat unrealistically high added concentrations; 48 hr to 96 hr LC 50 values for larval fish are reported to lie in the range 2.7 mg l⁻¹ to 83 mg l⁻¹ (U.S. EPA, 1980). Such concentrations exceed the solubility of zinc in sea water. More realistic data exist for the effects of zinc on crustacea and molluscs, with 48 hr to 96 hr LC 50 values normally being reported in the 100 μ g l⁻¹ range. Abnormal shell growth has been reported to occur in oysters (Crassostrea gigas) after exposure to only 50 μ g l⁻¹ (Nelson, 1972) and delayed development of larvae of the crustacean Rhithropanopeus harisii was observed at concentrations of 70 μ g l⁻¹ (Benijts-Claus and Benijts, 1975). Egg production by fathead minnows (Pimephales promelas) was reported to be inhibited by exposure to 180 μ g l⁻¹ (Brungs, 1969).

However, there is considerable evidence that marine organisms develop a tolerance to zinc if exposed for long periods. Bryan (1980), for example, has shown that crabs from a high zinc exposure area were appreciably more tolerant to added zinc than those from other areas. Greater tolerance in fish species probably stems from their ability to regulate their zinc uptake.

Public Health Aspects

Zinc is not particularly toxic to humans when taken via the oral route. There are relatively few reports of accidental zinc poisoning through food sources and at least some of these may well have been caused by cadmium present as an impurity. The normal response to excessively high oral intakes is nausea and vomitting, with no lasting ill-effects although lethargy and fever may occur in some individuals. Zinc has in fact been used for therapeutic purposes, with up to 660 mg per day of zinc sulphate being administered in the treatment of leg ulcers. The levels of zinc found in marine animals used for human food purposes do not present a threat to human health and no record could be found of public health standards or action limits for fisheries products. Zinc is a vital element in the human diet and there is evidence from recent studies of zinc in the human diet as a whole which suggest that the typical, modern, developed world diet may even be deficient in zinc (H.M.S.O., 1981).

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References

- Benijts-Claus, C and Benijts, F, 1975. The effect of low lead and zinc concentrations on the larval development of the mud crab <u>Rhithropanopeus</u> <u>harisii</u> (Gould). <u>In</u> Sub-lethal effects of toxic chemicals on aquatic animals. Elsemier Scientific Publications Co., Amsterdam, 43.
- Bruland, K W, 1980. Oceanographic distribution of cadmium, zinc, nickel and copper in the North Pacific. Earth and Planetary Science Letter 47, 176-198.
- Brungs, W A, 1969. Chronic toxicity of zinc to the fathead minnow, <u>Pimephales promelas</u> (Raffinesque). Trans. Am. Fish Soc. <u>98</u>, 272-279.
- Bryan, G W, 1969. The absorption of zinc and other metals by the brown seaweed Laminaria digitata. J. Mar. biol. Assoc. UK 49, 225.
- Bryan, G W, 1980. Recent trends in research on heavy metal contamination in the sea. Helgolander Meeresunter. <u>33</u>, 6.
- Buat-Menard, P and Chesselet, R, 1979. Variable influence of the atmospheric flux in the trace metal chemistry of oceanic suspended matter. Earth and Planetary Science Letters, 42, 399-411.
- Gutnecht, J, 1965. Uptake and retention of caesium-137 and zinc-65 by sea weeds. Limnology and Oceanog. 1965, 10, 58.
- H.M.S.O., 1981. Survey of Copper and Zinc in Food. The fifth report of the steering group on food surveillance and the Working Party on the Monitoring of foodstuffs for heavy metals. Food Surveillance Paper No. 5. pp. 50.
- Li, Y H, 1981. Geochemical cycles of elements and human perturbation. Geochim. et Cosmochim. Acta <u>45</u>, 2073-2084.

- Murray, A J and Portmann, J E, 1984. Metals and organochlorine pesticide and PCB residues in fish and shellfish in England and Wales in 1976 and trends since 1970. Ministry of Agriculture, Fisheries and Food, Aquatic Environment Monitoring Report. No. 10, pp. 79.
- Nelson, D A, 1972. Effects of Strontium-90 plus Yttruim-90, zinc-65 and chromium-51 on the larvae of the Pacific oyster <u>Crassostrea gigas</u>. <u>In</u> The Columbia estuary and Adjacent Ocean waters, Bioenvironment Studies. University of Washington Press. Seattle, Washington.
- National Academy of Sciences, 1979. University Park Press, Baltimore, USA. pp. 471.
- Nriagu, J O, 1980. Zinc in the environment. Part 1. Wiley-Interscience, New York.
- Pentreath, R J, 1973. The accumulation and retention of 65-Zn and 54-Mn by the plaice <u>Pleuronectes platessa</u> (L). J. exp. mar. Biol. Ecol. <u>12</u>, 1-18.
- Pentreath, R J, 1976. Some further studies on the accumulation and retention of 65-Zn and 54-Mn by the plaice <u>Pleuronectes platessa</u> (L). J. exp. mar. Biol. Ecol. 21, 179-189.
- U.S. EPA, 1980. Ambient Water quality for zinc. Ref. No. EPA 440/5-80-07.
- Willis, J N and Sunda, W G, 1984. Relative contributions of food and water in the accumulation of zinc by two species of fish. Mar. Biol. <u>80</u>, 273-279.
- Young, M L, 1975. The transfer of Zn-65 and Fe-59 along a <u>Fucus</u> serratus (L) <u>Littorina obtusata food chain.</u> J. mar. biol. Assoc. UK 55, 583.

ANNEX 8

- 97 -

REPORT OF THE FIRST MEETING OF THE ICES WORKING GROUP ON BALTIC SEALS* 20-22 April 1983

1. INTRODUCTION

In response to requests from the Helsinki Commission and the International Baltic Sea Fisheries Commission, the ICES Council resolved that a Working Group should be established to:

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

The Working Group met at the ICES Headquarters in Copenhagen from 20 to 22 April 1983 under the chairmanship of J Harwood, who also acted as rapporteur. The Agenda shown in Appendix 1 was adopted. A list of participants is given in Appendix 2, and a list of the working papers submitted to the Group in Appendix 3. Copies of these papers may be obtained from their authors.

Three species of seal now occur in the Baltic: the ringed seal (<u>Phoca hispida</u>), the grey seal (<u>Halochoerus grypus</u>) and the harbour seal (<u>Phoca vitulina</u>). There are historical records of harp seals (<u>Phoca groenlandica</u>) in the Baltic, but there have been no regular sightings for several hundred years.

The Working Group decided to consider the seal populations occurring in the Baltic Sea and the Kattegat-Skagerrak area separately. It did not consider the populations of ringed seals in Lake Saimaa and Lake Ladoga, although the river systems of these lakes do lead into the Baltic. The Working Group believed that there was no significant interchange of individuals between them and the Gulf of Finland. Figure 1 shows the location of all of the sites referred to in this report.

2. POPULATION SIZE IN 1900

The only data for estimating the size of the Baltic seal populations at the beginning of this century come from the records of bounty schemes which started in 1889 in Denmark, the 1890s in Sweden, and 1909 in Finland. Although the species and approximate age of each seal killed was recorded, these identifications are not entirely reliable. However,

*This report was originally presented as Doc. ICES C.M.1983/N:3

between 1963 and 1974 a jaw from each seal taken in Sweden was supplied to the Swedish Museum of Natural History, and it has been possible to correct some of the hunters' identifications.

2.1 Ringed Seals

Over 100 000 ringed seals were killed in the period 1910-1920 (Almkvist et al., 1980), and over 20 000 were killed in some years. A significant proportion of these animals were females and their pups. On this basis, Almkvist (1982) has estimated that there must have been several hundred thousand ringed seals in the Baltic in 1900.

2.2 Grey Seals

Approximately 30% of the seals taken in Finland and Sweden before 1935 were grey seals. It is probable that the proportion of adult females and their pups in this catch is even higher than for ringed seals. These figures suggest that there may have been about 100 000 grey seals in the Baltic in 1900.

The situation in the Kattegat is even less clear. Grey seals were traditionally hunted on Anholt untl the end of the nineteenth century, but this was carefully regulated by the local inhabitants. However, when the bounty scheme was introduced up to 1 500 seals were killed each year in Danish waters, including the Wadensee. It is not known how many of these were grey seals, and it is not possible to estimate the size of the population in 1900.

2.3 Harbour Seals

At one time harbour seals were found throughout much of the southern Baltic, in the Skagerrak and Kattegat.

Up to 360 harbour seals were taken each year at the beginning of this century on the west and southeast coast of Sweden and an unknown number of seals was also taken along the German Baltic coast and in Poland. As noted above, up to 1 500 seals were taken each year in the Danish waters. This includes both grey and harbour seals taken in the Baltic, Kattegat, Skagerrak and Danish Wadensee. Unfortunately, the location of these catches is not known and it is impossible to estimate separately the size of the Baltic and Kattegat populations at the beginning of this century. However, the ages of a sample of the harbour seals taken in Danish waters in 1889-1890 were determined. Eighty-five per cent of these animals were pups and Heide-Jørgensen (1980) has used this to estimate that approximately 3,000 pups (equivalent to a total population of 10-15 000 animals) were born each year at this time.

3. CHANGES IN POPULATION SIZE

Information on changes in population size was available from three sources: changes in recorded catches of seals; changes in distribution; and a comparison of current estimates of population size with historical ones.

3.1 <u>History of Exploitation</u>

All three species of seal were hunted in the Baltic during the nineteenth century but catches decreased at the end of the century, probably because of a decline in the value of seal products. However, about this time the

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bounty scheme referred to in Section 2 was introduced. The scheme was intended to increase fisheries yields by reducing the seal populations and was, in fact, recommended by ICES in 1909. Bounty payments were abolished in 1927 in Denmark, 1974 in Sweden, and 1976 in Finland.

In Finland about 70% of the seals killed were ringed seals (Helle, 1979). The same was true in the Swedish Baltic until 1935, but from that time onwards approximately equal numbers of grey and ringed seals were killed (Almkvist <u>et al.</u>, 1980). In the Kattegat it appears that grey seals were rapidly reduced to very low numbers, and most of the animals taken were harbour seals.

The average age of the animals has varied. Until the Second World War, many of the ringed seals killed in the Gulf of Finland were taken at their breeding lairs, which were located with specially trained dogs. However, after the war this stopped and most ringed seals were killed when they were basking on the ice. Some seals were also taken in a net fishery in the Bothnian Bay. Pups or young of the year made up about 20% of the total Finnish catch of ringed seals between 1956 and 1975 (Helle, 1979).

Although some grey seals were shot at haul-outs along the coast, most of the hunting was on the breeding grounds and a very high proportion of the catch was mothers and their pups. Between 1932 and 1939 two thirds of all the grey seals taken by Sweden and Finland were less than one year old (Almkvist <u>et al.</u>, 1980). Approximately 45% of the Finnish catch between 1956 and 1975 was juvenile animals (Helle, 1979).

Catches of both ringed and grey seals in the Baltic were high in the period 1910 to 1920, averaging about 19 000 per year in total. They were lower between 1920 and 1940, but still exceeding 15 000 in some years. However, catches declined markedly after the Second World War, apart from a brief increase around 1964 when the value of the bounty was doubled (Helle, 1979). This decline was not due to a decrease in the number of hunters applying for bounties (Helle, 1979). Between 1956 and 1975 approximately 900 ringed seals and 400 grey seals were taken each year in Finland, while approximately 300 of each species were taken in Sweden.

In the Kattegat a total of 40 000 seals was taken between 1889 and 1927, but catches fell rapidly from 1 500 in 1900 to only 56 in 1927 (Heide-Jørgensen, this meeting).

3.2 Changes in Distribution

At the beginning of this century ringed seals were hunted along the east coast of Sweden as far south as Stockholm, but these catches declined from 1910 to 1950 and ringed seals are no longer seen in this area. Similarly, ringed seals are seen much less frequently than in the past in the southwest archipelago of Finland.

Grey seals have disappeared from a number of traditional sites in Sweden, most noticeably from Harstena where tens of thousands of grey seals used to haul out (Almkvist, 1982). Harbour seals are now rare in Gotland where they used to be seen frequently, and are no longer found in Poland and along the Baltic coast of Germany.

There have been no major changes in distribution in the Kattegat.

3.3 Current Population Size

Seals are now hunted only in Finland, and Stenman reported that these catches are low - only a few dozen animals in the Gulf of Finland and a few hundred in the Bothnian Bay. Thus, estimates of population size must be based on direct surveys, with different techniques required for each species.

Ringed Seal

The only time when ringed seals can be readily counted is during late April or early May, when animals can be seen basking on what remains of the winter ice. Helle (1980a) carried out low-level surveys in the Bothnian Bay in 1975 and 1978 and used line transect techniques to estimate ringed seal density along the survey line. He calculated that there were 3 000 ringed seals hauled out in Bothnian Bay in each year. Almkvist reported that Soviet scientists had carried out aerial surveys of suitable ringed seal habitats in the Soviet waters of the Gulf of Finland and the Gulf of Riga during spring. They had counted about 2 600 seals in 1982 and estimated that they had missed 20% of the seals on the ice (Tormosov, pers. comm.). Allowing for these missed animals gives a figure, comparable to Helle's, of 3 000 seals. In addition, Stenman reported that in recent years no more than 100 ringed seals had been counted in April on the Finnish side of the Gulf of Finland. Thus, 6 000 is a minimum estimate of the current ringed seal population in the Baltic. However, it is very unlikely that the entire population will be basking at the same time. Canadian ringed seals are reported to spend 50-70% of their time basking in spring (Smith, 1973; Finley, 1979), but Soviet scientists believed that seals in the Gulf of Finland spend 88-90% of their time basking (Tormosov, pers. comm. to Almkvist). Thus, the current size of the population may be 7 000 - 12 000 animals.

Grey Seals

In the North Atlantic grey seal populations are usually censused by counting the number of pups born each year. However, this is a less satisfactory method in the Baltic because:

- (1) Pup numbers can only be readily converted to an estimate of total population size if the population has a stable age structure and if the age structure is known. This is certainly not the case in the Baltic. If fecundity rates are changing, as they may be in the Baltic, pup numbers do not even provide a reliable index of population size.
- (2) Baltic grey seals whelp on ice in small groups. The position of these groups is unpredictable from year to year and they are difficult to spot from the air. Thus aerial surveys are expensive and unreliable.

In Sweden, the numbers of seals hauled out during the summer have been counted since 1975. There are two problems: how to find all the haulout sites and how to count the seals at these sites. Sites have been identified from traditional information and postal surveys. It is believed that most of the sites in the central Baltic have been identified, but less is known about sites in northern Sweden. The largest number of seals is ashore in May-June, and surveys are usually conducted at this time either from the air, or by boat. Boats are particularly useful for finding new sites. The maximum number of seals counted at any one site is only 200, but a total of 750 animals has been counted at a number of sites over a short period. At the large haul-outs, the number ashore is relatively constant from April until November when it declines, presumably because the seals move to the Gulf of Bothnia and the Gulf of Finland. Similar surveys have been conducted in Finland, but not for so long. In the southwest archipelago the largest numbers are seen in the autumn; in the Gulf of Finland there is some evidence that the largest numbers occur in December. Stenman notes a report from an experienced seal hunter in the Gulf of Finland who had seen 500-750 grey seal pups on drifting ice in 1975. Soviet scientists also carry out surveys of skerries used by grey seals and they record any grey seals seen on ringed seal surveys.

From the results of these surveys, Almkvist (1982) suggested that the Baltic population is 1 000 - 1 500 seals, with 750 in Sweden, 300 in Finland and 100 - 150 in the USSR. About 25 grey seals, mostly males, are found in the Kattegat. They are counted during surveys for harbour seals (see below). A dead grey seal pup was found in the Kattegat in 1982 (Dietz and Heide-Jørgensen, 1982).

Harbour Seals

Harbour seals appear to occur in small groups, each having a rather restricted range. In the Swedish Baltic they are principally found at Falsterbo and in southern Karmarsund; they may also still occur in southern Gotland. In the Danish Baltic they occur around southern Sjælland. These localities have been surveyed occasionally using similar techniques to those described for Swedish grey seals. There may be about 200 harbour seals in the Baltic (Almkvist, 1982).

In the Kattegat harbour, seals occur on both the Danish and Swedish coasts and, as part of a co-operative project between these two nations, all the known sites have been surveyed from the air in a single day each year since 1979. The maximum numbers are hauled out in late August, and counts of these animals have increased from 2 300 in 1979 to 3 100 in 1981 (Heide-Jørgensen, this meeting). This figure includes seals in the Skagerrak.

3.4 Summary

The Working Group noted that all of the seal populations in the Baltic occur in the waters of more than one nation and, in most cases, in international waters also. This has made it difficult to coordinate surveys.

All the available evidence indicates that there has been a dramatic decline in all of the Baltic seal populations during the last 80 years. These populations are now between one tenth and one hundredth of their size is 1900. The harbour seal population in the Kattegat is probably no longer decreasing, but the exact status of the other populations is unknown.

4. POPULATION PARAMETERS

Much of the decline in Baltic seal populations has clearly been caused by excessive exploitation. Very few seals have been deliberately killed by man since 1976, yet only for the Kattegat harbour seal population is there any evidence of stabilization.

There is some evidence that fecundity and age at sexual maturity have declined recently, and there has been speculation (e.g., Almkvist <u>et al.</u>, 1980) that natural mortality has increased.

4.1 Fecundity

There are reliable estimates of fecundity (Helle, 1978, 1980b) for only one species (the ringed seal) in one area (the Bothnian Bay). These estimates are based on examination of the reproductive tracts of 225 females caught between 1973 and 1979 in the net fishery and 28 females shot in the same area. There is also some information on regnancy rate from animals taken in this fishery in 1957 to 1964, because bounties were paid on foetuses as well as adults. Bounties were paid on 1 158 animals over one year old and 372 foetuses in this period (Helle, 1978). If 50% of these animals were females and the catch had the same age structure as that observed by Helle (1980b) in 1973-78, this represents a fecundity of 68%.

Only 28% of the sexually mature females examined in 1973-79 carried a foetus (Helle, 1980b), although 98% of them had ovulated. Five per cent of the females had either decomposing or retarded foetuses, and 25% showed no signs of pregnancy. The remaining females had occlusions in either one or both uterine horns. The latter animals were clearly incapable of sustaining a pregnancy, making them effectively sterile. Only one of the 46 females with one occlusion was pregnant. Thus, the presence of a single occlusion appears to reduce fecundity by much more than half.

Estimates of fecundity for other Baltic and Skagerrak-Kattegat seal populations are uncertain. Material for studies of anatomy and pathology has been collected from seals around the Swedish coast including seals found dead. So far only preliminary results from 65 animals are available (Bergman et al., 1981). Occlusions were reported in 12 out of 20 ringed seals, 16 out of 38 grey seals, and 4 out of 7 harbour seals. Further data from this study are soon to be published. Stenman reported that some additional material had also been collected in the Gulf of Finland, and a few cases of occlusions have been identified.

4.1.1 Nature of Reduction in Fecundity

There appear to be three classes of sexually mature female ringed seals in the Baltic: Females with apparently normal reproductive tracts, most of these ovulate but in the Bothnian Bay area only approximately half of them actually give birth to a pup; females with one uterine horn occluded - most of these animals ovulate but only a small proportion complete a pregnancy; and females with both horns occluded, which are effectively sterile.

The Working Group noted that these different reproductive categories should be taken into account in any modelling of the dynamics of Baltic seal populations.

4.1.2 Causes of Reduced Fecundity

Reijnders (this meeting) reviewed the available information on the possible causes of reproductive failure in pinnipeds.

Pollutants, particularly PCBs and DDT, have been suggested as a cause of abortion in Californian sea lions <u>Zalophus</u> californius (Gilmartin <u>et al.</u>, 1976); failure of implantation or early resorbtion of the foetus in Dutch harbour seal (Reijnders, 1982); and resorbtion, abortion and occlusion formation in Baltic seals (Bergman <u>et al.</u>, 1981).

At present the only direct experimental evidence for the effect of pollutants on reproduction in carnivores comes from studies of mink (<u>Mustella</u> <u>vison</u>) in Canada, the United States and Sweden (Platanow and Karstad, 1973, Bleavins et al., 1980, Jensen et al., 1977). In all of these, reproductive success declined as the level of PCBs in the food was increased. In the Swedish experiments, mink fed fish with similar PCB levels to those found in the Baltic developed similar levels of PCBs in their body fat to those found in Baltic seals. Although implantation occurred normally, foetal deaths occurred after about one-third of the pregnancy time (Olsson, pers.comm. to Almkvist). However, none of the experimental animals developed uterine occlusions.

An experiment with harbour seals, in which two groups of seals are given food with different content of pollutants, has been started by Reijnders in Holland. The hormonal levels in the blood are monitored in order to describe and follow differences in the reproductive cycle. A first report is expected this autumn.

Baltic seals carry high levels of PCBs, similar to those causing reproductive failure in mink, and a working hypothesis is that these are responsible for their low reproductive rate (Bergman <u>et al.</u>, 1981). However, it is not clear how PCBs could cause uterine occlusions, although Bergman <u>et al.</u> (1981) suggest that they may form as a result of infection at the site of an abortion or resorbtion. Outside the Baltic and Swedish west coast, occlusions have been observed only in two grey seals from the Faroe Islands (Boyd, pers. comm. to Almkvist, and Harwood), and these may not be identical to those observed in the Baltic. The Working Group recommended that reproductive tracts from any female seals sampled outside the Baltic should be examined carefully for signs of occlusions.

It is possible that the reproductive failures observed in the Baltic may be caused by the particular combination of PCBs found there, or by a synergistic effect between PCBs, DDT and other pollutants (Helle, 1981). In addition, the Working Group noted that increasing disturbances could have made seals more vulnerable to the effects of pollutants. Stressed animals often have lower thresholds of tolerance to toxic substances.

Disturbance, particularly due to the increase in ice breaker traffic in the Bothnian Bay and Gulf of Finland since 1970, may have a direct effect on fecundity and juvenile survival, the latter effect is discussed in Section 4.2. Ringed seals, and perhaps grey seals, copulate in the water at the end of lactation and mating pairs may be particularly vulnerable to disturbance. Such an effect could account, in part, for the low fecundity in animals without occlusions observed by Helle (1980b). In parts of Shetland and the Wadensee, a reduction in the proportion of pups in the local harbour seal has been associated with an increase in disturbance, particularly from boats (SMRU and Reijnders, unpubl. data). However, this reduction may be the result of a redistribution of breeding animals.

4.1.3 Trends in Fecundity

Helle (1980b) observed a significant increase in the proportion of female ringed seals with occlusions at Simi in the Bothnian Bay from 1974/1975 to 1977/1979. However, there is no other information on the probability that an animal will move from one to another of the reproductive categories described in Section 4.1.1. In particular, it is not clear whether the total or partial sterility caused by the occlusions is reversible. Helle (1980b) believes that the material from Simi provides some indication that the occlusions can heal. On the other hand, Bergman (pers. comm. to Almkvist), after studies of the histopathology of the occlusions, has the opinion that most occlusions involve irreversible lesions.

Because of these problems and because the cause of the low fecundity and occlusions is not known with certainty, the Working Group was unable to make any predictions about future changes in fecundity.

4.2 Age at Sexual Maturity

The only long time series of information on age at sexual maturity comes from Soderberg's (1978) analysis of grey and ringed seal teeth collected as part of the Swedish bounty scheme. He used Hewer's (1964) conclusion that a change in the structure of annual laminae in the cementum, which is observed in most seal teeth, indicates the attainment of sexual maturity, and found that this age declined from about five years for seals born in the 1930s to about three years for seals born in the 1960s. However, Helle (1980) found no sexually mature animals less than five years old in his samples collected in the 1970s, whereas Soderberg's results suggest that many of those seals should have been mature. Similar trends in age at sexual maturity have also been observed in samples of ear plugs from a number of baleen whale species, but such results must always be interpreted with caution because older maturing animals from the most recent year classes are inevitably underrepresented and this can give a false impression of a decline in age at sexual maturity (Cook & de la Mare, 1983).

4.3 Juvenile Survival

There are no direct estimates of survival during the first year of life for any Baltic seal population, although the number of harbour seal pups found dead in the Kattegat has been recorded in recent years. Helle (1980) estimated that 84% of all ringed seals die in the first 10 years of life (equivalent to an annual survival of 83%) by applying age-specific fecundity rates for Canadian ringed seals to the age structure of the female seals caught in nets in the Bothnian Bay.

The Working Group identified three possible sources of juvenile mortality that may have arisen in recent years: early desertion of ringed and harbour seal pups due to disturbance; destruction of ringed seal lairs by ice breakers; and entanglement of seals in fishing nets.

Burns <u>et al.</u> (1982) found that Alaskan ringed seals within 150 m of seismic search lines were twice as likely to desert their ice lairs as those further away. It is therefore possible that the noise created by ice breakers may cause some female ringed seals in the Bothnian Bay and Gulf of Finland to desert their pups before they are completely weaned. This could result in a reduced growth and survival of pups. However, this is mere speculation and research is needed on the level of noise during the ringed seal whelping season and its effect on the seals. Such disturbance in the breeding areas is less likely to affect grey seals, but heavy boat traffic is known to disturb harbour seals.
Observers on ice breakers sometimes report that their vessel has cut through a ringed seal lair. This almost certainly results in the death of the pup, although the female may escape. Such reports are rare, but days are short at this time of year and accidents of this sort may be more frequent than these reports suggest. Grey seal pups are usually born on thick, compacted ice which is avoided by ice breakers, so they are probably less vulnerable than ringed seals. Almkvist <u>et al.</u> (1980) reported that of 100 grey seals tagged as pups in the Baltic, 20 were recovered drowned in fishing nets within six months of tagging. Entanglements of this sort may be a significant source of juvenile mortality, although in Finland young seals do not appear to be particularly vulnerable to entanglement (Helle, 1979, Table 1).

There are reports that eagles (<u>Haliaeetus albicilla</u>) and wolves (<u>Canis lupus</u>) used to prey on grey seal pups. These predators are now much less abundant than in the last century and presumably mortality from this source is much reduced.

4.4 Adult Survival

Hunting of seals in the Baltic virtually ceased in 1976, and this should have increased the survival rate for adults. However, there are no reliable estimates of adult survival. Age structure cannot be used to estimate this because all of the seal populations have suffered varying levels of exploitation.

4.5 Summary

The fecundity of ringed seals in the Bothnian Bay is unusually low for a seal species. This is partly because a high proportion of the females has been rendered sterile by uterine occlusions. Of the remaining females, less than 60% are pregnant. The fact that similar occlusions have been observed elsewhere in the Baltic suggest that fecundity may be low in all the populations. The exact cause of these low rates, and particularly of the uterine occlusions, is not known.

There is no evidence for a decline in either juvenile or adult survival, but survival rates are notoriously difficult to estimate precisely. The Working Group identified some factors which may cause reduced juvenile survival, and noted that the dynamics of populations of long-lived animals are more sensitive to changes in survival than to changes in fecundity (see, for example, Goodman, 1980).

5. PREDICTED CHANGES IN THE SIZE OF BALTIC SEAL POPULATIONS

Harwood (this meeting) presented a paper describing possible future changes in the ringed seal population of the Baltic. The predictions were based on the assumption that the population was stationary in the 1950s, with a pregnancy rate of 70%, and an age at sexual maturity of 6. If these assumptions are true, and if the fecundities observed at Simi by Helle (1978) apply to the entire Baltic population, then the population is decreasing by about 6% each year and will be reduced to half its current size in 13-14 years. If, however, the average age at sexual maturity is only 3, as estimated by Söderberg (1978), then the rate of decrease is rather less (about 4% each year) with the population halving in size every 20 years. If the decline in fecundity can be reversed, so that new females which are recruited to the breeding population do not develop occlusions, then the rate of decline in population size will gradually be reduced and, eventually, the population will stabilize at a new, low size (if the age at sexual maturity is 6 years) or begin to increase (if the age at sexual maturity has declined to 3 years). In the first case the decline will continue for up to 30 years, whereas in the second the population will begin to recover within 10 years. Both of these examples assume that females with occlusions remain sterile for the rest of their lives. If some do become fertile again then, with sexual maturity at 6 years, the decline will not continue for so long or, with sexual maturity at 3, the population will begin to recover almost immediately.

Harwood stressed that these predictions were highly speculative and merely gave an indication of the type and scale of any changes that might occur in the near future. They took no account of the possibility that juvenile survival may also have decreased since the 1950s. It was impossible to estimate the effects of this.

The estimates of current population size for all of the Baltic seal stocks are rather imprecise and the predicted changes in population size are small. Therefore, it will be difficult to detect the effects on population size of any changes in fecundity or survival rates.

6. CONCLUSIONS

With reference to the items which ICES Council asked the Working Group to consider, the Group concluded that:

- (I) If the fecundity rates estimated for ringed seals in the Bay of Bothnia apply to the entire Baltic population and to Baltic grey seals, then the populations will continue to decline, but relatively slowly - at most by about 6-7% each year. Aerial surveys of the harbour seal population in the Kattegat and Skagerrak indicate that it is probably no longer declining.
- (II) The Working Group could find no evidnece for a direct link between high levels of PCBs, DDT and other pollutants and the low level of reproductive success observed in Baltic seals. However, it concluded that at least part of the reduction in fecundity, particularly the failure of otherwise fertile females to carry a pregnancy to term, could, on the basis of tests with mink, be due to effects of PCBs during the first third of pregnancy.
- (III) Because of the rather weak conclusions above, it is not possible to predict the effects of changes in pollutant levels. However, levels of PCBs and DDT in guillemot (Uria aalge) eggs collected from Gotland over the last 13 years show a significant decline since the early 1970s. Decreases since the early 1970s in PCB levels have also been documented for pike (Esox lucius) in southwest Finland (Moilanen et al., 1982) and the Baltic herring (Clupea harengus) in the Gulf of Finland (Paasivirta and Linko, 1980). If these are true indications of environmental levels in the Baltic, and if these pollutants really are responsible for most of the observed decline in fecundity, then the rate of decline of the population described in (I) should reduce and the populations may eventually begin to increase. However, all of these changes will be small and difficult to detect.

- (IV) The Working Group concluded that environmental disturbance, particularly increased ice breaker traffic on the breeding grounds of grey and ringed seals and general disturbance around haul-out sites used by harbour seals, could cause a reduction in juvenile survival and possibly in fecundity. However, there was no direct evidence for either effect in the Baltic.
- (V) Recommendations for conservation and research are described in Section 7.

7. CONSERVATION AND RESEARCH

7.1 Current Conservation Measures

In Denmark all species of seal are fully protected, in the USSR grey seals have been protected since 1975 and ringed seals since 1980. In Sweden all seals are generally protected but fishermen are permitted to kill seals around their nets. In Finland grey seal are completely protected but ringed seals may be hunted in the Finnish sea area (excluding Åland) between 20 March and 10 June. There is no formal protection of seals in international waters but it is illegal to import skins into the countries of any of the signatories of the Gdańsk Convention.

Sweden and Denmark have established a network of seal sanctuaries (see Figure 1). The regulation of the Swedish sanctuaries varies from place to place, but in all of them admittance over a radius of between 1 km and 1 nm is forbidden for at least part of the year, although fishermen are allowed to pass through this area on the way to their fishing grounds. Research is possible with special permission, but fishermen are not allowed to kill seals within the sanctuary. In some areas over-flying by aircraft is forbidden. There are three Danish sanctuaries, two in the Baltic and one in the Kattegat. At present there are no sanctuaries in Finland, but one has been proposed as part of a 400 km² marine park on the north shore of the Gulf of Finland. This is the second most important area for grey seals in Finland. Within the sanctuary, hunting of ringed seals will be prohibited, and other forms of hunting will be restricted.

Almkvist reported that a captive group of two male and two female grey seals had been established near Uppsala in the grounds of a nuclear power station. The seals are being fed on fish from the North Atlantic and any pups that are produced will be released near existing small grey seal groups.

7.2 Recommendations for Conservation

The Working Group took into account and endorsed the recommendations of the 2nd and 3rd Symposia on the Conservation of Baltic seals in Haikko, Finland in 1977 and Konstancin, Poland in 1980. It also took note of the recommendations for Soviet-Swedish Seal Research Co-operation prepared by the Soviet-Swedish Working Group on Environmental Problems in the USSR on 10-15 April, 1983.

The following actions are necessary:

1. Existing seal sanctuaries in Sweden and Denmark should be maintained, and the seal sanctuary proposed for Finland should be established as soon as possible. It may be necessary to establish additional sanctuaries in Finland.

- 2. Efforts should be made to reduce disturbance in seal breeding areas, the exact action to be taken will depend on the results of the research recommended in 7.3
- 3. A studbook should be compiled of all Baltic seals held in captivity by zoological gardens and seal-breeding centres. Warsaw Zoological Garden has agreed to compile such a studbook.
- 4. The research described below should be conducted as soon as possible.

7.3 Recommendations for Research

In addition to recommending that all existing studies of Baltic seals (such as routine monitoring of population size, and studies of the pathology and anatomy of the reproductive organs) should be continued, the Working Group also identified a number of areas where further research is needed.

- 1. It is particularly important to be able to monitor trends in pregnancy rates and age at sexual mortality. To this end as much material as possible should be collected from seals taken in by hunters in Finland, and the possibility of obtaining additional information from laminar structures in teeth should be investigated. The validity of estimates of age at sexual maturity from changes in these laminae should also be checked.
- 2. The effect of disturbance to ringed seals on their breeding grounds should be investigated. Information is required on the distribution of ringed seal birth lairs with respect to the routes normally followed by ice breakers in the Bothnian Bay and Gulf of Finland, the amount of noise produced by the ice breakers and how it is propogated through the ice, and the effect of the noise on maternal and sexual behaviour. Ice breaker captains should be asked to keep a record of the number of seal lairs they hit, and the length of time during each voyage when this could be observed.
- 3. There is a lack of information on the normal anatomy, histology and pathology of the seal species occurring in the Baltic. ICES members are encouraged to collect, or make available, appropriate material for comparison with samples from the Baltic.
- 4. Some study is needed to see whether the grey seals in the Baltic merit sub-species status.

7.4 Seals and Fisheries

Even the most optimistic predictions about the Baltic seal stocks suggest that they will not increase by more than a few per cent each year. It will, therefore, be many years before they can recover to their levels in the 1950s, let alone the levels at the beginning of this century. Therefore, the Working Group concluded that at present the Baltic seal populations cannot pose any significant threat to commercial fisheries.

The Working Group noted that if the diet of Baltic seals is to be studied in greater detail, faecal analysis is a more efficient and less destructive technique for this than shooting seals to collect stomachs. 8. References

- Almkvist, L. 1982. Baltic marine mammals a status report. Doc. ICES C.M. 1982/N:16.
- Almkvist, L, Olsson, M and Söderberg, S. 1980. Sälar i Sverige. Svenska Naturskyddsföreningen, Stockholm. 80 pp.
- Bergman, A, Olsson, M and Reutergårdh, L. 1981. Lowered reproductive rate in seal population and PCB. A discussion of comparability of results and a presentation of some data from research on the Baltic seals. Doc. ICES C.M. 1981/N:10.
- Bleavins, M R, Aulerich, R J, and Ringer, R K. 1980. Polychlorinated biphenyls (Arochlors 1016 and 1242): Effects on survival and reproduction in mink and ferrets. Arch. Environm. Contam. Toxicol. 9, 627-635.
- Burns, JJ, Shapiro, L H, and Fay, F H. 1981. Ice as marine mammal habitat in the Berring Sea. <u>In</u>: The Eastern Berring Sea Shelf: Oceanography and Resources (Hood, D W and Calder, J A, Eds.) Vol 2, pp. 781-797.
- Cooke, J G and de la Mare, W K. 1983. Some notes on the estimation of time trends in the age at sexual maturity in baleen whales from transition layer data. IWC SC/A83/AW3.
- Dietz, R and Heide-Jørgensen, M P. 1982. A new breeding attempt of grey seals (Halichoerus grypus) in the Kattegat. Doc. ICES C.M.1982/N:12.
- Finley, K. 1979. Haul-out behaviour and densities of ringed seals (<u>Phoca hispida</u>) in the Barrow Strait area, NWT. Can. J. Zool. 57, 1985-1997.
- Gilmartin, W G, Delong, R L, Smith, A W, Sweeney, J C, de Lappe, B W, Risebrough, R W, Griner, L A, Dailey, M D, and Peakall, D B. 1976. Premature parturition in the California sea lion. J. Wildl. Dis. <u>12</u>, 104-115.
- Goodman, D. 1980. Demographic intervention for closely managed populations. <u>In</u>: Conservation Biology: An Evolutionary-Ecological Perspective. (Soulé, M E and Wilcox, B A, Eds.). Sinauer Associates Inc., Massachusetts. pp. 171-195.
- Heide-Jørgensen, M P. 1980. Sælbestandene i de danske farvande. <u>In</u>: Status over den danske plante- og dyreverden. Fredningsstyrelsen. pp. 292-306.
- Helle, E O. 1978. On the reproductive success in the Bothnian Bay population of the ringed seal and future prospects for the species. Finnish Game Res. <u>37</u>, 32-35.
- Helle, E O. 1979. Structure and numbers of seal populations in the northern Baltic Sea: a study on Finnish bounty statistics, 1956-1975. Aquilo. Ser. Zool. <u>19</u>.

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Helle, E O. 1980a. Aerial census of ringed seals (<u>Pusa hispida</u>) basking on the ice of the Bothnian Bay, Baltic. Holarct. Ecol. <u>3</u>, 183-189.

- Helle, E O. 1980b. Lowered reproductive capacity in female ringed seals (<u>Pusa hispida</u>) in the Bothnian Bay, northern Baltic Sea, with special reference to uterine occlusions. Ann. Zool. Fennici <u>17</u>, 147-158.
- Helle, E O. 1981. Reproductive trends and occurrence of organochlorines and heavy metals in the Baltic seal populations. ICES C.M.1981/E:37.
- Hewer, H R. 1964. The determination of age, sexual maturity, longevity and life-table in the grey seal (<u>Halichoerus grypus</u>). Proc. Zool. Soc. Lond. <u>142</u>, 593-624.
- Jensen, S, Kihlström, J E, Olsson, M, and Orberg, J. 1977. Effects of PCB and DDT on mink (<u>Mustella vison</u>) during the reproductive season. Ambio 6, 239.
- Moilanen, R, Pyysalo, H, Wickström, K, and Linko, R. 1982. Time trends of chlordane, DDT and PCB concentrations in pike (<u>Esox lucius</u>) and Baltic herring (<u>Clupea harengus</u>) in the Turku archipelago, northern Baltic Sea, for the period 1971-1982. Bull. Environm. Contam-Toxicol. 29, 334-340.
- Paasivirta, J and Linko, R. 1980. Environmental toxins in Finnish wildlife. A study of time trends of residue content in fish during 1973-1978. Chemosphere <u>9</u>, 643-661.
- Platanow, N S and Karstad, L H. 1973. Dietary effects of polychlorinated biphenyls in mink. Can. J. Comp. Med. 37, 391-400.
- Reijnders, P J H. 1982. Diminished fertility in seals in the Netherlands, possibly resulting from exposure to large amounts of polychlorinated biphenyls. Tijdschrift Diergeneesk. <u>107</u> (10), 363-367 (in Dutch, with English summary).
- Smith, T G. 1973. Population dynamics of the ringed seal in the Canadian eastern Arctic. Fish. Res. Board Can., Bull. <u>181</u>, 1-55.
- Söderberg, S. 1978. Falling age at sexual maturity in Baltic seals. Finnish Game Res. <u>37</u>, 27-31.

APPENDIX 1: AGENDA

- 1. Introductory remarks
- 2. Past changes in the size of the Baltic seal populations
- 3. Recent changes in population parameters 3.1 Reproduction 3.1.1 Effects of pollution 3.1.2 Effects of disturbance
 - 3.2 Survival
- 4. Predicted changes in the size of Baltic seal populations
 4.1 With no change in the environment
 4.2 If appropriate changes are made
- 5. Recommendations for the conservations of Baltic seal stocks

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APPENDIX 3: WORKING PAPERS

WP1	Harwood, J	Future trends in Baltic seal populations
WP2	Heide-Jørgensen, M P	Monitoring seal stocks in the Kattegat - with an appendix on seal herds in the Øresund and the western Baltic
WP3	Reijnders, P J H	Man-induced environmental factors in relation to fertility changes in pinnipeds



ANNEX 9

PLANS FOR THE 1985 BASELINE STUDY OF CONTAMINANTS IN FISH AND SHELLFISH

BALTIC COMPONENT

An excellent response was received from the countries around the Baltic Sea. Although not all the persons written to responded directly, a response was received from all countries, including one of the Republics of the USSR. There appears to be firm intentions to sample all areas of the Baltic Sea. In most cases countries did not indicate how many samples would be collected from each area, but where this was indicated it would appear that 1-3 samples will be taken per area. Poland indicated that it hoped to collect samples on two occasions during the year, although official confirmation of Polish participation had still not been received by mid-September 1984. The species listed are those intended for sampling; not all species may be available, therefore these data represent the best picture.

Of the so-called mandatory metals, only arsenic will not be analysed by all countries and mercury will not be analysed by Poland.

Most countries, USSR and Denmark are the exceptions, indicated that they would analyse for organochlorine residues; Denmark did indicate that they hoped to do so but were not sure where the work would be done.

The samples to be collected are listed below according to ICES fishing areas.

AREA 21 -	Coast shared by Sweden (east) and Denmark (west)						
Sweden	will collect cod, herring, dab and mussels						
	will analyse for Hg, Cu, Zn, Cd, Pb, DDT and PCBs						
Denmark	will collect cod, herring, plaice, flounder and possibly mussels						
	will analyse for Hg, Cu, Zn, Cd, As, Cr, and Ni in selected tissues						
<u>AREA 22</u> -	Coast shared by Denmark, Federal Republic of Germany and German Democratic Republic						
Denmark	will collect plaice, flounder and possibly mussels						
	will analyse for Hg, Cu, Zn, Cd, As, Cr, and Ni in selected tissues						
Federal	will collect cod and herring						
Republic of Germany	will analyse for Hg, Cu, Zn, Cd, Pb, As, HCH, DDT group, PCBs, HCB, dieldrin and chlordane						

	German	will collect cod, herring and flounder
	Democratic Republic	will analyse for Hg, Cu, Zn, Cd, Pb, and possibly Ni, Cr, Mn, DDT, PCBs and possibly HCH and HCB
	AREA 23 -	Coast shared by Denmark and Sweden
	Denmark	will collect cod, herring, plaice, flounder and possibly mussels
		will analyse for Hg, Cu, Zn, Cd, As, Cr, and Ni in selected tissues
	AREA 24 -	Coast shared by Sweden (north) and Denmark, German Democratic
		Republic and Poland
	Denmark	will collect plaice, flounder and possibly mussels
		will analyse for Hg, Cu, Zn, Cd, As, Cr, and Ni in selected tissues
	Federal	will collect cod and herring
	Republic of Germany	will analyse for Hg, Cu, Zn, Cd, Pb, As, HCH, DDT group, PCBs, HCB, dieldrin, chlordane
	German	will collect cod, herring and flounder
2	Democratic Republic	will analyse for Hg, Cu, Zn, Cd, Pb, DDT, PCBs and possibly Cr, Ni, Mn, HCH and HCB
	Poland	will collect cod, herring, flounder, mussels (plus sprat and <u>Macoma</u>) from one sub-area
		will analyse for Cu, Zn, Cd, Pb, DDT group and PCBs
	AREA 25 -	Coast shared by Sweden, Poland and Denmark
	Sweden	will collect herring, flounder and mussels
		will analyse for Hg, Cu, Zn, Cd, Pb, DDT and PCBs
	Denmark	will collect mussels
		will analyse for Hg, Cu, Zn, Cd, As, Cr and Ni
	Poland	will collect cod, herring, flounder, mussels (plus sprat and <u>Macoma</u>) from up to 3 sub-areas
		will analyse for Cu, Zn, Cd, Pb, DDT group, PCBs
	AREA 27 -	Sweden
	Sweden	will collect herring, flounder, mussels
		will analyse for Hg, Cu, Zn, Cd, Pb, DDT and PCBs

-	Sweden (west) and Finland (east)						
	will collect herring and possibly cod						
	will analyse for Hg, Cu, Zn, Cd, Pb, DDT and PCBs						
	will collect cod, herring, Mesidotea and Macoma						
	will analyse for Hg, Cu, Zn, Cd, Pb, DDT group and PCBs						
-	Sweden (west) and Finland (east)						
	will collect herring						
	will analyse for Hg, Cu, Zn, Cd, Pb, DDT and PCBs						
	will collect cod, herring, Mesidotea and Macoma						
	will analyse for Hg, Cu, Zn, Cd, Pb, DDT group and PCBs						
-	Finland, USSR, Sweden						
	will collect samples of cod, herring, Mesidotea and Macoma						
	will analyse for Hg, Cu, Zn, Cd, Pb, DDT group, PCBs						
-	Finland and USSR						
	will collect cod, herring, Mesidotea and Macoma						
	will analyse for Hg, Cu, Zn, Cd, Pb, DDT group and PCBs						
-	USSR						
	will collect cod, herring and mussels, 2 samples of each species						
	will analyse for Hg, Cu, Zn, Cd, Pb, Cr, Ni, Mn, Co, Sr, Ca and Mg						
	will collect cod and analyse for Hg, Cu, Zn, Cd, Pb, DDT group and PCBs						
-	USSR and Poland						
	will collect cod, herring, flounder, mussels (and sprat and Macoma) from one sub-area						
	will analyse for Cu. Zn. Cd. Pb. DDT group. PCBs						
	with anotype for out bing out i be bbt proupe forb						

NORTH SEA - NORTH ATLANTIC COMPONENT

The response from the countries bordering the North Atlantic was, by comparison to that received from the Baltic group, disappointing.

As will be apparent from the details summarised below, the coverage which can be expected ranges from extensive to minimal. From the responses received, it seems probable that on the eastern side of the Atlantic there will be no sampling in areas Vb, VIb, VII, c, h, j or k; X, XII, XIVa, XIVb. However, there seems likely to be good coverage of the North Sea, Irish Sea, English Channel (both sides) and the Norwegian coast, with mussels collected at sites along most countries' coastlines and at least cod and plaice being collected from most areas (generally several samples). Norway also indicated that a few extra samples could be collected in the Barents Sea if this is regarded as necessary.

On the western side of the Atlantic, coverage is generally likely to be poor, as only 3 areas will be sampled by the USA and only 4 samples of direct relevance will be collected by Canada. The determinands to be analysed in that area also seem likely to be restricted.

Of the eastern Atlantic countries, all have indicated that they intend to analyse for all the "mandatory" metals and most have also indicated their intention to analyse for the common organochlorine pesticide residues and PCBs, although Denmark had still (mid-September 1984) not confirmed whether they had analytical facilities available for organochlorines.

<u>NORWAY</u> will analyse samples from areas I, IIa, IIb, IIIa, IVa and IVb for Hg, Cu, Zn, Cd, Pb, As, HCH, HCB, DDT group, dieldrin and PCBs (plus hydrocarbons, PAHs and PCB isomers).

Area

I	will be sampled for cod, plaice and herring; 2 sites
IIa	will be sampled for cod, plaice, herring and mussels; 2 sites, and cod plus herring; 1 site
IIb	will be sampled for cod and herring; 1 site
IIIa	will be sampled for cod, plaice and mussels; 2 sites
IVa	will be sampled for cod, plaice and mussels; 2 sites
IVb	will be sampled for cod and mussels; 1 site.

DENMARK will analyse samples from areas IIIa, IVa, and IVb for Hg, Cu, Zn, Cd, Pb, As, plus Cr and Ni in mussels and possibly organochlorines.

Area

IIIa	will be 3 sites	sampled	for	cod,	plaice,	herring	and	pos	sibly	muss	sels;
IVa	will be	sampled	for	cod,	plaice	and herr	ing;	2	sites		
IVb	will be 2 sites	sampled - possib	for ly m	cod,	plaice,	herring	and	mus	sels;	at	least

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SWEDEN will analyse samples of flounder and mussels from area IIIa for Hg, Cu, Zn, Cd, Pb, DDT and PCBs.

FEDERAL REPUBLIC OF GERMANY will analyse samples from at least 2 sites in the Inner German Bight area of IVb for Hg, Cu, Zn, Cd, Pb, As, HCH, HCB, DDT group, dieldrin, PCBs and chlordane.

Area

IVb will be sampled for cod, plaice, flounder, dab and mussels.

<u>NETHERLANDS</u> will analyse samples for Hg, Cu, Cd, Pb, As, HCH, HCB, DDT group, PCBs, dieldrin and in the case of cod and hake liver, only chlordanes. Mussels will also be analysed for PAHs. Samples will be collected as follows:

Area

IVc	flounder,	3-4 sites;
	herring,	2 sites;
	cod,	1 site; and
	mussels,	6-7 sites
IVa & 1	cod, herring,	2 sites; 1-2 sites

Areas VIIb-c, VII g-h, VIId e and VIII up to 4 samples, one from each area, of hake.

BELGIUM will analyse samples from area IVc on their coast and from up to 4 other areas in either IVc or IVb for Hg, Cu, Zn, Cd, Pb, As, Ni, Cr, HCH, HCB, DDT group, PCBs, dieldrin and heptachlor epoxide.

Area

IVc will be sampled for cod, flounder, plaice and mussels; at least 1 site.

FRANCE will analyse samples of mussels and plaice from areas VIId-e and VIII for Hg, Cu, Zn, Cd, Pb, and DDT group, HCH, PCBs and PAHs. The number of samples to be analysed from each area are 190 and 200, respectively.

SPAIN - No reply.

<u>PORTUGAL</u> will analyse samples of mussels from several sites along the <u>coast of</u> Portugal (Area IX). These will be analysed for Hg, Cu, Zn, Cd, Pb and organochlorine compounds. Data normally submitted to the JMP of the Oslo and Paris Commissions will also be supplied. These include data on Hg in fish flesh.

ICELAND will analyse samples of cod (4 sites), herring (1 site), plaice (2 sites) and mussels (4 sites) from area Va. These samples will be analysed for Hg, Cu, Zn, Cd, Pb, As and chlorinated hydrocarbons.

GREENLAND - Not participating.

IRELAND will analyse samples of cod, plaice, herring and mussels from at least one site in each of the following areas: VIIa, VIIg, VIIj, VIIb, VIa. Each sample will be analysed for Hg, Cu, Zn, Cd, HCH, HCB, DDT group, dieldrin and PCBs. ENGLAND AND WALES will analyse samples from IVb, IVc, VIIa, d, e, f and g for Hg, Cu, Zn, Cd, Pb, As, HCH, HCB, DDT group, PCBs, dieldrin.

- Area IVb will be sampled for cod, plaice, flounder, dab and mussels; at least 2 sites VIc will be sampled for cod, plaice, flounder, dab and mussels; 2 sites for fish, plus mussels 9 sites will be sampled for cod, plaice, flounder and dab; VIId 1 site, plus mussels 5 sites VIIe will be sampled for cod, plaice, flounder and dab; 1 site, plus mussels 4 sites VIIf will be sampled for cod, plaice, flounder and dab; 2 sites, plus mussels 7 sites VIIg-k will be sampled for cod, plaice and hake; 1 site
- VIIa will be sampled for cod, plaice, flounder and dab; 3 sites, plus mussels 9 sites

SCOTLAND will analyse samples from areas IVa, IVb, VIa and VIIa for Hg, Cu, Zn, Cd, Pb, As, HCH, HCB, DDT group, PCBs, dieldrin, chlordane. All fish and shellfish samples will be analysed for metals and most will be analysed for the organochlorines.

Area

IVa	will be	sampled	for (cod	and plaice,	3-4 sites;
	herring	and muss	sels.	12	sites	

- IVb will be sampled for cod and plaice, 1-2 sites; herring, 1 site; flounder, 4 sites; and mussels, 19 sites
- VIa will be sampled for cod and plaice, 4 sites; herring, 2 sites; flounder, 1 site; and mussels, 24 sites
- VIIa will be sampled for flounder, 1 site; and mussels, 7 sites

USA will analyse samples from blocks 5%, 5% and 6A for Cu, Zn, Cd and Pb, possibly Ni, Hg, As, Cr, Se, Sn and Mn.

Area

5 Z e	will	be	sampled	for	winter	flounder	;	
5 Z w	will	be	sampled	for	winter	flounder	and	mussels;
6A	will	be	sampled	for	winter	flounder	and	mussels

<u>CANADA</u> will analyse samples of cod from areas 4W, 30, 3M and 4T. All samples will be analysed for organochlorines and those from 4W, 30 and 3M will also be analysed for Cd, Cu, Zn, Se, Ag and Hg. In addition, samples of scallops will be taken from areas 52e, 4X and 4T and all will be analysed for Cd and some also for Pb. Herring will be taken from 3L (Trinity Bay) and will be analysed for organochlorines.

Lobsters will be taken from 4Vn (Sidney Harbour) and will be analysed for PAHs.

The word organochlorines here means PCBs, HCB and γ -HCH plus toxaphene.



ICES Statistical Rectangles in the Baltic Sea.



ICES Fishing Areas in the Northeast Atlantic and NAFO Fishing Areas in the Northwest Atlantic.



ICES FISHING AREAS

ANALYSTS FOR METALS

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USSR		Only contact (probably <u>not</u> analyst) is Director. Dr G Andrushaitis Academy of Sciences of Latvian SSR Institute of Biology Riga 229021

NOTE

 All analysts should take part in the quality assurance programme devised by the Marine Chemistry Working Group (MCWG) (for details, see Doc. ICES, C.M. 1984/E:45). For supplies of the appropriate samples, analysts should contact

> Dr S Berman National Research Council Division of Chemistry Ottawa, Ont. K1A OR9 CANADA.

(2) There is some doubt about the overall comparability that can be achieved in the analysis of arsenic and lead. Special measures may be necessary to resolve this. All analysts who plan to determine these elements should, therefore, ensure that they are made aware of the decisions of the MCWG on this issue after its meeting in late February 1985.

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ANALYSTS FOR ORGANOCHLORINES, etc.

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<u>USA</u> Mr R Grieg Milford Laboratory NMFS/NOAA, 212 Rogers Avenue Milford, Connecticut 06460

USSR

NOTE

It is unlikely that a quality assurance scheme or intercalibration exercise for organochlorine compounds will be offered in connection with the 1985 Baseline Study. It is therefore recommended that analysts who carry out work on these substances for this study should:

- (a) attempt to retain duplicate material for subsequent check analysis (store at not less than -20°C);
- (b) attempt to ensure some overlap in their sampling with that undertaken by other analysts;
- (c) ensure, to the best of their ability, that their results are accurate and precise, e.g., by national quality assurance schemes.

Procedures to be followed for sample collection, preparation and analysis

The aim of the proposed study is to meet monitoring objective 2 of ICES, i.e., to provide, over a wide geographical area, an indication of the health of the marine environment. The fish and shellfish used therefore are intended to serve as indicators of the level of contamination of the marine environment and the samples to be collected should therefore be as comparable as possible. It is also important that the samples be treated in a similar way and that the analytical procedures used are as comparable as practicable. In an attempt to ensure the latter, analysts are being requested to take part in an analytical quality control exercise for metals (and organochlorine pesticide and PCB residues).

The procedures for sampling and analysis have been agreed previously and most are published in ICES Cooperative Research Report No. 126, Appendix 1. However, for the sake of convenience and easy reference, the relevant details are reproduced below. Sample Collection

All samples should be collected in 1985, preferably in the first six months.

- (a) A sample should consist of 25 fish or 50 mussels.
- (b) Fish should be selected so as to be representative of the area in question, i.e., they should not be very recent immigrants to the area or on passage through it. Each sample should consist of the same or similar sized fish.
- (c) Mussels should be between 20 and 50 mm in size and preferably as close to the lower end of this range as possible. 20-30 mm is strongly recommended for all areas, especially those in the Baltic Sea.
- (d) Sampling should take place prior to spawning of the species concerned.
- (e) All fish should be aged and only 2-year-old fish (2-ring herring) should be used to make up the sample.
- (f) Mussels should be collected from a position on the shore such that they are immersed in water for at least 6 hours of each tidal cycle.

Storage and pre-treatment of samples prior to analysis

- (a) Fish samples should be collected ungutted and preserved (deep frozen) as soon as practicable after collection; length and weight should be determined before freezing.
- (b) Mussels should be held live in clear (settled) sea water from the area of collection for 12-24 hours to allow discharge of pseudo-faeces. The shell length of each individual, even if used as part of a composite, should be measured as a maximum value regardless of direction of orientation.
- (c) After cleaning and measuring the mussels, the individual animals should be carefully freed from their shells by cutting the adductor muscle. The shell cavity liquor can then be drained and discarded by placing the opened shells vertically in a filter funnel for 5 minutes. The remaining shell contents may then be preserved either individually or as pooled samples. The weight of the dry shells should be measured and recorded (see Doc. ICES, C.M.1984/E:41 for details).
- (d) In order to reduce the number of analyses which have to be performed, pooled samples of fish may be used. These should be prepared as described below and analysed in duplicate.
- (e) An equivalent quantity of muscle tissue must be taken from each fish, e.g., a whole fillet of every fish. If the total quantity of tissue so yielded would be too large to be handled conveniently, the tissue may be sub-sampled, but a fixed proportion of each tissue must then be taken, e.g., 10% of each whole fillet or 10% of each whole liver, the sub-sample being taken after homogenisation of the whole fillet/liver or in the form of complete longitudinal sections.

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Reporting of Results

- (a) Results should be reported on a wet weight basis. In addition, results of analyses of mussels for metals should also be reported on a dry weight basis. All results of analyses for organochlorine compounds must be reported also on an extracted fat weight basis or as a minimum be accompanied by a fat weight determination result.
- (b) Dry weight determinations should be carried out in duplicate by airdrying to constant weight at 105°C of sub-samples of the material analysed for the contaminants.
- (c) Fat weight should be determined on a sub-sample of the extract used for the organochlorine compound analyses. The results should be accompanied by a brief description of the method used for extraction.
- (d) Results should be submitted to the ICES Environment Officer not later than 30 June 1986, using the ICES Interim Reporting Format for Contaminants in Fish and Shellfish. These results should be accompanied by the name of the contributing laboratory(s) and the name of an individual contact in the event of queries. The contributors should specify the most recent ICES intercalibration exercise in which they took part. A brief commentary on the data would also be welcomed.
- (e) Whether or not a commentary is provided, the results should be accompanied by details of the size range of the sample, details of the site, date and method of collection and, if appropriate, the method of preserving the sample prior to analysis. Brief details of the method of analysis used should be provided and if PCBs are determined these details should include the formulation or congener(s) and the method of quantitation used.

ANNEX 10

IMPACT OF WASTES FROM

THE TITANIUM DIOXIDE INDUSTRY DISCHARGED INTO THE NORTH SEA

- 1. The following figures and assumptions have been used in the subsequent calculations:
 - Volume of the North Sea = $5 \times 10^{13} \text{m}^3$
 - Area of the North Sea = $5.8 \times 10^{5} \text{km}^2$
 - Flushing time of the North Sea = 2 years
 - Net movement of water along the Belgian, Netherlands, Federal Republic of Germany coastal belt = 1.9 km · day⁻¹ (Topping, 1978)
 - Average iron (Fe) content of North Sea sediments = 3%
 - Aggregate rate of dumping/discharge of wastes from the TiO₂ industry by the Federal Republic of Germany, the Netherlands and Belgium is 5 900 tonnes • day⁻¹ (see attached table)
 - Aggregate rate of dumping/discharge of iron (Fe) in wastes from the TiO₂ industry by the Federal Republic of Germany, the Netherlands and Belgium is 460 tonnes day⁻¹ (see attached table)
 - Aggregate rate of dumping/discharge of iron (Fe) in wastes from the TiO₂ industry by the Federal Republic of Germany, the Netherlands, Belgium and the United Kingdom is 639 tonnes day⁻¹ (see attached table)
 - Discharge of wastes from the TiO₂ industry by France is 1 000 tonnes • day⁻¹ with iron content similar to that of wastes dumped/discharged by other countries
 - The lowest concentration of wastes from the TiO_2 industry in water causing a detectable sub-lethal effect on marine life is 1 part waste in 45 000 parts water (Kayser, 1969). This corresponds to a concentration of waste in water of 2.2 x 10^{-5} (or 22 ppm).
- 2. Assessment of the effects of waste from the TiO_2 industry on organisms in the North Sea as a whole (Best Case Assessment).

If it is further assumed that the waste discharged becomes uniformly distributed throughout the entire body of the North Sea, the volume of water available annually for waste assimilation/dilution is

$$\frac{\text{Volume of the North Sea}}{\text{Turnover Time}} = \frac{5 \times 10^{13} \text{m}^3}{2 \text{ yrs}} = 2.5 \times 10^{13} \text{m}^3 \cdot \text{yr}^{-1}$$

The effective concentration of TiO_2 waste in water of the North Sea will be

Annual discharge of waste Mass of water available for assimilation/dilution

$$= \frac{6 \times 10^3 \text{ tonnes } \cdot \text{ day}^{-1} \times 365 \text{ day } \cdot \text{ yr}^{-1} \times 5^*}{2.5 \times 10^{13} \text{m}^3 \cdot \text{yr}^{-1}}$$

= $4.4 \times 10^{-7} \text{ tonnes } \cdot \text{m}^{-3}$

assuming the density of North Sea water = 1 tonne \cdot m⁻³.

The concentration derived from this calculation, i.e., 4.4×10^{-7} tonnes $\cdot m^{-3}$ or 0.44 ppm, is a factor of 50 lower than the lowest concentration at which detectable sub-lethal effects on marine life occur (i.e., 2.2 x 10^{-5} tonnes $\cdot m^{-3}$ or 22 ppm). Therefore, while deleterious effects on marine life in the North Sea as a whole are most unlikely, it is probable that effects do occur on smaller spatial scales, since complete mixing of the wastes throughout the North Sea is unlikely.

3. Assessment of effects on organisms within the Belgium, Netherlands, Federal Republic of Germany coastal zone (Worst Case Assessment).

If it is assumed that the wastes from the TiO_2 industry discharged or dumped by Belgium, the Netherlands and the Federal Republic of Germany are all retained within a 30 km-wide belt (of average depth 25 m) along the western North Sea coast, the volume of water available for assimilating/diluting these wastes is

Volume of the coastal belt = cross-section area x Mean Water Transport = $30 \text{ km} \times 25 \text{ m} \times 1.9 \text{ km} \cdot \text{day}^{-1} = 1.4 \times 10^{9} \text{m}^3 \cdot \text{day}^{-1}$.

The concentration of wastes in this coastal belt then becomes

Mass of waste dumped/discharged per unit time Mass of water available for waste assimilation per unit time

$$= \frac{6 \times 10^3 \text{ tonnes } \cdot \text{ day}^{-1}}{1.4 \times 10^9 \text{ tonnes } \cdot \text{ day}^{-1}} = 4.3 \times 10^{-6}$$

The concentration derived from this calculation $(4.3 \times 10^{-6} \text{ tonnes} \cdot \text{m}^{-3} \text{ or } 4.3 \text{ ppm})$ is only a factor of 5 lower than the lowest concentration at which detectable sub-lethal effects on marine organisms occur $(2.2 \times 10^{-5} \text{ tonnes} \cdot \text{m}^{-3} \text{ or } 22 \text{ ppm})$. Furthermore, this safety factor must be viewed against the probability that the coastal water flow may already be contaminated by wastes arising from countries situated "upstream" of this flow, for example, France. Clearly, deleterious effects over scales comparable with that of such a coastal belt must be expected and are likely to be most evident in sub-areas of slightly smaller spatial scales. Any periodicity in the discharge/dumping practices in the area may result in significantly greater impact in the receiving areas but is unlikely to affect the North Sea as a whole.

The factor of 5 introduced here is to allow (conservatively) for all additional discharge/dumping of wastes from the TiO_2 industry into the North Sea by countries other than the Netherlands, the Federal Republic of Germany and Belgium.

TABLE

Discharges/Dumping of Wastes from the TiO₂ Industry by Countries Bordering the North Sea

Country of Origin	Wastes Discharged/Dumped	Iron Content	Rate of Iron Discharged/Dumped in Wastes tonnes.day-1
Federal Republic of Germany	1 300 tonnes•day ⁻¹	14 %	165
Netherlands	4 000 tonnes day^{-1}	7 %	280
Belgium	600 tonnes day ⁻¹	2 %	12
	Sub-t	otal	457
United Kingdom	22,700 m ³ .day ⁻¹	0.8%	182*
	Total		639

Assuming the wastes have a specific gravity of 1.0.

4. Impact on North Sea sediments (Best Case)

In order to determine the likely extent of contamination of North Sea sediments by the discharge and dumping of wastes from the TiO₂ industry, the following calculation is provided.

It is assumed that the wastes become uniformly distributed over North Sea sediments and that they become uniformly mixed throughout the upper 10 cm of the surficial sediments by bioturbation and physical mixing.

Background or baseline quantity of iron in North Sea sediments

- = Area of North Sea x Average Fe content of North Sea sediments x depth of uniform mixing
- = $5.8 \times 10^{11} \text{m}^2 \times 30 \text{ kg Fe} \cdot \text{m}^{-3} \times 0.1 \text{ m}$

 $= 1.74 \times 10^9$ tonnes.

The quantity of additional iron provided to the sediments through the discharge/dumping of wastes from the TiO_2 industry is

639 tonnes \cdot day⁻¹ x 365 day \cdot yr⁻¹ = 2.3 x 10⁵ tonnes \cdot yr⁻¹. The percentage increase in iron incorporated into North Sea sediments annually through the disposal of wastes from the TiO₂ industry is

 $\frac{2.3 \times 10^5 \text{ tonnes}}{1.74 \times 10^9 \text{ tonnes}} \times 100\% = 0.013\%.$

Even if we allow for the disposal into the North Sea of a further 300 tonnes day^{-1} of iron through the disposal of wastes from the TiO₂ industry by countries other than Belgium, the Netherlands, the Federal Republic of Germany, and the United Kingdom, the proportional increase in the iron content of the sediments is only 0.02%. Furthermore, this calculation takes no account of the dilution arising from the particles with which the iron is sedimented.

It is clear that broad-scale consequences on the composition of North Sea sediments are essentially negligible.

5. In the next case, the smaller scale western North Sea coastal belt will be examined as it was earlier in the case of water assimilation and dilution.

Assume a distribution of the iron such that the iron in the wastes disposed of by Belgium (2 dump sites), the Netherlands (1 discharge point) and the Federal Republic of Germany (3 dump sites) is deposited within one day close to each of the six zones of input. The area affected in each case is assumed to be about 4 km^2 , i.e., 1.9 km (the net movement north per day) by about 2 km to represent dispersion across the current.

The amount of iron already present in the top 0.1 m of the sediments in the six areas affected will be

 $4 \times 10^{6} \text{m}^{2} \times 0.1 \text{ m} \times 30 \text{ kg} \cdot \text{m}^{-3} \times 6 \text{ areas}$ = 7.2 x 10⁷ kg

The amount of iron added per year to the six areas is 1.67×10^5 tonnes, i.e., the percentage increase per year is

$$\frac{1.67 \times 10^5 \times 10^3 \text{ kg} \times 100\%}{7.2 \times 10^7 \text{ kg}}$$

= 231.9%

i.e., more than a two-fold increase per year.

As it is known that the inputs in the German Bight at least are never supposed to be dumped in the same place and total deposition in one day only is unlikely, the above clearly indicates the very worst possible situation. Nevertheless, it does indicate that in the area of input and down current thereof, detectable increases in the iron content of the surface sediments must be expected. This is in fact understood to be demonstrable in the German Bight case. These calculations demonstrate that while deleterious sub-lethal effects on marine organisms and compositional changes in sediments caused by the disposal of wastes from the TiO₂ industry are unlikely to occur throughout the North Sea as a whole, effects on smaller areas within the coastal zones of countries carrying out these waste disposal practices are to be expected.

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REFERENCES

Kayser, H. 1969. Züchtungsexperimente an Zwei Marinen Flagellaten (Dinophyta) und ihre Anwendung im toxikologischen Abwassertest. Helgoländer Wiss. Meeresunters., 19, 21-44 (1969).

Topping, G. 1978. Sewage and the Sea, in "Marine Pollution". Ed. R. Johnston, Academic Press, N.4., London.

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Indication of spine colours

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

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