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REPORT OF THE MARINE CHEMISTRY WORKING GROUP

Helsinki, Finland, 18-21 February 1986

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TABLE OF CONTENTS

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1 OPENING OF MEETING

The Chairman, Dr G Topping, opened the meeting at 9.30 hrs on 18 February 1986 and welcomed the participants.

Professor A Voipio, Director of the Finnish Institute of Marine Research, welcomed the participants to Helsinki and to his Institute. He mentioned a few of the problems experienced in chemical oceanographic studies 25 years ago and noted that the types of problems, though not the subjects, are similar today. He wished the Group every success in its work. Dr Topping thanked Professor Voipio for his words of welcome and for the opportunity of meeting in Helsinki.

Each member then introduced him- or herself, indicating the main areas of research interest and responsibilities in marine chemistry.

2 ADOPTION OF AGENDA

The Working Group reviewed the draft agenda and adopted it without change. The agenda is attached as Annex 1. The list of participants is contained in Annex 2.

The Working Group agreed that most of the discussion during the meeting should take place in three sub-groups, as follows:

1) Trace Metals Sub-Group (Chairman: Dr G Asmund)

2) Organics Sub-Group (Chairman: Dr. L Reutergårdh)

3) Chemical Oceanography Sub-Group (Chairman:Dr M Perttilä)

It was agreed that each Sub-Group should prepare a report on the results of its discussions before the end of the Working Group meeting. The ICES Environment Officer, Dr J Pawlak, served as Rapporteur for the plenary sessions of the Working Group.

3 REPORT OF THE 73RD STATUTORY MEETING

The Working Group took note of the relevant Council Resolutions from the 1985 Statutory Meeting. It was reported that the subject of contaminant concentrations in marine mammals and their possible effects had been discussed at several sessions during the Statutory Meeting. Biologists studying the effects of organochlorine contaminants on marine mammals had requested the MCWG to provide advice on appropriate methods for the determination of organochlorines in fatty marine mammal tissues and perhaps coordinate an intercalibration exercise on such determinations. The Chairman reported that, on the basis of this request, he had written to a number of people to obtain reprints of reports on the results of analyses of organochlorine concentrations in marine mammals and had received several responses. The Working Group felt that studies of possible effects of contaminants on marine mammals should encompass a broad range of organochlorine compounds, including dibenzofurans and dibenzodioxins; these studies

should also include analyses for trace metals. It was agreed that detailed consideration of this topic should take place under agenda item 7.2.3.

4 REPORTS OF RELATED ACTIVITIES

4.1 JMG of the Oslo and Paris Commissions

The MCWG reviewed the results of the January 1986 meeting of the Joint Monitoring Group (JMG) of the Oslo and Paris Commissions, as reported in a paper by Dr A Jensen. The JMG had experienced difficulty in assessing the monitoring data taken for human health risk assessment purposes, owing to disagreement on the fish/shellfish consumption patterns and the criteria levels for threats to human health used in different countries. The Commissions have been requested to decide whether monitoring for this purpose should be continued.

From 1986 the Joint Monitoring Programme (JMP) has been expanded to include copper, zinc, lead and lindane, in addition to the existing parameters mercury, cadmium and PCBs. This addition generally applies to all three media monitored - biota, sea water, and sediments - but for those contaminants for which the results of intercalibration exercises have not been acceptable or for which no intercalibration has yet been held, formal monitoring will not begin until a successful intercalibration has been completed.

It was noted that the monitoring of nutrient concentrations in sea water had been discussed by the JMG, which had recommended that nutrients should be included in the JMP on a voluntary basis beginning in 1987. This nutrient monitoring should preferably be carried out on transects from the coastline and should be conducted in the winter months, as a minimum requirement. The JMG requested ICES to prepare an overview of the nutrient data held in the ICES data bank; this overview should cover as many years (at least 20 years) and as much of the Oslo/Paris Convention area as possible.

The JMG had discussed the plans for the intercalibration exercise on trace metals in estuarine waters and had approved them.

The Environment Officer then reported on the discussions that had led to the proposal that the initial assessment of data on samples from the Oslo/Paris Convention area taken for the 1985 Baseline Study of Contaminants in Fish and Shellfish should be carried out by a joint ICES/OSPARCOM/HELCOM group. The Chairman expressed disappointment over this proposal, pointing out that as ICES had designed and coordinated the Baseline Study, ICES should take the lead in the assessment and evaluation of the results, which would then be made freely available to the Commissions. While some members of the MCWG agreed with this position, others felt that there should be a joint evaluation of the data. The MCWG agreed to return to this topic later in the meeting.

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

The MCWG took note of the main activities coordinated by the ICES/SCOR Working Group on the Study of the Pollution of the Baltic. The most important project is the conduct of the Joint International Multi-Ship Investigation of Patchiness in the Baltic Sea (PEX), which will be conducted in the southern Gotland Basin in late April and early May 1986 by 15 research vessels from six countries around the Baltic Sea. It was noted that there are still some problems regarding intercalibration of the methods to be used in this investigation. Another important project of this Group is the review of data on contaminants in sediments in the Baltic Sea and the development of recommendations regarding sediment monitoring.

4.3 Activities under the Helsinki Commission

Dr Perttilä reported on some of the relevant activities that are being carried out under the Baltic Marine Environment Protection Commission (Helsinki Commission). One important area of work involved the development of a data base management system for the compilation and analysis of the data collected in the Baltic Monitoring Programme. The Finnish Institute of Marine Research is in the process of developing this system for the Helsinki Commission and it will be completed by September 1987. A new major assessment of the environment of the Baltic Sea has recently been completed; the overall conclusions of this assessment and the scientific background material will be published by the Commission in the summer of 1986. A thorough review of the Baltic Monitoring Programme will take place in 1986-1987. This review process will begin with a Baltic Monitoring Symposium in Tallinn in March 1986, where scientific papers on national results of the BMP will be presented.

In the discussion of Helsinki Commission programmes, the question was raised as to whether a programme has been developed to measure the atmospheric input of substances to the Baltic. Atmospheric input was felt to be a major source of input to this area, particularly for PAHs, DDT, lead and possibly arsenic. At least in some areas, atmospheric input may also be a significant source of nitrates. It was noted, however, that there are still a number of outstanding questions related to the methodology for measuring atmospheric deposition and net atmospheric input.

4.4 Intergovernmental Oceanographic Commission (GIPME/GEMSI/GEEP/GOPPS)

The Chairman presented his note on the seventh session of GEMSI (IOC/UNEP Group of Experts on Methods, Standards and Intercalibration), at which a number of items of interest to MCWG had been considered. Among these were included the preparation of standards and reference materials for contaminants in marine media, the analysis of individual organic contaminants, and the use of marine organisms in monitoring programmes.

4.5 Other relevant activities

Dr Wells presented a progress report on the work of the Community Bureau of Reference (EEC BCR) Working Group on PCB Analysis. He gave the results of recent intercalibration work and stated that present work includes the analysis of a freeze-dried, homogenized mussel tissue and the analysis of a sludge extract for the CB congeners under consideration in this programme. In addition, preparations are being made to certify two fish oil reference materials for these seven CBs, namely, IUPAC Nrs: 28, 52, 101, 118, 138, 153, and 180. The CB levels in one fish oil will be around 500 µg/kg, while the other fish oil will contain CBs in the range of 10 to 100 µg/kg.

5 REPORTS ON PROJECTS AND ACTIVITIES IN ICES COUNTRIES

Dr Cofino reported that the Dutch Rijkswaterstaat has been reorganized. A new institute has been established, the Dienst Getijdewateren, DGW (Tidal Water Division), which is a technical and scientific institute reponsible for work in Dutch coastal waters. As a result of this reorganization, the former Governmental Institute for Sewage and Waste Water Treatment (RIZA), is no longer engaged with measurements in the marine environment.

Dr Berman presented a paper on the recent activities of the Marine Analytical Chemistry Standards Program of the National Research Council of Canada. The following reference materials are in the final stages of preparation:

1) A filtered, acidified sample of St Lawrence River water, designated SLRS-1, is being certified for trace element concentrations.

2) Spray-dried, acetone extracted samples of dogfish muscle and liver, designated DORM-1 and DOLT-1, respectively, are undergoing certification for trace metal concentrations. These concentrations are relatively low.

3) A set of five 0.5 ml aliquots of a standard solution of synthetic 2,2', 4,4', 5,5'-hexachlorobiphenyl (IUPAC No. 153), uniformly labelled with ^{13}C in isooctane, is being prepared. Designated CLB-2, this material has been designed for use as an internal standard for analysts determining chlorinated biphenys by GC-MS.

4) A set of four harbour sediments and one estuarine sediment for determination of polycyclic aromatic hydrocarbons will be issued soon.

5) Reference material projects under active study include the preparation of a marine sediment with higher metal concentrations than in MESS or BCSS, an estuarine water for trace metals, a lobster hepatopancreas for trace organics, and a dogfish liver oil for trace organics.

Dr Berman also reported that significant advances have been made concerning hydride generation atomic absorption spectrometry, with *in situ* concentration of the analyte hydride in a graphite furnace.

Dr Reutergårdh informed the Working Group that the National Swedish Environmental Monitoring Programme had recently been reviewed. Copies of this review, entitled "Monitor 1985", can be obtained from the Swedish National Environment Protection Board.

6 REQUESTS FROM ACMP AND REGULATORY AGENCIES

The Working Group reviewed the relevant requests from the Oslo and Paris Commissions and agreed that all of them would be discussed under the most relevant agenda items. These requests had already been reflected in the additional items added to the terms of reference for this MCWG meeting, as proposed by ACMP at the 1985 Statutory Meeting.

REPORTS ON SESSIONAL SUB-GROUP DISCUSSIONS

The MCWG divided into three sub-groups to discuss agenda items 7 through 13. The sub-groups met concurrently and produced written reports which were reviewed in detail on the last day of the meeting. At the start of each day, MCWG met in plenary to review the progress of the sub-group work and to allow the sub-groups to seek advice from the Group on any problems they had encountered in their deliberations. The sub-group reports are contained in their entirety in the next three sections, as follows:

Section A. Report of the Trace Metals Sub-Group

Section B. Report of the Organics Sub-Group

Section C. Report of the Sub-Group on Chemical Oceanography

Main points from the discussion of these reports in the MCWG as a whole are contained in Section D.

A. REPORT OF THE SUB-GROUP ON TRACE METALS

The Sub-Group on Trace Metals consisted of the following members: Dr G Asmund (Chairman), Dr S Berman (Rapporteur), Dr L Brügmann, Dr W Cofino, Dr D Cossa, Dr V Tervo, and Dr S Westerlund.

7A.1 Intercalibration and Other Quality Control Activities Regarding Trace Metals

7.1.1 Status reports on (a) 7/TM/BT (Part 2) and (b) 1/TM/SM

The current status of the Seventh Intercalibration Exercise on Trace Metals in Biological Tissues - Part 2 (7/TM/BT (Part 2)) is described by the Coordinator of the exercise, Dr S. Berman, in the following paragraphs. The Sub-Group noted that the exercise is on schedule and that a draft final report should be available by the end of the year. The exercise is not open to new participants.

The 7/TM/BT exercise is in two phases. The first has been completed and a preliminary evaluation has been made of the results for the six core metals, copper, zinc, arsenic, cadmium, mercury and lead.

All laboratories which participated in Part 1 of 7/TM/BT were invited to participate in Part 2. Other laboratories were also allowed to join.

Fifty-five sets of samples (codfish liver, dogfish liver, dogfish muscle, dogfish composite and Mytilus edulis) were sent out in January 1985. The original deadline for the first phase was postponed from 30 June 1985 to 31 December 1985 on the recommendation of the MCWG. Forty-two sets of results were received by 31 January 1986. Nineteen of these sets had been sent to laboratories participating in the 1985 Baseline Study of Contaminants in Fish and Shellfish. Fifteen of these laboratories submitted results and were sent another set of samples with a deadline for submitted values of 30 June 1986.

Because the laboratories participating in Part 2 of this exercise have yet to submit their second set of results, the actual consensus values and precision estimates for Part 1 cannot yet be released. A full report will be presented at the 1987 MCWG meeting.

On the whole, there appear to be improvements evident in the analyses for all metals except mercury. Mercury was already being handled competently by most laboratories (about 70%) which analyse for this metal. The most dramatic improvement is with low ppm levels of lead, but there are still problems at the sub-ppm level.

A disproportionate percentage of poor results came from laboratories which did not participate in Part 1 of the exercise. This may be interpreted as heartening evidence that all this is really worthwhile after all.

The "Baseline Study" laboratories have generally performed well. The Coordinator intends to discuss some specific problems with a few of these laboratories before they submit results for the second part.

Another outstanding feature of this exercise was the relatively high number of arithmetic errors made by several laboratories. Most of these were (hopefully) cleared up through correspondence.

In terms of the report on the results of the First Intercomparison Exercise on Trace Metals in Suspended Matter (1/TM/SM), the Sub-Group noted that the publication of this report in the Cooperative Research Report series had been approved at the 1985 Statutory Meeting.

7.1.2 Method sheets based on procedures used in 5/TM/SW and 7/TM/BT

Dr Berman reported that no leaflets based on procedures used by "successful" laboratories from the Fifth Round Intercalibration on Trace Metals in Sea Water (5/TM/SW) or 7/TM/BT (Part 1) have

yet been prepared. Work has begun on the leaflets concerning trace metals in sea water, but descriptions of methods to determine trace metals in biological tissues will not be prepared until the termination of 7/TM/BT (Part 2).

7.1.3 Performance charts for 5/TM/SW

Dr Berman informed the Sub-Group that he had prepared performance charts based on the results of 5/TM/SW, as requested at the last MCWG meeting. These charts indicate individual laboratory precision for the core metals as well as laboratory bias with respect to the presumed trace metal concentrations. These performance charts have been included in the report of 5/TM/SW, which has been published as Cooperative Research Report No. 136.

7.1.4 Plans for JMG I/C on trace metals in estuarine waters

The Sub-Group reviewed the plans for the intercalibration exercise on trace metals in estuarine waters, described in Annex 4, which is being conducted for the Joint Monitoring Group. There was some discussion concerning the type of bottle and closure to be used for the mercury sample. However, it was noted that the coordinators are committed to using a borosilicate glass bottle with ground glass stopper, similar to that used by Olafsson in the intercalibration he conducted, and there is not adequate time available to make any changes. It was, however, felt that a teflon stopper or seal might be superior to ground glass.

7.1.5 Other proposals/plans for I/C exercises

The Sub-Group noted that there are no other intercalibration exercises coordinated under MCWG in progress at the present time.

In considering what possible new intercomparison activities to propose, Dr Cossa agreed to prepare a paper for the 1987 MCWG meeting on the feasibility of conducting an intercomparison exercise for mercury, emphasizing organic mercury (methyl-Hg), in marine biological tissues. Recognizing the fact that the toxic effect of mercury is mainly from the organic form, the paper will survey the various methods used to analyze organic forms of mercury and, if appropriate, present a proposal for an intercomparison exercise.

The Sub-Group felt that work should continue on the analysis of contaminants in suspended matter and, accordingly, agreed that Dr P Yeats should be approached to consider the feasibility of conducting a full-scale intercomparison exercise on the analysis of trace metals in suspended particulate matter. It was noted that this topic will be considered in greater detail at the meeting of the Working Group on Marine Sediments in Relation to Pollution.

Dr Cossa announced that the IFREMER Centre de Nantes proposes to send to interested laboratories a sub-sample of an oyster homogenate in order to compare analytical results for concentrations of total tin and different forms of organo-tin. This sample should be available in early autumn 1986 and can be obtained from Mr P. Michel, IFREMER, Centre de Nantes, B.P. 1049, F-44037,

Nantes-Cedex, France. This will be an informal inter-comparison exercise as a first step to a possible ICES exercise on this subject.

7A.4 Proposals for Manual on "Good Laboratory Practice"

A paper on this topic by Dr Topping was considered. The Sub-Group agreed that this paper covered the principles of good laboratory practice, but felt that it was written in a form that was too general for application in ICES. Rather than writing a new, more specific paper, the Sub-Group agreed to ask Dr Cofino, with the assistance of Dr Berman, to identify a selection of published papers on this subject and to write a short introduction to the papers. These papers and the introduction should then be sent to the ICES Secretariat. From there, with the appropriate permission of the publishers of the papers selected, they would be available for distribution to any interested laboratories.

7A.5 Reference Materials

Dr Berman reported that there is an excellent document published by the International Atomic Energy Agency (IAEA) which describes all the biological and environmental reference materials available at the present time. This document may be obtained by writing to: International Atomic Energy Agency, Wagramerstrasse 5, P.O.Box 100, A-1400 Vienna, Austria. A similar document, with more elaborate detail, is under preparation by the U. S. National Oceanic and Atmospheric Administration. This document is entitled "Standards and Reference Materials for use in Marine Science" and is being compiled by Dr. Adriana Cantillo, NOAA, US Department of Commerce, Rockville, MD, USA.

The Sub-Group then discussed the need for a reference material of marine mammal liver and kidney with a high concentration of cadmium. The Sub-Group felt that there is a need for such a reference material and, accordingly, requested Dr Berman to investigate whether it would be possible for the National Research Council of Canada to prepare this type of reference material. In the event this is possible, Dr Asmund agreed to provide the necessary raw materials.

In connection with the discussion of reference materials, the Sub-Group noted with great pleasure C.Res. 1985/3:4 and looked forward to a successful programme of cooperation between IOC/UNEP and the producers of reference materials.

8A. SPATIAL AND TEMPORAL TRENDS FOR TRACE METALS IN SEAWATER

After an initial discussion of this topic, Dr Brügmann prepared a draft report on how trends could be determined for trace metals in sea water. The Trace Metals Sub-Group discussed this draft and agreed that it was a very good and useful beginning for a document on this subject. All members of the Sub-Group agreed to provide Dr Brügmann by correspondence with comments and proposals for additions or amendments to his paper. Dr Brügmann will then redraft the paper for presentation at the 1987 MCWG meeting.

9A. NET FLUXES FROM RIVERS TO OCEANS AND MASS BALANCE ESTIMATES

In terms of programmes to measure riverine fluxes, Dr Cossa informed the Trace Metals Sub-Group that a two-year project will commence in France in 1987. The river Seine will be sampled twice per month and the samples analyzed for mercury, cadmium and PCBs in both the dissolved and particulate phases.

The Sub-Group then reviewed the ACMP advice on "Methods of Assessing Gross Riverine Discharges of Trace Metals and Organohalogens into the Marine Environment", which is contained in Annex 6 to the 1982 ACMP report (Coop. Res. Rep. No. 120 (1983)). The Sub-Group felt that this is a very valuable document. It noted, however, that the procedures described in the document are derived from work in rivers with relatively low concentrations of suspended particulate matter. A supplement for measurements in rivers with high SPM levels would enhance the value of this document.

The Sub-Group questioned the complete neglect of the bedload in the input calculations, as the material may release heavy metals into the estuarine environment (e.g., cadmium).

In clarification of the above comments, the Sub-Group noted that the composition of the SPM is an important factor to measure. These measurements should include parameters characteristic for the mineral phase (e.g., Al, Sc, conservative elements) and the organic phase (e.g., organic carbon, loss on ignition).

It was also considered that inputs from major industrial and population centers near the river mouth have to be accounted for in a better way than that proposed in the document.

The Sub-Group then considered the ACMP document "Estimation of River Composition and Riverine Influxes of Chemicals to the Marine Environment" contained in Annex 1 to the 1984 ACMP report (Coop. Res. Rep. No. 132). This document deals with the very difficult problem of the "net flux" of materials to the ocean. While the Sub-Group felt that the document represented a good introduction to this topic, it was obvious that there is presently a lower state of understanding of this subject when compared to that of "gross flux". It was noted that in the first approach covered in this document, which considers specific influxes and effluxes, the important influxes due to direct discharges (e.g., dumping of wastes and dredged materials, petroleum exploitation, mining and manufacturing activities, etc.) have been omitted.

The second approach, concerning salinity/contaminant relationships, seems to be promising in view of recently available literature on the subject (e.g., Kauls, L W, and Froelich, P N jr., 1984. Geochim. Cosmochim. Acta 48: 1417 - 1433).

10A. OVERVIEWS

The Trace Metals Sub-Group noted that the list of candidate substances suggested by ACMP for the preparation of an overview included arsenic, copper, chromium and nickel.

The Sub-Group agreed that Mr P Michel, IFREMER, Centre de Nantes, should prepare an overview document on arsenic in the marine environment. Dr Cofino agreed to try to find a colleague to prepare an overview on copper and Dr Cossa and Dr Topping agreed to try to find colleagues to prepare overviews on chromium and nickel.

The need for an updated overview on mercury, emphasizing organic mercury compounds, in the marine environment was discussed. Drs Cossa and Topping volunteered to prepare such an overview.

11A. GLOBAL OCEAN FLUX STUDY AND SIMILAR PROGRAMMES

The Trace Metals Sub-Group did not feel that it had the competence to address this item at the present time.

13A. ANY OTHER BUSINESS

The Trace Metals Sub-Group reviewed a revised version of the Interim Reporting Format for Contaminants in Sea Water. This revised format was found to be generally quite acceptable for the reporting of inorganic data. Some minor modifications were discussed. The Sub-Group suggested that a different format be adopted for organic contaminants in order to maintain maximum simplicity.

The Sub-Group also sugested that a common definition of "limit of detection" be established, so that data from various laboratories could more readily be compared and evaluated. A sample definition based on the variance of the procedural blank was supplied for inclusion in the description of the format.

B. REPORT OF THE ORGANICS SUB-GROUP

The Organics Sub-Group consisted of the following members: Dr L Reutergårdh (Chairman), Mr R Law (Rapporteur), Dr J Calder, Dr J de Boer, Dr M Ehrhardt, Dr H Haahti, Dr J Klungsøyr, Dr A Knap, Dr A Niemenen, Dr K Palmork, Dr D Wells.

The discussion of this Sub-Group will be summarised under agenda items 7 through 13, although many of the topics are interconnected and the direction of discussion often crossed these arbitrary boundaries.

7B.2 Intercalibration and Other Quality Control Activities Regarding Organics

7.2.1

(a) Status Report on 2/HC/BT

No subsequent report to that available at the 1985 MCWG meeting was presented on the results of the Second Intercomparison Exercise on Hydrocarbons in Biological Tissue (2/HC/BT). It was anticipated that the Coordinator of this exercise, Dr J Farrington, would circulate the draft report to the participants in the near

future. The final report will then be submitted to ICES for publication as a Cooperative Research Report. Mr Law and Dr Klungsøyr agreed to review this report on behalf of the MCWG.

(b) Status Report on 2/HC/BT

Concerning the Third Intercomparison Exercise on Hydrocarbons (PAHs) in Biological Tissue (3/HC/BT), it was understood that the report presented by the Coordinator, Dr J Uthe, at the 1985 MCWG meeting is regarded as the final report for this exercise.

(c) Status Report on Oil Pollution Research Unit intercalibation exercise

Mr R Law presented a short paper updating progress with this exercise, which involved hydrocarbon determinations in marine sediments. This exercise is being conducted by the UK Oil Pollution Research Unit (OPRU). Samples were sent to 30 laboratories and data have been submitted by 16. Six of these were "ICES" laboratories.

Samples were analysed by UV-fluorescence, gravimetry, capillary GC and capillary GC-MS. The coordinator, Dr S Howells, has indicated that a draft report should be ready to circulate to participants by summer 1986. Mr R Law agreed to report on the results to the MCWG in 1987.

7.2.2 Proposals for 1/HC/SW

The Sub-Group considered a proposal by Dr E Levy and Dr J M Bewers for an intercalibration exercise for dissolved/dispersed hydrocarbons by UV-fluorescence. A similar paper had been considered by the Sub-Group at the 1985 MCWG meeting and the advice given to ACMP at that time was that this approach was not viable. A separate proposal detailing a method for carrying out such an exercise had been put forward in the 1985 MCWG report.

The Sub-Group felt that an intercalibration exercise is not necessary at the present time. Of the numerous techniques available for hydrocarbon measurements in a variety of matrices, UV-F measurements in sea water and sediments represent the only areas in which there seem to be few problems. For sediments, the results of the first ICES exercise showed most laboratories to be capable of returning reasonably comparable data. For sea water, the results of the three major exercises conducted already have been more encouraging. These were the Kiel exercise carried out in 1981 (Baltic Sea Environment Proceedings, No. 6) and those held in Bermuda in 1984 (Knap et al., Mar. Pollut. Bull., in press) and 1985 (Ehrhardt and Knap, Environ. Sci. Technol., in press). The Sub-Group also directed interested parties to IOC Manuals and Guides No. 13, which details a suitable method for these determinations. The Sub-Group did not, therefore, see any need to deploy effort in this area when it could much more usefully be directed to problem areas, such as the analysis of specific aromatic compounds by GC-MS and HPLC-UVF.

7.2.3 Proposals for 1/OC/MM (Marine Mammals) and descriptions of methods

A survey has been conducted of laboratories known to be, or to have been, carrying out research on the concentrations of organochlorine residues in marine mammals. Anyone with information on laboratories involved in this type of work is requested to send details to Drs Reutergårdh or Knap, as this survey is currently felt to be incomplete.

The data on analytical methodology submitted so far suggest that the majority of the work is being performed on packed columns and using standardization based on technical formulations of PCBs, though in some cases this information (based on submitted reprints) may be out of date. Based on experience with other sample types, the Sub-Group felt that data coming from different laboratories are unlikely to be comparable, and that there is no basis at the moment for conducting an intercalibration exercise. Advances in methodology adopted in other areas (capillary GC and the determination of individual chlorobiphenyl congeners, hereafter CBs) should also be taken up by analysts working with marine mammal tissues, if necessary assisted by contact with laboratories already skilled in the use of capillary GC techniques.

Interest has concentrated on PCBs because the diseases seen (Cushing's syndrome and chloracne) are particularly associated with these chemicals. Concern was expressed, however, that other substances which may be associated (such as heavy metals, polychlorinated dibenzofurans, and polychlorinated dibenzodioxins) have not been included in studies carried out so far; they should be included in future studies.

In order to fully investigate the connection between contaminant levels and disease incidence in marine mammals, the Sub-Group proposed that a special meeting be held by ICES in 1987, to take place immediately before the meeting of MCWG. This must involve analysts, biologists with expertise in the area of marine mammals, and experts on the diseases mentioned above. Prior to this meeting, Drs. Knap and Reutergårdh will prepare a paper on methodology improvements suggested by IOC and their own research.

The Sub-Group then considered two papers : "Organochlorine Analysis in Marine Mammals" by Dr A.Abarnou, and "An Evaluation of the Individual Congener Approach for Quantitation of PCBs in Environmental Samples (Marine Mammals)" by Dr J C Duinker *et al*. Both were submitted for information, comments were also requested on the first of these papers.

A number of other papers on organochlorine determinations in marine mammals were mentioned during the discussion and Drs Knap and Reutergårdh agreed to produce a critical review of the methodology currently in use for presentation at the 1987 MCWG meeting. All members of MCWG and others with information are requested to send reprints of relevant articles to Dr Knap and Dr Reutergårdh for inclusion in the review.

It was agreed that an approach should be made to organisations involved in the preparation of standard reference materials to request the preparation of a reference material for individual CBs (and possibly other organic contaminants) in a high fat ma-

terial. This would be invaluable in method development for CB (and OC) compounds in tissues from marine mammals. Dr A Knap agreed to contact the U.S. National Bureau of Standards (NBS), Dr K Palmork will contact IAEA, and Dr L Reutergårdh will contact the National Research Council (NRC) of Canada.

7.2.4 Other proposals/plans for intercalibration exercises

1) The Sub-Group was asked to consider the feasibility of, and to make proposals for the conduct of, an intercalibration exercise for the determination of Lindane (γ-HCH) in biota and sediment samples. This remit, which was based on a request from the Joint Monitoring Group of the Oslo and Paris Commissions, was extended at the meeting to include sea water.

   The Sub-Group felt that it is currently feasible to carry out an intercalibration exercise for Lindane in all three matrices, and Dr D Wells had prepared a paper summarising the basic structure of a suitable exercise. This proposed a simple step-wise approach to intercalibration that has also been proposed in other contexts, and has been successfully applied to CB analysis within the BCR. A copy of this paper is attached as Annex 3.

   It was noted by the Sub-Group that the inclusion of Lindane in the Joint Monitoring Programme is intended to allow the use of Lindane as a tracer of anthropogenic inputs of organic contaminants/pollutants to the marine environment, specifically to sea water, biota and sediments. The view of the Sub-Group was that whilst this would be a satisfactory choice for sea water, Lindane would be an entirely inappropriate choice for the other two matrices. The solubility of Lindane is such that it would be expected to move rapidly from sediments to sea water, and not to be concentrated in biota. It was also felt that laboratories employing standard methodology for PCB determinations may encounter some difficulties with Lindane because of its high vapour pressure and volatility. Attention was drawn to Section 8C.4 of the 1985 MCWG report, in which further information was requested on the reasons for including Lindane in the JMP:

   "The Sub-Group requested that any firm requirement by the Regulatory Commissions for analysis of Lindane in any matrix be suggested by a position paper clearly stating the background and justification for the request. This should include collated data currently available on levels in different environmental compartments, any known acute or chronic effects and measures to restrict usage and/or manufacture."

   No further information has been forthcoming.

2) The current status of intercalibration on hydrocarbons was very thoroughly discussed, and the general feeling was that after three ICES exercises we are no further forward in the analysis of specific hydrocarbons than after the first

exercise (Coop. Res. Rep. No. 117, 1982). Two of the comments made in the assessment of this exercise are particularly relevant to the discussion which took place in the Sub-Group:

"An international intercalibration exercise of this size obviously requires a huge input of time and effort, by all the participants as well as the organising laboratories. At least one analyst reported devoting 1 man-month to the analyses. Thus, the dispatch costs of ca. £50 per participant are only a small proportion of the total costs involved in the conduct of such an exercise and such an input of resources requires that some progress be made towards greater comparability between results generated at different laboratories."

"It would be a useful aid to assessing GC and GC/MS results if a standard solution were circulated and analysed in addition to the samples, so as to facilitate the interpretation of interlaboratory differences."

Following the experiences of the exercises 2/HC/BT and 3/HC/BT, Sub-Group now felt that to make progress we must first take a number of steps backwards. This should involve an exercise structured according to the BCR experience, which will first address the basics and then improve comparability in a step-wise manner. The Sub-Group appreciated that this may disappoint some people who hoped for dramatic improvements immediately, but this was felt to be the best way of improving the present poor level of comparability.

The proposal is as follows:

Aim: To check instrument calibration for the determination of specific aromatic hydrocarbon concentrations by GC/MS and HPLC-UVF.

Co-ordinator: Dr K Burns, Bermuda Biological Station, will be approached by Dr Knap with a view to acting as co-ordinator for this exercise.

Requirements: Ideally 12-15 participating laboratories. Any laboratories with GC/MS or HPLC-UVF who are interested in taking part should contact:

Mr R Law
Fisheries Laboratory Burnham-on-Crouch
Essex, England CM0 8HA

Plan: To circulate for analysis the following solutions:

1) A standard solution containing 6 aromatic hydrocarbons at declared concentrations.

2) Solution 1, containing the same 6 compounds at concentrations which are approximately indicated, to be determined.

3) Solutions 2 and 3, containing the same 6 compounds at unknown concentrations, higher in one solution than in the other, to be determined.

4) Blank solution for analysis.

5) Internal standard solution containing deuterated aromatic hydrocarbons for use with CG-MS analysis and, if feasible, a separate solution for use with HPLC-UVF.

The operation of this first phase will depend on the availability of funding to cover the costs of some aspects of the programme. It is felt that it is no longer possible to make progress solely on the goodwill of the participants, and provision needs to be made to cover the following expenses:

1) The cost of the standard materials to be used in preparation of the solutions listed above.

2) The cost of a pre-exercise meeting at which all participants can discuss and agree the conduct of the exercise in detail. This meeting is felt to be essential for the success of the exercise, and is based on the BCR approach. the cost could be minimized by allocating extra time at the start or end of the 1987 MCWG meeting, as a number of the participants are likely to be members of MCWG.

   At the conclusion of the first phase of the exercise, the analysts must meet to discuss the results and to plan the next phase of the exercise.

7.2.5 Monitoring organochlorines in fish and birds

Two papers were tabled for discussion under this item, "Marine monitoring of organochlorine compounds, selection of media in relation to trends and detection levels" by Drs Reutergårdh and M Olsson, and "Proposal for an international programme to monitor trends in ocean pollutants" by Dr J Elliot and Dr M Gilbertson.

At the 1985 MCWG meeting a proposal by Dr Gilbertson that sea bird eggs may be very suitable for monitoring purposes had been discussed. The second paper expanded this suggestion into a proposal for a large-scale multinational trend monitoring programme and early warning system using sea bird eggs.

The paper by Drs Reutergårdh and Olsson summarised Swedish monitoring data gathered since 1969 for herring and cod muscle, and guillemot eggs. Concentrations of organochlorine residues were at least ten times higher in the bird eggs than in the fish on which they feed, which makes the analysis more reliable and narrows the confidence intervals placed around the concentrations. This is especially beneficial in cleaner areas where concentrations are lower. The data suggest, however, that the peak concentrations found in eggs lag behind production peaks for the chemicals concerned by 7 to 10 years. The decreasing trend of concentration was much more evident in sea bird eggs than in fish tissue, amply demonstrating the value of long-term data sets.

On the proposal made by Drs Elliott and Gilbertson, the Sub-Group felt that while the time-lage for uptake does call into question the validity of the early warning concept, the large-scale trend monitoring programme still seems to be of value. The Sub-Group

felt that there were various aspects of the programme on which information was lacking, such as the distribution of the birds throughout the North Atlantic area, and their migratory habits. Accordingly, it was felt that it was premature to support the establishment of a monitoring programme.

Further work on the use of sea bird eggs was encouraged by the Sub-Group, and Dr Reutergårdh urged all members of MCWG to send him any data which may be available from their own countries.

7.2.6

a) Method Sheets on Organochlorine Analysis

The Sub-Group considered a draft leaflet by Dr Ehrhardt on "A versatile apparatus for extracting solid materials used for concentrating lipophilic organic trace constituents from sea water". The use of solid adsorbents to concentrate organics from large volumes of sea water (of the order of 100-1000 liters) is necessary to allow analysis of e.g., single specific hydrocarbons, present at very low concentrations, by techniques such as GC and GC-MS. During discussion, Dr Ehrhardt informed the group that with some minor modifications the technique may also be used for the extraction of sediments, mussel tissue, etc.

The method was felt to be very useful, and with an additional note to the effect that the recovery efficiency of XAD-2 resin is not universally high (for aliphatic hydrocarbons, for example, the recovery may be only 20%), the paper was accepted for publication by ICES in the leaflet series 'Techniques in Marine Science'.

b) Method Sheets on Hydrocarbon Analysis

It was agreed that there was a need for a critical review of methodology currently in use for the analysis of hydrocarbons in all matrices. Such a review does not exist in the scientific literature, and the Sub-Group agreed to prepare one for the 1987 MCWG meeting. The division of labour was agreed as follows:

Analysis of:	seawater	: M Ehrhardt
	sediments	: R Law
	atmosphere	: A Knap
	biota	: J Klungsøyr

Draft submissions are to be sent to M. Ehrhardt by September 1986.

Dr J Uthe will also be contacted for an input to the section on biota, and Dr J Farrington will be asked to act as reviewer of the compiled draft. If appropriate, the final review may be submitted for publication in the open literature following discussion of it at the 1987 MCWG meeting.

7B.4 Proposals for Manual on "Good Laboratory Practice"

This item had been raised at the 1985 MCWG meeting at the request of ACMP, and the MCWG had responded that the subject was well covered in the open literature. A reference list had been provided in which particularly relevant articles were identified. The Organics Sub-Group felt that the production of a guide on this subject by MCWG is a waste of time, as the subject is already adequately covered in the literature.

7B.5 Reference Materials

Discussion on this topic covered two main areas: the current availability of, and further requirements for, standards and reference materials. The philosophy underlying the Organics Sub-Group's current proposals for intercalibration exercises requires the availability of certified standard reference materials for use both in the exercises themselves and in subsequent quality assurance programmes.

Dr Calder is currently compiling a looseleaf handbook of available reference materials from all sources, with full information on certified values. This will be made available to ICES when completed, and will help to ensure that the Sub-Group does not request materials that are already available.

All the chlorobiphenyls (CBs) on the ICES primary list are now available from BCR. Dr J C Duinker is currently carrying out work to assess whether or not this list is fully appropriate for investigations in the marine environment. When this work is complete, BCR will consider synthesizing additional CBs as necessary.

The standard CB solutions produced by the National Research Council of Canada were felt to be very useful, but they do not contain all the CBs found in the marine environment. When they are used, care should be taken to ensure the integrity of the solutions, and one or two CBs should be available as pure compounds to allow the preparation of solutions for cross-checking concentrations.

The most urgently required reference materials felt to be:

1) A material with a high fat matrix, for use primarily in the analysis of marine mammals.

2) Fish muscle or mussel homogenate.

The organic compounds for which certified concentrations could be most usefully provided were identified as:

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

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

8B. SPATIAL AND TEMPORAL TRENDS FOR CONTAMINANTS IN SEA WATER

The assessment of spatial variability of organic contaminants in sea water is possible, especially in areas close to sources where concentration gradients are steep. The study of temporal trends requires much greater confidence in determined concentrations than can currently be achieved, as the changes are not so great. The ability to detect spatial and temporal trends is governed by the precision of the method used; only changes greater than about three times the standard deviation of the method can be reliably detected. The Sub-Group could not suggest any case in which temporal trends for the concentrations of organic contaminants have been demonstrated to be statistically significant, though decreasing tendencies have been noted (e.g., in stranded tar).

9B. NET FLUXES FROM RIVERS TO OCEANS AND MASS BALANCE ESTIMATES

The Organics Sub-Group considered the issue of contaminant fluxes and mass balances, though the Sub-Group felt that it lacked the expertise to tackle the question thoroughly. It is clear from the results of intercomparison exercises completed to date that the ability to generate the high resolution, high quality data for all compartments needed to support flux and mass balance calculations does not exist generally throughout ICES countries.

The Sub-Group requested that the ACMP in future provide MCWG with guidance on the relative priority of such activities vis-a-vis monitoring activities. If flux and mass balance calculations are considered to be of relatively high priority, then additional expertise must be brought to bear on the problem.

Lack of time prevented the Sub-Group from discussing agenda items 10, 11 and 12.

13B. ANY OTHER BUSINESS

13B.1 Item 8.C.3 from the 1985 MCWG report

The mussel homogenates mentioned in this section have not so far been distributed. NOAA laboratories have produced consensus values based on levels of chlorination, whereas European users would carry out analysis for individual CBs. This calls into question the value of using these mussel homogenates in connection with the Baseline Study on Contaminants in Fish and Shellfish, and the question of what to do with this has not yet been resolved.

13B.2 CB congeners

GEMSI has discussed the ICES lists of CB congeners to be analysed for routine monitoring purposes, and has been somewhat critical of the choice. GEMSI would prefer CBs to be easily separable on an average quality SE-54 column and has suggested their own list. As the ICES lists are only provisional, and as they take account of more factors than simply chromatographic behaviour, it was agreed to leave the ICES primary list as agreed previously. The Sub-Group decided to add chlorobiphenyl IUPAC numbers 194, 206 and 209 to the secondary list.

C. REPORT OF THE SUB-GROUP ON CHEMICAL OCEANOGRAPHY

The Sub-Group on Chemical Oceanography consisted of the following members: Dr M Perttilä (Chairman), Dr M O'Sullivan (Rapporteur), Dr S Fonselius, Dr L Føyn, Dr F Koroleff, Dr O Vagn Olsen, and Dr G Weichart.

7.3 Nutrients

7.3.1 Analysis of nutrients in seawater

The Sub-Group discussed problems associated with the automated analysis of nutrients in sea water.

Mr Vagn Olsen presented the results of his investigations on the effects of turbidity on nutrient analysis (phosphate, silicate,

nitrate, nitrite) using an autoanalyser. Two species of phytoplankton were used to provide samples with a defined turbidity. At a concentration of 20 mg/m^3 chlorophyll-a, the highest value normally measured in a "bloom" situation, a slight turbidity effect was observed. It was concluded that in most situations phytoplankton would not be a major source of turbidity. It was estimated that high turbidities were only observed in one percent of nutrient data from the current measurements, mainly in near-bottom samples from the northern Kattegat, although ten percent of the data obtained in March and April show high turbidity due to the presence of diatoms. Normally, it was not necessary to take turbidity into account, however, appropriate corrections should be made for very turbid samples. It was pointed out that the autoanalyser used for this study is unique (see Doc. ICES C.M. 1984/C:19). A report of a similar investigation by the Finnish Institute of Marine Research using Technicon and AKEA autoanalysers was also discussed. The results of this work indicated that turbidity should always be measured when nutrient concentrations are low.

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

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

A new method for the analysis of total nitrogen in sea water using high temperature catalytic oxidation has been described (Suzuki, Y., Sugimura, Y. and Hoh, R., Mar. Chem. 16, 83 - 97 (1985)). This was discussed by the Sub-Group. The results obtained for sea water using this method are significantly higher than those obtained using the persulfate oxidation method. The authors attribute the difference in results to the low oxidation capacity of the wet oxidation method against high-polymer organic matter dissolved in sea water. However, it was pointed out that the results obtained by Kjeldahl analysis for total nitrogen are in agreement with the results obtained using the wet oxidation method. It was suggested that the Organics Sub-Group consider the forms in which organic nitrogen is present in sea water and, if possible, propose suitable model compounds which could be used to compare the efficiency of the different analytical methods. If necessary, further investigations will be conducted. A literature review will be carried out on the oxidation capacity of the wet method.

The Sub-Group was satisfied that suitable standard reference materials (Sagami standards) are available and that, at present, there is no need for an international intercalibration exercise for nutrients in sea water.

However, bilateral or multilateral intercalibration exercises should be carried out between ships whenever it is possible to do so.

7C.4 Proposals for Manual on "Good Laboratory Practice"

The Sub-Group on Chemical Oceanography discussed the paper on general guidance for good laboratory practice in relation to the collection and analysis of marine samples (Doc. MCWG 1986/7.4) and came to the following conclusions:

1) This paper is very general, suitable as a preface to a manual of sea water analysis or as an introduction to a course in chemical oceanography. The Sub-Group suggested that the paper be included as an introduction in the series of leaflets on marine methods produced by ICES.

2) In its present form, this paper is not very useful for the laboratories in the ICES community. If it is distributed to developing countries, the Sub-Group felt that ICES may be interfering with the tasks of IOC, FAO, UNEP or other international organisations carrying out education in oceanography (marine chemistry) in developing countries.

3) paragraph should be added to the paper stressing the importance of collecting routine hydrographic information and also the necessity of filling in the proper oceanographic data sheets. These sheets should be filled in correctly, as this information may be required in the future.

8C. TEMPORAL TREND MONITORING FOR NUTRIENTS

The Sub-Group on Chemical Oceanography stated that three approaches can be used when carrying out temporal trend monitoring programmes for nutrients in sea water. They are:

a) Single stations.

b) Transects from the coast into the open sea.

c) Grid of stations.

The choice of approach to use will depend on the type of area (estuarine, coastal or sea) being monitored and on the available background data. The frequency of sampling for b) and c) above should be decided using the information that is available on seasonal and annual variations. To reduce biological interference it is recommended that samples for nutrient trend analysis be taken during the winter months. The parameters which can be monitored in this type of programme include phosphate, nitrate, nitrite, ammonium, silicate, total phosphorus and total nitrogen.

Salinity and temperature measurements are mandatory components of all nutrient monitoring programmes. It is desirable that measurements of biological activity (primary production, chlorophyll)

also be included to provide background information which would enable a more comprehensive interpretation of the data. Standard depths, as recommended by ICES, should be sampled.

As a preliminary step in identifying those areas where trends might be monitored, it is recommended that ICES request countries in the Oslo and Paris Conventions area to provide information on the available nutrient data. An inventory can then be compiled which would assist in the identification of gaps in the existing nutrient data. Countries should be encouraged to continue their monitoring studies and to make the data available to ICES.

Countries are also requested to provide papers on the results of their trend monitoring activities.

9C. NET FLUXES FROM RIVERS TO OCEANS AND MASS BALANCE ESTIMATES

The Sub-Group on Chemical Oceanography felt that the measurement of riverine and atmospheric inputs was outside its scope, because in most countries this area is dealt with by different authorities, e.g., hydrological institutes. It was pointed out that the use of coastal sampling stations in the determination of atmospheric inputs to the sea can lead to serious inaccuracies in the results. However, if the MCWG decides that it is necessary, a leaflet on the methodology used for the assessment of riverine and atmospheric inputs can be prepared intersessionally.

11C. GLOBAL OCEAN FLUX STUDY AND SIMILAR PROGRAMMES

The Sub-Group on Chemical Oceanography agreed that it did not have sufficient information to evaluate the compatibility of current marine chemical programmes within the ICES community with the proposed Global Ocean Flux Study (GOFS). This study was welcomed in principle and it was proposed that ICES make the organisers aware of ICES activities in the areas of chemical, biological and physical oceanography.

As the resources of ICES member countries are limited, duplication of research activities should be avoided. It is recommended that the GOFS group take account of existing programmes within ICES member countries when drafting their programmes.

13C. ANY OTHER BUSINESS

There were no matters raised under this agenda item.

D. DISCUSSION IN PLENARY OF SUB-GROUP REPORTS

D.1 Trace Metals Sub-Group Report

The MCWG reviewed the report of the Trace Metals Sub-Group and its action list.

Noting that no information was given on the atmospheric deposition of trace metals into the sea, it was pointed out to the Group that there are several relevant papers on this topic, including several papers from the Symposium on Contaminant Fluxes through the Coastal Zone (Nantes, 1984).

The question was raised as to whether this Sub-Group had considered the issue of the speciation of individual trace metals, but it had not as no questions regarding speciation had been directed toward it.

D.2 Organics Sub-Group Report

The MCWG considered the report of the Organics Sub-Group and noted its response to the request from the JMG for advice on the feasibility of conducting an intercalibration exercise for analyses of Lindane in biota and sediments. It was pointed out to the Group that Lindane is the subject of an EEC Directive, so all EEC countries are required to monitor Lindane (γ-HCH) in biota, sea water and sediments. This was one of the reasons that Lindane was added to the Joint Monitoring Programme. Another reason was that Lindane was one of the substances singled out at the International Conference on the North Sea in Bremen in November 1984 as a candidate for inclusion in the JMP. The MCWG took note of this information and felt that the response of the Organics Sub-Group was adequate.

The MCWG noted that on the subject of good laboratory practice, the Organics Sub-Group had a different approach from that of the Trace Metals Sub-Group.

In terms of the issue of a reference material for organochlorine analysis for use in the Baseline Study, it was noted that there had been a number of problems with the distribution of the mussel homogenate that Dr Calder had mentioned at last year's meeting. Accordingly, the MCWG agreed that for purposes of validating the organochlorine component of the Baseline Study, it was too late to distribute reference materials to be analysed along with samples from the Baseline Study because many of these analyses may already be completed. The MCWG emphasized, however, that there should have been built into the guidelines for the Baseline Study a requirement that a reference material must be analysed to allow validation of the organochlorine data.

The MCWG approved all the recommendations of the Organics Sub-Group. These will be covered in more detail under agenda item 14.

D.3 Report of the Sub-Group on Chemical Oceanography

The MCWG reviewed the report of the Sub-Group on Chemical Oceanography. Noting the section on good laboratory practice, the Sub-Group was requested to provide references to several key papers on good laboratory practice in terms of nutrient analyses.

An extensive discussion was held on the Sub-Group's view that no international intercalibration exercise was needed on the analysis of nutrients. The Chairman of the Sub-Group, Dr Perttilä, pointed out that the problem with nutrient analyses is that the

best conditions cannot be attained with preserved samples and, accordingly, the Sub-Group felt that an intercalibration exercise on preserved nutrient samples would not be useful. On the other hand, it is very difficult to hold an intercalibration workshop to carry out analyses of nutrients in fresh seawater samples. However, the Sub-Group has recommended that intercalibrations be held whenever a joint exercise is carried out, such the International Investigation of Patchiness in the Baltic Sea, and on any other occasion when research vessels meet.

Based on this discussion, Dr Perttilä agreed to review the extent to which nutrient intercalibrations have been conducted between ships when they have met, covering the past 15 years. In this work, he will attempt to obtain the results of these intercalibrations and determine the level of comparability achieved.

In terms of riverine inputs and atmospheric deposition of nutrients, the MCWG felt that more information was available than indicated by the Sub-Group. Dr Knap informed the Group that he is preparing a paper on the atmospheric deposition of nutrients to the sea and the effects on primary production in the open ocean.

8 SPATIAL AND TEMPORAL TRENDS FOR CONTAMINANTS IN SEA WATER

The discussion of this item took place in the three sub-groups and is recorded in Sections 8A, 8B and 8C.

9 NET FLUXES FROM RIVERS TO OCEANS AND MASS BALANCE ESTIMATES

In addition to the discussion of this topic in the Sub-Groups (see Sections 9A, 9B, and 9C), the MCWG as a whole discussed the atmospheric input component of mass balance estimates. It was reported that the IOC has a programme on atmospheric deposition and will prepare descriptions of methods to determine contaminants in rain water and dry deposition to the sea. It was expected that these methods descriptions would be available from IOC in approximately one year.

Noting the request from the Paris Commission concerning an assessment of the input of contaminants from the atmosphere to the sea and advice on the most appropriate methodologies for quantifying inputs from this source, it was agreed that several members of MCWG should review the information available from the Paris Commission's Working Group on Atmospheric Deposition and prepare a response to this request. This sub-group will be coordinated by the Chairman, Dr Topping, and will consist of Drs Brügmann, Cofino, Cossa, Ehrhardt, Føyn, Knap, Law, O'Sullivan, Palmork, and Reutergårdh. The Environment Officer agreed to send the appropriate papers to this group in late spring.

10 OVERVIEWS

10.1 PAHs in the Marine Environment

The MCWG reviewed the document "Polycyclic Aromatic Hydrocarbons in the Marine Environment: An Overview" by Mr. Law and accepted it for transmission to ACMP. Noting that this paper had been the subject of many years of work and had undergone a number of re-drafts, the Working Group expressed its great appreciation to Mr Law for his excellent paper and for his patience and tolerence in dealing with the numerous requests for the insertion of additional data in his paper.

10.2 Use of Organisms for Monitoring Purposes

No paper had been prepared on this topic, but the Working Group noted that the Organics Sub-Group had discussed the topic in terms of the relative value of the use of organisms in monitoring marine contamination and which organisms should be used. It was felt that there are clearly different uses for monitoring organisms on the different scales. It was generally felt that some biota, particularly bird eggs, cannot be used as an early warning system for new contaminants.

10.3 Review of, and Proposals for, Overviews

The discussion of proposals for new overviews by the Trace Metals Sub-Group is contained in Section 10A, above. The Organics Sub-Group, however, was unable to discuss this item owing to lack of time. Accordingly, the consideration of possible overviews on organic contaminants was carried out in the MCWG as a whole.

The MCWG noted that the US Environmental Protection Agency has prepared a two-volume book describing every priority pollutant, including its toxic effects, environmental fate, etc. This book could serve as a useful basis for the development of overviews on individual contaminants. Dr Knap agreed to send the full citation for this book to the Environment Officer.

The US Environmental Protection Agency has also prepared reports on Lindane and on chlordane. Dr Reutergårdh agreed to send the full citations on both these reports to the Environment Officer.

Dr Reutergårdh offered to ask a colleague whether he would be able to prepare an overview on surface-active substances.

11 GLOBAL OCEAN FLUX STUDY AND SIMILAR PROGRAMMES

This agenda item was discussed in the Sub-Group on Chemical Oceanography, as reported in Section 11C, above. The Trace Metals Sub-Group felt that it did not have the competence to discuss this item and the Organics Sub-Group did not have adequate time to consider it.

12 NEW CONTAMINANTS

Dr Ehrhardt mentioned that studies in the Baltic Sea have shown that diphenylsulfone occurs in concentrations ten times higher than any PAH. Additionally, oxygenated and degraded hydrocarbons are often found at much higher concentrations in water and air than the respective parent compounds; often these compounds are much less degradable than the parent compounds.

It was suggested that it could be useful to study the toxicity of such compounds in the surface microlayer and determine their possible effects on biota.

13 ANY OTHER BUSINESS

The MCWG reviewed the action lists for intersessional work that had been agreed by each of the three Sub-Groups and the work agreed for members of the MCWG as a whole. The full action list is contained in Annex 5.

There was no other business in the plenary meeting of MCWG, however, the Trace Metals Sub-Group and the Organics Sub-Group had several items of other business that are reported in Sections 13A and 13B, above, respectively.

14 RECOMMENDATIONS

The MCWG considered again the evaluation of the data from the 1985 Baseline Study of Contaminants in Fish and Shellfish, which had been discussed earlier under agenda item 4.1, above. The MCWG agreed to recommend that these data should be validated and assessed by a sub-group of MCWG together with scientists nominated by the Joint Monitoring Group and the Helsinki Commission. Noting that this Baseline Study is being coordinated under three ICES Working Groups, namely, the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic, the MCWG, and the ICES/SCOR Working Group on the Study of the Pollution of the Baltic, it was agreed that the ACMP should nominate the Chairman of this evaluation group for the Baseline Study on Contaminants in Fish and Shellfish. The recommendation for the establishment of this group is contained in Recommendation 1 (Annex 6).

The MCWG proposed the following persons for possible membership in this group: Dr S Berman, Dr L Brügmann, Dr W Cofino, Dr U Harms, Dr A Jensen, Mr R Law, Dr M Olsson, Dr M O'Sullivan, Dr K Palmork, Dr M Perttilä, Dr L Reutergärdh, and Dr D Wells; in addition, either Dr J Uthe or Mr H Lassen should provide advice on statistical handling of the data.

In terms of reporting data to ICES from the Baseline Study on Contaminants in Fish and Shellfish, the MCWG agreed that these data should be reported no later than 1 August 1986. These data should be reported using the Interim Reporting Format for Contaminants in Fish and Shellfish, either on paper forms or, preferably, on magnetic tape. Copies of the paper reporting formats will be sent to all laboratories participating in the Baseline Study in mid-May by the ICES Sectretariat, while instructions for

reporting on magnetic tape are available on request. Quality control data should also be reported; this information should be submitted on paper.

While noting that the Baseline Study of Trace Metals in Coastal and Shelf Sea Waters is scheduled to run until 1987, the MCWG agreed that an evaluation of the data available from 1985 should be made by a sub-group of MCWG which should meet immediately following the meeting of the evaluation group for the Baseline Study of Contaminants in Fish and Shellfish. The recommendation for this meeting is contained in Recommendation 2 (Annex 6). The MCWG agreed that data from the Seawater Baseline Study should be submitted to the ICES Secretariat by 1 September 1986, according to the Interim Reporting Format for Contaminants in Sea Water (Version 2) or its magnetic tape equivalent. This reporting format will be available for distribution from the middle of June.

The MCWG then reviewed and accepted the recommendation of the Organics Sub-Group that a two-day special meeting be held (a) to review the data on contaminants in marine mammals and the analytical procedures used to obtain these data, (b) to evaluate the observations of disease conditions in marine mammals in terms of disease incidence and prevalence in the respective populations and estimate the impact on these populations, (c) to prepare a list of reported toxicants that may be implicated in these diseases and indicate any other contaminants that might be implicated on the basis of known toxicological, structural and physical properties, and (d) to identify future needs for a programme to fill the gaps in understanding. This meeting should be held immediately prior to the next meeting of the MCWG. The ACMP should nominate a suitable convener for this special meeting and identify appropriate participants, bearing in mind the need to include representatives from MCWG, the Marine Mammals Committee, and the Baltic Seals Working Group. The convener should thereafter invite the relevant experts for participation and prepare the meeting in detail. This recommendation is contained in Recommendation 3 (Annex 6). The MCWG further agreed that in preparation for this special meeting, a paper should be prepared reviewing the methodology used to determine organochlorines in marine mammals and evaluating the data that have been reported on these contaminants in marine mammals. This paper should be prepared by Dr A Knap and Dr L Reutergårdh in a meeting at the Bermuda Biological Station from 14 July to 7 August 1986. A recommendation for this preparatory meeting is also contained in Recommendation 3.

The MCWG then took note of the portion of the Organics Sub-Group report concerning analysis of specific hydrocarbons and agreed that, given the lack of progress currently being made in the improvement of specific hydrocarbon analysis, a new approach to improving comparability should be recommended for adoption within ICES. This approach is based on the experience within the EC's Bureau of Community References (BCR) on standardizing methods in the preparation of reference materials. This approach consists of the selection of competent laboratories who can undertake a commitment to the full programme of work required to complete the exercise, which will extend over several years. The MCWG advised that, if this commitment cannot be made by any given laboratory, it should not undertake to participate in this work. An essential component of this approach is that the participating analysts

meet regularly to set specific aims for each phase of the exercise and to critically review progress that has been made in achieving these aims. A full description of this approach, written for the intercalibration of Lindane analyses but applicable to any class of organic compounds, is given in Annex 3. The MCWG recommendation that ICES adopt this approach for the intercalibration of analysis of specific hydrocarbons is contained in Recommendation 4 (Annex 6). As the first step in this programme, the MCWG recommended that a preliminary meeting of analysts participating in this programme be held for one or two days immediately preceding the next MCWG meeting to draw up an outline of the programme and to agree the first steps. This meeting should be convened by Mr R Law (see Recommendation 4).

The MCWG then discussed its next meeting and agreed that it should be held for five days in late February or early March 1987 at ICES headquarters. The following topics should be considered:

a) the reports on the results of the Baseline Study of Contaminants in Fish and Shellfish and the Baseline Study of Trace Metals in Coastal and Shelf Sea Waters;

b) the results of Part 2 of 7/TM/BT;

c) the results of the intercalibration exercise on trace metals in estuarine water;

d) the results of the questionnaire survey on nutrient data in the northeast Atlantic;

e) the paper on a possible intercalibration exercise on analysis of organo-mercury compounds;

f) overview papers on certain contaminants in the marine environment;

g) monitoring to determine spatial distribution and temporal trends of contaminants and nutrients in sea water;

h) a possible intercalibration exercise on nutrient analyses in sea water.

This is Recommendation 5 in Annex 6.

The MCWG noted that the full series of meetings called for in the five recommendations above would cover two weeks and should be scheduled as follows:

<u>First Week</u>

Monday - Thursday	Joint ICES/OSPARCOM/HELCOM group to evaluate the results of the Baseline Study on Contaminants in Fish and Shellfish
Friday - Saturday	Sub-Group of MCWG to evaluate 1985 results of the Baseline Study on Trace Metals in Coastal and Shelf Sea Waters

Wednesday - Thursday	Special Meeting on contaminants in marine mammals and their possible effects
Friday - (Saturday)	Meeting of analysts participating in the programme to optimize analysis of specific hydrocarbons

Second Week

Monday - Friday	Meeting of the Marine Chemistry Working Group

For the 1988 meeting of MCWG, Dr Knap offered that the meeting could be held at the Bermuda Biological Station. Dr Cofino stated that, if it proves not to be feasible to meet on Bermuda, he to would invite the Group meet in the Netherlands. The MCWG fino for thanked Drs Knap and Cotheir generous offers.

As all business had been completed, the Chairman thanked all members for their very constructive work during the meeting.

On behalf of the entire Working Group, the Chairman expressed warm appreciation to the host of the meeting, Dr Perttilä, for the excellent facilities and assistance provided. The Chairman asked Dr Perttilä to convey the Group's appreciation also to the Director of the Finnish Marine Research Institute, Professor Voipio, and his staff.

The Chairman then closed the meeting at 17.00 hours on Friday, 21 February 1986.

ANNEX 1

MARINE CHEMISTRY WORKING GROUP

Helsinki, Finland, 18-21 February 1986

AGENDA

1. Opening of Meeting
2. Adoption of the Agenda
3. Report on the 73rd Statutory Meeting
4. Reports of related activities
   - 4.1 JMG of the Oslo and Paris Commissions
   - 4.2 ICES/SCOR Working Group on the Study of the Pollution of the Baltic
   - 4.3 Activities under the Helsinki Commission
   - 4.4 Intergovernmental Oceanographic Commission (GIPME/GEMSI/GEEP/GOPPS)
   - 4.5 Other relevant activities
5. Reports on Projects and Activities in ICES Countries
6. Requests from ACMP and regulatory agencies
7. Intercalibration and other Quality Control Activities
   - 7.1 Trace Metals
     - 7.1.1 Status reports on (a) 7b/TM/BT and (b) 1/TM/MS
     - 7.1.2 Method sheets based on procedures used in 5 TM/SW and 7a/TM/BT
     - 7.1.3 Performance charts for 5 TM/SW
     - 7.1.4 Plans for JMG I/C on trace metals in estuarine waters
     - 7.1.5 Other proposals/plans for I/C exercises
   - 7.2 Organics
     - 7.2.1 Status reports on (a) 2 HC/BT and (b) 3 HC/BT
     - 7.2.2 Proposals for 1/HC/SW
     - 7.2.3 Proposals for 1/OC/Marine Mammals and descriptions of methods
     - 7.2.4 Other proposals/plans for I/C exercises
     - 7.2.5 Monitoring O/Cs in fish and birds
     - 7.2.6 Methods sheets on (a) O/Cs and (b) H/C analysis
   - 7.3 Nutrients
     - 7.3.1 Analysis of nutrients in seawater
   - 7.4 Proposals for manual on 'good laboratory practice'
   - 7.5 Reference materials
8. Spatial and temporal trends for contaminants in seawater
9. Net fluxes from rivers to oceans and mass balance estimates
10. Overviews
    - 10.1 PAHs in the marine environment
    - 10.2 Use of organisms for monitoring purposes
    - 10.3 Review of, and proposals for, overviews
11. Global Ocean Flux Study and similar programmes
12. New Contaminants
13. Any other business
14. Recommendations

ANNEX 2

MARINE CHEMISTRY WORKING GROUP

(Helsinki, 18-21 February 1986)

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ANNEX 3

DISCUSSION PAPER FOR ICES MCWG (ORGANIC SUB-GROUP) ON THE REQUEST BY JMG FOR AN INTERCOMPARISON EXERCISE FOR THE ANALYSIS OF LINDANE (γ-HEXACHLOROCYCLOHEXANE) IN BIOLOGICAL TISSUE AND SEDIMENT

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1. Introduction

This paper has been prepared as a starting point for discussion and is not intended as a definite comment on any proposed intercalibration exercise for lindane by this or any other group.

There is now a large data bank of information on intercalibration exercises for a wide number of pesticides (Smart, 1984, 1985; Storet, 1982), and some including γ-HCH (Lindane, γ-BHC) (Palmork, 1980). The general procedures and methods of testing are well known and documented (Horowitz, 1981; ISO, 1981). However, it would be useful for discussion to highlight discrete areas which require consideration prior to embarking on an exercise for γ-HCH, or any other determinand.

In Figure 1, the flow diagram outlines the checklist/analytical exercises necessary to build up a reliable intercalibration study, with the appropriate critical review stages.

2. Approach

In the past, a number of intercomparison exercises (Holden 1980, 1983) have been less successful than they might have been for one or more of the following reasons:

1) Poor coordination and slow response of participants in meeting deadlines. This occurs when a large exercise is conducted over a wide time scale.

2) The initial (or sometimes final) expectations of laboratory's performance are too high.

3) The euphoric atmosphere of the planning session often sets too big a task, or too many tasks, to be achieved in a single exercise at any one step. Often the work is either rushed with consequent errors, only partially complete, late or deferred due to other pressing priorities.

4) The tasks themselves and the exact goals to be achieved may not, in some cases, be defined exactly, leaving room for interpretation where it was not intended. The initial group of participating laboratories may have widely different ranges of experience and expertise and this is often reflected in the variance in the data obtained.

Many of these difficulties can, in some measure, be overcome as follows:

1) Initially a limited number of laboratories should be selected, 10 or 12, with the required laboratory support and staff experience. This may be a difficult task if there are a number of potential laboratories involved, but this should be done objectively on the basis of proven analytical capability and quality control for the determinands in question.

2) Membership of that initial group should not be regarded as exclusive or necessarily an elite band, but simply appropriate for the task. The group should agree to the work programme and to the deadlines set, for the best progress of the group as a whole, and for the other laboratories awaiting the outcome of the Ring Tests.

3) If the group can be financially supported by a central body, this is desirable as it encourages progress and entitles that body to request the results within the timescale, particularly when support is withdrawn if the results are not forthcoming.

4) The programme should be set out at the beginning of the I/C exercises, possibly along the lines of the flow diagram (Figure 1) and agreed by the participants. This should be actively reviewed at each step of the programme.

5) Although tangible progress is essential, the pace must be one where all participants can contribute and improve (refine) their techniques. This will often require small steps to be taken with a single objective. In the long run, this is more efficient, since the study rarely has to be repeated.

Horowitz (1982) has shown that a group of laboratories working together on a common analytical problem rarely obtains good comparability on the initial exercise and that improvement to the minimum CV obtainable by that group may take up to four exercises and group meetings (four years on an annual cycle).

Therefore, even with some degree of selection, it may not be possible to obtain first time success. Generally with such exercises there are a number of direct improvements in methodology and approach which will only come to notice following the initial steps in the programme (Tuinsta et al., 1985).

3. Analytical Methods

Although there are a larger number of laboratories who are currently analysing for lindane, there should be common agreement on suitability of these methods, now and for the foreseeable future. Since this compound is usually determined by gas chromatography (GC) at the same time as a number of other organochlorine resi-

dues, it is important to select a method which, in general terms, can also be applied to these other components. With these general points in mind, the following specific questions must be addressed.

3.1 Availability of suitable pure primary standards

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

3.2 Written methods for the preparation of standard solutions

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

3.3 Internal standards for quantitation and retention index markers for identification

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

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

3.4 Method of Determination

Capillary Column Chromatography with Ni-63 Electron Capture Detection is currently preferred as the method for the analysis of organochlorine residues, including lindane. Therefore, this should be the basic method used in such an intercalibration exercise. The use of autosamplers/integrators/computer-controlled systems may be regarded as optional and their use discussed in the intercalibration Working Group.

3.5 Chromatographic Conditions

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

1) Injector, detector and initial oven temperature.

2) Carrier gas purity and linear velocity.

3) Split time, if splitless injector system is used.

4) The length, id, film thickness and stationary phase of the capillary column.

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

4. Certification of Reference Material

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

1) An evaluation of the wider demand and applicability of the selected candidate RMs.

2) Assistance in the location and preparation of RMs, including homogeneity and storage testing.

3) Possible financial support for (1) and (2), above, and assistance in certification.

4) Wider credibility for the RMs once the analysis has been completed.

5) A central reference point for a future source of the RMs for participating and other laboratories.

5. Selection of the Matrix

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

The common points which require detailed group discussion are:

1) The selection of the matrix and the expected range of contamination. The starting reference material should be obtained as a natural, unspiked sample and the content certified by analysis.

2) Sufficient quantities of these materials should be identified, not only to cover the initial I/C, but for a longer term use as RMs.

3) Methods of extraction and clean-up, and information on the postextraction stability and storage of the samples are particularly valuable (Mowrer and Jensen, 1982).

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

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

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

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

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FIGURE 1

Flow Diagram for an Intercomparison Exercise for Lindane

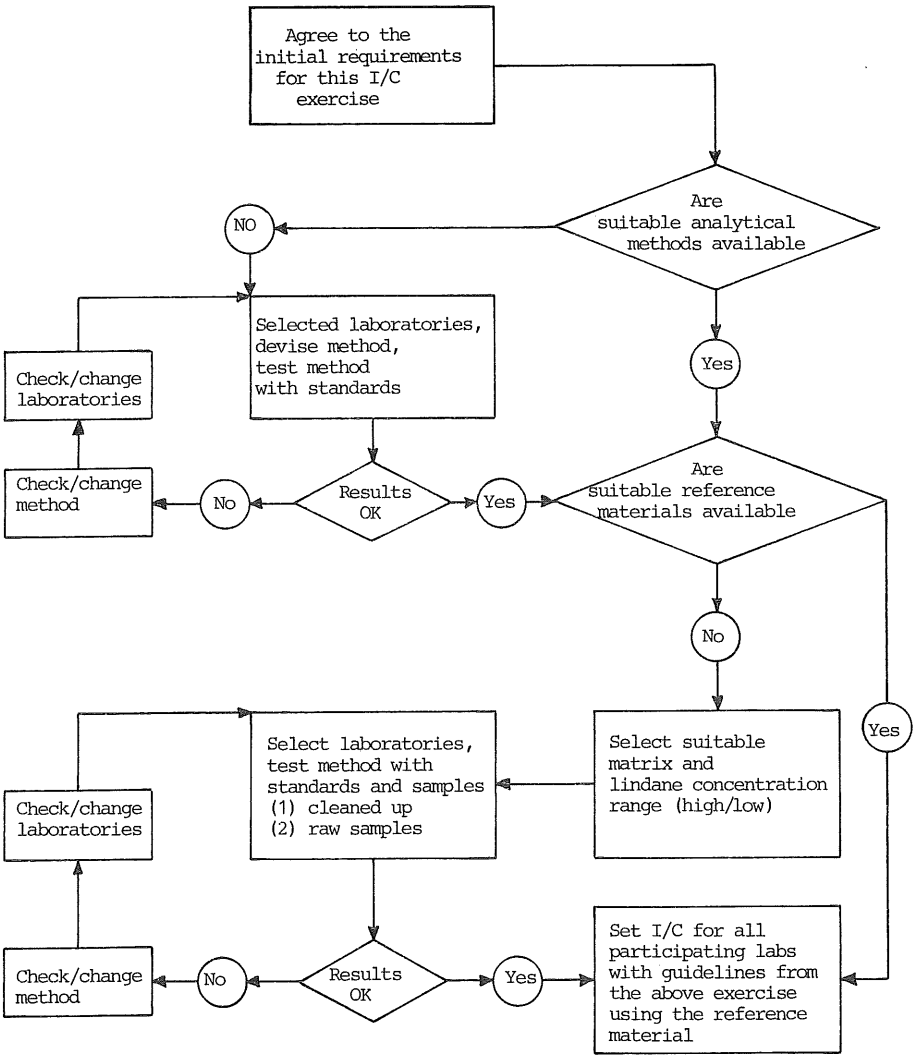

TABLE 1

γ-HCH IN SEDIMENTS

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

TABLE 2

γ-HCH IN BIOLOGICAL TISSUE

		Wet Weight		Lipid Weight		
		Mean µg/kg	Range µg/kg	Mean µg/kg	Range µg/kg	
Freshwater						
Lake Ontario	1976		10-36			Freshwater Fish STORET (1976)
River Tweed	1979		2-19			Trout Liver FFL-DAFS
			1-5			Trout Muscle
River Stour UK	1980	23				Dace Muscle FFL-DAFS
		216				Dace Liver
Marine						
North Sea/Dutch Wadden Sea	1974	3.2		0.2		Mussel
		11.3		0.29		Herring 0(M))
		3.3		0.2		Plaice 0 (M))Ten Berg and
		6.4		0.1		Herring 3(M))Hillebrand 1974
		2.0		0.08		Plaice 3 (M))
English catch	1970-73		<1-66			Many species Portmann (1979)
Firth of Clyde	1980		4-31			Herring Liver FFL-DAFS
			4-11			Herring Muscle
Sogndals fjord and Dalsfjord	1982	10	6-16			Cod (L))
		9	4-15			Haddock (L))Skare et al
		1	1-3			Lemon Sole (L))1985
		1	nd-2			Flounder (L))

ANNEX 4

JMG INTERCALIBRATION EXERCISE ON THE DETERMINATION OF TRACE METALS IN ESTUARINE WATERS

Shier Berman

Plans for this exercise are now well advanced. The collection of two samples of water for the trace metals copper, zinc and cadmium and one sample for mercury will take place during the latter part of May, probably in one of the estuaries of the Scheldt River.

The plan is to prepare a "high" and a "low" sample for copper, zinc and cadmium, increasing the value of the exercise at but little extra cost for the exercise. Only one sample will be prepared for mercury.

The exercise is on schedule as previously planned:

May 1986	Collection and bottling of water. Distribution of samples.
September 30, 1986	Deadline for receipt of results.
January 1987	Presentation of draft report to JMG.
February 1987	Presentation of draft report to MCWG for review and comment.
June 1987	Review of final report by ACMP, prior to transmission of the Oslo and Paris Commissions.

In order to carry out this schedule the deadline for the receipt of results will have to be ruthlessly adhered to. The January 1987 JMG meeting allows for almost no slippage for this deadline. Laboratories will have about three and a half months to carry out the analyses.

The water will be gathered in 50-litre polypropylene carboys by peristaltic pumping through 0.45 µM high capacity filters and simultaneously acidified with high purity nitric acid. The samples will be homogenized in a polyethylene tank at the Rijkswaterstaat laboratory in Lelystad, bottled and shipped to the participants from the Netherlands.

Sufficient samples are being prepared so that any ICES country laboratory that wishes to participate in the exercise may do so. I hope that many non JMG laboratories will take advantage of this opportunity.

ANNEX 5

MARINE CHEMISTRY WORKING GROUP

ACTION LIST FOR 1986

ORGANICS SUB-GROUP

Dr Reutergårdh	- to send references on EPA report on Lindane and Chlordane to the Environment Officer
	- to consider with his colleague the feasibility of an overview on surface active compounds
	- to write to Dr Abarnou with the Subgroup's comments on his paper on monitoring of organics using marine mammals
Drs Reutergårdh and Knap	- to review methods for the analysis of organochlorines in marine mammals and prepare paper at Bermuda Biological Station for coinsideration by MCWG at its 1987 meeting
	- to assess feasibility of reviewing riverine inputs of organic compounds to sea
Dr Knap	- to assess atmospheric input of organic compounds to the sea
	- to send reference on EPA Priority Pollutants to the Environment Officer
Dr Law	- to obtain OPRU report on the intercalibration exercise for hydrocarbons in seawater for 1987 MCWG
Dr Wells	- to contact BCR in relation to the availability of reference materials for individual CBs
Dr Calder	- to assess the availability of reference materials for individual CBs and report to Dr Reutergårdh intersessionally
Drs Erhardt, Knap, Law and Klungsøyr	- to prepare critical review of the methodology currently used for the measurement of hydrocarbons in all marine matrices for 1987 MCWG (this group will be assisted by Drs Uthe and Farrington)

TRACE METALS SUB-GROUP

Dr Cossa	- to discuss with Dr P Michel the possibility of preparing an overview on arsenic
	- to prepare a paper on the feasibility of conducting an intercalibration exercise for mercury, emphasing organo-mercury in marine biota tissue
	- to discuss with Dr P Buat-Menard the possibility of preparing a paper on the state of the art of methodology for assessing atmospheric input of trace metals to the coastal zones
and Dr Topping	- to discuss with colleagues the possibility of preparing overviews on chromium and nickel, respectively
Dr Cofino	- to discuss with colleagues the possibility of preparing an overview on copper
	- to send reference on Lindane to the Environment Officer
and Dr Berman	- to send papers on good laboratory practice, together with a covering note, to the Environment Officer
Dr Berman	- to prepare report on 7b/TM/BT
	- to discuss with Dr P Yeats the feasibility of conducting an extended version of the intercomparison exercise for trace metals in suspended matter
	- to prepare leaflets in connection with 7/TM/BT and 5/TM/SW
Dr Brügmann	- in conjunction with colleagues from the Sub-group to finalise the draft paper on temporal trend monitoring of trace metals in seawater

CHEMICAL OCEANOGRAPHY SUB-GROUP

Dr Perttilä	- to finalise questionnaire and covering letter in connection with the inventory of nutrient measurements in seawater and to distribute it to appropriate ICES laboratories
	- to examine the inter-ship comparisons of nutrient sampling and measurement and prepare report for 1987 MCWG

CHAIRMAN

- to contact Dr Uthe to determine status of the report on 3/HC/BT
- to send copies of correspondence on organochlorines in marine mammals to Dr Reutergårdh
- to send papers on atmospheric inputs of trace metals to Dr Cossa

ENVIRONMENT OFFICER

- to send details of the intercomparison exercise for trace metals in inshore waters to all members of MCWG
- to inform participants in the ICES baseline study of the deadline for submitting results to ICES and send copies of data reporting formats
- to send copies of appropriate papers from the Paris Commission's Working Group on Atmospheric Deposition to MCWG members who have agreed to review them

ALL MEMBERS OF MCWG

- to provide comments and suggestions on the reporting format for contaminants in seawater
- to inform Dr Law about laboratories in their country who wish to participate in the exercise on methodological improvement for hydrocarbons in marine samples
- to remind colleagues about the deadline for submission of results for 7b/TM/BT and the JMG I/C exercise for trace metals in seawater

ANNEX 6

RECOMMENDATIONS

Recommendation 1

The Marine Chemistry Working Group recommends that a joint ICES/OSPARCOM/HELCOM group be established to carry out the initial validation and assessment of the data from the 1985 Baseline Study of Contaminants in Fish and Shellfish; this group should meet for four days in February 1987 at ICES headquarters to conduct this work.

Recommendation 2

The Marine Chemistry Working Group recommends that a sub-group of the MCWG, convened by Dr G Topping, meet for two days in February 1987 at ICES headquarters to review the data collected in 1985 for the Baseline Study on Trace Metals in Coastal and Shelf Sea Waters.

Recommendation 3

Noting the serious discrepancies in the analyses of contaminants in marine mammals, the Marine Chemistry Working Group recommends that

i) a special meeting on marine mammals (Convener:) be held for two days in February 1987, during the week preceding the MCWG meeting, at ICES headquarters with the following terms of reference:

   a) to review critically the analytical procedures used to determine organochlorine residues in marine mammals and the data on these contaminants currently available in the literature;

   b) to evaluate the observations on disease conditions in marine mammals in terms of disease incidence and prevalence in the respective populations and estimate the extent of the impact on these populations; in this evaluation, similar disease syndromes in terrestrial mammals should also be considered;

   c) to draw up a list of reported toxicants that may be implicated in these diseases and indicate any other contaminants that might be implicated on the basis of known toxicological, structural and physical properties;

   d) to prepare a statement of findings and identify future needs for a programme to fill the gaps in understanding of, e.g., the pathology and reproduction of marine mammals, effects of habitat, etc.

The Convener should invite relevant experts for participation in this meeting.

ii) In preparation for the above meeting, a background paper should be prepared by Dr A Knap and Dr L Reutergårdh in a working session at the Bermuda Biological Station from 14 July to 7 August 1986 which should review the methodology presently used to determine organochlorine residues in marine mammals and evaluate the data reported in the literature on concentrations of these contaminants in marine mammals.

Recommendation 4

The Marine Chemistry Working Group recommends that

i) recognizing the lack of progress currently being made in the improvement in specific hydrocarbon analysis, a systematic programme to optimize methods to determine hydrocarbons, including polynuclear aromatic hydrocarbons, in marine samples should be initiated within ICES according to the general strategy given in Annex 3 to the MCWG report. This strategy provides for the stepwise development of analytical methods among a group of competent laboratories who can undertake a commitment to the full programme of work, which will extend over several years. Certain expenses associated with this programme, including the cost of the reference materials used and travel expenses for participating analysts to take part in meetings, should be met by ICES to ensure the success of this programme.

ii) As the first step in the programme to optimize specific hydrocarbon analysis, a preliminary meeting of analysts participating in this programme should be held for one or two days at ICES headquarters immediately preceding the 1987 MCWG meeting to draw up an outline of the programme and agree the first steps. This meeting will be convened by Mr R Law.

Recommendation 5

The Marine Chemistry Working Group recommends that it meet for five days in February or early March 1987 at ICES headquarters with the following terms of reference:

i) to review the reports on the results of the Baseline Study on Contaminants in Fish and Shellfish and the 1985 results of the Baseline Study of Trace Metals in Coastal and Shelf Sea Waters;

ii) to review the results of Part 2 of the Seventh Intercalibration on Trace Metals in Biological Tissue (7/TM/BT);

iii) to review the results of the intercalibration exercise on trace metals in estuarine water;

iv) to consider the results of the questionnaire survey on nutrient data in the Northeast Atlantic;

v) to consider the paper on the possible need for an intercalibration exercise on the analysis of organo-mercury compounds;

vi) to review the overview papers that have been prepared on certain contaminants in the marine environment;

vii) to consider the issue of monitoring to determine spatial distribution and temporal trends of contaminants and nutrients in sea water.