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REPORT OF THE ADVISORY COMMITTEE ON MARINE POLLUTION, 1982

List of Members

Dr A D McIntyre  
Chairman

Dr J B Pearce  
Chairman, Marine Environmental Quality Committee

Dr L Otto  
Chairman, Hydrography Committee

Dr K Vagn Hansen  
Chairman, Biological Oceanography Committee

Co-opted Members

Dr (Ms) MC de Barros
Dr R H Cook
Dr V Dethlefsen
Dr I Dundas
Prof. G Kullenberg
Dr J Lassig
Dr M Parker*
Dr D Phelps
Dr J E Portmann
Ms F Soudan
Dr (Ms) A Trozinska*

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

*) Prevented from attending the meeting 29 March–2 April 1982.
INTRODUCTION

1. The Advisory Committee on Marine Pollution (ACMP) has been 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. It is a firm procedure within the Council that reports of other subsidiary bodies must pass the Advisory Committee on Marine Pollution.

2. 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.

3. The present membership of the Committee is found on page 1.

ISSUES RELATED TO INTERCALIBRATION

4. The ACMP noted with approval the proposal by the Marine Chemistry Working Group (MCWG) to simplify the references to intercalibration exercises. It agreed that the titles of the exercises should be given in full when first used on any occasion, but that thereafter a short-form coding system should be used in the form

   \[ N/XX/YY \]

   where \( N \) refers to the number of the intercalibration, \( XX \) to the contaminant class (\( TM \) - trace metals; \( OC \) - organochlorines; \( HC \) - hydrocarbon compounds; \( NT \) - nutrients) and \( YY \) to the environmental compartment (\( SW \) - sea water; \( MS \) - marine sediments; \( BT \) - biological tissues). Thus, the ICES Fifth Round Intercalibration of Trace Metals in Sea Water should be referred to as ICES-5/TM/SW.

Trace Metals

5. The ACMP noted the outcome of the intersessional work on the analysis of lead in biological tissue, which identified matrix interference as one of the problems to be considered to achieve good accuracy at lead concentrations up to 2 mg/kg (wet weight), particularly if atomic absorption spectrophotometry (AAS) with a graphite furnace is used. Further work by a small group of analysts will be pursued. Chemists are advised always to investigate the matrix effect of each type of material analysed. If this effect cannot be overcome by the technique used, other methods should be sought.

6. In anticipation of the new baseline study which is being considered for 1985, preparations for the 7th ICES Intercalibration Exercise on Trace Metals in Biological Tissues (coded ICES-7/TM/BT) have been initiated by the MCWG. It was noted that this exercise will utilize several different reference samples consisting of different tissues (fish liver, shellfish muscle or bivalve soft body) and several different concentration ranges for the trace metals under study: cadmium, lead, mercury, copper, zinc and arsenic. By using these different materials, some of the questions regarding matrix effects can be covered in the intercalibration. It is expected that this intercalibration exercise will be carried out in 1983.

7. The ACMP was informed of the progress made in planning for the ICES Fifth Round Intercalibration Exercise on Trace Metals in Sea Water (ICES-5/TM/SW), which will take place in September 1982, with the support of a research vessel from the Netherlands North Sea Directorate, and using the laboratory facilities of the Institut Scientifique et Technique des Pêches Maritimes in Nantes. The exercise will concen-
trate on determining the intercomparability of different procedures for the separation of dissolved and particulate fractions of metals in sea water, but will also consider the measurement of suspended matter concentrations, and problems involved in sampling for mercury determinations. In addition, provision will be made for training/advice sessions on aspects of sampling and sample treatment for analysis of trace metals in sea water, which can be attended by 20 to 30 participants. Additionally, bottled sea water samples will be distributed to laboratories unable to participate in the on-site work. The core experiment will be conducted mainly by laboratories that have successfully participated in the previous rounds of this intercalibration programme, but invitations for participation in the other activities will be sent to the Paris, Oslo and Helsinki Commissions.

Organochlorines

8. After being informed that the recent intersessional work on PCB analysis showed a large interlaboratory variation in results and suggested that some isomers are being identified differently by different laboratories, the ACMP noted that a new exercise, aiming at further studying the residue determination of PCB isomers, is being launched by the MCWG. The new study (ICES-5/OC/BT), which is coordinated by Dr J Uthe from Canada, will utilize samples of unspiked fish oil and fish oil spiked with known amounts of four or five individual PCB isomers, small amounts of which will also be made available. The exercise will concentrate on capillary gas chromatography techniques and the major objective will be the development of new methods of quantifying PCBs, which can be adopted by ICES. Participants will also be asked to compare results using Florisil with those using alumina as clean-up agents. Meanwhile, to prepare for the next intercalibration exercise on organochlorines that is needed to control the quality of data for the 1985 baseline survey, studies will be conducted to investigate the preparation and stability of a suitable fish tissue substrate to be used instead of fish oils in intercomparison exercises. The use of such a fish tissue substrate would permit an investigation of the extraction efficiency of PCBs from fish tissues as well as the comparability of analytical techniques. Since extraction efficiency has not been studied in previous exercises, the tissues to be included should be indicated by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNNA), but a minimum of three tissues with different fat contents and PCB concentrations will have to be included.

Petroleum Hydrocarbons

9. The ACMP was informed that the planned intercomparison exercise on analyses of petroleum hydrocarbons had been delayed due to funding problems, but that there is a possibility of samples being available by late 1982 or early 1983. The MCWG is also considering the possibility of conducting intercomparison studies on the analysis of dissolved/dispersed hydrocarbons in sea water. In addition, studies are being envisaged on analytical methods for the determination of photodegradation products of high molecular weight and high solubility in sea water, which are suspected of being very toxic.

10. Because high concentrations of polycyclic aromatic hydrocarbons (PAH) are being measured in some areas of the marine environment, a first intercomparison exercise on the analysis of these compounds in biological tissue is being planned. The details of this exercise will be considered at the 1982 Statutory Meeting.
Other Studies

11. The ACMP also took note of other intercalibration studies which are being carried out in relevant fields of marine sciences. In particular, it was noted that an intercomparison workshop on biological methods and nutrient analyses will be conducted under the auspices of the Helsinki Commission in August 1982. In addition, an ICES Workshop on Intercomparison of Techniques in Measurements of Primary Production is being planned and will possibly be held in 1984.

ICES Quality Assurance Programme

12. Taking the discussions reported from the Marine Chemistry Working Group meeting as a basis, the ACMP considered the general philosophy of intercalibration and intercomparison studies in the context of present knowledge of the state-of-the-art of analytical methods and the status and needs of ongoing or planned work within ICES and in collaboration with the pollution regulatory commissions.

13. It was noted that the first intercalibration exercises had been conducted with the intention of identifying the level of accuracy that could be achieved with the various analytical methods used for the determination of contaminants. As problems of inaccuracy or lack of comparability were identified, options to solve them were studied and exercises, loosely referred to as intercalibrations, were developed to cater for these problems. At its 1982 meeting, the MCWG had assessed the status of the intercalibration programme in relation to the determination of contaminants in marine samples.

14. In this assessment, the MCWG had evaluated the present ability to determine contaminants and the comparability among laboratories with respect to the three groups of contaminants studied, namely, trace metals, organochlorine residues, and petroleum hydrocarbons, in the different compartments of the marine environment, i.e., biota, sea water and sediments. It was concluded that for several of the contaminants in several of the compartments a good comparability of data was now achievable. However, in some cases further work is still needed to improve methodology or to identify sources of errors. A modified version of the MCWG assessment of the status of intercalibrations is attached as Annex 1.

15. In view of these conclusions, the ACMP considered that a new approach is now possible for trace metals and certain organochlorines in biological tissues. This approach, along the lines proposed by the MCWG, recognizes that the need is for intercalibration exercises which are conducted essentially as a method for quality assurance of the data provided under cooperative monitoring programmes with a periodicity compatible with these programmes (4 to 5 years). Blind samples could be available throughout the period between the exercises. These samples would meet the needs of new laboratories joining ongoing activities or analysts newly engaged in marine pollution work. It was noted that the MCWG has, in fact, proposed that the issue of longer term availability of blind samples be considered in the planning for the 1983/84 intercalibration study, and has further suggested that the Fisheries Laboratory in Halifax be nominated to serve as the first intercalibration coordination center for biological tissue to facilitate, inter alia, the preparation of blind intercalibration sample material for continued testing of laboratories taking part in cooperative monitoring studies.

16. The ACMP also stresses that the main aim of the baseline or monitoring programme must be taken into consideration when devising the quality assurance programmes, because this dictates which substrates should be included as well as the contaminants and the range of concentrations. It was recalled that the WMFPHA has already developed different protocols for monitoring studies of contaminants
in biological tissues when aiming at protection of human health, analysis of geographical distribution or trends in concentrations (to be issued as a Cooperative Research Report). The objective of the programme is also highly relevant when decisions are taken on the level of detection required and, in some cases, on the minimum level of accuracy or comparability that has to be achieved.

17. Recognizing that new substances are likely to be identified which should be incorporated into collaborative monitoring programmes, the ACMP agreed that intercalibration studies should be devised for all such substances along the same lines that have been used for earlier intercalibrations. These studies should explore all aspects of the methodology for sampling, preservation, storage and analysis in order to attain the best possible interlaboratory comparability as is appropriate to the chemical and the substrates under study. Participants in such intercalibration exercises should always consider the results obtained in order to improve their performance, as necessary. In this respect, it might be necessary to have one or more laboratories conduct particular studies on specific problems. The intercalibration exercises that have been conducted on trace metals in sea water and on organochlorines and trace metals in biological tissues are examples of how to develop intercalibration studies for new contaminants (see Coop.Res.Rep., Nos. 80 (1978), 105 (1981), 108 (1981), 110 (1981), 111 (1982), 115 (1982) for the results of these exercises).

18. It should always be borne in mind that as soon as good comparability among laboratories has been achieved for the new contaminants under investigation, the intercalibration studies should develop into programmes for quality assurance with a convenient periodicity and should make use of blind reference samples, taking into account the aims of the studies to be undertaken.

ISSUES RELATED TO MONITORING

1980 Coordinated Monitoring Report

19. The ACMP reviewed the draft report of the 1980 results of the Coordinated Monitoring Programme of contaminant levels in fish and shellfish. Data were included from Belgium, Denmark, England/Wales, the Federal Republic of Germany, Ireland, and the Netherlands, giving the concentrations of heavy metals and certain organochlorine residues in several species of fish and shellfish. The draft report had been reviewed and approved by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic, subject to the addition of relevant data which may be received subsequent to the Working Group meeting. Further data had later been submitted by Belgium and the Netherlands.

20. Given that the report will be revised by the addition of further data and the preparation of graphs requested by the ACMP, it was decided that the draft report should be reviewed again at the next ACMP meeting. It was further decided that the report should be held for later publication together with the report to be prepared on the 1981 coordinated monitoring results, as these will be the last two reports on the Coordinated Monitoring Programme as carried out under the protocol contained in Annex II to the 1978 ACMP Report (Coop.Res.Rep. No. 84 (1979)). This joint publication should also update the overall review of the results of the programme which had been made in the Six-Year Review of ICES Coordinated Monitoring Programmes (to be issued as a Cooperative Research Report) and would be appropriately illustrated with graphs and charts.

21. Concerning the new ICES Cooperative Monitoring Studies programme which is beginning in 1982, the ACMP felt that the guidelines for the sampling procedures, sample composition, and reporting for this new programme should be publicized as widely as possible to ensure that all prospective participants will be made aware of them.
Trend Monitoring using Marine Organisms

22. The ACMP noted that three developments had occurred at the recent meeting of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic concerning the specification of appropriate methods to use in the monitoring of trends in contaminant concentrations in marine organisms. First, precise recommendations had been made on the best way to compose a sample of fish according to length stratification. Second, the guidelines for trend monitoring had been amended to include these new recommendations on length stratification as well as a clearer indication of the species of fish which can be selected for trend monitoring and the data reporting requirements. Third, a coordinator had been appointed to review trend monitoring packages to ensure that comparable techniques for sampling and statistical analysis will be used and to provide an overview of trend monitoring programmes in terms of species, contaminants and areas covered. The Coordinator is Mr H Hill, MAFF Fisheries Laboratory, Lowestoft, England, and the ACMP noted that all laboratories which have developed or will develop plans for trend monitoring as part of the ICES Cooperative Monitoring Studies programme have been requested to send their detailed plans for trend monitoring to him.

The ICES Cooperative Monitoring Studies Programme

23. Given that there were generally still some misunderstandings concerning the Guidelines for the new ICES Cooperative Monitoring Studies programme, the ACMP again stated that the Six-Year Review of ICES Coordinated Monitoring Programmes in the North Atlantic had shown that the same sampling protocol cannot be used to meet different aims of monitoring using marine organisms. Thus, three separate protocols for sampling, sample composition and reporting have been developed to meet the three different aims of monitoring agreed within ICES. For monitoring to provide a continuing assurance of the quality of marine foodstuffs with respect to human health, the samples should be composed of species of fish and shellfish normally consumed and selected so as to reflect the size distribution of the commercially exploitable portion of the catch of each species selected. The 25 fish in the sample may be pooled before analysis and the bulk sample analyzed in duplicate. The frequency of sampling should be every second year.

24. For monitoring conducted to provide an indication of the health of the marine environment over a wide geographical area, it is important to select species which have a wide distribution over the North Atlantic, so as to permit a comparison of concentrations between areas. The fish selected, however, should be representative of the area in question and samples should be collected from as many locations as practicable throughout the ICES area. The 25 fish in a sample may be pooled and the bulk sample analyzed in duplicate. The frequency of sampling to meet this objective is every fifth year.

25. The third objective in the programme is trend monitoring, i.e., the analysis of trends over time in the concentrations of contaminants in fish and shellfish in selected areas. The sampling requirements to meet this objective are much more stringent than those for the other objectives because it is necessary to reduce as much as possible the variability in samples from year to year. The species of interest should be selected in the light of information on fish stock composition and history, and it is preferable to use a species which continues to grow throughout its life. Species of particular interest which have so far been identified are as follows: cod (Gadus morhua) or hake (Merluccius merluccius), plaice (Pleuronectes platessa), flounder (Platichthys flesus), mackerel (Scomber scombrus), mussel (Mytilus edulis) and common shrimp (Crangon crangon). For fish, samples of 25 individuals should be composed based on a length stratification scheme, which once developed for a particular species and area, should be adhered
to strictly for a number of years. A number of biological variables should be recorded and the fish should be analyzed individually. The results obtained should be subjected to multiple regression analysis according to an agreed programme. The sampling frequency is once a year and generally only a few critical areas will be studied by each country using this protocol.

**ADP Handling of Monitoring Data**

26. The ACMP noted that, at the 1981 Statutory Meeting, the Council had approved the establishment of a computerized data bank in ICES for storing and processing data on the concentrations of contaminants in marine organisms. It was further noted that the Joint Monitoring Group, the Technical Working Group of the Paris Commission and the Standing Advisory Committee for Scientific Advice of the Oslo Commission had recommended that data on contaminants in organisms from the Joint Monitoring Programme should be handled by ICES, and that a common reporting format for ICES and JMG data should be developed by ICES. Furthermore, ICES had earlier been requested by the Helsinki Commission to prepare a reporting and exchange format for data on harmful substances in organisms, so the format to be developed should meet the needs of all four organizations.

27. The ACMP welcomed these developments and urged that the work to implement this system be carried out as rapidly as possible, so that the data handling needs of ICES as well as the Commissions could be met at the earliest practicable date. It was expected that the work would begin with the development of a data entry format, after which an overall data exchange format will be developed. Beginning on a relatively simple level, there will be a gradual build-up of sophistication in the handling and exchange of pollution data as experience is gained. It was requested that the background work be carried out with the aim of being able to enter 1981 ICES coordinated monitoring data before the end of 1982.

**ISSUES RELATED TO DUMPING**

**Updating of Annex I to the 1977 ACMP Report**

28. The ACMP considered a report prepared intersessionally by Dr Cook entitled "Considerations Relevant to the Selection and Monitoring of Dumping Grounds". This report was developed in the light of a proposal by the Australian delegation to the ad hoc Scientific Group of the London Dumping Convention and incorporated ICES experience gained since the last ACMP advice on this subject was given in 1977. Several members considered that this report would be of assistance to the Commissions as it would draw attention to the current information associated with site selection and monitoring of dumping operations. However, it was recognized that the report of the GESAMP Working Group on Sea Disposal Studies was now available in final draft form and would soon be published. This GESAMP study has already given comprehensive consideration to most of the points raised in the report under discussion and some members suggested that it would be duplicative to issue this report as it stands. Following a discussion, it was noted that the report included observations on topics such as the adequacy of the hydrographic considerations regarding transport and mixing, the relevance of biological considerations, and the use of incineration and its acceptability for disposal of persistent toxic chemicals as well as associated technical observations. The ACMP therefore felt that the report provided a useful updating of the ICES experience since 1977 in the field of ocean dumping. Thus, the ACMP decided that the report should be revised to focus specifically on this experience. This revised report is attached as Annex 2.
Incineration at Sea

29. Having previously reviewed the European situation concerning the frequency of incineration at sea, the types and amounts of waste so disposed, and the controls on operating conditions, the ACMP had requested Dr J B Pearce to conduct a comparable review of American activities on incineration at sea.

30. This review stated that the U.S. Environmental Protection Agency has estimated that tens of millions of tonnes of hazardous waste are generated annually in the United States (57 million metric tonnes of industrial hazardous waste in 1980). Many of these wastes are incinerable and controlled high-temperature incineration, whether on land or at sea, has been deemed by the U.S. EPA as a most effective method for the destruction of combustible hazardous wastes (e.g., toxic organochlorines), destroying 99.99 per cent of the wastes. Incineration that occurs at sea removes the destruction site from populated areas and the vulnerable freshwater environment, which is of special importance when incinerating the most toxic wastes. In 1974, 1975 and 1977 three officially-sanctioned United States at-sea incineration operations were successfully conducted on the foreign incinerator ship M/T VULCANUS. Eight shiploads of industrial organochlorine wastes and three shiploads of Air Force Herbicide Orange were destroyed under research, special and interim permits issued by the U.S. Environmental Protection Agency. It was considered that these operations and those in Europe have demonstrated incineration at sea of combustible liquid chemical wastes to be an industrial operation which can be implemented without much of the preliminary testing that other ultimate disposal alternatives may require.

31. In 1980, an interagency work group in the United States undertook a study of at-sea incineration technology and the alternatives available to the U.S. Government for encouraging the design, construction and operation of U.S.-flag incineration ships. The work group examined previous incineration operations, various federal assistance programmes, safety and control measures, incinerator ship conceptual designs, environmental impacts, and waterfront facilities. The work group's report concluded that chemical waste incineration at sea aboard specially designed and equipped ships is a cost-effective, technically efficient, and environmentally acceptable technology for the destruction of many types of combustible hazardous wastes.\(^1\)

32. The U.S. Environmental Protection Agency has designated an incineration site in the Gulf of Mexico and is in the process of designating one in the North Atlantic.

33. After discussing this information, the ACMP concluded that the information at hand indicates that incineration at sea can be an effective and acceptable way of destroying a range of toxic organic wastes, e.g. certain persistent pesticides, PCBs and other chlorinated hydrocarbons, provided that the present codes of practice are strictly adhered to. In coming to this conclusion, the ACMP noted that it was not in a position to consider land-based incineration. Additionally, it considered that there are still some open questions concerning incineration at sea, the most serious of which involves the effect of meteorological conditions on the transport and dispersal of the plume gases.

BIOLoGICAL EFFECTS STUDIES AND MONITORING

Fish Diseases and Pollution

34. The ACMP has been examining the possibility of adding a biological component to on-going routine chemical monitoring programmes. Following the ICES Workshop on Monitoring the Biological Effects of Pollution in the Sea, held in Beaufort, N.C., U.S.A. in 1979, which identified some 50 techniques that could be appropriate to biological monitoring, the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA) had proposed that certain aspects of fish pathology might be particularly amenable to cooperative monitoring. ICES member countries were therefore asked to make observations on tumours, finrot and skeletal anomalies and to report the results to the ICES Secretariat on a special reporting form which was circulated. The first results of this exercise were discussed by ACMP.

35. Reports covered 12 species of fish and many thousands of individual specimens from the Baltic Sea, North Sea, Irish Sea and off the east coasts of Canada and the USA. Particularly notable was the high incidence of skeletal deformities in one species of fish in the Baltic Sea near effluents from metal works and pulp and paper industries. However, relatively high frequencies of deformities were also observed at some distance from pollution sources.

36. The ACMP also had before it two discussion papers reviewing fish (and shell-fish) diseases in relation to marine pollution. One of these papers highlighted the lack of quantitative information linking records of disease with data on the concentrations of contaminants in water, sediments or in the tissues of the diseased organisms. It stressed the value of laboratory experiments designed to reproduce disease symptoms. The second paper examined the case against a relationship between pollution and fish diseases, including the arguments that fish diseases existed before pollution in specific areas; that their incidence may be high in "clean" areas and low in some pollution hot-spots; and that factors unconnected with pollution may be responsible (stress from fishing gear, parasites, poor nutrition). It emphasised the complexity of the problem and the comparative simplicity of many current approaches, suggesting the need for careful extensive baseline studies.

37. In the discussion that followed, the ACMP noted there still was uncertainty in many cases about whether there is a cause-and-effect relationship between pollution and disease, and endorsed the suggestion of the WGMPNA that additional information on diseased fish (e.g. size, sex, age, weight, liver weight) should be sought so that the relationship between the observed anomalies and the condition of the fish could be investigated. These factors should be taken into account and reported, whenever possible. Where a specific input was known or suspected, body burdens of likely contaminants should also be determined if possible. The ACMP
also endorsed the proposals of the WGMPNA to take into account the common interests of the Working Group on Pathology and Disease of Marine Organisms and encouraged this latter Working Group to become actively involved in the work to elucidate the possible relationship between pollution and fish disease.

38. The special case of effects from the dumping and discharge of wastes from the TiO2 industry, which had been raised by the Oslo and Paris Commissions, was considered. In its 1981 Report, the ACMP had recognized that there are new observations in relation to the biological effects of dumping TiO2 wastes and had expressed more caution concerning such dumping. It was noted that information has been accumulated on the dumping ground in the German Bight and that a major study is currently under way, financed by the Federal Republic of Germany. An interim report on the results of this study would be available next year and will provide input for a new assessment. Other relevant information will also be collected.

39. The ACMP felt that one effective way of advancing the studies discussed above would be to arrange a workshop on methods to be used in fish disease surveys in relation to pollution. The aim would be to bring together scientists actively engaged in studies of fish pathology in conjunction with environmental effects to discuss the diagnosis of relevant fish diseases. The workshop would preferably be held at sea during a fish disease survey cruise, thus giving the opportunity to inspect living material under field conditions.

Other Biological Effects Monitoring Techniques

40. Although, as indicated above, the main cooperative effort from ICES on biological effects studies is at present focussed on pathology, other approaches have not been neglected. At the level of biochemical effects, one technique which is in use at several laboratories is the study of enzyme induction as an indicator of the presence of contaminants. This has proved useful in relation to oil contamination around drilling platforms. At the other end of the spectrum, in the field of ecology, a number of programmes are examining changes in the community structure of macrobenthos, plankton and fish populations as a warning of adverse conditions. Additional approaches listed in the Beaufort Workshop Proceedings (Rapp. P.-V. Réun. Cons.Int. Explor. Mer No.179 (1980)) are being evaluated in the field, including microsomal fragility, scope for growth in molluscs, and bioassays using oyster larvae.

Biological Effects Monitoring Strategy

41. Finally, the ACMP discussed a strategy for biological effects monitoring. This had been considered in detail by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic, which had adapted the GESAMP suggestions (reproduced in Annex 3) and agreed that three elements were relevant:

1. the identification of biological changes,
2. the quantification of associated effects, and
3. the analysis of their causation.
The order in which these elements were dealt with (and even the question of whether they are all needed for a particular situation) would depend on the circumstances of the specific study. Different biological techniques would be required for each of the three parts of the strategy. Some of these techniques were still being developed, while others had been well tested and were already in use in several laboratories. However, it was considered premature to recommend specific procedures for immediate inclusion in internationally coordinated monitoring programmes, although a recommendation on this may soon be possible as a result of the ICES initiatives described above.

THE STUDY OF POLLUTANTS IN SEDIMENTS

42. This subject was considered on the basis of the first two reports from the new ICES Working Group on Marine Sediments in Relation to Pollution as well as on information on a sediment study planned for the Baltic Sea under the ICES/SCOR Working Group on the Study of the Pollution of the Baltic. It was noted that the Working Group on Marine Sediments in Relation to Pollution had before it a request from ACMP to review work on pollutants in sediments and to advise on the role of sediments as monitoring devices in marine pollution programmes. On the latter issue, the Working Group had provided preliminary advice but stated that more concrete information will be available after certain scientific problems have been solved. The Working Group was also preparing a decision tree to be used in determining which types of sea bottom areas would be suitable for sediment monitoring aside from those locations (such as dumping grounds) where it was already clear that monitoring would be required. Regarding the methods to be used in studies of pollutants in sediments, the Working Group had decided that descriptions should be prepared of agreed methods of sediment characterization and analysis for publication in the "Techniques in Marine Chemistry" series. Finally, progress in the planning of the Pilot Sediment Study in the German Bight and the Pilot Sediment Study in the Skagerrak had been reviewed, and it was noted that these exercises would begin in 1982.

43. In discussing these reports, the ACMP noted that sandy sediments may be of considerable interest in pollution studies. Changes in the quality of overlying water may have a significant impact on the biology of such sediments, even in the absence of appreciable sedimentation.

44. The ACMP was then informed about the initial plans for a pilot study of sediments in the Baltic Sea, to be coordinated by the ICES/SCOR Working Group on the Study of the Pollution of the Baltic. This study would be carried out to determine the pollution history of dated Baltic Sea sediment cores and answer questions related to the monitoring of sedimentation rate and pollutants in sediments in the Baltic Sea. Additionally, the role of the sediments as a sink for materials and a source of materials to the water column will be studied in relation to processes occurring at the sediment-water interface.

45. The ACMP endorsed the conduct of these three pilot sediment studies and noted that as the conditions in the three areas are very different, information about pollutant deposition in a range of sediment types will be produced. The ACMP stated that it hopes to be able to review results from these studies within two years.

REGIONAL ASSESSMENTS

46. At its meeting in connection with the 1981 Statutory Meeting, the Advisory Committee on Marine Pollution had conducted an extensive discussion on the subject of regional assessments of the health of the marine
environment and how they should be carried out. The ACMP stressed the importance of regional assessments and agreed that it would be very useful to develop a general framework for the conduct of assessments in the ICES area. This framework would help to ensure that all appropriate subjects would be covered in the assessments and would promote comparability in approach so that it would be easier to compare results between regions.

47. To begin work on this subject, the ACMP had requested the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic to (1) develop a general format for the assessment of the state of the health of the marine environment of an area using existing information, and (2) consider the best way to carry out such a regional assessment. The ICES/SCOR Working Group on the Study of the Pollution of the Baltic had also been requested to consider the issue on the basis of the experience already gained in assessing the effects of pollution in the Baltic Sea.

48. The ACMP then took note of the results of the discussion of this subject in WGMPNA. This Working Group had agreed that the conduct of regional assessments of the health of the marine environment was a logical progression from the monitoring programmes with which it has been concerned and would be very valuable. The Working Group had further agreed that all regional assessments should follow a generally similar approach. The assessments should contain a succinct description of the physical, chemical and biological conditions of the region and any changes which may be occurring due to natural causes. The anthropogenic influences and their impacts on the environment of the region should then be described. Regarding the choice of marine areas for the conduct of an assessment, the WGMPNA had suggested that the criteria for selecting a region should be that it is a reasonably natural hydrographic entity; that there is reason to believe that anthropogenic activities have an effect on the marine environment of the region; and that there is readily available published information on the region. With these comments from the groups before it, the ACMP reconsidered the matter.

49. The ACMP recognised that significant amounts of information were available on many areas with respect to general ecology, pollution inputs and the various uses and requirements of mankind. It would be useful to bring together this information in a concise form. The assessment documents would not require new data but would draw on existing information. They would allow comparisons to be made of the information available on each area with a view to assessing the extent of pollution and other changes brought about by man's activities and indicate gaps in knowledge; they would document the state of the environment at a given time and so establish a benchmark; they would be valuable to those concerned with administrative or regulatory matters in the environment, helping to set the uses of the areas in an overall context and indicating options.

50. It was envisaged that each document would be prepared by a small interdisciplinary group of scientists who would draw on the expertise of their colleagues as required. To be of value, the assessments should not be generalised descriptions, but would need to deal with specific topics relevant to an understanding of the area in question. In this connection, it was mentioned that the Helsinki Commission has decided to carry out periodic assessments of the health of the Baltic Sea environment.

51. The ACMP noted that the WGMPNA is working intersessionally by correspondence to produce a draft set of guidelines for regional assessments, and to delineate the areas to be assessed. The ACMP looked forward to reviewing this work at its next meeting.
52. In its 1981 report, the ACMP had recognised a distinction between short-term storage (<1 year) of biological materials prior to chemical analysis, long-term storage (1-5 years) and specimen banking (>5 years). Dr J B Pearce had been asked to expand his paper on short-term storage and Dr D Phelps to contribute a paper on specimen banking.

53. The ACMP discussed these papers in detail. It was clear that many scientists hold samples of tissues and sediments which will be used for analysis of contaminant levels one to five years after collection. Techniques now advocated include chemical preservation, radiation sterilization, freeze drying, ashing and rapid or deep-freezing. It was the consensus of investigators queried that deep freezing is now the preferred way of retaining samples for future contaminant analysis. Some reports suggest that marine tissues or sediments should be frozen immediately in dry ice or liquid nitrogen and stored at -70 to -80°C in the dark, noting that substances such as pp'-DDT and related compounds could break down due to biological processes when held at approximately -14°C. Other reports indicated that there may be some loss of organics or pesticides if samples are dried or freeze-dried. In general, however, it was recommended that the lower the temperature the better. Temperatures of -80°C or colder were suggested for certain purposes, but many scientists use freezers holding at -20°C or -40°C. Alternative methods of storage, in addition to the various freezing protocols, include preparation of hexane-lipid extracts of tissues in sealed glass ampoules and preservation using MgSO4 salts blended with equal amounts of biological tissues.

54. In discussing these papers, the ACMP noted that ideally the storage procedure should be tailored to fit the requirements of each collection and that no single protocol would be universally applicable. Thus, for microbiology the speed of first entry to freezing is of crucial importance and a change of 20°C during storage could be damaging. It was recognised that the rate of freezing is an important question that requires further research. For enzyme work, very low temperatures are required. If parts of collections are to be analysed at intervals, it is desirable to make provision for this at the beginning by dividing the sample into sub-samples, rather than removing portions from a single sample later. The ACMP endorsed a call for research which would emphasise efforts to determine changes in the levels of materials of interest during long-term storage and which would lead to the development of new storage procedures and techniques capable of holding samples for years or decades.

55. Finally, it was recognised that during the past two or three decades "new contaminants" have been found but generally there have been no benchmarks against which contemporary levels of contaminants in environmental samples and biological tissues could be compared. The problem of short- and long-term storage of such samples has become even more critical with the development of new biological effects techniques for measuring contaminant effects; physiologists and biochemists now routinely use certain biochemical responses and assays to indicate the stress which contaminants might have had upon organisms held in the laboratory or collected from the field. It is now known, for instance, that enzyme activity can be affected by relatively short periods of sample retention, even when the samples are supposedly well-refrigerated or frozen. A major difference between long-term storage of samples for pollutant analysis and specimen banking is that for the latter there could be a need to analyse the samples for new, presently unknown substances. The ACMP noted that materials originally intended for limited storage might ultimately be retained for longer periods and thus become specimen banks.
therefore important that investigators use proper procedures when beginning to preserve samples. The need to avoid temperature fluctuations is particularly emphasised.

Specimen Banking

56. The subject was discussed at length on the basis of the paper, "Review of Environmental Specimen Banking Philosophy and Experience", which is attached as Annex 4 to this report. The ACMP agreed that specimen banking (i.e., the indefinite storage of material for retrospective analysis) has scientific merit, and current activities in this field in the Federal Republic of Germany and the United States of America were noted with interest. It was suggested that a major power failure would be a significant threat to this type of enterprise, and that a site in the Antarctic might have advantages. Although the connection between specimen banking and monitoring environmental contaminants was clear, it was felt that new activities of specimen banking should not be encouraged within the ICES member countries at the present time due to the large investment required, especially in view of the lack of enough experience in the area to be certain of the nature, extent and applicability of expected returns.

57. It was recognized that the on-going specimen banking activities in the Federal Republic of Germany and the United States would produce methodology pertinent to questions of long-term storage of specimens for more general analytical purposes and that this would represent a useful source of technological information.

PLANKTON BLOOMS

58. Plankton blooms have been a subject of interest to ICES for some years and have been discussed in the past by ACMP. Recent events on both sides of the Atlantic have highlighted the topic. The ACMP had before it a paper by Dr Parker on unusual plankton blooms and their relation to fisheries. This provided the basis for a discussion on the definition of blooms, their impact on the dynamics of food chains, and their causes. It was recognised that the session on exceptional blooms planned for the 1982 Statutory Meeting would provide a substantial addition of information on the subject. Further discussion was, therefore, deferred until the outcome of the Statutory Meeting session was available.

TRANSFER AND CYCLING OF SUBSTANCES IN THE MARINE ENVIRONMENT

Transport of Lead in the Marine Environment

59. The ACMP considered an overview paper on lead in the marine environment which had been prepared by Dr M Waldichuk, Dept. of Fisheries and Oceans, Vancouver, Canada. It had been the subject of detailed discussion by the Marine Chemistry Working Group, and had also been reviewed by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic. In the light of the comments from these two Working Groups, a number of clarifications and changes had been made to the paper which now had the status of an endorsed Working Group report.

60. In reviewing the paper, the ACMP noted that the distribution of lead is apparently not significantly affected by biological processes, although its distribution in the marine environment has been greatly influenced by man's activities.
As a consequence, the concentrations of lead in the water column and in sediments in coastal, shelf and oceanic areas are now appreciably higher than those which could have been found if inputs had been of natural origin only. The ACMP approved the report, as an addition to the series of overviews on pollutants of topical interest prepared on behalf of ICES, and agreed that it should be appended to its Report as Annex 5.

Methods for the Assessment of River Inputs

61. The ACMP noted that the Marine Chemistry Working Group had, in accordance with the ACMP's request, developed a series of guidelines on methods for the assessment of riverine inputs. These guidelines, entitled "Methods of Assessing Gross Riverine Discharges of Trace Metals and Organohalogens to the Marine Environment", had originally been prepared by Dr J M Bewers and Dr J C Duinker. It was recognised that this type of guidance had specifically been requested by the Oslo and Paris Commissions and for this reason the ACMP agreed that the full report should be included as Annex 6 to its report.

62. It was, however, agreed that in transmitting the guidelines to the Commissions a number of explanatory remarks should be drawn to the attention of potential users. In particular, the ACMP emphasized that the guidelines catered only for the quantification of gross inputs from rivers to estuaries. In many instances these are likely to be appreciably different from the net flux out of the estuary into the coastal areas and the open oceans. However, the measurement of gross inputs is a necessary first step in the evaluation of net inputs. It is also apparent that the general state-of-the-art of the methodology needs to be developed further to allow net inputs to be estimated. However, in the context of the Commission's interest in assigning control priorities and in monitoring trends in response to such control measures, it is probably adequate to be able to assess gross river inputs because control measures have to be implemented on a local basis after agreement at a regional or global level.

63. It should be noted that the guidelines have been developed with the assessment of inputs of major rivers, i.e., fluxes greater than 1000 m$^3$ sec$^{-1}$, in mind, and as such reflect some of the Marine Chemistry Working Group's current interest in overall mass balance assessments. For such very large rivers, the ACMP agreed that short-term fluctuations and accidental or episodic inputs are irrelevant in their effect on overall long-term fluxes from river to estuary. However, on a more regional or local scale, such fluctuations may be important. It was noted that almost all the rivers in the areas of interest to the Oslo, Paris and Helsinki Commissions can be expected to be subject to quite marked seasonal and even short-term variations in flow and composition. For this reason, it is essential that the suggested sampling frequency of once or twice a month be regarded as a minimum requirement, which might well have to be increased in the light of local conditions, as revealed by the preliminary surveys advocated in the early section of the guidelines.
64. It was noted that the recommendation to use 0.4 µm as the separation point between dissolved and particulate matter is unavoidably an arbitrary decision and the ACMP agreed that in general terms it is satisfactory. However, it was pointed out that in certain circumstances such a separation could lead to misleading information as to what is dissolved and readily biologically available and what is not. In the particular instance of phosphate, for example, under some conditions a 0.4 µm filtration might reveal available dissolved phosphate which in reality is bound in bacterial cells. Under such circumstances, a further filtration through a 0.2 µm filter might be advisable.

65. Subject to these additional notes, it was agreed that the guidelines developed via the Marine Chemistry Working Group should, if followed carefully, allow the user to establish and follow sampling and analytical procedures which will enable the collection of good quality data on river inputs to the marine environment. However, further work on the estimation of net inflow from estuaries to the sea was thought to be necessary and as new results become available these will be considered by the ACMP with a view to developing strategies for the assessment of net fluxes.

PROGRESS IN WORK REQUESTED BY THE OSLO AND PARIS COMMISSIONS

66. The ACMP considered the programme of work which ICES had been requested to perform by the Oslo and Paris Commissions, on the recommendation of their subsidiary bodies, and noted the progress in this work as reported in the following paragraphs. Several of the items have been dealt with earlier in this report and so are merely referenced.

Specimen Banking

67. This subject is covered in paragraphs 52 to 57, above, and in Annex 4. These sections of the report reflect the present state of knowledge on sample storage and specimen banking. On the question of shorter term storage, the ACMP recalled that the sampling guidelines (to be issued as a Cooperative Research Report) in relation to monitoring using fish and shellfish make specific recommendations on sample storage. It was also noted that the Marine Chemistry Working Group had briefly discussed the question at their 1982 meeting. The ACMP agreed that the MCWG should be asked to consider whether or not further information should be collected on the changes which may take place in contaminant concentrations under the storage procedures commonly adopted for water, sediment and biological tissue samples.

Transport of Lead in the Marine Environment

68. An overview transmitted via the Marine Chemistry Working Group is attached as Annex 5, and the ACMP felt that this, together with the comments recorded in paragraphs 59 to 60, above, fulfilled the request for information on this subject.

Methods for the Assessment of River Inputs

69. The ACMP consideration of this request is reported in paragraphs 61 to 65, above, and a set of guidelines to be followed in assessing gross riverine discharges of trace metals and organohalogenes to the marine environment is attached as Annex 6. The ACMP recognized that, as work on the measurement of river inputs progresses, it should be possible to develop strategies
for the assessment of net fluxes and, accordingly, it was agreed to review this topic after the 1984 Symposium on Contaminant Fluxes through the Coastal Zone.

**Sampling Guidelines for Monitoring Using Fish and Shellfish**

70. The ACMP has approved the additional guidance on this subject (see paragraphs 22 to 25 above), especially that developed in relation to trend monitoring, and noted that a complete set of amended guidelines would be sent to the Oslo and Paris Commissions Secretariat by the end of April 1982. It was noted, however, that from time to time it might be necessary to extend or amend the guidelines further as new knowledge is collected; in particular, some aspects of trend monitoring are still under active consideration. The ACMP therefore agreed to keep this matter under review.

**ADP Handling of Marine Pollution Data**

71. Discussions of collaboration on this topic between ICES and the Oslo and Paris Commissions are currently under way and are outlined in paragraphs 26 and 27, above. In noting that the JMG has agreed to cooperate with ICES in the development of an ADP-compatible reporting format for common use, the ACMP agreed that this matter would have to be considered in detail by the ICES Working Group on Marine Data Management, but it was stressed that users' specifications of requirements must be the starting point for this work.

**Analytical Methods and Intercalibration Exercises**

72. Plans have been prepared for the conduct of the Fifth Round Intercalibration Exercise in relation to the measurement of metal concentrations in sea water (5-18 September 1982, Nantes) and are described in paragraph 7, above.

73. The ACMP noted (see paragraph 8) the plans for an investigation into the quantification of PCBs in biological tissues using capillary column gas chromatography and considered that if this goes according to plan, it ought to be possible to develop guidelines on a more accurate method for quantifying PCB concentrations in marine environmental samples.

74. It was further noted that the MCWG had held some preliminary discussions on the feasibility of an intercalibration exercise for analysis of hydrocarbons in sea water (see paragraph 9). It was recognised that such an exercise might be extremely difficult to conduct and that the involvement of a large number of laboratories may be precluded by practical considerations. The ACMP, however, confirmed its support and encouragement for such an activity and considered that it ought to be conducted as soon as the practical difficulties can be solved.

75. The ACMP's initial consideration of the more general request for advice on the rationale for intercalibration exercises is recorded in paragraphs 12 to 18, above.

**Biological Effects Studies**

76. Progress is being made on biological effects studies and the ACMP's current views on the matter are recorded in paragraphs 34 to 41, above. A portion of the GESAMP strategy for biological effects monitoring, which provide a basis for the deliberations of the ACMP, is attached as Annex 3.
Studies on Sediments in Relation to Pollution

77. The main responsibility for investigations under this topic rests with the Working Group on Marine Sediments in Relation to Pollution and the ACMP's comments on this Working Group's reports are recorded in paragraphs 42 to 45, above. Further, it was noted that an additional pilot study on sediments in relation to pollution is being undertaken under the ICES/SCOR Working Group for the Study of the Pollution of the Baltic and that this can also be expected to yield information which will be of interest to the Oslo and Paris Commissions.

New Tasks

78. It was noted that among the items on the work programme for the period up to and including 1983 were new requests for advice on the effects of dumping wastes from TiO₂ production at sea, capping of contaminated dredge spoil deposits and atmospheric inputs. Members of ACMP were identified to take lead responsibility for these tasks (see paragraph 38 regarding TiO₂ wastes) so that they could be discussed in depth at the 1983 mid-term meeting. It was further noted that the question of plankton blooms was a matter of interest to the Commissions, and the ACMP has arranged to study this topic further as outlined in paragraph 56, above.

Work Requested by the Helsinki Commission

79. The ACMP took note of the request which the Helsinki Commission had submitted to ICES, which had invited ICES continuously to assess the condition of the seal populations of the Baltic Sea, particularly in view of the strong indications that the serious decline in the reproductive rate of seals in the Baltic Sea Area is due to pollution.

80. The ACMP agreed that there was considerable cause for concern and recalled that it had on a number of previous occasions reviewed information on the association between effects on seals and the levels of contaminants found in their tissues and the environment. Although the cause-and-effect relationship has not definitely been confirmed and may well be a complex issue, given the observed changes in abundance and distribution of seals and the body burdens of certain contaminants and their possible effects, there is a clear need for a comprehensive review of the problem. It was noted that a paper on this subject had been provided by Dr L Almkvist for the ACMP to review the present status of Baltic marine mammals. Furthermore, the Marine Environmental Quality Committee and the Marine Mammals Committee have requested that a special review of the various factors which may be related to the uptake of contaminants by marine mammals and their consequent effects should be undertaken at the 1982 Statutory Meeting.

81. Accordingly, it was agreed that, on the basis of the various papers already available and in the light of the outcome of discussions at the 1982 Statutory Meeting, the ACMP ought to be in a position to comment on the issue next year. The matter will subsequently be kept under review and reports will be made to the Helsinki Commission at appropriate intervals.

82. In reviewing the progress in other work requested by the Helsinki Commission, the ACMP noted that the development of species code lists for Baltic Sea invertebrates was progressing and the preparation of a reporting format for ADP handling of data on contaminants in fish and invertebrates would be completed by the end of 1982.

Progress in the Study of the Baltic Sea

83. At its 1982 meeting, the ICES/SCOR Working Group on the Study of Pollution of the Baltic dealt with a wide range of topics. The results of its consideration of these topics are summarised below.
Cooperative Studies

84. The Working Group intends to collect summaries of the results obtained through the Baltic Open Sea Experiment (BOSEX) 1977 for a joint publication, covering physical, chemical, biological, sedimentological and trace metal studies.

85. On the basis of the BOSEX observations as well as results of other studies, the Working Group has decided to pursue investigations of the patchiness, or inhomogeneity in distributions, of physical, chemical and biological variables in the Baltic Sea. Several national or bilateral pilot studies were carried out during 1981, giving further evidence of inhomogeneous distributions of various properties. These results emphasize the need for further joint studies, both to obtain a better understanding of natural variability and to generate a better basis for the interpretation of monitoring data. Accordingly, further pilot studies will be carried out during 1982 and, during a workshop in early 1983, plans for a cooperative study will be formulated on the basis of the results from different areas in the Baltic Sea. Cooperation will be sought with the Baltic Marine Biologists in this work.

86. The formulation of mass balances for selected substances as well as models of the cycling or fluxes of some elements has been attempted on a national or bilateral basis for sub-areas of the Baltic Sea, such as the Gulf of Bothnia. Here a fairly substantive data base has been obtained on nutrients and some harmful substances. The budgets help identify gaps in the information and focus the attention on research needs. On the basis of the present results, it can be concluded that fragments of cycles are now understood for sub-areas, and it was decided that an attempt should be made to cover the whole Baltic Sea, probably starting with some nutrients. In this connection, it should be noted that unusually low oxygen concentrations were observed in some areas of the Baltic Sea and the Kattegat during the autumn of 1981, and that the oxygen conditions in the whole Baltic Proper seem to have deteriorated during 1981. A link with eutrophication has been suggested. The report on the matter from the ICES/SCOR Working Group is given in Annex 7.

87. Biological effects studies are being carried out in several areas of the Baltic Sea, e.g., the Transition Area and the southwestern Baltic, the northern Baltic Proper and the Gulf of Bothnia. There is considerable interest in establishing a regular contact between the groups involved in these studies in the Baltic and the groups conducting similar studies in the North Sea region. This will be pursued by the Working Group.

Sediments and Sediment-Water Exchange Studies

88. A framework for a programme to study sediments, sediment processes and the exchange of substances between sediments and the water column has been developed, dealing with sampling, analysis and interpretation. This has been carried out in response to Council Resolution 1981/2:16. The work will be further pursued with the aim of establishing coordinated sediment studies in the Baltic Sea.

Other Pollution Studies

89. The Working Group strongly recommended that the Baltic Sea countries participate in the baseline study planned for the entire North Atlantic for 1985, and in the relevant preceding intercalibration exercises. This has been brought to the attention of the Helsinki Commission, and it was noted with great
satisfaction that the Commission has endorsed the recommendation.

90. Several problems requiring further study had been identified in the Baltic Assessment Document (Assessment of the Effects of Pollution on the Natural Resources of the Baltic Sea, 1980, HELCOM Baltic Sea Environ. Proc. No. 5B (1981)), some of which have been considered above or elsewhere in this report. In relation to new contaminants it was noted that the Council had passed a resolution in 1978 (C.Res. 1978/4:13) encouraging studies of new, possibly harmful, substances and requesting that the results be reported to ICES. The Working Group reiterated this request and especially the need for the development of appropriate analytical techniques as well as studies of the inputs of these substances.

91. In relation to the identified requirement for further research on the distribution, cycling and effects of pollutants and nutrients in coastal areas, the Working Group was aware that the Symposium and Workshop on "Pollutant Fluxes through the Coastal Zone", planned for 1984, will be relevant. Scientists from the Baltic Sea countries involved in this field were reminded to participate and present their results at that meeting.

92. The ACMP took note of the proposals and activities of the ICES/SCOR Working Group on the Study of the Pollution of the Baltic, as set out in paragraphs 83 to 92, above, and endorsed them.

**OTHER MATTERS FROM THE MARINE CHEMISTRY WORKING GROUP**

93. The ACMP was informed that the Marine Chemistry Working Group had, in addition to the matters mentioned earlier, considered international activities related to the study of the CO2 system in the ocean. It had also discussed studies of nutrients, especially in the Baltic Sea, and had reviewed intersessional work on the analysis of lead in biological material, which was nearly complete. Finally, the MCWG had approved a format for the leaflets on "Techniques in Marine Chemistry" and had received commitments from several members to produce leaflets. The ACMP noted this information with interest and expressed its satisfaction that some leaflets would be ready for publication in due course.

**OTHER MATTERS FROM THE WORKING GROUP ON MARINE POLLUTION BASELINE AND MONITORING STUDIES IN THE NORTH ATLANTIC**

94. The ACMP was informed that the WGMPCNA had considered national priorities in the choice of contaminants for monitoring and had concluded that the contaminants studied in the ICES Coordinated Monitoring Programme (mercury, cadmium, lead, copper, zinc, dieldrin, DDT isomers and PCBs) were still of sufficient importance for monitoring of them to continue. However, several other substances were mentioned as priorities by some countries, and as a result the Working Group arranged that short review papers would be prepared on: polynuclear aromatic hydrocarbons, petroleum hydrocarbons, nutrients, zinc, HCB, and toxaphene. These papers would enable the WGMPCNA to decide what its reaction, if any, should be.

95. In addition the WGMPCNA proposed a notification procedure by which members would submit papers on "new" or additional contaminants so that the ICES community could be alerted to potential problems.

96. The ACMP noted these activities with approval.
ANNEX 1

ASSESSMENT OF THE STATUS OF INTERCALIBRATIONS ON THE
DETERMINATION OF CONTAMINANTS IN MARINE SAMPLES

1. TRACE ELEMENTS IN SEA WATER

Dissolved phase

a) Sampling

The accompanying table (Table 1) indicates which elements can be satisfactorily sampled. This means, for instance, that following the results of the IOC/UNEP/WMO Sampling Intercalibration (PANCAL-80), a modified GO-FLO or Niskin bottle on a clean stainless steel or plastic-coated hydrowire can be considered adequate for the elements listed as satisfactory, and probably also for the ones in parentheses, although they were not tested as such in PANCAL-80.

As the Table points out, the main requirement at present is for an intercalibration of sampling techniques for Hg. Pb also needs to be intercalibrated, but it is realized that the difficulties involved and the means required will greatly limit the ability of average laboratories to make viable deep ocean Pb measurements. Finally, Se, Sn, and possibly As, were identified as elements for which sampling needs to be investigated, with Se being given a higher priority among these three.

b) Pre-treatment

For open-ocean waters, filtration is unnecessary and, indeed, it could very often become a possible source of contamination when working with very low levels.

A very high priority is identified for the intercalibration of filtration procedures for coastal waters.

c) Storage

Acidification and storage in containers made of the proper clean material (depending on the elements considered) seem to be satisfactory over long periods (one or two years) for the elements listed as such in the Table. The metals in parentheses have not been studied as fully, but are felt to be adequately preserved.

There may be a problem for Pb from the open ocean, but that is not a concern for most ICES or JMG laboratories.

A medium priority need was identified for Se and a low priority for As and Sn.

d) Analysis (including pre-concentration)

The elements considered satisfactory are listed in the Table, but those in parentheses are not as well-documented.

Although Pb analysis is very difficult, it was felt that it was possible to analyze for Pb at concentrations greater than 20 ng/l. Analysis below that threshold was considered problematic and requires further work.

It was also noted that the analysis of As, Se, Sn and Co presents greater difficulties and needs to be examined, with Se getting the highest priority among that group.

Particulate phase

No intercalibration work has so far been conducted for any of the stages of the measurement of the concentration of particulates and of their trace element content. While no proposal is made at this time for open-ocean particulates, a high priority is placed on the sampling, pre-treatment and measurement of particulates in coastal waters. The storage of filters and the analysis of the trace element content of particulates have yet to be intercompared.

Other Remarks

Depending on the requirements of other ICES Working Groups or even of other MCWG sub-groups on trace elements in biota or in sediments, it is possible that trace elements not presently included in the Table should be added for various reasons (e.g., Be, Sb, Ag, etc.).
Table 1. Trace elements in sea water.\(^{\star} \)

<table>
<thead>
<tr>
<th></th>
<th>Satisfactory</th>
<th>Problematic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sampling</strong></td>
<td>Fe, Mn, Ni, Cu, Zn, Cd (Al, Co, Mo, V, Cr)</td>
<td>Sn (As)</td>
</tr>
<tr>
<td><strong>Pre-treatment</strong></td>
<td>Open-ocean N/A</td>
<td>Pb</td>
</tr>
<tr>
<td><strong>Storage</strong></td>
<td>Fe, Mn, Ni, Cu, Zn, Cd Hg (Al, Co, Cr, V, Mo)</td>
<td>Se</td>
</tr>
<tr>
<td><strong>Analysis (incl. pre-concentration)</strong></td>
<td>Fe, Mn, Ni, Cu, Zn, Cd Hg (Cr, Al)</td>
<td>Hg</td>
</tr>
</tbody>
</table>

\(^{\star} \) Elements such as Be, Sb, Ag have never been considered but could be included if the need arises.

**PARTICULATE (Coastal Waters)**

<table>
<thead>
<tr>
<th></th>
<th>Status</th>
<th>Priority</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sampling</strong></td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td><strong>Pre-treatment (phase separation)</strong></td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td><strong>Concentration measurement</strong></td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td><strong>Storage</strong></td>
<td>□</td>
<td>1</td>
</tr>
<tr>
<td><strong>Analysis</strong></td>
<td>Total</td>
<td>□</td>
</tr>
<tr>
<td></td>
<td>Fractions</td>
<td>□</td>
</tr>
</tbody>
</table>

Key:
- N/A = not applicable
- □ = no proposals for the work at present
- V = assessment completed
- 0 = assessment in planning stage
- Priority: 9 = high, 5 = medium, 1 = low
2. ORGANOCHLORINES IN SEA WATER

In the determination of organochlorines in sea water, the following steps can be distinguished:

<table>
<thead>
<tr>
<th>State of development</th>
<th>Further work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samplirig</td>
<td>in progress</td>
</tr>
<tr>
<td>Phase separation</td>
<td>in progress</td>
</tr>
<tr>
<td>Extraction</td>
<td>in progress</td>
</tr>
<tr>
<td>Storage</td>
<td>not considered</td>
</tr>
<tr>
<td>Sample clean-up</td>
<td>not considered</td>
</tr>
<tr>
<td>Separation of fractions</td>
<td>not considered</td>
</tr>
<tr>
<td>GLC separation and quantification</td>
<td>in progress</td>
</tr>
</tbody>
</table>

The development of the methodology to analyze organochlorines in sea water is presently at a relatively low level as compared to trace metals. Work is in progress in some laboratories. Several details of the steps defined above have been studied during the IOC/WMO/UNEP intercalibration exercise for sampling procedures of selected pollutants in open-ocean waters (PANCAL-80, Bermuda 1980).

Work is planned by IOC for the near future related to a comparison of extraction procedures for sea water by XAD-2 resin adsorption and liquid-liquid extraction techniques to be carried out by the Bermuda Biological Station in close cooperation with the Institute of Marine Research (Bergen) and the Netherlands Institute for Sea Research (Texel). These Institutes are presently carrying out preparatory studies, using capillary column techniques for the measurement of specific compounds whenever possible. Accomplishment of this step in the entire procedure is essential before measurement of levels in sea water solution is to be attempted.

Sampling procedures should be tested at that stage and, in fact, such activities are planned as IOC activities as a follow-up to the development of the extraction methodology at Bermuda. This may eventually lead to an appraisal of the techniques for measuring open-ocean levels of organochlorine compounds.

3. TRACE METALS IN BIOLOGICAL TISSUE

The intercalibration studies that have been carried out since 1971 show that the majority of the participants have the capability of producing comparable data for the following metals at the given concentrations:

- Copper: all concentrations $\geq 0.3 \text{ mg/kg}$ (dry weight basis)
- Zinc: all concentrations $\geq 5 \text{ mg/kg}$ (dry weight basis)
- Mercury: all concentrations $\geq 0.05 \text{ mg/kg}$ (dry weight basis)
- Lead: all concentrations $\geq 2 \text{ mg/kg}$ (dry weight basis)
- Cadmium: all concentrations $\geq 0.8 \text{ mg/kg}$ (dry weight basis).

More detailed information on the current status of trace metal measurements in marine biota is given in Table 2.
Table 2. Status of Trace Metal Determinations in Marine Biota

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Current Status</th>
<th>Future Plans</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of sample</td>
<td>(fish and shellfish muscle)</td>
<td>0, (fish liver and representative shellfish homogenate)</td>
</tr>
<tr>
<td>Sampling</td>
<td>Contamination problems associated with Pb only. Work in progress to assess sample size required for trend monitoring</td>
<td>X, to continue present statistical work regarding sample size</td>
</tr>
<tr>
<td>Pre-treatment</td>
<td>work in progress to assess contamination problems during sample processing</td>
<td>X, to continue present work, particularly for lead analysis (MCWG Sub-group)</td>
</tr>
<tr>
<td>Analysis</td>
<td>(a) Digestion - outstanding problems apply only to Pb analysis</td>
<td>To continue present work (MCWG Sub-group)</td>
</tr>
<tr>
<td></td>
<td>(b) Matrix - problem recognized. Can be overcome by modification of digestion procedure and/or by extraction technique</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(c) Quantification - Cd, Pb, Hg, Cu, Zn and As (completed during ICES intercalibration exercises)</td>
<td>To continue current work</td>
</tr>
<tr>
<td></td>
<td>Range of concentration - complete coverage for Cu, Zn and Hg Limited coverage for Cd, Pb and As</td>
<td>0 - to be considered in ICES 7/7M/HT</td>
</tr>
<tr>
<td></td>
<td>Form of metal - total measurements made in relation to public health and trend monitoring programme</td>
<td>□ - No proposals to change present approach</td>
</tr>
</tbody>
</table>

Key:  
V - assessment completed  
♀ - assessment partially completed  
X - assessment in progress  
0 - assessment in planning stage  
□ - no proposals for the work at present.
4. ORGANOCHLORINE COMPOUNDS IN BIOLOGICAL TISSUE

Three groups of interest are identified:

1. Polychlorinated biphenyls (PCBs)
2. Organochlorine pesticides (Σ DDT, dieldrin, etc.)
3. Polychlorinated camphenes (PCCs)

PCBs have been subject to investigations as regards intercalibration work as have some organochlorine pesticides but little, if any, investigation has been carried out in the case of polychlorinated camphenes (toxaphene) beyond identification in marine biotic tissues.

It is recognised that there would be no point in further intercalibration studies of the analysis of low concentrations of organochlorines or of the manipulations such as sampling, autopsy, and storage involved in this work until certain problems concerned with marine oil analyses (at relatively high levels of organochlorines) are solved.

Current philosophy suggests that if the problems concerned with PCB analysis are solved, no major problem should be encountered with the intercalibration of analysis of organochlorine pesticides other than questions concerning long-term storage.

There is a need to investigate the preparation and suitability of fish tissue, ground with Na₂S₀₄ as an ambient temperature-stable material for intercalibration analysis.

5. PETROLEUM HYDROCARBONS IN MARINE SAMPLES

The present status is summarized in Table 3.

The sampling of sea water for petroleum hydrocarbons is under consideration by the IOC under MARPOLMON-P. A non-volatile sampling intercalibration was held in the Baltic Intercalibration Workshop at Kiel, where sea water samples were analyzed for gross hydrocarbon content. More work needs to be done on this subject in both coastal and open-ocean waters. The subject of storage has not been assessed. Extraction techniques were assessed by the Baltic Intercalibration Workshop. However, further work is needed on extraction to provide more reliable information on interlaboratory variations. The levels so far have been up to 5-6 ppb total hydrocarbon by UWF but a wider range of concentrations should be assessed.

There have been a few intercomparison exercises for analyses of petroleum hydrocarbons in tissue. The effects of type of sample, pre-treatment and storage methods have not been investigated adequately by past intercalibrations. The extraction techniques were assessed to some extent by the ICES first round intercalibration, but the results indicated that this is a high priority item for further work. The concentration range for the total hydrocarbon content was 50 µg/g wet weight and this concentration should be used for the next ICES round.
The sampling of sediments and sub-sampling intercalibration is also a very high priority item. The question of storage has not been addressed, but sampling and extraction are high priority items. The results of the ICES first round show again that there has not been an adequate answer reached for interlaboratory variability.

The whole analytical procedure has not been adequately intercalibrated but gravimetric and infrared analyses may not be recommended. UV and UVF for gross content is adequate but depends on the standardization procedure used. Packed column gas chromatography can also give some idea of gross hydrocarbon content as well as some specific compounds, providing the sample extract has been pre-treated. Capillary gas chromatography, GC/MS, LC/MS and HPLC give the most information on individual components of petroleum hydrocarbons.

Overall, the entire subject of petroleum hydrocarbon intercalibration needs to have a very high priority in all compartments.
Table 3 Status of intercalibrations of measurement of Petroleum hydrocarbons

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Sea water (dissolved + particulate)</th>
<th>Tissue (all high priority)</th>
<th>Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling</td>
<td>• IOC</td>
<td>□</td>
<td>□ High</td>
</tr>
<tr>
<td></td>
<td>X Kiel (Brackish water)</td>
<td></td>
<td>priority</td>
</tr>
<tr>
<td>Pre-treatment</td>
<td>N/A</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>Storage</td>
<td>□</td>
<td>□</td>
<td>□</td>
</tr>
<tr>
<td>Extraction</td>
<td>• IOC</td>
<td>• ICES</td>
<td>• ICES</td>
</tr>
<tr>
<td></td>
<td>X Kiel (Brackish water)</td>
<td>• IDOE</td>
<td>• ICES</td>
</tr>
<tr>
<td>Concentration</td>
<td>up to 5 µg/l</td>
<td>~50 µg/g wet</td>
<td>~30 µg/g dry</td>
</tr>
<tr>
<td>range</td>
<td>(Total HC by UVF)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methods</td>
<td>Analysis 1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gravimetric</td>
<td>• ICES</td>
<td></td>
</tr>
<tr>
<td></td>
<td>IR</td>
<td>• ICES</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UV</td>
<td>• ICES</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UVF</td>
<td>• ICES</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• IOC/WMO</td>
<td>• Kiel</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GC</td>
<td>• ICES</td>
<td>• EPA</td>
</tr>
<tr>
<td></td>
<td>HPLC</td>
<td>• ICES</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GC/MS</td>
<td>• ICES</td>
<td>• EPA</td>
</tr>
<tr>
<td></td>
<td>LC/MS</td>
<td>• ICES</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• EPA</td>
<td></td>
</tr>
</tbody>
</table>

Recommended Methods
For PAH analysis: capillary GC
   GC/MS
   LC/MS
   HPLC
For THC (total hydrocarbon determinations):
   Packed column and capillary GC
   UV
   UVF

Key □ = no proposals for the work at present  X = assessment in progress
• = under consideration  N/A = not applicable

1) Analysis is considered as one item because most samples are analyzed by similar techniques.
CONTAMINANTS IN SEDIMENTS

The only international intercomparison exercise on sediments which has been performed has been organised by the Joint Monitoring Group of the Oslo and Paris Commissions. The conclusions drawn were that the participating laboratories were able to analyse most elements studied to a satisfactory degree in sediments which are polluted, whereas the results for non-contaminated sediments were unsatisfactory for some elements. A trial to estimate the bioavailability by a weak acid attack gave very unsatisfactory results (Table 4).

The next step in the JMG programme, which will start in spring 1982, involves the distribution of a frozen wet sample. The participants will be requested to sieve the sample, dry the different particle-size fractions, and analyse some fractions for metals, nitrogen, phosphorus and organic carbon.

The third step which ought to be done should include intercomparisons of sampling procedures.

No international intercomparison exercise has yet been made concerning organochlorines in sediments. There is a great need for starting such an exercise, which should involve the same steps as in the intercomparison exercises for metals.

There is a great need for research to develop a method for estimating the bioavailability of pollutants in sediments.

There is also a need for international agreement on which basis the results should be expressed, e.g., on the basis of the total sample, or a fraction of the sample, organic content, etc., and how samples will be characterized physically and chemically.
Table 4: Results of the JMG intercalibration on trace elements in sediments

Types of sediments:
1. Dried river sediment, highly polluted (NBS)
2. Dried natural estuarine sediment, contaminated
3. Dried natural estuarine sediment, non-contaminated

Elements (30 participants) and Ranges in ppm

<table>
<thead>
<tr>
<th>Element</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>0.02-1.7</td>
</tr>
<tr>
<td>Cd</td>
<td>0.05-10</td>
</tr>
<tr>
<td>Pb</td>
<td>5-700</td>
</tr>
<tr>
<td>Zn</td>
<td>20-1700</td>
</tr>
<tr>
<td>Cu</td>
<td>2-110</td>
</tr>
<tr>
<td>Fe</td>
<td>4000-45000</td>
</tr>
<tr>
<td>Mn</td>
<td>150-700</td>
</tr>
<tr>
<td>Cr</td>
<td>4-25000</td>
</tr>
<tr>
<td>Ni</td>
<td>3-40</td>
</tr>
<tr>
<td>As</td>
<td>4-45</td>
</tr>
<tr>
<td>Co</td>
<td>1-5</td>
</tr>
</tbody>
</table>

Sampling: 10 (high priority)

Pre-treatment:
- drying: 0
- sieving: 0

Storage: 1 (low priority)

Analysis:
- total strong attack: V
- bioavailability: V/□

Key:
V = assessment completed
V = assessment partially completed
□ = no proposals for the work at present
□ = assessment in planning stage
ANNEX 2

CONSIDERATIONS RELEVANT TO SELECTION AND MONITORING OF DUMPING GROUNDS

The advice provided by ICES in 1978 relevant to the selection and monitoring of dumping grounds (contained in Annex I to the 1977 ACMP Report (ICES, 1978)) has been reviewed. It was originally considered that an updated version of that report should be prepared which would take due account of (i) the comments made by Australia (LDC,1980) to the fourth meeting of the ad hoc Scientific Group of the London Dumping Convention (LDC), (ii) the dispersion and mixing processes in deep oceans (ICES, 1980) as related to deep ocean dumping, and (iii) various ICES reports on dumping which have been presented since 1977.

However, although a preliminary draft was prepared on these lines, it was later considered that the GESAMP XII/4 Working Group Report on Sea Disposal Studies (GESAMP, 1982), publication of which is imminent, covers almost all the same points and, in some cases, does so in considerably more detail. Accordingly, it was decided that the most appropriate activity for ACMP would be the preparation of a summary of information conveyed to ICES through the medium of reports and papers delivered at its Statutory Meetings, and which have extended the experience and understanding available since the preparation of the ICES report on selection and monitoring of dumping grounds in 1977. The summary which follows is based mainly, but not exclusively, on such papers.

General Considerations

The work of the ICES Study Group on the Flushing Time of the North Sea and earlier related work (Otto, 1976; ICES, In prep.) are relevant to the general problem of estimating exchange rates and, in particular, how the dilution which can be achieved within a generally confined area such as specific parts of the North Sea is dependent on the flushing time for that area. In addition, the decomposition of organic wastes can release nutrients which may, in turn, lead to massive algal blooms. It has been noted that living or decaying blooms can often result in fish and shellfish mortalities (Eleftheriou et al., 1981).

The strongly acidic waste water from titanium dioxide production which contains high concentrations of FeSO₄ and H₂SO₄ has been shown to cause only a slight and temporary decrease in sea water pH because of inherent buffering capacity and rapid dilution (Weichert, 1977). Sewage sludge poses a health hazard by virtue of pathogenic bacteria and viruses contained in it. Although the number of pathogenic bacteria of sewage origin are reduced gradually in sea water due to the effect of sunlight and salinity, the processes affecting viruses are more complex and less well understood; dilution is one important element in the reduction of virus hazards (Graikoski, 1981).

Consideration should also be given to activities, other than fisheries, in potential dumping areas. Sea bed drilling, ocean bed mining, shipping traffic, etc., may well lead to future increases in the ambient levels of contaminants in the vicinity of marine dumping sites. In particular, ocean bed mining involves benthic collectors, lift systems and shipboard separation and discharge systems that create benthic and surface plumes of fine suspended particulate matter which may persist for considerable periods (Burns et al., 1980; Osturgat et al., 1980).
Appropriate water and waste characteristics will obviously have to be determined in order to establish the appropriateness of an area or region for dumping the wastes under consideration (Calder, 1981).

To follow the dispersion and settlement patterns of dumped materials (e.g. sewage), advanced acoustic monitoring techniques can be used (Thomas and O'Reilly, 1981) as well as the application of tracers.

**Biological Effects**

Industrial wastes can also cause demonstrable effects. In laboratory studies on the effects of dilutions of titanium dioxide wastes on herring (*Clupea harengus*) embryos and larvae, it was observed that the brownish iron hydrate precipitates covered developing embryos to the extent that gaseous exchange between the embryo membrane and the surrounding water was inhibited. Higher concentrations of these wastes reduced the successful fertilization and survival of the eggs (Kinne and Rosenthal, 1967). Comparable results have been determined with Goby (*Pomatoschistus microps*) and Solea solea larvae (Kinne and Schumann, 1968). Certain diseases of dab (*Limanda limanda*) have also been monitored in relation to the dumping of wastes from the titanium dioxide industry in the North Sea (Dethlefsen and Watermann, 1980).

In addition to the direct lethal effects of ocean dumped chemicals on marine organisms, indirect or sublethal effects such as alteration of schooling behaviour may occur (Wildish et al., 1977). Techniques such as short-term elutriate tests and remote sensing have proved useful in assessing potential long-term impacts of the dumped materials on the water column (Plumb and Brannon, 1981; Schmidt, 1977). The bioaccumulation of cadmium in oysters (*Crassostrea gigas*) and the effects of metals on herring eggs and larvae (von Westerhagen et al., 1979) have also been studied in relation to dumping areas.

A review of the recent research strongly suggests that bioavailability of chlorinated hydrocarbons and heavy metals in sediments is controlled mainly by the adsorption-desorption process. The route of uptake of chlorinated hydrocarbons and heavy metals by marine organisms may be directly from sediment, from contact with or ingestion of fine suspended particulates, from compounds dissolved in the water, by ingestion of "contaminated" food or by a combination of these routes. The potential for accumulation of chlorinated hydrocarbons by aquatic organisms is not as great from food as from water although, because of their low solubility in water, food may also be an important source (Ray and McLeese, 1980).

Bioaccumulation results when the rate of uptake is greater than the rate of excretion or degradation. Heavy metals, petroleum, and chlorinated hydrocarbons will accumulate in organs such as liver or hepatopancreas where there is a high lipid content. Concentration factors (concentration in organism/concentration in water or sediment) may be large (Dethlefsen, 1977) and may produce lethal or sublethal effects in marine organisms (Mounib and Eisan, 1977; von Westerhagen et al., 1978).

**Deep Ocean Dumping**

The selection criteria for deep ocean dumping have been based on a conceptual view of the processes in deep ocean areas (ICES, 1980). In brief, the benthic boundary layer, usually 10-100 m thick, is considered to be well mixed with its properties being sharply discontinuous with those at the upper boundary. Mixing from the boundary layer into overlying water usually is rather slow. However, within the boundary layer, the horizontal dispersion will be relatively rapid. Abyssal circulation from tidal, internal and aperiodic water movements, and abyssal mean flow are discussed.
Soluble wastes in deep-ocean areas are likely to mix throughout the benthic layer, be transported horizontally by abyssal circulation and eventually undergo vertical mixing at ocean boundaries (continental slopes and near-land masses) where biological productivity is high (Vaccaro et al., 1980).

Escape of material from the benthic layer will depend to a minor extent on lateral intrusion of water, although for several reasons dispersion will still be more horizontal than vertical. Vertical mixing is expected to be enhanced at the ocean boundaries because of slope mixing (breaking of internal waves against the slope, bottom roughness, and large mean currents).

The renewal of abyssal water masses, especially from the overflow over the Faroe-Iceland-Greenland ridges, has been one of the major fields of research in the ICES hydrography community in recent years (Willebrand and Meincke, 1980).

The mean residence times used in these projections of oceanic circulation were taken from Worthington (1976), and have been discussed by McCartney and Talley (1980) on the basis of new estimates of production rate to Labrador sea water. Their findings suggest larger oceanic deep-water upwelling than previously estimated, indicating the need for further study of the processes of deep-water formation.

Marked northward currents occur along the African and European Atlantic Shelves (Ellett et al., 1979, Ellett et al., 1980; Mittelstaedt et al., 1980). It is not yet clear whether these currents constitute one system or whether they should be considered as more separate phenomena. Slope water processes occur along islands and isolated oceanic banks (Dooley and Henderson, 1980; Gould and Catler, 1980). Coastal upwelling is especially important as a mechanism for transport of water and nutrients into the euphotic zone. New data are available on upwelling off Northwest Africa (Meier-Fritsch and Mittelstaedt, 1980; Hagen and Zahn, 1980). Deep ocean circulation observations, as made in connection with the NEADS (North East Atlantic Dynamics Study), have contributed to the knowledge of circulation variability in the northeast Atlantic. Long-living eddies have been observed in both the eastern and western parts of the Atlantic and these may be of great significance for the transport of dumped substances in the ocean. New techniques are now being deployed to study these eddies (Bradley and Tillier, 1980). These hydrographic observations will allow an improved understanding of the fate of dumped materials in the open oceans.

**Human Health Effects**

There are also considerable hazards to human health associated with ocean dumping and these were given considerable attention in the Australian proposal (LDC, 1980) including (a) exposure to persons engaged in the dumping operation, (b) exposure to contaminants in the marine environment (viz. pathogenic micro-organisms), and (c) transfer of contaminants to humans through the food chain.

**Incineration**

The incineration of contaminants at sea is receiving increasing attention and ICES has been keeping abreast of these developments. At this time, the most effective method of destroying toxic organics (environmentally persistent pesticides, herbicides, PCBs and other chlorinated hydrocarbons) appears to be by incineration. Incineration of chlorinated hydrocarbons on land requires treatment of stack
gases because of the presence of hydrochloric acid vapors (Fish, 1977). Incineration at sea does not require treatment of stack gases because the residual alkalinity of the sea water neutralizes the hydrochloric acid (Paulson, 1977; Dunn, 1979).

A recent report (Company, 1980) has reviewed the operational characteristics of the three incineration ships currently in service. This report shows that organochlorine wastes were destroyed with efficiencies exceeding 99.98% under optimum conditions. The destruction of PCBs was not attempted, however, the prospects for an acceptable level of destruction appeared good. None of the studies has revealed any adverse effects on the marine ecosystem.

Dredge Spoils

There has been considerable investigation in recent years of dumping areas receiving dredge spoils. The effects of the disposal of such wastes include the physical blanketing of the bottom (Norton, 1978, 1980). In addition, these spoils may be contaminated with heavy metals, oil, or organochlorine compounds, causing adverse effects on zooplankton and benthic shellfish populations (Feng et al., 1978; Capuzzo, 1980), among others.

New dredge spoil disposal sites should be selected on the basis of a lack of interference with navigation, fisheries, amenities, and on several other considerations. For example, surveys before dumping site selection should cover the seabed topography and sediment structure, normal variations in water quality and suspended solids, hydrographic conditions, the benthos and its chemical quality. Such background or benchmark information is required for comparison with conditions after disposal commences.

Because original or background conditions may no longer exist, dredge spoil disposal sites which have been used for many years generally require a lower level of monitoring in order to assess the biological impact of varying types of dredge spoil deposits, to assess the possible transfer of contaminants to the water column and marine life and to investigate the changes after dumping such as physical movements of the spoil, weather, or recolonization of biota.

References


42. Weichart, G., 1977. The pH in the waters of the German Bight as influenced by primary production and respiration and by acid TiO2 wastes. ICES Doc. C.M.1977/C:3 (mimeo.).


STRATEGY FOR MONITORING THE BIOLOGICAL EFFECTS OF POLLUTION

There are several possible monitoring objectives: for input control; the protection of human health; the determination of spatial and temporal trends in contamination and its effects on the ecosystem; the provision of environmental management data. Constraints of time and resources often make it necessary that a single monitoring exercise subserve several requirements, but the programme, whether single or multi-purpose, may usefully be built up according to a consistent strategy that will enable the requirements of different objectives to be identified and appropriate techniques used.

In developing such a strategy, the Working Group recognized three phases:

Phase I identification: detecting a change in time and/or space;
Phase II quantification: establishing the degree or extent of the change;
Phase III causation: determining the cause of the observed change.

The recognition of these phases is important because techniques appropriate to one phase will usually be less appropriate to another. For example, it has been pointed out that many of the readily observable biological changes can be produced by a wide variety of causes, not all related to pollution, but by selecting a suite of non-specific biological effects measurements, changes from the normal state, however caused, can be quickly identified and quantified. On the other hand, the measurement of biological effects specific to one particular pollutant will not identify effects produced by other pollutants.

These phases may be regarded as a temporal sequence of discrete investigations for monitoring biological effects of pollution. It should be noted that in many cases (for example, when hot-spots are already known) phase I, which concentrates on chemistry and involves biology largely to detect a signal, may have been accomplished before the start of the investigation. It is then possible to begin with phase II. At each phase, techniques could be used to increase the precision or sensitivity before the next phase was entered into. Furthermore, at any point within this strategy, an evaluation of the situation based on scientific or economic considerations could indicate that further investigation is unwarranted.

Implementing the Strategy

We may now examine how the variables evaluated in the earlier sections can be drawn into this framework to produce practical guidelines for a monitoring programme. It is useful for descriptive purposes to consider spatial and temporal aspects separately, although the components of both are essentially the same.

Phase I. In the context of spatial variability, the identification phase is concerned with mapping potential or actual effects and thus pinpointing "hot-spots" of pollution. This allows the effort in the later phases to be concentrated at those sites where biological effects are most likely to occur.

* Taken from:
Potential "hot-spots" of effects can be inferred from the distribution of contaminating inputs and from areas with elevated levels of contaminants in water, sediment and biota. Increased resolution may be achieved using chemical analysis of sessile suspension feeders of wide geographical distribution (such as Mytilus); mobile species (such as fish) may also be used but they provide poorer resolution. Spatial discrimination by these methods can be very high.

Biological variables in phase I must be sensitive and precise. That is, they should be responsive to very slight changes in the chemical composition of their environment but, at the same time, they should be capable of precise measurement and discrimination against normal variability - they should have a high "signal to noise" ratio. Also, to be useful on a wide scale, they should be cheap and generally applicable. The incidence of abnormal morphological and pathobiological conditions in fish, as defined earlier, appears to be highly suitable for broad-scale discrimination and over long time periods. Bioassays of sea water samples, although probably subject to greater temporal variability, fulfil all other requirements, and resolution can be increased merely by increasing the intensity of the sampling grid. Observations on lysosomal stability of the bioassay organisms can also be a useful additional technique.

Phase II. The demonstration of a "hot spot" by the above-mentioned procedures does not of itself indicate biological damage. Confirmation and quantification is then required, and this constitutes phase II, which relies on the examination of more ecologically significant variables. Since one purpose of biological monitoring is to ascertain the health of the ecosystem, gross measurements at community level are important. This approach would have been advocated in phase I but for its relatively high cost, for its insensitivity, and for the problems of interpretation. The Working Group endorsed the conclusion reached by the Ecological Panel of the ICES Workshop on Pollution Effects Monitoring, that analysis of the benthic and epibenthic communities, including littoral communities, is likely to be more cost-effective than plankton work. As indicated earlier, however, the case for detailed analysis of benthic communities in a monitoring role is not yet proven, and the Working Group recommends that only gross measures such as total abundance, total biomass, etc., be done initially. To obtain increased sensitivity, it is recommended that general physiological measurements, such as scope for growth and biochemical measurements, be made.

Phase III. At this stage it may be possible to ascribe the causes (where these are not already known) of any effects using circumstantial evidence, and this can be enhanced by increased chemical sampling, with specific analyses using advanced techniques. It may be noted that phase III requires a rather different type of chemistry from that likely to be used in phase I. The later phases are concerned with quantification and with understanding dose/response relationships so that knowledge of the speciation of chemicals and of their partition in different biological compartments is needed. Bioassays on seawater samples modified in specific ways to alter their chemical quality is a relevant biological approach, and it is at this stage that the extensive use of laboratory experiments on the effects of substances (i.e., retrospective testing) becomes particularly useful.

For a limited number of substances, or types of substances, specific biological effects can be sought, but it should be noted that effects will often be produced by the interactions of numerous contaminants rather than by single substances acting alone.

The essential aspects of the strategy are set out in the following Table.
Elements in Studying the Distribution of Biological Effects

Phase I Identification: Distribution of known inputs:
- chemical analyses of water, sediment and biota;
- selected bioassay of organisms (e.g., estimates of lysosomal fragility);
- elevated incidence of morphological/pathological abnormalities in fish populations;
- bioassay of surface/deep water with oyster/echinoderm larvae, hydroids.

Phase II Quantification: To be implemented on detection of spatial variability of any phase I determinations. In order:
- survey of benthic community structure;
- survey of benthic population parameters;
- physiological indices (e.g., scope for growth) in selected widespread species (e.g., Crassostrea, Mytilus);
- biochemical indices in above-mentioned species.

Phase III Causation: To be implemented on confirmation of significant effect assessed by the above-mentioned procedures:
- by specific chemical analyses of water, sediment, biota for suspected contaminants;
- bioassay, with specific chemical modifications to water samples;
- biochemical techniques specific to chemicals or chemical classes.

Temporal aspects. Study of changes in intensity with time is concerned with establishing trends. This can be done: (i) in conjunction with a spatial mapping exercise to demonstrate changes in geographical distribution, one spatial survey identifying the distribution being repeated on an appropriate time sequence; or (ii) by repeated observations at the same site to demonstrate station-specific trends. The approach can clearly be applied over various time scales, depending on the nature of the contaminant inputs.

The strategy for determining temporal changes is similar to that for spatial changes as set out in the Table, except that the objectives become the identification of changing inputs, changing levels of chemicals in the environment, changing incidences of morphological modifications in fish, and changing size and frequency of hot-spots. The use of bioassays provides a good basis for measuring changes in water quality, as long as a suitable baseline such as synthetic sea water can be established. In such work, variations in water quality due to seasonal influence, blooms, changes in coastal run-off, etc., must be taken into account. An adequate
trend-monitoring study will require a suite of biological procedures covering, in particular, sensitivity, causation and ecological relevance, drawn from the possibilities listed under phases II and III of the spatial study.

Geographical scales

Application of the strategy will vary, depending on the geographical scale, and in general three ranges may usefully be recognized. First, at the local level, one can think in terms of point-source pollution from individual discharges or of localized hot-spots on dumping grounds or around industrial terminals, where the details of the input may be known and the strategy may therefore be more finely focused. The Working Group discussed this aspect, but in view of its terms of reference, concentrated on the second level: the regional, which will encompass the sum of the effects of the local-scale pollution and include diffuse inputs from land and river run-off and from the atmosphere.

At the third level, the global scale, the Working Group concluded that there was sufficient reason to modify its strategy with respect to open oceans.

There is increasing evidence that the division between estuarine and shelf waters, on the one hand, and the open oceans, on the other, is surprisingly firm in that "leakage" of pollutants between the two is slight. Since most of the inputs of contaminants are to shelf waters (by main rivers, land run-off, direct discharge), it is to be expected that biological effects will occur in these regions more quickly than in the open oceans. Accordingly, the greater proportion of monitoring effort should be concentrated on these shelf waters.
ANNEX 4

REVIEW OF ENVIRONMENTAL SPECIMEN BANKING PHILOSOPHY
AND EXPERIENCE

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INTRODUCTION

After considering a preliminary report on environmental specimen banking during the October 1981 meeting of the Advisory Committee on Marine Pollution, it was decided to revise the paper with attention paid to weighing specimen banking expense against the value of the expected return.

DEFINITIONS

A distinction exists between the routine storage of environmental samples and environmental specimen banking. The former activity is usually relatively short-term, covering a time span of days, weeks, months, and occasionally years. The purpose is generally to set aside samples for state-of-the-art analyses, either to accommodate limited analytical capabilities or to re-check results or accomplish some additional analyses over a relatively short time span (see Pearce, 1981, for a detailed discussion).

Environmental specimen banking, on the other hand, is defined as the systematic collection and storage of samples, with minimal changes, for deferred examination (chemical analysis or other evaluation). The examination may be deferred for a period of years or even decades following collection. The reasons for storing such materials would be to: (1) measure levels of new contaminants; (2) measure levels of contaminants which are not now considered important but may be so in future years; (3) re-measure materials in samples with the more accurate analytical tools of the future; and (4) provide a historical documentation of changes in contaminant levels for the litigation, legislation or regulatory actions of the future.

PHILOSOPHICAL VIEWS ON ENVIRONMENTAL SPECIMEN BANKING

At the ACMP meeting in March 1981, it was agreed to survey the opinions of selected scientists regarding specimen banking - its appropriateness and desirability from practical as well as conceptual considerations.

The survey was designed to develop a philosophical consensus from concerned researchers about environmental specimen banking as distinct from a solicitation of suggested methods for developing facilities or management structures. Relative priority compared to other activities that depend on the limited resources, logistical practicality and, finally, need, were subjects identified as appropriate for consideration.

The survey results demonstrate that the concept of specimen banking generates a high level of interest. However, serious considerations beyond the conceptual level lead to considerations and concerns of the practicality of realizing a full-scale specimen banking operation.
The greatest dilemma revolves around concern for setting in motion quality control procedures, which obviously reflect existing state-of-the-art analytical capabilities, yet which are expected to be suitable for as yet unidentified chemical pollutants or greatly increased sensitivities for determining known environmental contaminants.

A second consideration of major importance is the need for statistically sound sampling designs for collecting appropriate specimens. The concern is that the number of samples required to achieve meaningful trend analyses may rapidly over-load banking facilities, thereby suggesting that logistical aspects may prove prohibitive in achieving the goals of specimen banking. The collection of meaningful time-series data appears, in some instances, to be equally prohibitive.

The question of ownership and control of banked specimens was raised. Does the individual collector, his institution or agency, the country, or the international organization involved own the banked specimens? Who controls access?

The cost of adequate large-scale facilities, based on sample freezing, caused concern. Alternative suggested storage methods, considered to be less costly, included:

1. solvent extraction and storage,
2. canning in appropriate containers,
3. air drying.

Additionally, museum storage is relevant, since specimens from museums can sometimes be used to provide data.

In view of the problems that still need to be solved, it is suggested that new specimen banking activities should be given a low priority.

STATUS OF SPECIMEN BANKS

"Ad hoc" specimen banks (i.e., those that happen as an adjunct activity to specimen collections for other than specific banking purposes) are widely distributed within the ICES community. Specimens, thus archived, fall in a limbo between those routinely stored and those collected and stored specifically for specimen banking. "Ad hoc" specimen banks usually accrue from environmental monitoring programs as a result of planned or accidental surpluses of collected material and the default of passing time.

The main activity in relation to specimen banks is in the Federal Republic of Germany and the United States of America. A bilateral agreement between the Federal Republic of Germany and the United States resulted in a cooperative program for development of protocols for the preparation, analysis and storage of samples for the determination of organic and inorganic chemical residues. Pilot specimen banks were developed in both countries. The Federal Republic of Germany now has an operational specimen bank currently in Julich. The United States activity remains in the pilot stage of development.

There have been three international workshops, sponsored in part by the Federal Republic of Germany and the United States, concerned with specimen banking and environmental monitoring. The first, held in Brussels, Belgium, dealt primarily with human specimen banking considerations. The second, in West Berlin in 1978, was entitled "Monitoring Environmental Materials and Specimen Banking"
(Luepke, 1979). It focused on other-than-human environmental specimen banking considerations. A third workshop was held in Saarbrücken, Federal Republic of Germany, in May 1982. Its purpose was to report on experiences to date in specimen selection and analysis within existing specimen banking programs. It was noted that specimen banking activities exist in only four countries: The United States, Federal Republic of Germany, Canada and Japan. The most developed program, that of the Federal Republic of Germany, is to move from the pilot phase into a "real" banking phase in 1983. Approximately 25 different specimen types, each from two locations, will be banked. The United States program, remaining in a pilot phase, is limiting its environmental specimen banking to Mytilus edulis for the time being. Canada retains a bank of frozen wildlife specimens collected from various monitoring programs. Japan has established a small pilot bank in conjunction with the development of reference materials.

Recommendations from the meeting include:

1) Standard Reference Materials (SRMs) should be included as a part of specimen banking activities. Existing SRMs should be banked. New SRMs, having matrices similar to banked environmental specimens, should be developed and subsequently banked.

2) Knowledge obtained since the last specimen banking workshop (1978) indicates that specimen banking activities should be continued and that pilot programs are currently providing data which will be useful in the implementation of full-scale specimen banking efforts.

3) An "executive committee" on specimen banking should be formed with the purpose of obtaining wider international interest.

COST CONSIDERATIONS

There is relatively little information on the cost of environmental specimen banking except for the development of pilot programs in the U.S.A. and the Federal Republic of Germany (Luepke, 1979). The specimen bank in Jülich has been operative for only a relatively short time, and true cost estimates would, therefore, be premature - even if available for this report.

Both German and American specimen banking activities have combined human (liver) specimen banking with other "environmental" specimen banking activities, giving higher priority to the former. This fact confounds the estimation of cost considerations for specimen banking on two counts: (1) the joint nature of the program (human liver as well as other environmental specimens) tends to obscure the true cost of developing a system for marine environmental specimen banking alone; (2) the nature of priority setting (giving highest priority to the human specimen program) provides little in the way of actual (cost) experience in other than human specimen banking.

However, with the qualifications stated above, the U.S. pilot banking program is used below as an example for cost estimation, keeping in mind the assumption that costs should be comparable whether or not a multi-use type of program exists. The U.S. pilot effort is jointly funded by the Environmental Protection Agency (EPA) and the National Bureau of Standards (NBS). Table 5, provided in part by the Office of Exploratory Research, EPA, presents a breakdown of proposed and actual costs, on an annual basis, since the inception of the pilot banking program.
The original proposal for the U.S. pilot bank included four components: man, marine bivalve molluscs, terrestrial species (honey bees and earthworms), and air biomonitor (as yet to be designated). The result of reduced funding levels has been to slow the schedule of the pilot bank to the extent that only the first component (human liver) has been realized as a functional pilot program. The second component (marine bivalve molluscs) is in the stage of protocol development for sample collection, storage and analysis for both organic and inorganic chemical compounds. Little progress has been made on the remaining components - terrestrial and air.

In a very broad sense, the adjusted cumulative actual cost (see Table 5) of the U.S. pilot bank to date i.e., 2 million U.S. dollars, may be used as a reasonable cost model for facility development in support of a single-component (i.e., marine) pilot specimen bank. The U.S. pilot facility has been designed to accommodate a total of 30,000 samples, but no predictions are available on the rate of sample accumulation. However, the step from a pilot facility to a full-fledged banking facility would represent a very significant financial investment.

According to Luepke (1979), the major expense for running a specimen bank, once established, is to acquire and retain sufficient competent personnel needed to assure the best possible performance of the total facility system. His estimate is that manpower costs would represent 45-50% of an annual operating budget.

Early personnel estimates for the U.S. pilot banking program projected growth to seven permanent, full-time persons by year five. Attainment of a fully operational specimen bank may, at a conservative estimate, result in a 50% increase initially in total personnel required or approximately ten permanent, full-time people. Using an approximate figure of $50,000 for the total cost per individual (salary, overhead, etc.), personnel costs would run at about half a million U.S. dollars annually. Using Luepke's (1979) estimate that personnel costs are expected to reflect 50% of the total operating cost, a total annual cost of operation estimated at one million U.S. dollars is indicated.

Specimen banking can usefully be linked with an active monitoring program. In the U.S. the Mussel Watch Program provides a monitoring link for the marine component. The average annual cost of Mussel Watch during its seven years of operation has been approximately one-half million U.S. dollars. A significant fraction of that total must reflect a hidden, but real, cost for the development and operation of the specimen banking program.

Early planning for a specimen banking program should emphasize a need for relatively sophisticated adjunct data handling facilities. The developmental costs of such a capability, scaled only on the basis of whether the data facility is a separate one developed exclusively for specimen banking or one that represents a blend with an on-going data handling system, remain another significant but hidden cost consideration in the full program development.

In summary, the estimated cost for a single-component (marine) environmental specimen bank, in rough terms, would be as follows in millions of U.S. dollars:
CONCLUSION

Dedicated environmental (marine) specimen banking represents a very significant undertaking from the point of view of financial and other resource considerations. Cost estimates, based on the U.S. pilot specimen bank experience, verify the point.

As yet, the limited experience on the part of both the Federal Republic of Germany and the United States programs has failed to allay basic philosophical questions regarding the likelihood of realizing the original goals (in other than human specimen banking activities especially), and practicality of meeting logistical support requirements in order to achieve a meaningful end product. Yet both programs have made significant investments.

As a result of this review of specimen banking activities, it is suggested that new programs in this field of interest might usefully await the further experience from on-going operations, and that, in the meantime, a low level of priority is appropriate.

REFERENCES


GENERAL

USEPA Environmental Health Effects Research Series, Health Effects Research Laboratory, USEPA, Research Triangle Park, North Carolina, 27711 U.S.A.:


EPA-600/1-79-017 May, 1979. The National Environmental Specimen Bank Research Program for Sampling, Storage, and Analyses.

EPA-600/1-81-025. Pilot Program for the National Specimen Bank Phase I.
Table 5. Proposed costs and actual funding levels for a five-year pilot specimen banking program. Figures represent millions of U.S. dollars.

<table>
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<th>Fiscal Year</th>
<th>1) EPA Funding</th>
<th>2) NBS Funding</th>
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<th>Cumulative Total</th>
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<td>1983</td>
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*Adjusted Cumulative Total: $4.95, $2.05

* It should be noted that three years of development of chemical analytical methods (sample storage and analysis) at a cost of $150,000 per year (total, $450,000) to NBS had preceded the establishment of the pilot bank facility in 1979. Only inorganic methods were done by NBS. Organic methods were developed cooperatively with the Federal Republic of Germany.

The differences between the actual and proposed levels of funding do not reflect unrealistic planning but rather realism of the funding situation. The question of EPA's continued support has not as yet been answered for fiscal year 1983.

1) U.S. Environmental Protection Agency
2) U.S. National Bureau of Standards
INTRODUCTION

This summary on behaviour, fluxes and distribution of lead in the marine environment was prepared in response to requests for information on a number of topics related to marine pollution by the ICES Marine Chemistry Working Group at its meetings in May 1979 in Lisbon, Portugal, and February 1980 in Copenhagen, Denmark.

An attempt has been made to utilize the latest information available by competent scientists in the field, recognizing that sampling and analytical techniques for lead in water require extreme precautions to avoid contamination and only skilled analysts with sophisticated instrumentation in ultra-clean laboratories are capable of measuring lead with the accuracy and precision needed for mass balance evaluations (Schaul and Patterson, 1980; Settle and Patterson, 1980). There are a number of monographs available on the geochemistry of lead in the environment (e.g., Wedepohl, 1975; Garrels et al., 1975; and Nriagu, 1978) and on the effects of lead in the environment (NAS, 1972, 1980; WHO, 1977; Jaworski, 1978; Boggess and Wixson, 1979; Forstner and Wittman, 1979). Man has had a considerable impact on the global geochemical cycling of lead. The natural levels of lead in ancient ice of Arctic and Antarctic glaciers have been determined to establish prehistoric atmospheric concentrations (Murozumi et al., 1969; Ng and Patterson, 1981). The anthropogenic effects on lead concentrations in the human environment and in the sea have been examined in a number of studies (e.g., Patterson, 1965; Patterson et al., 1976; Barltrop, 1979; Burnett and Patterson, 1980a; Settle and Patterson, 1980). Lead precipitation fluxes at tropical oceanic sites, as determined in the SEAREX (Sea-Air Exchange) Programme, have been reported recently by Settle et al. (1982a, b).

It is not the intention here to review the literature on the effects of lead on marine organisms and on humans, except incidentally and where biological uptake may be significant in the cycling of lead through the marine environment.

NATURAL SOURCES AND CONCENTRATIONS OF LEAD

Lead is ubiquitous in nature. It is estimated that the earth's crust contains 3.8 x 10¹⁴ tonnes of lead and the soil 4.8 x 10⁹ tonnes. The predominant form of lead in the earth's crust is galena or lead sulphide (PbS). Minor amounts of lead are present as cerussite (PbCO₃) and anglesite (PbSO₄), which are secondary minerals formed by weathering processes acting on galena. About 200 other lead-containing minerals have been described, but they are inconsequential in terms of contributing to the total amount of lead in the earth's crust. The concentration of lead in the earth's crust ranges from 5 to 30 mg·kg⁻¹
(Wedepohl, 1975) and is usually accepted at an average of 16 mg·kg$^{-1}$ (Barltrop, 1979). The lead concentration in ores and in ferromanganese nodules in marine sediments may reach 1 000 mg·kg$^{-1}$. In uncontaminated soils, the lead concentration ranges from 5 to 25 mg·kg$^{-1}$. This varies with the pH of the soil; acidic soils generally have a lower lead concentration than alkaline soils. Organic matter in soils plays a role in establishing the lead content, but whether it helps to retain lead by fixation or facilitates movement out of the soil is still uncertain.

The annual contribution of dissolved lead to the sea by rivers in pre-industrial natural discharge has been estimated at 1.7 x 10$^4$ tonnes (Patterson, 1965). The concentration of lead in uncontaminated groundwaters and surface fresh waters ranges from 1 to 60 µg·kg$^{-1}$; this varies according to the pH and hardness of the water. Soft, acidic fresh waters tend to have a higher concentration of lead than hard, alkaline waters. Deep-ocean sea water, free of contamination, usually has a concentration of less than 10 ng·kg$^{-1}$. At least one report (Burnett and Patterson, 1980b) suggests that a concentration of more than 1 ng·kg$^{-1}$ in sea water is indicative of environmental contamination and/or contamination of the sample during collection.

It has been estimated that about 1.0 x 10$^4$ tonnes of lead are introduced into the atmosphere from natural sources and are eventually washed out by precipitation into the oceans. The main contributions are from suspended dust (85%), plant exudates (10%) and forest fires (5%) (Craig, 1980). The natural lead concentration in the atmosphere is about 0.6 ng·m$^{-3}$.

**MAN-MADE SOURCES OF LEAD**

Man is known to have affected the natural geochemical cycling of lead in the global environments for at least four thousand years. It has been estimated that 70 million tonnes of lead were smelted before A.D. 1850, and that there was a per capita production of lead within the Roman Empire which was equivalent to about one-fifth of that within today's industrial nations.

In 1940, the world lead production was 1.9 million tonnes of which 36 000 tonnes was burned in leaded fuels. The annual world production of lead had reached 3.5 million tonnes in 1966 with about 310 000 tonnes being burned in leaded fuels, and it had stabilized at about 3 million tonnes by 1968. The world production and consumption of lead in 1979 were estimated at 3.6 x 10$^6$ tonnes and 5.4 x 10$^6$ tonnes, respectively. The annual world production of lead has not varied a great deal from 1975 to 1980. The consumption figure includes secondary recycled and refined lead and is constituted, on the average, of the following uses: 51% for storage batteries, 22% for tetraalkyl lead, 6% for cable sheathing and 21% for miscellaneous uses including lead alloy production. It is estimated that 380 000 tonnes of tetraalkyl lead were produced in 1973 and that this declined to 300 000 tonnes in 1975 (WHO, 1977), as curbs were placed in various countries on the use of lead in automobile fuels. About 70% of this total is likely to enter the environment as inorganic lead compounds from the combustion of organic lead compounds. Paints are estimated to release to the atmosphere 50% of the lead used in their formulation, while other applications of lead-containing materials result in local contamination only.

The total annual present-day release of lead to the atmosphere is estimated at 0.44 x 10$^6$ tonnes, of which 61% arises from combustion of leaded gasoline, 23% from production of steel and other metals, 6% from lead mining and smelting, and 5% from fossil fuel burning. The current average concentration of lead in
the atmosphere is estimated to be 3.5 ng·m⁻³ of which 3.1 ng·m⁻³, or 84%, of the total, can be attributed to man-made sources. This lead has a residence time of about two weeks in the atmosphere (Schaule and Patterson, 1980) and is believed to enter the sea through washout by precipitation.

Rivers now contribute annually a total of 0.74 x 10⁶ tonnes of lead, of which 32% is dissolved and 68% is particulate. It is estimated that 99% of the lead in particulate form settles to the bottom on the continental shelves. Of the 0.24 x 10⁶ tonnes of dissolved lead that enters the sea with river runoff, most of it reaches the open sea.

The sources and fluxes of anthropogenic lead are shown in Figure 1.

**LEAD IN SEA WATER**

Lead may be present dissolved in sea water in a number of forms: Pb²⁺, PbOH⁺, PbHCO₃⁻, Pb(OH)Cl, PbO₂, PbSO₄²⁻, PbCl₂ and PbCl³⁻, with PbCO₃ probably being the main form of labile lead in the sea (FAO, 1971; Sipos et al., 1980). The distribution of lead between dissolved and particulate forms in sea water is not yet precisely known, but indications from some early experiments on lead in filtered water and plankton were that about half of the total lead in sea water is in dissolved form (FAO, 1971). More recent studies (Schaule and Patterson, 1981) show that the dissolved fraction is closer to 90% of total lead in sea water. Lead compounds, with the exception of those arising from combustion of leaded gasolines, are generally quite insoluble in sea water and tend to have a high affinity toward adsorption on surfaces of both inorganic and organic particles. Sedimentation and adsorption of lead on bottom sediments leads to a low concentration of lead in sea water.

Quantitative analysis for lead in sea water is very difficult and requires much skill to avoid contamination and to achieve high precision in measurement. The isotope dilution technique, using a mass spectrometer for analysis, (Tatsumoto and Patterson, 1963) is considered to be the most reliable method for lead analysis. Other methods of analysis, such as concentration by solvent extraction and analysis by atomic absorption spectrophotometry (Brooks et al., 1967), give results that may be an order of magnitude higher than those obtained with isotope dilution. But even with isotope dilution and mass spectrometry, the refinement in sampling and analysis by this technique over a 17-year period (Tatsumoto and Patterson, 1963; Burnett and Patterson, 1980b) has led to a lowering of the estimated lead concentration found at 1000 metres in the sea from 30 ng·kg⁻¹ to 1 ng·kg⁻¹. Lead concentrations in coastal sea water are usually considerably higher than in the deep sea because of environmental contamination and can be measured by techniques having a higher limit of detection and lower degree of sensitivity than those used for analyses of open ocean waters (Patterson, Settle, and Glover, 1976).

Estimations have been reported by Schaule and Patterson (1980) of the prehistoric and present-day concentrations, standing crops and fluxes of lead in the open North Pacific. These models are reproduced in Figure 2. The present flux of lead from the atmosphere to the sea is estimated at 60 ng·cm⁻²·yr⁻¹, compared to the prehistoric flux of <0.5 ng·cm⁻²·yr⁻¹, while the present-day flux from the sea water to the sediments is 50 ng·cm⁻²·yr⁻¹, compared to 3 ng·cm⁻²·yr⁻¹ in prehistoric time. The present concentration of lead in the upper mixed layer is more than 16 times higher than the prehistoric level, and the present standing crop between the 100-m level and 4300 m is 1180 ng·cm⁻², compared to 420 ng·cm⁻² during prehistoric time.
The distribution of dissolved lead in the surface and deep waters of the Northeast Pacific, as observed in a section between California and Hawaii, is shown in Figure 3. It is clear from this figure that the highest concentrations of dissolved lead are in the surface layer, below which there is a decrease in concentration with depth. This is opposite to the type of vertical distribution noted for other metals, e.g., cadmium, which exhibit an increase in concentration with depth, at least for the upper 1000 m.

The highest concentration shown, of almost 15 ng Pb·kg⁻¹, was observed in the western section of the transect near Hawaii. About 14 ng·kg⁻¹ was observed adjacent to the coast of California. Surface concentrations of dissolved lead did not vary a great deal from about 10 ng·kg⁻¹. Concentrations in deep water below 3500 m depth, however, were about an order of magnitude lower, at 1 ng·kg⁻¹. Schaule and Patterson (1981) showed that in surface and deep water samples (to 5000 m) collected in the Northeast Pacific between California and Hawaii, dissolved Pb was by far the largest fraction (more than 90%) of the total Pb in most of the samples analyzed. The vertical lead concentration profiles below the upper mixed layer are probably not in a steady state. These lead concentrations are increasing in response to the increase in anthropogenic input. The estimated lead residence times are about 20 years in the thermocline and 80 years in the deep waters. Calculations based on a 10-fold increase in lead input and concentration in the surface mixed layer of the Northeast Pacific, since the mid-eighteenth century, show that the 10 ng·kg⁻¹ average concentration between 100 and 900 m is 2 to 5 times larger, and the 1.8 ng·kg⁻¹ concentration between 900 and 5000 m is about 2 times larger, than it was in the mid-eighteenth century. How well these models represent the global picture is unknown at present, but it can be expected that higher values of lead would prevail in the North Atlantic and lower values in the southern hemisphere.

**BIOAVAILABILITY AND BIOLOGICAL CYCLING OF LEAD IN THE MARINE ENVIRONMENT**

Lead has no known nutritional value to marine organisms. It is generally toxic to all aquatic organisms. Much of the research on the biological uptake of lead has been confined to mussels (Schulz-Baldes, 1974; Phillips, 1976; and Popham et al., 1980) and phytoplankton (Schulz-Baldes and Lewin, 1976). In order that lead can impose a toxic stress or be bioaccumulated by marine organisms, it must be in a biologically available form. This generally means that the lead must be present in a soluble form which can be assimilated by marine organisms. While the particulate form of lead may be taken up by filter feeders, it is believed that most of this lead is excreted. It is unknown how the different ionic species of lead affect plants and animals. Lead present in particulate form is usually unavailable biologically, unless it is solubilized within the gut of a marine animal. Some forms of particulate lead, however, may be biologically available by virtue of their solubility in sea water.

Certain ions present in water reduce the solubility and toxicity of lead. This particularly applies to fresh water, and it is well known that hard fresh water with a high calcium content dissolves lead rather poorly and gives a comparatively low toxicity of lead to exposed fish. The toxicity of lead was found to decrease in the presence of phosphate during bioassays on Hyallela azteca, and this was believed to be due to a reduction in the concentration of water-soluble lead (Freedman et al., 1980). Lead is not as acutely toxic to marine organisms as other metals, e.g., mercury, silver, copper, zinc and nickel. However, the sub-lethal effects are only poorly understood.
Lead can be accumulated to rather high concentrations by some organisms, particularly filter feeders. The effect of this bioaccumulation on the organism itself is not too well known, although efforts are being made to study the effects on the enzyme systems and endocrinology of exposed animals. The reproductive capability of exposed organisms may be affected. So far, it is not known whether metal-binding proteins, such as metallothionein which binds cadmium, are available to combine with lead and thereby reduce its toxicity to marine animals. The hazard with high concentrations of lead lies more with the consumer than with the organism that has accumulated the lead.

Marine organisms do not appear to play a major role in the cycling of lead in the water column. Unlike cadmium, lead exhibits the highest concentration in the surface mixed layer of the sea and then decreases to low levels at abyssal depths. As noted earlier, in most cases 90% or more of the total lead in the water column of the open ocean is in the dissolved form, so that at any given time there is comparatively little lead associated with particulate organic or inorganic material. The lead that eventually reaches the sediments as part of or adsorbed onto particulate matter is generally considered as being mobilized there by incorporation into authigenic minerals. The picture may be somewhat different in coastal waters where there is usually a higher concentration of suspended particulates than in the open sea. However, the limited amount of good quality data on concentrations of lead in waters of the Pacific Coast of Canada show that more than half of the total lead is in the dissolved form (Stukus and Wong, 1981).

Sedimentary lead, because it is regarded as being fixed, is usually considered as being unavailable for uptake by marine organisms. This is not entirely true, because the availability of metals from sediments depends on the presence of other metals and organic substances and on complex diagenetic processes which take place in the sediments with time. For example, it has been shown that the presence of iron in sediments can reduce the availability of sediment-bound lead to the estuarine bivalve Scrobiculaira plana (Luoma and Bryan, 1978). The presence of organic substances also reduces the bioavailability of lead. The flux of lead from the sediments to the overlying water as a result of various processes is unknown, but it is probably small in comparison to the downward flux.

The formation of alkyl-lead compounds in marine sediments by bacteriological action has not yet been conclusively demonstrated, although it has been shown to occur in freshwater systems (Wong et al., 1975), and there is some evidence of slight methylation (0.03%) of lead as the nitrate in incubation experiments with marine sediments (Thompson and Crerar, 1980). Tetraalkyl lead compounds have been detected in fish tissue (Sirota and Uthe, 1977), but it is uncertain whether the presence of these compounds can be attributed to methylation of lead in sediments or in the fish, or whether they were present in the water from other direct sources. If methylation of lead does indeed occur by natural biological processes in the sea, its contribution to the cycling of lead in the marine environment by virtue of mobilizing the lead from sediments would be probably small and insignificant from the point of view of the total biogeochemical cycle of lead in the sea. However, its biological impact could be great, if one draws on the analogy with mercury.
CONCLUSIONS

(1) The anthropogenic impact on the natural geochemical cycle of lead in the marine environment is highly significant, in that it is now estimated that the annual industrial inputs of lead to the total oceans (300 000 tonnes yr⁻¹) exceed the natural inputs (114 000 tonnes yr⁻¹) by nearly a factor of 3.

(2) Rivers contribute $7.4 \times 10^5$ tonnes of lead annually of which about 70% is in particulate form and is deposited almost entirely in coastal waters. The natural pre-industrial input of lead from rivers has been estimated at $0.17 \times 10^5$ tonnes yr⁻¹.

(3) The annual present-day atmospheric input of lead to the oceans is estimated at $2 \times 10^5$ tonnes, which is about equal to the lead reaching the open ocean from rivers.

(4) A major contributor to atmospheric lead is the combustion of leaded gasolines (61%).

(5) The vertical lead distribution in the sea shows the effect of surface introduction of lead, with a high concentration at the surface (10-15 ng kg⁻¹) and decreasing to one-tenth of that concentration at depths below 3500 m.

(6) There appears to be little biological effect on lead distribution in the water column. More than 90% of the total lead measured in water samples taken in the deep sea, from the surface to depths of 5000 m in the Northeast Pacific, is in the dissolved form.

(7) Because of the low solubility of lead compounds in sea water, much of the particulate lead in runoff and discharge from industrial plants and urban centres is deposited in coastal sediments.

(8) The release of lead from sediments to overlying waters depends on many factors, such as the presence of iron and the concentration of sedimentary organic matter. However, the flux of lead from sediments to bottom water is considered to be small.

(9) The bioavailability of lead in sea water depends on the solubility of different species of lead and on the uptake of these species by marine organisms. It is believed that in order for lead to be biologically available, it must be present in ionic form, whether this be in the sea water or in the gut of an organism.

(10) The natural methylation of lead by micro-organisms in marine sediments has not been conclusively proven. If it does occur, however, it can be considered to contribute to the recycling of lead from sediments, by virtue of the higher solubility of methylated forms of lead. The amount recycled in this way would be probably very small. On the other hand, its potential hazard to marine organisms and human health should be borne in mind.

REFERENCES


Figure 1. Schematic representation of the global distribution, concentrations and cycling of lead through various environments (T = tonne(s); $\tau_r$ = residence time; concn = concentration; ng = nanograms; µg = micrograms)
AT PRESENT

Degtn

Cone.

Stllldiffl

Flua

cop

II.

ng/119

ng/cm²

0

---J.---

P1Hlui

10

---J.---

100

---J.---

2000

---J.---

4300

Figure 2(a). Oceanic outputs, river and atmospheric inputs, and reservoirs (estimated) of soluble lead during prehistoric times in the open North Pacific. Soluble lead entering the shallow reservoir is removed with particles to the sediments where it is chemically transformed to authigenic minerals. Fluxes of lead in terrigenous silicates which do not contribute significant amounts of soluble lead are not shown. (From Schaule and Patterson, 1980).

PREHISTORIC

Depth

m

Conc.

ng/cm²

Flux

ng/cm²y

Standing
crop

ng/cm²

0

0.6

0

0.6

---J.---

100

230

950

50

50

50-300 yrs. res.

6

420

Figure 2(b). Oceanic outputs, river and atmospheric inputs and reservoirs of soluble lead at the present time in the open North Pacific. (From Schaule and Patterson, 1980).
Figure 3. Dissolved lead distribution in the Northeast Pacific Ocean between Hawaii and California, shown in a three-dimensional representation. Surface values are plotted as open circles; concentrations at depth are represented by solid circles. The separate profiles at the far right refer to stations occupied in the near-shelf area at different times. (From Schaule and Patterson, 1980).
METHODS OF ASSESSING GROSS RIVERINE DISCHARGES OF TRACE METALS AND ORGANOHALOGENS INTO THE MARINE ENVIRONMENT

PREFACE

The following paper was produced by two members of the ICES Marine Chemistry Working Group on the question of how to assess riverine inputs to the marine environment. After modification to take account of comments made by that Working Group and the Working Group on Marine Pollution in the North Atlantic, the paper was considered by ACMP. It was recognised that the Joint Monitoring Group of the Oslo and Paris Commissions had expressed an interest in a similar question, so the paper is also being transmitted to the JMG.

It should be noted that the JMG expression of interest related to the net flux out of an estuary into the open sea, whereas the paper attached relates to the quantification of gross inputs from rivers to estuaries. In many instances these are likely to be appreciably different from the net flux out of the estuary into the coastal areas and the open oceans. However, gross inputs are a necessary first step in the evaluation of net inputs and it is apparent that the present state of the art is not such as to allow a general methodology to be developed according to which net inputs can be estimated. Moreover, in the context of the Commissions' interest in assigning pollution control priorities and monitoring trends in response to such control measures, it is probably adequate to be able to assess gross river inputs because control measures have to be implemented on a local basis after agreement at a regional or global level.

It should be noted that the guidelines have been developed in a detailed context with the assessment of inputs of major rivers, i.e., rivers with fluxes greater than 1000 m$^3$ sec$^{-1}$, in mind, and as such reflect some of the Marine Chemistry Working Group's current interest in overall mass balance assessments. For such very large rivers, short-term fluctuations and accidental or episodic inputs are irrelevant in their effect on overall long-term fluxes from river to estuary. However, on a more local or regional scale, fluctuations may be important. Almost all the rivers in the areas of interest to the Oslo, Paris and Helsinki Commissions can be expected to be subject to quite marked seasonal and even short-term variations in flow and composition. For this reason, it is essential that the suggested once or twice a month sampling frequency be regarded as an absolute minimum requirement, which might well have to be increased in the light of local conditions as revealed by preliminary surveys advocated in the early section of the guidelines. It should be noted that hydrological aspects of river fluxes will be a subject of discussion at the 1984 ICES Symposium on Contaminant Fluxes in the Coastal Zone and the outcome of this Symposium will be considered in this context. In the meantime, the ACMP has arranged to examine current information on techniques to measure the inputs from fresh water in the light of existing national programmes.

Finally, it was noted that the recommendation to use 0.4 µm as the separation point between dissolved and particulate matter is unavoidably an arbitrary decision. The ACMP agreed that in general terms it is satisfactory, however, in certain circumstances such a separation could lead to misleading information as to what is dissolved and readily biologically available and what is not. In the particular instance of phosphate, for example, under some conditions a 0.4 µm filtration might reveal available dissolved phosphate which in reality is bound in bacterial cells. Under such circumstances a further filtration through a 0.2 µm filter might be advisable.
INTRODUCTION

Estimates of the fluxes of chemicals across ocean boundaries provide important contributions to the elucidation of geochemical processes and chemical fluxes within the ocean itself. Thus, the exchanges of chemicals at the air-sea interface, and the influxes of chemicals to the ocean through continental runoff are of considerable value to the marine chemist, both in establishing the sources and rates of introduction of materials to the ocean and in estimating the relative importance of anthropogenic and natural chemical mobilization processes. Material is carried across the continental/ocean boundary by glaciers, rivers and groundwater but, of these, rivers are the most important carriers of dissolved and particulate material on a global basis. The rivers also carry the majority of the material which enters the ocean as a consequence of human and industrial activity and it is for these reasons that attention to the composition of rivers is most valuable in the context of oceanic geochemistry and pollution.

The first comprehensive review of world river composition was published by Livingstone in 1963. At that time fairly comprehensive and reliable data on the major ion composition, and total dissolved solids concentrations, for the major rivers draining the six populated continents were available. Data for the trace constituents of rivers were, however, not only meager but unreliable due to the limitations of the sampling and analytical procedures then available. Only relatively recently have reliable trace element data for time-series samples from some major rivers become available. Examples of these are provided in papers by Carpenter et al. (1975) for the Susquehanna River, Trefry and Presley (1976) for the Mississippi, Gibbs (1977) for the Amazon and Yukon, and Yeats and Bewers (1982) for the St. Lawrence. While we are sure that there are many other rivers for which routine measurements of trace composition have been or are being made, we regard the approaches and interpretation exemplified by these cited studies as being the most appropriate for application to other major rivers in order to define more reliably the discharge of trace metals and organohalogens from rivers to the ocean.

It can be argued that, with the rapid improvement in our understanding of the processes controlling the dispersion and transport of trace constituents in the ocean that has occurred during recent years, more balanced attention to the influxes of chemicals, particularly contaminants, to the ocean is long overdue. We believe that the benefits to both individual nations and to international organisations through the conduct of accurate and precise time-series measurements of potential contaminants at the mouths of major rivers are considerable. This document was prepared in order to outline approaches and methods for gaining more and better information on the fluxes of trace organic and inorganic
constituents in river discharge. Our aim is to provide a basis upon which to measure the discharges of trace metals and organohalogen compounds from individual rivers and, hopefully, to stimulate greater attention to such measurements within the framework of marine pollution assessment.

Not all the material discharged by rivers can logically be said to represent an influx to the ocean as a whole. A certain proportion of the constituents of rivers is retained within estuarine and nearshore sediments and does not succeed in reaching the truly offshore marine environment. Thus, the measurements advocated here apply solely to the gross fluxes of trace constituents within river discharge. Of equal interest, from a marine chemistry and pollution perspective, are the net fluxes of these same constituents that represent the proportions of the gross fluxes that survive nearshore removal and sedimentation to be transported into the deep offshore marine basins. The determination of net fluxes is, however, considerably more complicated than the measurement of gross fluxes and we have left the subject of net riverborne fluxes to another document.

The Approach

We will assume that the subjects of these investigations are fairly major world rivers, typically rivers with water discharges greater than 1000 m³ s⁻¹ (≈ 3 x 10¹³ yr⁻¹) or about 0.1% of the aggregate global river runoff. We need to be able to define the longitudinal and transverse locations for sampling, the frequency of sampling, and the sampling and analytical methods most suitable for obtaining reliable estimates of the annual fluxes of trace metals and organohalogen compounds in river discharge. No fixed definition of such criteria as sampling locations and frequencies can be given that would be immediately applicable to all rivers, but we will endeavour to develop a rationale by which they may be determined.

The highest signal-to-noise ratios for the detection of contaminants that might ultimately degrade the environment are gained as close to their individual sources as possible. However, detection and quantification of emission rates of contaminants at their source does not allow direct estimates to be made of their fluxes into the marine environment because a proportion of these emissions will be retained in the terrestrial sphere. Therefore, at the cost of a reduction in signal strength but with the advantage of needing fewer sampling sites, it is preferable to measure the discharges of contaminants to the ocean as close to the ocean/land boundary as possible. In the case of rivers, appropriate sampling sites are within the freshwater regime as close to the river estuary as possible but at locations where marine influences are relatively minor. Unfortunately, the mouths of major rivers are often the sites for major population and industrial centres and in such cases it will be necessary to shift the sampling location upstream to avoid local and frequent variations in river composition that result from nearby discharges.

Preliminary Surveys

As a first step, all available hydrologic and water quality data for the downstream portions of the river of interest should be acquired in order to reduce the extent of preliminary survey work that, in the absence of any such information, would have to be carried out. It might initially appear that the most appropriate location to make measurements for flux estimates might be just upstream of the limit of salt intrusion. However, periodic reversals of river flow direction can occur upstream of the limit of salt intrusion and this can permit the ingress of marine suspended material to such locations. Therefore, it is necessary to establish a sampling section for flux measurements at a place further upstream of the limit of salt intrusion at which unidirectional downstream flow is always maintained over the entire depth range of the river. Often sufficient hydrologic data are available to permit easy selection of the most suitable location but,
if they are not, a short survey of potential sites can be made with a current
timeter over a few tidal cycles during a low river flow season. In northern
temperate areas, for which the runoff regime is mainly controlled by rainfall
and warm season evaporation, the lowest runoff period is in mid-year (typically
between June and August). These conditions apply to rivers in the south central
and southeastern United States and in western Europe (the Thames is a typical
river of this type). The flow characteristics of other rivers in northern
temperate climes are mostly controlled by cold season snowfall and warm season
rainfall. The minima in flow are, in such cases, in the early or late parts of
the year and the winter months (December to February) are the most appropriate
periods in which to carry out low-flow hydrological surveys.

Once the choice of axial location for sampling has been made, a more detailed
survey of the hydrologic conditions in a cross section of the river of interest
is required. An arbitrary grid of sampling positions on a cross-section should
be selected to enable the extent of horizontal and vertical gradations in major
dissolved properties and suspended particulate concentrations to be determined.
Obviously the more complex is this sampling grid, the more thorough becomes the
determination of property gradients. However, it is generally adequate to limit
the number of sampling points to about ten for rivers with a single channel
having no abnormal bathymetric features. Two alternative approaches can be
adopted for rivers with deltaic mouths. The first is to shift the measurement
cross-section upstream beyond the confluence of the major distributaries. The
second is to carry out the preliminary survey within each major discharge channel.
In terms of overall cost-effectiveness the first alternative is probably the
most appropriate. In the case of single channel rivers, we can follow normal
hydrologic practice and restrict the number of sampling points to, say, three
depths (surface, mid-depth and near-bottom) at stations one-quarter, half and
three-quarters of the way across the chosen section. Once the grid has been
established, samples should be collected at each sampling point daily for periods
of two weeks during each of the major flow regimes, particularly during highest
and lowest flow. For rivers whose regimes are controlled by rainfall and warm-
season evaporation, highest and lowest flows correspond to winter and summer
seasons, respectively. Rivers whose flow is strongly affected by snow-melt have
their highest flows in the spring and lowest flows in winter months. It is also
desirable to install current meters at each of the grid locations in order to
estimate the contributions of flow for each segment of the cross-section. However,
hydrologists can often be persuaded to carry out analyses of river channel flow
which would be valuable adjuncts to both the preliminary survey and actual measure-
ment phases of a river analysis program.

The samples collected from the sampling grid should be analysed for suspended
particulate matter and some major ions such as calcium, magnesium, sodium, chloride
and sulphate. In general, analysis for two or more major ions will suffice to
show the degree of river stratification. The concentration of suspended parti-
culate matter can be conveniently determined by filtering a known volume of river
water through a pre-weighed Nuclepore filter and subsequently reweighing the
filter paper after drying. Nuclepore filters maintain remarkably constant tare
weights through wet and dry cycles which is often not the case with other types
of filter. For this reason we would recommend the use of 0.4 µm Nuclepore filters
for this work. The most convenient filter diameter to use is probably 47 mm since
a variety of simple filter holders are available for this size filter. A 47 mm
diameter 0.4 µm Nuclepore filter can handle up to 1 or 2 mg of suspended material
without serious clogging problems and trial and error can be used to determine
the most suitable volumes of river water to filter routinely in the case of an
individual river. It is important, however, to ensure that the volume chosen is representative of the bulk sample and not biased by settling effects in the sampling device. The water sample retrieved from the river should be homogenised by thorough agitation before the subsample intended for filtration is drawn and this subsample should be filtered in its entirety. Suspended matter concentrations can vary widely both within a single river and between rivers and this is why the trial and error approach has to be used to determine the most suitable size of sample to filter. Rivers in northern temperate areas can be expected to contain between 10 and 1000 mg.l⁻¹ of suspended material. The analysis for the major dissolved cations can be carried out by applying flame atomic absorption spectrophotometry to the filtrate from the suspended matter samples. Chloride and sulphate ion concentrations can be measured by titration and colourimetric methods, respectively. All the major ions suggested for measurement exist at concentrations in excess of 1 mg.l⁻¹ in normal rivers and use of these procedures should present only minor difficulties.

**Sampling Design for Trace Constituents**

We will now turn to the design of sampling methodology for determining the fluxes of trace metals and organohalogen compounds in river discharge. The results of the preliminary survey should enable the selection of a number of cross-sectional sampling locations that can account for inhomogeneities in the river composition. In fast flowing rivers there is often little stratification, but in slowly flowing rivers there can be pronounced stratification of the flow due to limited mixing of the waters from tributaries or other discharges to the river. In this respect, the further downstream the chosen section is from industrial outfalls and the confluence of tributaries, the more homogeneous in properties the river is likely to be. However, many rivers, like the Mackenzie in northern Canada, remain horizontally stratified for several hundred miles downstream of the confluence of major tributaries. If the preliminary survey reveals little spatial variability in major constituents, only one or two sampling points need to be selected for the trace constituent sampling series but as the river inhomogeneity increases this number should be increased.

In estimating the fluxes of the trace constituents, we are primarily interested in the dissolved and suspended phases. The suspended sediment flux will comprise both material in continuous suspension and material being transported downstream by saltation. However, both types of material can be regarded as important and relevant to the discharge of trace constituents by the river. We will ignore bed load since such material will become trapped in the vicinity of the estuarine "null zone" where the average time-integrated flow is zero. Exclusion of bed load material in time series samples is achieved simply by ensuring that the near-bottom samples are collected no closer than half a metre above the river bed.

In choosing repetitive sampling locations it is useful to consider the logistics of sample collection such as the ease with which the chosen stations can be occupied throughout the year. In this respect, proximity to shipping channels and the possibility of ice coverage and rafting should be considered. Sampling should be avoided soon after the passage of deep-draught vessels that may cause sediment resuspension by the propeller wash. The difficulties of occupying stations during periods of ice flow can be pronounced. In a recent case in which the St. Lawrence River was monitored for trace metal constituents, the cross section was chosen to be underneath a large road bridge that enabled the sampling devices to be lowered from it under all climatic and weather conditions. It should be stressed that a perfect sampling grid might involve a large number of sampling points but that it is usually not possible to consider large sampling grids for long-term repetitive measurements for logistical or financial reasons.
This should not result in the program being abandoned. Time-series measurements at only two or three sampling sites on a cross-section are extremely valuable, especially if these data are acquired together with cross-sectional current profiles or major ion distributions. Therefore, rather than insisting on thorough account being taken of cross-sectional inhomogeneities, it is more important that a small number of sites be repetitively sampled and that the quality of the analytical results be assured.

Similar arguments can be advanced with respect to sampling frequencies. In general, the higher the sampling frequency the smaller becomes the error in the resultant flux estimates. However, as has been lucidly pointed out by Loftis and Ward (1979), there is a limit to the efficacy of increased sampling frequencies in water monitoring networks. In discussing sampling frequency we must always bear in mind the principal objective of the measurements that we are advocating, namely to permit "estimates" to be made of the fluxes of trace constituents in river discharge. We use the term "estimate" advisedly, since in the absence of much previous quantitative data we are not in a position to specify how accurate the estimate itself should be. In our view we should first collect data which enable a rather crude estimate to be made. We can always refine our sampling network and frequencies in the future if we subsequently require a more refined estimate.

Before discussing the sampling frequency for the trace constituents, it is necessary to define the essential ancillary data that are required during the period of the time-series measurements. The most essential information pertains to the river discharge rate. This is basic hydrologic information that, for most major rivers, is available from national inland water or river authorities. Usually flow information can be obtained from a calibrated section in the vicinity of the chosen monitoring section. Staff water gauges at calibrated sections usually yield a continuous record of river flow analogues that can be readily converted to flow by the hydrologic authority. Such information should be compiled during the course of the time-series measurements to enable integrated bi-weekly discharge volumes to be calculated. It is also desirable to have some information on suspended sediment discharges. In many cases, annual suspended matter discharge figures will be available from national records or from international compilations such as that of Holeman (1968). In general, annual discharges for suspended matter, when combined with weighted values for the trace constituent composition, are adequate for estimating particulate constituent discharges.

The most suitable sampling frequency for the long-term time-series sampling for the trace constituents is twice per month. The utility of increasing this frequency is a small gain in the reliability of the flux estimates but not a substantial one. To a large extent the necessity of increasing the sampling frequency depends upon the extent of high frequency variations in river composition that it is desirable to account for. The probabilities are that such high frequency variations, in the composition of a river of any reasonable size, are the result of injections of material just upstream of the sampling section and are, for the purposes of the main objectives of the proposed sampling program, best ignored. A large number of freshwater quality monitoring networks use monthly or quarterly sampling intervals and, as a result, are really only sensitive to fairly large and sustained changes in freshwater composition. In the case of flux measurements in rivers, the objectives are closer to those of water quality monitoring networks than those associated with the detection of transients such as spills or abnormal excursions in the quality of wastewater discharges. Thus, we would recommend a sampling frequency for the trace constituents of rivers, for the purposes of river discharge flux estimates, of bimonthly or monthly.
Sampling and Analytical Methods for Trace Metals

Two types of samples need to be collected for subsequent trace metal analysis: filtered water samples and suspended particulate material. Ideally these samples should be obtainable from a single sampling device with the aqueous and particulate fractions separated promptly after sample collection. In the case of trace metals, the major problem to be avoided is contamination of the samples by metallic constituents. The sampling procedure recommended here is based upon previous experience with determinations of trace metals in both seawater and freshwater. Samples should be collected by a hydrowire/sampling bottle combination of proven ability to obtain uncontaminated samples in waters of equal or lower ambient trace metal levels than those in the river of interest. The results of a recent intercomparison of seawater sampling devices for trace metals (IOC, 1981) can be used to select appropriate combinations of hydrowire and sampling bottle. Undoubtedly the best combination, from the perspective of obtaining unmodified samples of water, is plastic-coated steel hydrowire and modified GO-FLO samplers. The GO-FLO sampler modifications comprise replacement of the drain cock by one made of solid Teflon and, if necessary, the replacement of all internal "O" rings and seals by equivalents made of silicone. Unfortunately, GO-FLO bottles are susceptible to jamming of the ball-valve closure system if they are used in waters of high turbidity. We would therefore only recommend their use in rivers having suspended sediment concentrations less than 10 mg/L. This makes them undesirable for use in most rivers and the most suitable alternative device is a modified Niskin sampler. Again, the sampler should be modified by replacement of internal "O" rings by silicone "O" rings and replacement of the internal spring by a length of silicone rod or tubing. Niskin bottles are available in a variety of sizes but probably the most appropriate size to use in the case of river sampling is the 5-litre, since this bottle provides a considerable volume of sample whilst being easy to deploy from a small vessel or other structure. There may be other suitable types of samplers but their ability to collect unmodified samples of water for trace metal analysis would need to be established. We do not, for example, recommend the use of Hydro-Bias bottles, as these devices can cause sample contamination for some metals (IOC, 1981). Devices made of low-density (conventional) polyethylene, Teflon or polypropylene are probably also quite acceptable. However, such devices may contain other materials that can contaminate the sample. This is the case with the polypropylene samplers supplied by the National Institute of Oceanography (U.K.). Considerably more latitude can be taken with regard to "hydrowires" in the sense of the line or cable that is used to deploy the sampling device. It is unnecessary to use plastic-coated hydrowire. Virtually any plastic rope, such as nylon, polypropylene or Kevlar, may be used as can also clean stainless steel, although the latter should probably be avoided if clean plastic rope is available. The hydrowire can be weighted with any material of non-metallic composition, such as a metal or stone weight enclosed in an impervious plastic coating or container.

An entirely different approach to sampling, which is also quite acceptable, is the use of pumping systems. Peristaltic pumps operating on weighted polyethylene, polypropylene or silicone tubing are good methods of obtaining uncontaminated samples. Again, it would be necessary to ensure that the samples collected were truly representative of the water being sampled but as long as suitable uncontaminating plastic materials are used in the sampling devices, it is usually possible to obtain viable samples. A note of warning should be given with regard to current speeds in rivers. The larger the sampling device, the greater will be the drag imposed upon it by river flow. In the marine environment, current speeds are generally low but even there high wire angles can be experienced in certain
circumstances. Such problems will be more pronounced in rivers and substantially more weight may be needed on the bottom of the hydrowire to get the sampling bottle or pump inlet nozzle to the desired depth than is the case in the marine environment.

Methods for the Separation of the Aqueous and Particulate Phases

Separation of the dissolved and particulate components is not trivial. Chemicals in natural waters occur in truly dissolved, colloidal and particulate forms and the transition between these forms is continuous. Thus, we have to choose a method of separating the fractions which we wish to analyse and make appropriate operational definitions as to what the nature of these individual fractions are. In the case of trace metals, we usually wish to separate the sample into two fractions by filtration of the sample using a filter of small, but arbitrary, pore size. More classically, filters chosen were either 0.45 µm or 0.22 µm pore size which were commercially available as mixed ester fibre-mat type filters (typically Millipore). Unfortunately, these filters were susceptible to their effective pore size changing as filtration proceeded due to clogging (Sheldon and Sutcliffe, 1969). In recent years nearly all deep marine water filtration has been achieved using Nuclepore filters which have numerous advantages over Millipore filters. First, the rated pore-sizes of Nuclepore filters are fairly accurate but, more importantly, they remain constant throughout the filtration procedure, i.e., they behave as screens (Sheldon, 1972). Second, as we have already stated, Nuclepore filters maintain very constant tare weights through wet/dry sequences which facilitates their use for measuring the concentration of suspended particulate matter in units of mass/volume⁻¹. We would therefore recommend the use of Nuclepore filters for the river sampling program and the most appropriate pore size to use, in order to ensure comparability with common measurements in the marine environment, would be 0.4 µm.

In employing filtration to separate the particulate material from the collected samples, an operational definition needs to be used to define the nature of the filtrate and filtered material. Subsequent analysis of the material retained by the filters will be referred to as analysis of suspended particulate material. The suspended material in such a case is the material in suspension that is removable by filtration through a 0.4 µm Nuclepore filter. The filtrate contains metals both in solution and in colloidal forms that are able to pass through the filter and this can be referred to as "dissolved" material irrespective of the fact that some is fine particulate. Thus, the 0.4 µm pore size Nuclepore filter becomes the basis of our operationally defined dissolved and particulate phases.

Again, there are alternative procedures for separating the aqueous and particulate fractions. One of the common methods is centrifugation. In this case the sample is centrifuged for some pre-determined period at a certain g value. Centrifugation may be expected to result in a better-defined particle size/density cut-off than filtration and it can be used to process larger volumes of water than filtration. This latter advantage can be quite useful when the river of interest is quite turbid and several filtrations have to be employed to obtain sufficient filtrate for analysis. Also, if large amounts of suspended matter are needed for detailed analysis, the centrifugation method may be preferred. However, centrifugation may not be the method of choice if the effluent is to be analysed for trace metals since contamination can occur for some elements that are constituents of the bearings (e.g., Fe, Cr). On balance, therefore, we would still recommend the use of filtration as the preferred method of phase separation.

One or two provisos need to be mentioned here in respect to the actual experimental procedure of separation to be employed. It is equally important that the
samples are not contaminated during phase separation as it is when they are collected. The filter itself should be held within an inert plastic holder of which there are several commercially-available types. Millipore Swinnex holders are quite acceptable for this purpose if they are equipped with silicone "O" rings, are initially flushed with weak (\sim 1N) acid and then washed thoroughly in distilled, deionized water before use. These filter holders can be repeatedly re-used without the need for further acid treatment as long as they are maintained in clean condition and are flushed with distilled, deionized water after replacement of the filter membrane. In fact, the entire filter holder/filter membrane assembly can be washed in weak acid and subsequently flushed with pure water prior to use if Nuclepore filters are employed. As an alternative to distilled, deionized water, the water produced by Millipore "Super-Q" apparatus is quite suitable for washing such devices.

In order to determine the concentration of suspended matter in the collected samples, the Nuclepore filters should be preweighted before installation in the filter holders. Any microbalance that can measure weights of about 15 mg with an accuracy of better than 100 µg can be used to do this. It will be necessary to employ an ionizing device to prevent electrostatic charge effects during the weighing process. After filtration of the samples, the filters may be left within the filter holders and returned to the laboratory for washing (by passing pure water through the assembly) and removal of the filter membrane for subsequent drying (in a dessicator) and re-weighing. The volume of sample that has been passed through the filter, together with the difference between tare and gross weights, can be then used to calculate the suspended matter concentration in the original sample. As has been stated, it is necessary to filter, in its entirety, an aliquot of the homogenised sample in order to avoid biases associated with particle settling in the sample. This aliquot should be drawn directly from the sampling device into a noncontaminating plastic container, particularly if the filtrate is to be used for subsequent analysis of the dissolved fraction. The filtrate itself, if it is to be used for trace metal analysis, must also be collected in a similar container. There are a reasonable number of appropriate container types for these purposes. The most suitable, and most easily acquired, are low-density (conventional) polyethylene, polypropylene or Teflon separatory funnels or bottles, but all of these types of containers need to be thoroughly cleaned before use. The most commonly employed containers are of polyethylene and these may be cleaned by immersion in, or filling with, concentrated (~6N) hydrochloric or nitric acid for several hours followed by leaching with pure water. The filtrates from the sampling program that are intended for trace metal analysis may need to be stored for some time prior to analysis and we will deal with this aspect of the procedure next.

Sample Storage and Analysis

The phase separation procedure should result in the production of a suspended sediment sample on a filter membrane and a filtered aqueous sample contained in a plastic bottle.

The suspended matter sample can be stored in its dry form in an enclosure, such as a plastic petri dish, until it is required for analysis. The aqueous sample should be stored in a pre-cleaned plastic bottle sealed against evaporative losses or leakage of the sample. The bottle itself should then be placed inside a plastic (polyethylene) bag to protect it against undue surface contamination. Recent experience with seawater sample storage (Bewers et al., 1981) suggests that the samples should be acidified to ca. pH 1 with ultrapure hydrochloric or nitric acid rather than frozen to preserve the sample. Recovery of metals from thawed frozen samples does not appear to be as complete as it is from acidified samples.
The acid used should be either double-distilled in quartz or a commercial high-purity grade such as BDH "Ultrex" or better. The cleanest acid is undoubtedly the National Bureau of Standards high-purity grade, but it is very expensive. In the case of river water, contamination by the metallic constituents of the few millilitres of the slightly lower purity acids, such as Ultrex, is not severe enough to significantly bias the sample. Storage of acidified samples for periods of up to a year or two, with no measurable change in the concentrations of most metals, has been achieved routinely.

Before turning to a discussion of the analytical techniques, it is worthwhile to stress the ultimate importance of the final analytical operations to the viability and usefulness of the data. The levels of metals in river water exemplified by the most recent studies are, in many instances, considerably lower than might have been thought to be the case a few years ago. Indeed, in the cases of some trace metals, the precautions required to prevent artifacts arising during the analytical stages are almost as stringent as those required in the case of seawater analysis. Table 6 gives some measurements of metal concentrations in rivers that have been derived from recent careful work in the Amazon, St. Lawrence and Mississippi. Both the Mississippi and the St. Lawrence rivers are, to some extent, contaminated and therefore these levels might be fairly typical of lightly to moderately contaminated rivers. Since there is little point in embarking upon a detailed time-series sampling and analysis program for a river unless the viability of the analytical procedures can be guaranteed, it is desirable to pay first attention to the development and proving of the analytical techniques to be employed in the program. This should be done by establishing the capability to analyse samples obtained from a river with relatively low concentrations of metals. Perhaps the best way to achieve this is through participation in round-robin intercalibrations on river-water samples involving some participants with established and well-recognised analytical capability, much as was done in the recent series of ICES intercalibrations for trace metals in seawater (see Bewers et al., 1981).

The concentrations of the metals in solution can be determined by either flameless atomic absorption spectrophotometry or, in some cases (viz. cadmium and zinc), by anodic stripping voltammetry or pulse polarography. The best approach is probably to use atomic absorption analysis for most of the metals of interest, employing preconcentration techniques (e.g., solvent extraction) where necessary. There are a variety of individual techniques for sample preconcentration and instrumental analysis that would be appropriate to river water and it only remains to ensure that the technique employed is sufficiently accurate and precise to be useful.

The analysis of the suspended matter samples is somewhat more complicated than the analysis of the solutions. While it might be adequate to measure solely the concentration of the metals in the suspended material as a whole, total analysis yields data that have only limited interpretative value. We would argue strongly for a two-stage analytical process that yields both bulk analyses and measures of the non-detrital, or extra-crystalline, metal concentrations. This latter information is useful in determining the fractions of the particulate metal forms that are amenable to exchange with metals in the aqueous phase in the marine environment. Equally, the non-detrital phase contains essentially all the metal that is available for biological uptake and transformation in the ocean as well. The residual, detrital, metal is that associated with the crystalline mineral phases that can only be transported as part of the host material - at least until such time as the host mineral itself is decomposed or otherwise attacked by intense leaching action. It is in the context of potential bioavailability that the non-detrital metal measurements are most valuable and, for the additional effort involved, are well justified. It is to be hoped that future intercalibration
exercises involving the determination of metals in marine (suspended and de-
posited) sediment samples will be useful for the standardization of such tech-
techniques.

Sampling and Analytical Methods for Organochlorine Compounds

The information in the literature on appropriate methods for the determination of organochlorines in natural waters is considerably less comprehensive or reliable than in the case of trace metals. Indeed, there are no generally, or widely,
accepted methods that can be straightforwardly recommended for the purpose of a river discharge assessment such as that proposed here. The reasons underlying this situation are the difficulties of obtaining uncontaminated samples, the complex chemistry involved in the identification and quantification of the compounds of interest and the fact that suitable techniques for such work have only recently been developed. Some specific compounds belonging to the pesticide group, such as α- and γ-hexachlorocyclohexane and members of the DDT family, have been determined at regular intervals in some Japanese and United States river systems. However, for most river systems there are no data for these constituents nor for other organochlorine compounds.

The methods available for the analysis of organochlorine compounds in environ-
mental samples have been greatly improved during the last few years. In particu-
lar, the introduction of capillary column technology has resulted in the ability to separate many compounds that could not be distinguished by packed columns. In consequence, many results reported in the 1960s and 1970s have to be regarded as unreliable and there is currently no accepted best method for the determination of organochlorines in natural waters. Some investigations of procedures for sampling and analysis for organochlorines in seawater were carried out at the Bermuda Biological Station during the IOC/WMO/UNEP Sampling Intercalibration Workshop in January 1980 (IOC, 1981). This work involved the use of a Bodman-Bodega deep water sampler, an air-lift system for collecting large quantities of near-surface water samples, an XAD-2 resin extraction system, an all-glass sampling/extraction system for small sample volumes (a few litres), and temperature-programmed capillary column gas chromatography. The samples collected during this exercise were not filtered but, as a rule, river samples will need to be filtered since they contain much larger concentrations of sus-
pended matter and this particulate material should be analysed separately from the aqueous phase. Recent experience in the seston-rich waters of estuaries, coastal and offshore regions have shown that an air-lift system, constructed along the lines adopted by Tokar et al. (1981), can be an appropriate tool for the collection of uncontaminated samples from depths down to about 50 metres. The water is discharged into glass or stainless steel containers from which it may be transferred, under pressure, into a filter unit or a continuous-flow centrifuge. The volume required for analysis depends upon both the concentrations of seston and the analytes in the aqueous phase. For contaminated rivers, one to 10 litres should be adequate. Transfer lines should be of polytetrafluorethylene (PTFE) or stainless steel. All such materials, containers, and other equipment likely to come into contact with the samples need to be thoroughly cleaned before use and rinsed between samples either with n-hexane or with large volumes of new sample water. Parts exposed to the atmosphere should be covered with aluminium foil when not in use.*

Filters can be back-extracted in the laboratory by Soxhlet extraction using a solvent, or mixture of solvents, of appropriate polarity to extract the class of compounds of interest. Water can be extracted by the method described in the report of the IOC/WMO/UNEP Sampling Intercalibration Workshop (IOC, 1981). Solvent-solvent extraction methods should also be suitable and these are presently undergoing investigation. However, for the present, there seems to be no reason

* A detailed scheme for sampling, sample processing and GLC-ECD analysis will be available shortly (Duinker and Hillebrand, In press).
to rule out the use of XAD-2 columns, particularly when they can be employed on-board ship for immediate extraction of the samples in order to minimise or eliminate compound sorption by container walls. Further procedures of sample clean-up, separation of non-polar and polar compounds, and the gas chromatographic/electron capture detector conditions can be taken from the IOC Workshop report (IOC, 1981). Extreme care should be taken to build in a number of internal tests for contamination. This can be done by running blank determinations on filters and carrying out second or third extractions of samples previously extracted for analytical purposes. The only step that is not easily amenable to such checks is the sampling procedure. As in the case of trace metals, the best internal check is the application of the entire procedure to low-concentration natural waters having levels of particular compounds typically in the picogram to sub-nanogram per litre range.

References


IOC (Intergovernmental Oceanographic Commission), 1981. The scientific report of the intercalibration exercise of the IOC/WMO/UNEP Pilot Project on Monitoring Background Levels of Selected Pollutants in Open Ocean Waters. IOC Technical Series No.23 (In press).


Table 6. Dissolved metal concentrations in some major world rivers and in seawater.

<table>
<thead>
<tr>
<th>River</th>
<th>Al (µg.l(^{-1}))</th>
<th>Fe (µg.l(^{-1}))</th>
<th>Mn (µg.l(^{-1}))</th>
<th>Co (µg.l(^{-1}))</th>
<th>Ni (µg.l(^{-1}))</th>
<th>Cu (µg.l(^{-1}))</th>
<th>Zn (µg.l(^{-1}))</th>
<th>Cd (µg.l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. Lawrence(a))</td>
<td>93</td>
<td>68</td>
<td>7.7</td>
<td>0.20</td>
<td>1.8</td>
<td>2.7</td>
<td>10</td>
<td>0.11</td>
</tr>
<tr>
<td>Amazon/Yukon(b))</td>
<td>-</td>
<td>43</td>
<td>19</td>
<td>0.08</td>
<td>0.34</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mississippi(c))</td>
<td>-</td>
<td>4.9</td>
<td>9.9</td>
<td>-</td>
<td>1.6</td>
<td>1.9</td>
<td>9.9</td>
<td>0.086</td>
</tr>
<tr>
<td>Seawater</td>
<td>1</td>
<td>0.5</td>
<td>0.03</td>
<td>0.01</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.04</td>
</tr>
</tbody>
</table>

\(a)\) after Yeats and Bewers (1981)  
\(b)\) after Gibbs (1977)  
\(c)\) after Trefry and Presley (1976)
REPORT ON THE OXYGEN CONDITIONS AND EUTROPHICATION IN THE BALTIC SEA AREA IN 1981

The oxygen conditions in the whole Baltic Proper seem to have deteriorated during 1981. If we look at the conditions in the northern Baltic Proper, we can find that ecological changes have occurred during recent years, in particular, in that along the northern coast of the Gulf of Finland, the bladder wrack (Fucus vesiculosus) has diminished or even disappeared totally in some places. Simultaneously, epiphytic algae have increased considerably, also on the Fucus vegetation. An increase of epiphytic animals has also taken place. All these events have generated changes in the coastal water ecosystem. It has been suggested that increased eutrophication has caused the development described. Such changes have not been noted off the Swedish coast, except around Gotland, where some reduction in the Fucus vegetation has been observed.

Scientists from the German Democratic Republic and Sweden have observed a strong reduction in oxygen in the deep layers of the Bornholm and the Gotland Basins. In both basins, H2S has been observed in the bottom water in the summer and autumn of 1981. No indications of salt water influx to the deep layers have been observed during the winter of 1981, but some intrusions of salt water have been measured in the intermediate layers both in the Bornholm and the Gotland Basins. In the southwestern Baltic Sea, oxygen conditions were not unfavourable along the coast of the German Democratic Republic. Only a temporary presence of H2S was observed near the bottom in the Lübeck Bay and partly in the Mecklenburg Bight in September. In August and October oxygen conditions were nearly normal. Only in the Lübeck Bay were low oxygen values (0.5 ml/l) still observed at the end of October.

Plankton blooms (Cyanophyceae) were observed in the Bornholm and Gotland Basins in August and September, but it seems that these blooms were of a smaller extent than those in earlier years.

During routine research in the Kiel Bight and the Fjord of Eckernförde in August/September 1981, H2S was observed in some areas where it has not previously been found. An ad hoc survey of the oxygen/H2S situation was carried out which showed a considerable spreading of H2S in bottom waters in the Kiel Bight and Eckernförde Fjord and along the coast. The oxygen concentrations were extremely low even considering the time of the year. The survey was repeated after a three-week period. It was then found that in most bottom areas H2S was no longer present, while oxygen concentrations were still very low. In small basins, however, H2S could still be found. A simplified interpretation of the data indicates an unusual hydrographic situation caused by the coincidence of a special meteorological situation and considerably low oxygen amounts in bottom waters of that area (and presumably other Baltic areas as well).

Measurements of H2S, oxygen and salinity indicated a movement of higher salinity water masses which pushed the H2S, which is normally present in some small basins, into the fjords.
Considerable damage to the benthic fauna in the areas which came into contact with H₂S was reported for some species and a total deserting of benthic fauna occurred in areas where the H₂S stayed for periods of several weeks.

An unusual oxygen situation in the Baltic Sea, namely, low oxygen concentrations caused by increased plankton blooms, was indicated by the results of a Kattegat cruise of R/V "Poseidon" in December 1981. A Baltic outflow of water was measured with extremely high nitrite concentration (2-3 µmol/dm³) containing no other nutrients except some nitrate and minor NH₃ concentrations corresponding to the nitrite maxima. However, the oxygen saturation was about 85%. The nitrite concentrations were measured over more than a one-week period, because of the low temperatures (ca. 3°C) which are suggested to limit the kinetic process of nitrite oxidation.

During the summer and late autumn of 1981, oxygen depletion and mass mortalities of fish were observed in Danish waters. In the Kattegat, there was a case of fish mass mortality off the coast north of Djursland, and very low oxygen values were observed in the southeastern parts, extending into the Sound. This phenomenon has also been reported around Funen, Langeland and the fjords of southeast Jutland. Also off the west coast of Jutland, at Fjaltring Strand, dead fish were washed ashore, and here a poisonous species of phytoplankton was identified. Observations from Langeland and from the southern fjords indicate that a water mass of unusually saline water flowed through the Great Belt approximately by the middle of June.

The wind activity during the autumn was lower than usual, especially in September, and the run-off from land was very high in the winter 1980/81. The run-off has been increasing since the rather dry year of 1976.

During the autumns of 1980 and 1981, unusually low oxygen values were reported for the southeastern Kattegat and, in the Laholm Bight, H₂S and dead bottoms below the halocline were even observed. Fish escaped the Bight and occasionally dead fish and lobsters were found in the fishing nets. Large blooms of dinoflagellates were observed at the same times.
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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