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FOURTH REPORT OF THE MARINE CHEMISTRY WORKING GROUP

Copenhagen, 2-5 February 1982

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TABLE OF CONTENTS

	<u>Page</u>
1. OPENING OF MEETING AND ADOPTION OF AGENDA	1
2. REPORT ON 69th STATUTORY MEETING	1
3. OTHER ACTIVITIES OF INTEREST	1
3.1 Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA)...	1
3.2 ICES/SCOR Working Group on the Study of the Pollution of the Baltic	1
3.3 Joint Monitoring Group of Oslo/Paris Commissions ...	2
3.4 IOC/GIPME	2
3.5 GESAMP	2
4. REPORTS ON PROJECTS AND STUDIES FROM WORKING GROUP MEMBERS	2
5. REPORTS ON INTERSESSIONAL WORK ON ANALYSES OF LEAD AND PCBs	3
6. INTERCALIBRATION PHILOSOPHY - LONG-TERM PLANS AND OBJECTIVES OF ICES INTERCALIBRATION PROGRAMME	4
7. PLANS FOR FUTURE INTERCALIBRATION EXERCISES	6
7.1 PCBs	6
7.2 Petroleum Hydrocarbons	7
7.3 Fifth Round Intercalibration for Trace Metals in Sea Water	8
7.4 Trace Metals in Biological Tissue	9
8. CONDITIONS FOR PRE-ANALYTICAL STORAGE OF BIOLOGICAL MATERIALS	11
9. METHODOLOGY FOR MEASUREMENT OF RIVER INPUTS	11
10. INFORMATION ON "NEW CONTAMINANTS"	12
10.1 PCTs	12
10.2 Others	12
11. OVERVIEWS ON FLUXES AND TRANSPORT OF POLLUTANTS IN THE MARINE ENVIRONMENT	13
12. RELEVANT NUTRIENT STUDIES	13
13. REVIEW OF LEAFLETS FOR "TECHNIQUES IN MARINE CHEMISTRY"..	14
14. RELEVANT ISSUES FROM WORKING GROUP ON MARINE SEDIMENTS IN RELATION TO POLLUTION	16
15. OTHER BUSINESS	16
16. APPROVAL OF RECOMMENDATIONS AND DEADLINES	16

Table of Contents (ctd)

	<u>Page</u>
ANNEX 1: Agenda, Marine Chemistry Working Group	17
ANNEX 2: List of Participants, Marine Chemistry Working Group	19
ANNEX 3: Reports on Projects and Studies from Working Group Members	21
ANNEX 4: Meeting of the CO ₂ Sub-Group of the Joint Panel on Oceanographic Tables and Standards, Miami, 21-23 September 1981, by Dr A Poisson	29
ANNEX 5: Assessment of the Status of Intercalibrations on the Determination of Contaminants in Marine Samples	31
ANNEX 6: ICES Fifth Round Intercalibration for Trace Metals in Sea Water	44
ANNEX 7: New "Contaminant" Overview Papers	47
ANNEX 8: Action List	48
ANNEX 9: Recommendations	50

FOURTH REPORT OF THE MARINE CHEMISTRY WORKING GROUP

1. OPENING OF MEETING AND ADOPTION OF AGENDA

- 1.1 The Chairman, Dr J M Bewers, opened the meeting at 10.00 hrs on 2 February 1982 and welcomed the participants. He expressed his appreciation to the former Chairman, Dr (Ms) M C de Barros, for her excellent work during the first three years of the Working Group.
- 1.2 The draft agenda was considered and adopted with the addition of a new point under Agenda Item 4 on "Activities related to CO₂" and a new item 7.4 on "trace metals in biological tissues". The agenda is attached as Annex 1. The list of participants is contained in Annex 2. The ICES Environment Officer served as Rapporteur.

2. REPORT ON 69th STATUTORY MEETING

- 2.1 The Working Group took note of a list of relevant Council resolutions which had been adopted at the 1981 Statutory Meeting.

3. OTHER ACTIVITIES OF INTEREST

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

- 3.1.1 Some of the main activities of this Working Group were noted, including progress in the development of biological effects monitoring techniques and the on-going programme to monitor contaminant levels in fish and shellfish. It was further noted that WGMPNA is planning a baseline survey of contaminant concentrations in fish and shellfish in 1985 and a baseline survey of trace metals in coastal and shelf waters of the North Atlantic, also to take place in 1985. Finally, it was noted with interest that WGMPNA has been requested by the Advisory Committee on Marine Pollution (ACMP) to prepare a general format for the conduct of regional assessments of the health of the marine environment.

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

- 3.2.1 It was reported that among the activities of this Working Group were: (a) the preparation of an overall report on the results of the BOSEX 77 Experiment, (b) the conduct of pilot studies of patchiness (inhomogeneity in distribution) of physical, chemical and biological parameters in the Baltic Sea, and (c) the development of models of biogeochemical cycles of selected substances in the Baltic Sea.
- 3.2.2 In this connection, information on relevant activities conducted under the Helsinki Commission was also noted. These included the conduct of an intercalibration workshop on the analysis of petroleum hydrocarbons (fluorescing substances) in Kiel in 1981 and a forthcoming intercalibration on biological methods and nutrient analyses, which will be held on Bornholm in August 1982. The document "Assessment of the Effects of Pollution on the Natural Resources of the Baltic Sea, 1980", which had been prepared with the assistance of ICES, had been published in August 1981.

3.3 Joint Monitoring Group of Oslo/Paris Commissions

- 3.3.1 Information was presented on the recent activities under the Joint Monitoring Group. It was noted that the JMG, subject to the Commissions' approval, has requested ICES "to prepare a general rationale for intercalibration exercises and their frequency, including an examination of the use of standard reference materials." Another new JMG request concerns the automatic processing of marine pollution monitoring data by ICES and the preparation of ADP-compatible data reporting and exchange formats.

3.4 IOC/GIPME

- 3.4.1 The Chairman briefly summarized the recent activities of IOC/GIPME and reported that a baseline survey of trace metals and PCBs in the open ocean waters of the North Atlantic is being planned for 1985.

3.5 GESAMP

- 3.5.1 The Chairman reported on some of the GESAMP activities and stated that one particularly important activity which GESAMP has recently completed is a very large project on a review of the health of the oceans. The results of this project point to the need to assess the state of the health of the oceans on a regional basis.
- 3.5.2 Noting that the issue of assessments of the state of the marine environment had been mentioned in connection with the work of most of the groups discussed above and that, within the ICES structure, the WGMPNA has been requested to prepare a general format for the conduct of regional assessments, the MCWG expressed its particular interest in this work. It further took note of information that one possible approach to a framework for regional assessments being considered by WGMPNA was that such assessments should summarize, for the region under consideration, (a) the physical oceanography and man's impact on it, (b) the chemical conditions and man's impact on them, and (c) the biological conditions and man's influence on them. As an important part of this work would be concerned with chemical oceanographic issues, the MCWG felt that it should be given a chance to comment on the framework being developed by WGMPNA. One possible avenue for commenting will be in connection with the 1982 Statutory Meeting, as the WGMPNA intends to prepare a paper giving a draft framework for regional assessments for presentation to the relevant Standing Committees at that meeting. In closing the discussion on this subject, the MCWG agreed that there will be a number of gaps in the understanding of the chemical conditions in the regions covered by this work.

4. REPORTS ON PROJECTS AND STUDIES FROM WORKING GROUP MEMBERS

Each participant provided information on relevant studies at his or her institute. Summaries of this information are contained in Annex 3. It was agreed that next year only updating information should be given. This should be provided in written form, with the contact person identified and a list of references provided, where applicable. Null reports should be sent where no new projects have been undertaken. The reports should be sent to the ICES Environment Officer to arrive no later than 15 November 1982.

4.1 Activities related to CO₂

- 4.1.1 Dr Poisson informed the Working Group about the main points from a meeting of the CO₂ Sub-Group of the Joint Panel on Oceanographic Tables and Standards, which had been held in September 1981. He stated that the main purpose of this meeting had been to consider the information available on the thermodynamics of the CO₂ system in sea water and indicate where further work was needed. After reviewing the state-of-the-art of determining the different parameters governing the CO₂ system in sea water, Dr Poisson reported that the group did not formulate recommendations on the use of any of the parameters but rather recommended further work on various aspects of methodology. Dr Poisson's written report is attached as Annex 4.
- 4.1.2 The Working Group expressed its interest in this work and thanked Dr Poisson for providing this information.

5. REPORTS ON INTERSESSIONAL WORK ON ANALYSES OF LEAD AND PCBs

- 5.1 Dr Harms, coordinator of the intersessional work on lead analyses, reported on the progress in this work. He stated that the work had centered on determining the lead concentration in Sample "B" (processed fish meal) from the 6th trace metal intercomparison exercise and that the results had been studied for the use of different methods of analysis, different methods of decomposition and various separation techniques. The "true" concentration of lead in Sample "B" was found to be 2.5 - 2.7 ppm using the atomic absorption technique. The studies had shown that severe matrix effects are encountered in the analysis of lead in Sample "B" and other types of samples, especially when AAS with a graphite furnace is used. As the degree of the matrix effect depends on the material in the sample and cannot be compared from one material to another, each analyst should investigate the matrix effect of each type of material analyzed. If an analyst cannot overcome matrix effects using his own procedure, he should consider adopting either (a) use of an extraction procedure (several methods are available), or (b) use of the L'vov platform for flameless AAS. An alternative method is the ICP procedure, but this is not as sensitive as some other techniques.
- 5.2 Concerning future work, Dr Harms reported that some members of his sub-group will continue with the intersessional work. A paper will be presented at the 1982 Statutory Meeting which will describe the work conducted and give conclusions and recommendations.
- 5.3 The Working Group thanked Dr Harms and the members of his sub-group for their excellent work. In the discussion, questions were raised concerning the use of the standard additions technique when one encounters matrix effects. It was noted that the standard additions technique is the easiest way to determine when there are matrix effects but it does not always provide the correct result.
- 5.4 Dr Uthe, coordinator of the intersessional work on PCB analysis, then described the progress achieved. He stated that five laboratories taking part in this work had used capillary column gas chromatography to determine the levels of a number of chlorinated biphenyl isomers in Aroclor 1254 and in herring oil

and the same oil spiked with Aroclor 1254. The results of this study showed a large interlaboratory variance in the values obtained. Additionally, of all the PCB isomers studied, only a very few had been analyzed by all participants. Finally, Dr Uthe stated that the results suggest that some isomers are being identified differently by different laboratories; this may be due to impurities in or other problems associated with the commercial isomers.

- 5.5 The Working Group thanked Dr Uthe and his colleagues for their excellent work. Although the problems associated with PCB analysis had not been solved, there had been a rapid response to new ideas and a lot of work had been carried out very quickly.

6. INTERCALIBRATION PHILOSOPHY - LONG-TERM PLANS AND OBJECTIVES OF ICES INTERCALIBRATION PROGRAMME

- 6.1 The Chairman opened consideration of this subject by stating that ICES has coordinated a number of intercalibration exercises in the past, but the progress has been different for each contaminant depending on the difficulty of the analytical problems involved. He suggested that it would be very useful to consider the present status in the ability to determine contaminants and the comparability among laboratories so that a logical picture could be obtained of what had been achieved and what work needs to be done in the near future (next five years) to improve the methodology for sampling, preservation, storage and analyses in order to attain better interlaboratory comparability.
- 6.2 Agreeing with this approach, the Working Group conducted a general discussion of the subject in which a number of points were made. Several members felt that the ultimate aim of the ICES intercalibration programme was the preparation of a series of samples of different types of materials containing a range of concentrations of contaminants encountered in the marine environment. These samples should be supplied as unknowns and should be available on a continuing basis to avoid conducting overly frequent intercalibration exercises and still ensure the quality and comparability of data produced in monitoring programmes. Several members indicated their concern for good quality control so that the quality of data appearing in reports will be good; however, other members felt that intercalibrations alone cannot ensure good quality data in all cases. Individual laboratories producing poor results must be willing to take the steps needed to improve their methods. However, to allow a better follow-up of the results of intercalibration exercises, some members felt that a dissemination of information on the methods which had produced good results would be very useful, especially for laboratories with poor results. This could be achieved, for example, by publishing such methods in the "Techniques in Marine Chemistry" series.
- 6.3 In order to obtain a detailed picture of the status of the ability to determine the various contaminants in the different compartments of the marine environment, the Working Group decided to set up a small sub-group for each class of contaminants in each compartment to consider each step in the methodology (sampling, extraction, pre-treatment, analysis, etc.) and decide whether the capability is adequate for that step and, if not, what work needs to be done. Priorities should be set for the work so identified, It was agreed that the sub-groups and their respective chairmen should be as follows:

Sea water

Trace metals	-	Dr Bewers
Organochlorines	-	Dr Duinker
Hydrocarbons	-	Dr Palmork

Biological tissue

Trace metals	-	Dr Harms
Organochlorines	-	Dr Uthe
Petroleum hydrocarbons	-	Mr Law

Sediments

Trace metals	-	Dr Jensen
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- 6.4 Each sub-group met for 1½ hours and prepared matrices showing the general level of ability to carry out each step in the determination of the contaminants of interest in each compartment. The reports of the sub-groups, including their respective matrices, have been compiled and attached as Annex 5.
- 6.5 The full Working Group then reviewed the conclusions reached by the individual sub-groups and agreed that they represented a good summary of the status of intercalibration for the measurement of contaminants in marine samples. In closing the discussion on intercalibration status, the Working Group emphasized the importance of the use of samples for intercalibration exercises which are as similar to the natural samples as possible, both in terms of the concentrations of contaminants and the matrix.
- 6.6 The Working Group, noting the large number of intercalibration exercises which have been conducted or are being planned, agreed that there was a need to assign unambiguous titles for these exercises. This will avoid any confusion when attempting to identify a particular intercalibration among the many intercalibrations which are conducted for various classes of contaminants in various compartments of the marine environment. The titles of the intercalibrations should always initially be given in full, e.g., the ICES Fourth Round Intercalibration for Trace Metals in Sea Water, but in order to avoid repetition of the full title when individual intercalibrations are referred to in the text of papers, it was recommended that a short-form coding system be introduced that unambiguously relates to the intercalibration being discussed. The form of this coding system should be as follows:

N/XX/YY

where N refers to the number of the intercalibration,

XX refers to the contaminant class, and

YY refers to the type of marine compartment.

Thus, 2/TM/SW would identify the ICES Second Round Intercalibration for Trace Metals in Sea Water.

Codes for contaminant classes (XX) would be:

TM	Trace Metals
OC	Organochlorine Compounds
HC	Hydrocarbon Compounds
NT	Nutrients

Codes for the types of marine compartments (YY) would be:

SW	Sea Water
MS	Marine Sediments
BT	Biological Tissues.

In order to minimize the number of compartments, it would be appropriate that the designated letters refer to the general type of matrix to which the ultimate aims of the intercalibration series apply. Thus, although fish oils are sometimes used as intercalibration samples, the long-term objectives of the programme to which the intercalibration belongs are to improve the comparability, accuracy and precision of biological tissue analysis. Such intercalibrations should therefore be designated as Biological Tissue (BT) intercalibrations. A few intercalibrations may refer to more than one compartment so in these cases each of the compartments covered should be noted, e.g., the First ICES Intercomparison Exercise for Petroleum Hydrocarbons in Marine Samples: 1/HC/MS-BT, as samples of both marine sediments and biological tissues had been studied. Finally, in contexts where there could be confusion with intercalibration exercises conducted under other organizations, the code number should be prefaced by "ICES".

- 6.7 Having agreed to this coding system, the Working Group noted that the code for the ICES Fifth Round Intercalibration of Trace Metals in Sea Water planned for September 1982 in Nantes should be referred to as ICES-5/TM/SW. Similarly, the next intercalibration on PCBs in biological tissues to be coordinated by Dr Uthe in spring 1982 should be referred to as the ICES Fifth Intercalibration on Organochlorines in Biological Tissue: ICES-5/OC/BT.

7. PLANS FOR FUTURE INTERCALIBRATION EXERCISES

7.1 PCBs

- 7.1.1 Dr Uthe reported that, based on intersessional work which he had carried out with Dr C J Musial at his laboratory, and Dr Kerckhoff and Dr Palmork, agreement had been reached for the protocol for a fifth intercomparison exercise on PCBs in biological tissues (5/OC/BT) (see Doc. MCWG 1982/7.1/1). The samples will be as follows: (a) a fish oil, (b) the same fish oil with known amounts of four or five individual PCB isomers added, and (c) small amounts of each isomer used in spiking. Participants will be asked to prepare working standards from the isomers supplied and to use these along with their own isomeric standards to determine the amounts of these isomers present in the two oils. Additionally, participants will be supplied with a quantity of Florisil and requested to compare the results based upon the use of Florisil with those based upon the use of alumina, as clean-up agents. Dr Uthe further reported that intercalibration kits will only be sent to those analysts who request them by letter to him directly. Priority in the distribution of the kits will be given to analysts who state that they will use capillary gas chromatography to determine PCB isomers. Requests for intercalibration kits should be received by Dr Uthe by 30 April 1982.
- 7.1.2 The Working Group noted this information with interest and agreed that it would be a valuable exercise. The Working Group expressed its appreciation to the scientists who had carried out the planning work for this exercise, especially Dr Uthe and his laboratory in the

Department of Fisheries and Oceans, Halifax, Canada, for their time, expenses, and efforts in coordinating this intercalibration exercise. The Working Group members agreed to notify their relevant colleagues about this intercalibration and looked forward to a report on the results at the next meeting of the Working Group.

- 7.1.3 Concerning future plans for PCB intercomparison studies, Dr Utthe stated that on the assumption that the fifth PCB intercomparison exercise (5/OC/BT) is successful, i.e., that analysts identify all four PCB components correctly and at the same level, there are two avenues which must be pursued prior to the 1985 baseline survey of contaminants in the North Atlantic (which will be coordinated by WGMPNA). First, there is a need to develop a suitable fish tissue substrate to be used in intercomparison studies instead of fish oils so that the extraction efficiency of PCBs from fish tissues can be investigated and compared among laboratories. Accordingly, work should start immediately concerning the preparation of ambient-temperature-stable tissues. To this end, Dr Kerkhoff has agreed to investigate the preparation and stability of a Na_2SO_4 /tissue blend. Secondly, if this tissue blend is satisfactory, a minimum of three tissues: (a) a low-fat, low-PCB fish tissue, (b) a high-fat, high-PCB fish tissue, and (c) a shellfish tissue, should be prepared for a final intercomparative study prior to the 1985 baseline survey. The WGMPNA should recommend which species and tissues should be used in preparing these samples.

7.2 Petroleum Hydrocarbons

- 7.2.1 Dr Knap reported on the progress in the second intercomparison exercise on petroleum hydrocarbons in marine samples, which he and Dr J Farrington are coordinating. He stated that, owing to funding problems, the conduct of this intercalibration would have to be postponed for a number of months. There was some possibility, however, that mussel homogenate samples might be available by late 1982 or early 1983.
- 7.2.2 The Working Group took note of this information and requested Dr Knap and Dr Farrington to continue to seek support for the design and conduct of this intercalibration. In the event that progress is made on this issue in the near future, they were requested to submit a paper for the 1982 Statutory Meeting describing the design and plans for the exercise.
- 7.2.3 The Working Group then turned to the question of whether an inter-comparative study could be carried out on analyses of polycyclic aromatic hydrocarbons (PAH) in biological tissues. Dr Utthe offered that, subject to his laboratory's approval, he would be willing to coordinate such an exercise, using extracts of shellfish tissue. He stated that he could prepare samples which would consist of an acetone powder and the acetone-extractable, hexane-partitioned lipid phase. These samples should be analyzed for a suggested core group of non-alkylated PAH compounds, e.g., phenanthrene, fluoranthene, perylene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, o-phenylene pyrene, benzo(ghi)perylene, pyrene, chrysene, and triphenylene. Dr Utthe offered to prepare a short paper for the 1982 Statutory Meeting describing the intercomparison exercise in more detail.

- 7.2.4 The Working Group agreed that this would be a very useful exercise and, accordingly, passed a recommendation that it should be carried out (Recommendation 1).
- 7.2.5 The question was then raised of whether it would be possible to develop an intercomparison study on analyses of dissolved/dispersed hydrocarbons in sea water. It was considered that it would be very useful to conduct an intercomparison exercise utilizing water samples containing natural low, medium and high concentrations of petroleum hydrocarbons. It was further pointed out that, when studying the analysis of water-soluble components of oil, it was very important to consider the photodegradation products of oil. Recent findings indicate that photodegradation products of oil of high molecular weight and solubility in sea water are very toxic. These compounds are both more polar and water soluble than the majority of hydrocarbons usually analyzed, and are not extracted with the hydrocarbons using the methods commonly employed for this purpose. It was, therefore, felt to be of great importance to start to look for methods to isolate and analyze for these compounds in the marine environment.
- 7.3 Fifth Round Intercalibration for Trace Metals in Sea Water
- 7.3.1 The Chairman reported that an offer of a research vessel had been received from the Netherlands North Sea Directorate so that, with the previous offer of land-based laboratory facilities from the Institut Scientifique et Technique des Pêches Maritimes, Nantes, the necessary facilities were now available for the conduct of the Fifth Round Intercalibration for Trace Metals in Sea Water (ICES-5/TM/SW). The dates for the experiment have been set for 5-18 September 1982. A meeting of the Coordinating Group for the experiment had taken place on 1 February 1982 at ICES headquarters at which outline plans for the experiment had been drafted taking into account the facilities available.
- 7.3.2 The Chairman then presented the report from this meeting and highlighted the main points. He stated that the original design of the Fifth Round Intercalibration has been revised to reflect the outcome of the IOC/WMO/UNEP Sampling Intercalibration (PANCAL-80, Bermuda, 1980) which showed that, in general, the use of different hydrowires and different sampling bottles do not account for the large variances in results of determinations of trace elements in sea water. The core of the revised Fifth Round Intercalibration will now deal with the intercomparability of different procedures for the separation of dissolved and particulate metal fractions in sea water, which is an important issue in terms of studying coastal and continental shelf waters. This core part of the experiment will compare the use of a number of different filter types and filter holders and also the various methods of filtering the samples. Another part of the experiment will be concerned with the measurement of suspended matter concentrations by different gravimetric techniques. The core part of the experiment will be carried out by 4-8 laboratories of established reputation. In order to obtain basic information on the conditions in the area which will be used for the collection of samples, work will be carried out to determine the distribution of trace metals and particulate matter along a transect from the coast to an area 50 to 100 km offshore. This work will be carried out by one or two expert laboratories.

- 7.3.3 The Chairman further stated that, in addition to the core part of the experiment, provision could be made for training/advice sessions concerning sampling and sample treatment. Demonstrations could be made of techniques for sea water sampling, sample filtration, preservation and storage and participants would be given the opportunity to collect samples using their own equipment for later comparison with samples collected using a single technique. From 20 to 30 participants could be accommodated in this part of the experiment. Finally, for analysts unable to participate in the on-site work, bottled sea water samples could be prepared and distributed for analysis; samples could be made available for up to 100 laboratories.
- 7.3.4 The Working Group then discussed these plans and agreed that, of the work planned, the highest priority should be given to the following three components: (1) the intercomparison of various filtration techniques (which should be done by 1-2 laboratories); (2) the comparison of different gravimetric techniques for suspended particulate matter (6-8 laboratories); and (3) the study of the problems involved in sampling for mercury determinations. These items constitute the main purpose of the experiment and should not be adversely affected by the other activities. The items of secondary importance were listed as: (1) the determination of temporal and spatial variations in the sea area where sampling will be conducted; (2) the collection of samples by up to 30 participants using their own equipment; (3) training and advice (up to 30 participants), and (4) distribution of samples (effluents and filters) to up to 100 laboratories. It was suggested that, in order to avoid conflicts, the core part of the experiment could be conducted during the first week and the sampling inter-comparison and training activities could be carried out during the second week of the time allotted for the Fifth Round Inter-calibration. With these comments, the Working Group agreed to annex the report of the Coordinating Group (Annex 6).
- 7.3.5 Concerning the management structure for the experiment, the Working Group noted that there were two coordinators: Dr W van Eyden, Netherlands North Sea Directorate, who is responsible for all aspects concerning the vessel, the M/V "Holland", and M Claude Alzieu, ISTPM, who is responsible for all land-based arrangements. Together, Dr van Eyden and M Alzieu would be responsible for all management and administrative aspects of the intercalibration. In addition, there will be four scientific advisors to assist in the detailed planning and conduct of the experiment: Dr J C Duinker, Dr G Topping, Dr H Windom and Dr J M Bewers. Finally, it was noted that a list of eight core laboratories had been identified earlier and that renewed invitations for participation should be sent to them immediately.
- 7.3.6 In closing the discussion, the Working Group expressed its sincere gratitude to Dr van Eyden and the Netherlands North Sea Directorate for providing the ship and to M Alzieu and ISTPM for providing the land-based facilities to allow this important and long-delayed experiment to take place. The Group wished all success for the intercalibration and looked forward to receiving a preliminary report on the results at its next meeting.
- 7.4 Trace Metals in Biological Tissue
- 7.4.1 Dr Topping outlined the proposals for intercalibrations of trace metal analyses in tissues covering the next 3-4 years, as had been developed by the sub-group formed for this subject under Agenda

Item 6. He stated that the sub-group had agreed that intercalibration was important in terms of the following list of elements, proposed concentration ranges and tissues:

Element:	Cd	Pb	Hg	Cu	Zn	As
Concentration (ppm)	0.1 0.3 1.0	0.3 1.0 3.0	0.05 0.2 0.5	0.3 1.0 3.0	5	0.1 1.0 10.
Tissues	fish liver shellfish muscle bivalve soft body	fish liver shellfish muscle bivalve soft body	fish muscle shellfish muscle bivalve soft body	fish liver shellfish muscle bivalve soft body	fish liver shellfish muscle bivalve soft body	fish muscle shellfish muscle bivalve soft body

To cover these requirements, eight or nine reference samples will need to be prepared. By using this number of different materials, some of the questions regarding matrix effects can also be covered.

- 7.4.2 Dr Topping stated that work to identify the appropriate materials which contain the desired concentrations of contaminants should begin now so that a detailed programme can be prepared and submitted as a paper to the 1982 Statutory Meeting. This paper should identify the types of materials needed and who will be requested to prepare each type of material; on the basis of this paper, Council approval of the intercalibration will be sought. If such approval is obtained, the samples can be prepared and distributed in 1983 so that the results can be available by the beginning of 1984.
- 7.4.3 In the discussion of this proposal by the Working Group, some members felt that the procedure should be simplified by reducing the number of samples so that the intercalibration would not be so resource-demanding. However, other members felt that, with the amount of work which would be put into the 1985 baseline study as well as other monitoring activities, such a detailed intercalibration was justified. In conclusion, the Working Group agreed that the proposal was a good one and that the screening procedures for the appropriate materials should begin immediately. It was felt that such detailed work would be necessary to obtain the required information, as had been identified by the sub-group, and that the interseasonal work should go forward as proposed. It was decided that an intercalibration exercise should be conducted when the appropriate samples have been prepared. Accordingly, the Working Group passed a recommendation to this effect (Recommendation 2, Annex 9).
- 7.4.4 The following members agreed to assist in this programme: Dr Topping, Dr Uthe, Dr Berman, Dr Harms, Dr Thibaud, Dr Jensen and Dr Piuze.
- 7.4.5 Before closing the discussion on the general subject of intercalibration exercises for analyses of contaminants in marine organisms, the Working Group considered the question of whether a laboratory should be appointed to maintain an overall coordination of activities promoting improvements in methodology for the determination of contaminants in biological tissue and for the

development of high-quality intercalibration samples. The Working Group agreed that this should be done. Thus, recognizing the expertise in analyses of trace metals, organochlorine compounds, and polycyclic aromatic hydrocarbons of the Canadian Department of Fisheries and Oceans, Fisheries Laboratory, Halifax, N.S., the Working Group recommended that this laboratory be nominated as an Intercalibration Coordination Center for biological tissue in order to facilitate continued attention to improvements in the determination of these compounds in marine biota and to facilitate the preparation of blind intercalibration sample material for continued testing of laboratories taking part in cooperative monitoring studies (Recommendation 3, Annex 9).

8. CONDITIONS FOR PRE-ANALYTICAL STORAGE OF BIOLOGICAL MATERIALS

8.1 The Environment Officer gave the background for this Agenda item. She stated that, at the 1981 Statutory Meeting, the Marine Environmental Quality Committee and the Advisory Committee on Marine Pollution, noting the lack of uniformity in short-term storage procedures for biological samples prior to analysis which had been reported in Doc. C.M.1981/E:19, had agreed to draw MCWG's attention to this document and invite them to consider the matter and take whatever initiative appeared to be necessary. The ACMP had further requested to be informed on whether a protocol would be needed on this subject.

8.2 The Working Group felt that C.M.1981/E:19 provided a good record of the storage conditions presently in use and decided that there were no problems with the present practices. It was pointed out that the only time one can obtain values on a true wet weight basis is when fresh tissues are used. For frozen samples, the storage temperature is not so important; it is more important how the sub-sample is taken after thawing because the outer portion of the sample is freeze-dried. Concerning possible decomposition of organic contaminants, Dr Reutergårdh mentioned that a Swedish study had determined that after 14 years of storage of tissues at -20°C, no change in the organochlorines could be detected.

9. METHODOLOGY FOR MEASUREMENT OF RIVER INPUTS

9.1 The Chairman presented the paper "Methods of Assessing Gross Riverine Discharges of Trace Metals and Organohalogenes to the Ocean" (Doc. MCWG 1982/9/Rev.1), which he and Dr Duinker had prepared. He pointed out that the paper represented a first step in a process aimed at specifying how riverine fluxes of contaminants into coastal and pelagic waters might be determined. In this paper, a method is given to measure the gross flux of metals from a river into an estuary. The question of net fluxes is far more complex and would be left to the future.

9.2 The Working Group then discussed the paper and provided several suggestions for amendments. The authors were requested to revise the title of the paper by changing the word "ocean" to "marine environment". They were also requested to indicate the specific metals for which the proposed sampling procedures might be suitable. Further, it was requested that the authors insert more detail as to the procedures for the determination of the exchangeable phase composition of suspended matter. In response, the authors indicated that they would provide details of IN HCl and 25% HAc leaches, together with appropriate references concerning these leaching

procedures. It was noted that the units of $\mu\text{g}/\text{l}$ would have to be inserted on the table. Finally, it was recommended that the authors stress the utility of conducting time-series river composition measurements in combination with hydrologic surveys on the sampling section.

- 9.3 In conclusion, the Working Group approved the paper in principle for transmission to ACMP with the suggestions for amendments taken into account. The Working Group further encouraged ICES member countries to carry out measurements on gross riverine inputs as a first step in understanding the transport of materials to the sea. Finally, the Working Group thanked Dr Bowers and Dr Duinker for their excellent work in preparing this paper.

10. INFORMATION ON "NEW CONTAMINANTS"

10.1 PCTs

- 10.1.1 Dr Jensen reported that the paper on PCTs which is being prepared by his Agency was not yet finalized, but would be available for the next meeting of the Working Group.
- 10.1.2 The Working Group noted this information with interest and asked Dr Jensen to prepare a summary of this paper for next year's meeting.

10.2 Others

- 10.2.1 It was mentioned that chlordanes and chlorinated terpenes have been found in several different types of organisms, including fish and birds of prey, in the Baltic Sea area during recent years.
- 10.2.2 The general subject of by-products from the synthesis of organic chemicals was also mentioned as a source of new contaminants to the environment
- 10.2.3 Furanes and dioxin were also mentioned as new contaminants of concern. Dr O'Sullivan agreed to prepare an overview paper concerning these substances for the next meeting. This paper will cover the production of these substances, their transport to and movement in the marine environment, and their concentrations in the various marine compartments.
- 10.2.4 Noting that overview papers on new contaminants were also being prepared by WGMPNA, the MCWG discussed the difference in emphasis which should be given to the various topics handled in these papers. It was felt that MCWG overviews should be more concerned with the mechanisms by which such contaminants enter the marine environment and the processes governing their movement, distribution and fate in the marine environment. On the other hand, the WGMPNA should be more concerned with the distribution of these contaminants in marine organisms at various trophic levels, the effects of the contaminants on marine organisms, and possible public health implications. The MCWG then agreed on section headings for overviews to be prepared for its use and proposed section headings for overviews to be prepared for WGMPNA. These are given in Annex 7. It was felt that the use of such common formats for overviews would permit easier ranking of new chemicals in terms of their significance in the marine environment. The Chairman agreed to consult with the Chairman of WGMPNA concerning this issue.

11. OVERVIEWS ON FLUXES AND TRANSPORT OF POLLUTANTS IN THE MARINE ENVIRONMENT

- 11.1 The Chairman presented the paper "Lead in the Marine Environment: An Overview", which had been prepared by Dr M Waldichuk, Dept. of Fisheries and Oceans, West Vancouver, Canada (Doc. MCWG 1982/11).
- 11.2 The Working Group agreed that this was an excellent review of the marine geochemistry of lead in the marine environment and would be valuable to ICES as well as to other groups, such as JMG. There were, however, several comments concerning biological aspects of the paper, especially with regard to statements on the toxicity of lead to biota, the quantities of lead consumed as tetra-alkyl lead, and the use of the term bioaccumulation. It was agreed that these comments and other suggestions for minor amendments would be conveyed to the author via the Chairman so that the paper could be revised for presentation to ACMP at its next mid-term meeting. With these amendments, the Working Group approved the paper for transmission to ACMP.
- 11.3 In concluding the discussion on this paper, the Working Group expressed its great appreciation to Dr Waldichuk for the preparation of this excellent and valuable review, which had constituted an important contribution to the work of the Group.
- 11.4 Mr Law then presented the paper "Polycyclic Aromatic Hydrocarbons (PAH) in the Marine Environment" (Doc. MCWG 1982/11/1), which he had prepared in order to stimulate discussion on this subject.
- 11.5 The Working Group thanked Mr Law for preparing this paper and agreed that it was a good first step in the preparation of an overview on PAHs in the marine environment. Several members had comments and suggestions for amendments, so it was agreed that all comments should be given or sent directly to Mr Law. He would then take these into account in preparing a revised version of the paper for the next Working Group meeting.
- 11.6 The Working Group then considered suggestions for further overviews on the distribution, behaviour and fluxes of contaminants in the marine environment. It was agreed that information on these topics should be obtained concerning degradation products from the photo-oxidation of oil. Dr Palmork agreed to coordinate the gathering of information on this subject and all members agreed to seek information from colleagues for transmission to Dr Palmork.
- 11.7 The Working Group further considered it valuable to have a paper prepared on selenium, so Dr Knap agreed to contact Dr C Measures and Dr Wrench and invite them to prepare a discussion paper on the geochemical and biochemical aspects of selenium in the marine environment.
- 11.8 Finally, it was felt that it would be important to have a paper on the marine chemical aspects of the CO₂ problem in the environment. Dr Poisson was invited to prepare this paper.

12. RELEVANT NUTRIENT STUDIES

- 12.1 Members provided information on various studies concerning nutrients, mainly in the Baltic Sea. Dr Jensen stated that the final report on the results of the Belt Project was now available. In this project, physical, chemical and biological measurements had been

made in the Kattegat, Danish Belts and Baltic Sea from 1974-1978 to study the exchange of water and materials between the Baltic Sea and the North Sea. During the study period, nutrient measurements had been conducted monthly on 25 stations. One conclusion reached in this project was that nutrient concentrations in the areas studied have increased during the past 30 years. Primary production has also increased.

- 12.2 Information was also noted on long-term studies of nutrients in the Baltic Sea being conducted by scientists from the German Democratic Republic. The results of these studies give a good presentation of the nutrient situation in the Baltic Sea. It was further noted that a large amount of nutrient data concerning the Baltic Sea is being obtained in the Baltic Monitoring Programme under the Helsinki Commission; primary production is also being monitored in this programme.
- 12.3 Studies to investigate the temporal and spatial scales of patchiness or variability in certain parameters are also being conducted in the Baltic Sea. In this context, Dr Carlberg summarized the results of a study of micro-scale patchiness in nutrient distributions carried out by his institute. He noted that these results have been reported by Dr S Fonselius in ICES Doc. C.M.1981/C:20.
- 12.4 Information concerning primary productivity measurements was also considered and it was noted that ICES will sponsor a Workshop on Intercomparison of Techniques in Measurements of Primary Production in 1983.
- 12.5 In concluding the discussion on this item, the Working Group agreed that it was interested in receiving further information on assessments of methods to measure primary production and on the results of studies on spatial heterogeneity in the distribution of nutrients and other substances.

13. REVIEW OF LEAFLETS FOR "TECHNIQUES IN MARINE CHEMISTRY"

- 13.1 The Environment Officer reminded the Group that in 1980 the Council had approved the establishment of a new series of leaflet publications entitled "Techniques in Marine Chemistry". At last year's meeting, Editorial Boards for the leaflets had been set up with the following members:

<u>Nutrients</u>	<u>Metals</u>	<u>Organics</u>
Dr B Boutier	Dr A Berman	Dr M Kerkhoff
Dr S Carlberg	Dr U Harms	Mr R Law
Dr F Koroleff	Dr Y Thibaud	Dr P Michel
Dr S Fonselius	Dr G Topping	Dr K Palmork
		Dr J Portmann
		Dr J Uthe.

Additionally, a small group of members had been requested to consider the format to be followed when preparing the leaflets. Working by correspondence, this group had agreed that the format should be based on that used by ISO (International Standards Organization), with some minor modifications. The proposed format is as follows:

- | | |
|----------------------|-----------------------------|
| 1. Outline of method | 7. Sampling and storage |
| 2. Range | 8. Calibration |
| 3. Precision | 9. Reagent blank |
| 4. Interferences | 10. Pre-treatment of sample |
| 5. Equipment | 11. Analysis of sample |
| 6. Reagents | 12. References |

- 13.2 The Working Group considered this format and accepted it for use in preparation of the leaflets. It agreed that this format could also be applicable to methods for sampling, storage and pre-treatment.
- 13.3 The Working Group then discussed the types of methods for which leaflets should be prepared. In this connection, a discussion paper was introduced which suggested that an important "end product" of the ICES intercalibration work could be the preparation of leaflets describing the procedures which had been found to produce accurate and reliable results in an intercalibration exercise. There was general support for this suggestion and also for the view that the leaflets should contain well-tested methods which can confidently be recommended to new colleagues in the field. Finally, it was reconfirmed that leaflets could cover methods for any step in the process of determining concentrations of substances in marine samples: sampling, pre-treatment, storage, analysis.
- 13.4 Commitments for the preparation of specific leaflets were then sought. It was noted that Dr Harms has already prepared a leaflet on "Determination of Cadmium and Lead in Organic Matrices with Electrothermal (Furnace) Atomic Absorption Spectrophotometry." Dr Koroleff promised to prepare leaflets by 1 June 1982 on methods to determine the following nutrients: silicates, urea, phosphate, total phosphorus, ammonium, total nitrogen by the Kjeldahl method, and total nitrogen by persulfate oxidation. Dr Duinker and Dr Palmork agreed to prepare a leaflet on the determination of PCBs in sea water by April 1982. All members were encouraged to consider whether they themselves could prepare one or more leaflets and, further, to invite appropriate colleagues to contribute leaflets to this series.
- 13.5 Having accepted the format, the Working Group then gave the Editorial Boards the responsibility to obtain leaflets on the best methods and keep them under review. Although the Editorial Boards have great autonomy, the Working Group agreed that it will intervene should a conflict arise. Noting the composition of the Editorial Boards, the Editorial Board for Metals was requested to consider whether it would need an additional member with special expertise concerning determinations in sea water. Additionally, Dr Vagn Olsen was appointed to the Editorial Board for Nutrients. Finally, so that the Working Group could follow the progress in the preparation of leaflets and members not on the Editorial Boards could review specific draft leaflets of interest to them, the Environment Officer was requested to circulate to all Working Group members the title and name and address of the author of each draft leaflet when it is submitted.

14. RELEVANT ISSUES FROM WORKING GROUP ON MARINE SEDIMENTS IN RELATION TO POLLUTION

- 14.1 The activities of the Working Group on Marine Sediments in Relation to Pollution (WGMS) were considered, especially the pilot sediment studies. In terms of the latter, the MCWG encouraged the WGMS to use radionuclide techniques when studying the geochronology of sediments. WGMS was also encouraged to pay attention to other contaminants, such as PCBs and DDT.
- 14.2 Noting that one area of possible overlap between the work of the MCWG and that of WGMS is the intercalibration of methods for the determination of contaminants, the MCWG requested the WGMS to consider the assessment of the status of intercalibration exercises, contained in Annex 5 to this report, and determine whether there are any major problems with this scheme as drawn up for sediments and suspended matter. Although it was assumed that the WGMS would carry out their own intercalibration exercises when needed, the MCWG offered to provide assistance when requested. The MCWG further offered to provide advice or do work on specific marine chemical issues when requested by WGMS. Finally, the MCWG indicated that it will concern itself with suspended particulate matter.

15. OTHER BUSINESS

- 15.1 There was some discussion on the question of whether the Working Group should be more concerned with matters of classical chemical oceanography. The Chairman stated that he will consider this matter intersessionally and will consult with the Chairman of the Hydrography Committee to obtain his views.

16. APPROVAL OF RECOMMENDATIONS AND DEADLINES

- 16.1 The Working Group reviewed and approved the Action List, attached as Annex 8.
- 16.2 The Working Group then passed a recommendation concerning the next meeting of the Group (Recommendation 4) and reviewed and reaffirmed its earlier recommendations.
- 16.3 The Chairman then thanked the participants for their work during the meeting and their spirit in volunteering for new tasks. He closed the meeting at 11.30 hrs on 5 February.

ANNEX 1

MARINE CHEMISTRY WORKING GROUP

Copenhagen, 2-5 February 1982

AGENDA

1. Opening of meeting and adoption of agenda.
2. Report on 69th Statutory Meeting.
3. Other activities of interest.
 - 3.1 Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic.
 - 3.2 ICES/SCOR Working Group on the Study of the Pollution of the Baltic.
 - 3.3 Joint Monitoring Group of Oslo/Paris Commissions.
 - 3.4 IOC/GIEMME.
 - 3.5 GESAMP.
4. Reports on projects and studies from Working Group members.
 - 4.1 Activities related to CO₂
5. Reports on intersessional work on analyses of lead and PCBs.
6. Intercalibration philosophy - long-term plans and objectives of ICES intercalibration programme.
7. Plans for future intercalibration exercises.
 - 7.1 PCBs.
 - 7.2 Petroleum hydrocarbons.
 - 7.3 Fifth round - trace metals in sea water.
 - 7.4 Trace metals in biological tissue
8. Conditions for pre-analytical storage of biological samples.
9. Methodology for measurement of river inputs.
10. Information on "new contaminants".
 - 10.1 PCTs.
 - 10.2 Others.
11. Overviews on fluxes and transport of pollutants in the marine environment.
12. Relevant nutrient studies.

/Cont'd.

13. Review of leaflets for "Techniques in Marine Chemistry".
14. Relevant issues from Working Group on Marine Sediments in Relation to Pollution.
15. Other business.
16. Approval of recommendations and deadlines.

ANNEX 2

MARINE CHEMISTRY WORKING GROUP

Copenhagen, 2-5 February 1982

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ANNEX 3

REPORTS ON PROJECTS AND STUDIES FROM WORKING GROUP MEMBERS

BELGIUM

Marine Fisheries Laboratory, Oostende - Dr K Vandamme

This institute monitors the sand extraction and the dumping zones for industrial waste. Water and sediment samples are taken. All water samples are analyzed for their nutrient content and some for their Hg and Cd content.

In the sediment samples, the distribution of the benthic species is studied. The sediment samples from the two dumping areas for waste derived from TiO₂ production are analyzed for trace metal levels.

Organochlorines (PCBs and organochlorine pesticides) and hydrocarbons (n-alkanes) are measured in muscle and liver tissue of biota (mussels, shrimps and fish species (cod, flounder, sole)).

Toxicological studies are carried out on industrial waste.

CANADA

National Research Council of Canada - Dr S Berman

1. The distribution of the two marine sediment reference materials for trace metals, MESS-1 and BCSS-1, began in March 1981. These samples have reliable values for 13 trace metals and 12 major and minor components. They have been well received internationally - some 225 bottles have been sold to date.
2. Three marine sediment standards for the determination of PCBs will be available within the next couple of months. The samples (HS-1, HS-2 and CS-1) will contain a range of PCB concentrations from below 2 ppb to above 100 ppb. Two sets of data will be provided for each: (i) results of a conventional extraction, packed column GC and electron capture detection, and (ii) individual PCB component concentrations based on capillary column GC-MS.
3. Marine sediment standards for PAHs are in the initial stages of preparation.
4. Following extensive storage and container experiments, a sea water reference material, NASS-1, for about a dozen trace metals of interest has been prepared and should be available by April 1982. This is an open ocean sea water gathered at 1 300 metres off Bermuda. Except for lead, the water does not appear to have been significantly contaminated during the sampling, homogenization and bottling processes. The samples, adjusted to pH 1.6 with nitric acid, will be made available in 2-litre polyethylene bottles.
5. A significant advance in the separation and concentration of trace metals from sea water has been made using silica-immobilized ligands (e.g., 8-hydroxyquinoline). Rapid and quantitative yields are possible with concentration factors in the hundreds. Blanks are lower by an order of magnitude with respect to the chelation-solvent extraction or ion-exchange chelation procedures formerly used.

Centre Champlain des Sciences de la Mer, Ministère des Pêches et des Océans, Québec - Dr J Piuze

Trace Metals: (1) projects are conducted mainly on the distribution and biogeochemistry of Hg in water, biota and sediments, particularly in the Estuary of the St. Lawrence and the Saguenay Fjord. In the latter case, profiles in the water column of the Fjord, where the sediments have been contaminated with Hg, show higher levels near the bottom, suggesting diffusion from the sediments resulting from diagenetic processes. Furthermore, benthic organisms in the Fjord are still contaminated, and levels in the zooplankton are higher than those found in the Estuary; (2) several trace metals (Cd, Cr, Fe, Hg, Pb, Zn) are analyzed in blue mussels. Much effort is put into studying the influence of physiological factors on the metal content, and how the sampling schemes and techniques could be improved to enable use of the mussels as pollution indicators; (3) trace metals (Cd, Cu, Zn) are determined by ASV in the waters of the St. Lawrence Estuary, and possible relationships with biological productivity will be investigated.

Organics: (1) levels of 3,4-benzopyrene have been determined in blue mussels from the Estuary and Gulf of St. Lawrence and in sediments of the Saguenay Fjord. The values, both in sediments and in mussels, indicate a contamination of the Fjord; (2) a new project has recently begun to study PAHs in sediments of the Laurentian Channel in the Estuary and Gulf of St. Lawrence; (3) some work has been conducted on levels of PCBs in blue mussels from the Estuary and Gulf of St. Lawrence.

Fisheries and Environmental Sciences, Halifax Fisheries Laboratory -
Dr J F Uthe

1. Individual chlorinated biphenyl intercalibration: five participants, utilizing capillary gas chromatography, determined individual chlorinated biphenyls in a herring oil, a herring oil with a known amount of Aroclor 1254 added and Aroclor 1254 itself. The results were reported in Doc. ICES C.M.1981/E:49.
2. Time trend monitoring of chemical contaminants: the results of our three-year study of contaminant levels in a length-stratified sample of cod from the southern Gulf of St. Lawrence were reported in Doc. ICES C.M.1981/E:47.
3. Cadmium in lobster (Homarus americanus) associated with a lead smelter: as in 1980 (Tech.Rep.Fish.Aquat.Sci., No.968), cadmium levels were determined in digestive glands and claw and tail muscle from lobsters in the area of Belledune Harbour, New Brunswick. Levels in digestive glands from animals from the most contaminated area of the harbour have risen significantly compared with 1980 levels, whereas muscle levels have decreased, suggesting that the harbour is moving towards stabilization of the situation.
4. Toxaphene: recently we have determined that the herring oil used for the 4th organochlorine intercalibration also contains toxaphene-like material in an estimated concentration greater than the concentration of PCBs in the unspiked oil.
5. Silver/Copper in lobster nutrition: studies of juvenile lobster (Homarus americanus) have shown that dietary Ag and Cu are mutually antagonistic from a toxicity point of view. Best growth was also found with an Ag/Cu combination diet.

6. Polycyclic aromatic hydrocarbons (PAH): relatively high levels of PAH are present in both digestive gland and muscle from lobster (Homarus americanus) from within a harbour which receives discharges from a coal-coking facility. The geographical extent of this contamination is being determined.

DENMARK

National Agency of Environment Protection, Marine Pollution Laboratory -
Dr A Jensen

The final report of the Belt Project has just been published and it contains an evaluation of the physical, chemical and biological measurements for the period 1974 to 1978 for the Danish areas between the Kattegat and the Baltic Sea.

Besides carrying out the monitoring programme in connection with the Helsinki and Oslo and Paris Commissions, the Marine Pollution Laboratory has studied the pollution by hydrocarbons in the Danish Sea areas in sediments and Mytilus edulis. The study has now been concentrating on a fjord system where a town and an oil refinery are situated at one end of the fjord. A total input study of hydrocarbons, including atmospheric deposition, is nearly completed in this fjord with extensive examinations of sediments and Mytilus edulis.

A study concerning the total input of nitrogen, phosphorus and organic matter to the sea areas around Denmark has nearly been completed.

Geological Survey of Greenland - Dr G Asmund

The marine chemistry work is mainly dealing with control of pollution from a zinc-lead mine in northern Greenland. The distribution and dispersal of heavy metals in the marine environment is being monitored and sea water, sediments, mussels, seaweed, fish, benthos and marine mammals are being analysed. Additionally, background information and background samples in areas of possible future mining are being collected. Special attention is being given to the very high content of cadmium in Arctic marine mammals. It is anticipated that this subject will be studied further in collaboration with the Greenland Fisheries Investigations.

FINLAND

Institute of Marine Research - Dr F Koroleff and Dr M Perttilä

The monitoring programme in the framework of the Helsinki Convention takes much time, especially for trace metals and chlorinated hydrocarbons in fish tissues and benthic organisms. For several years, metals in water have been determined by AAS after a preconcentration step with $Mg(OH)_2$. This procedure will be compared with the freon extraction technique. All nutrient analyses are performed with a Finnish autoanalyzer system (4 channels). The effect of variable salinity on the system is under study.

The new pyrocatechol violet spectrophotometric method for aluminium (Koroleff) will be used for the determination of various forms of the metal in sea water. A comparison with the fluorescence Lumogallion procedure will be performed.

Chlordanes have been found in fish tissue using GC/MS. Work is continuing with other media. An analytical method is being developed for PCTs. A gas chromatographic method for the determination of heavy metals (as dithiocarbamate complexes) is being tested and compared to AA results.

FRANCE

(prepared by the Rapporteur)

Laboratoire de Physique et Chimie Marine, Université Pierre et Marie Curie, Paris

Work has begun on the first stage of a programme to study the CO₂ cycle in the ocean. Measurements were made in the western Mediterranean Sea in late 1981 using the technique recommended in the Transient Tracers in the Ocean programme. Plans are being developed for a larger scale expedition.

Institut Scientifique et Technique des Pêches Maritimes, Nantes

One of the programmes of this Institute is the measurement of the concentrations of heavy metals and organochlorine residues in organisms and trace metals in sea water from several areas along the French coast.

FEDERAL REPUBLIC OF GERMANY

Bundesforschungsanstalt für Fischerei, Hamburg - Dr U Harms

One study of interest concerns the bioaccumulation and biotransformation of mercury by biota from estuarine and coastal waters.

Young flounder migrate during their early life phase (i.e., 4-8 weeks after hatching) from the spawning areas in the sea into estuaries. Recent investigations have demonstrated very clearly that the young fish show a remarkable increase in their mercury burden when they enter the River Elbe estuary.

Hence, they are regarded and used as appropriate test organisms to indicate the bioavailability of mercury within different compartments of the marine environment.

In order to determine organically bound mercury (methylmercury) in small quantities (< 100 mg) of biological material, an analytical procedure based on "heterogeneous isotope exchange" and "sub-stoichiometric isotope dilution" has been developed. According to the investigations carried out so far, this technique allows a reliable determination of methylmercury at the ng/g level.

Institut für Meereskunde an der Universität Kiel - Dr K Kremling

Trace metal projects in the Department of Marine Chemistry include the following:

1. Investigations on the chemistry of trace elements in anoxic waters of the Baltic Sea (formation of sulfides and polysulfides; distribution of redox-dependent elements).
2. Studies on copper- and tin-organic substances in sea water (biogeochemical cycles; identification of structures).
3. Investigations on atmospheric transport of elements in the Baltic Sea by means of a buoy system (development of methodology; field work in the Kiel Bight).
4. Survey of Atlantic surface waters for Cd, Cu, Ni and Mn by means of a continuous pumping system. (3 meridional sections:

42°N - 23°S (Nov. 1980);
Azores-Scotland-North Sea (Aug. 1981);
Azores-Equator-African coast-English Channel-German Bight (April 1982)).

IRELAND

Department of Fisheries and Forestry, Fisheries Research Center,
Abbotstown, Castleknock, Co. Dublin - Dr (Ms) M O'Sullivan

The programmes in this laboratory are concerned with contamination and pollution in the marine and freshwater environments. Several major estuaries around the Irish coast are included in monitoring programmes. Amongst the persistent substances analyzed are (i) heavy metals in fish, shellfish and sediments and (ii) organochlorines (including PCBs) in fish and shellfish.

Another area of concern lies with organic and nutrient inputs from agriculture, sewage disposal and certain industrial wastes. Studies on the nutrient content of estuarine waters have been carried out in this regard.

NETHERLANDS

Netherlands Institute for Sea Research, Texel - Dr J Duinker

Attention is being given to the development of methodology for analysis of organochlorines in sea water and particulate suspended matter, in cooperation with Dr Knap (Bermuda Biological Station) and Dr Palmork (Institute for Marine Research, Bergen). Recent results for individual PCB components in the North Sea indicate that the partition over solution and suspension generally increases with molecular weight.

Contamination of samples has been minimized (and hopefully eliminated) by using a stainless steel gas-lift system and containers and teflon transfer tubing. A method using this equipment, involving pressurized filtration and continuous liquid-liquid extraction of 100-200 litre samples will be published shortly.

The effects of physical and chemical processes on the partition of contaminants in dissolved and particulate forms within estuaries and their transport through estuaries into coastal regions has been studied for the rivers Varde Å, Elbe, Weser, Ems, Rhine and Scheldt. Special attention has been given to effects caused by spring-neap tide variations and the effects of varying properties of particulate suspended matter (size, density, mineral and organic carbon content).

Rijkswaterstaat, RIZA (Government Institute for Wastewater Treatment) -
Dr P Hoogweg

During the past year, a new extraction technique developed by Dr A Dorneman (Federal Republic of Germany) was tested for sea water. HMA-HMDC is used as the chelating agent and DIPK/xylene as the organic solvent. The method has the advantage of stable extracts (1-2 weeks) and simple standard preparation from aqueous solutions. Limits of detection by flameless AAS were achieved of 0.01 (Cd), 0.1 (Cu, Pb) and 0.5 (Zn) µg/l.

A method for determining PAH by HPLC with fluorescence detection in water, sediments and organisms was developed. The concentration and accumulation of PAH in fresh water mussels will be determined in the River Rhine. Sediments and the water phase will also be taken into account.

Netherlands Institute for Fishery Investigations, IJmuiden - Dr (Ms)
M A Kerkhoff

This Institute is responsible for analysis of fish in marine as well as fresh water. On-going programmes include studies on the distribution of organochlorines in the environment based on samples of cod liver and eel. The concentrations of several individual PCB components have been determined during the last two years, mostly in fish, and occasionally in other samples. New projects include the study of the occurrence of polychlorinated benzenes (tri-up to hexa-) in eel and the distribution of mercury in pike-perch. We consider that for environmental assessment work, information about the degradability of xenobiotic compounds is needed and so we have started some work in this area. The results of this work to date are given in Doc. C.M.1981/E:36: Biodegradability in the marine environment. I. The chemostat as a model for the aquatic environment.

NORWAY

Institute of Marine Research, Bergen - Dr K Palmork

Projects related to marine chemistry include the following:

PCBs: Work is in progress on methods for analysis of PCBs as individual isomers in sea water, organisms and sediments.

Petroleum hydrocarbons and PAH in general: Sediments from projected drilling areas are collected for analysis of petroleum hydrocarbons as a baseline. Sediments are also collected to monitor petroleum hydrocarbons around drilling and production platforms; special attention is paid in the areas where drilling is performed using oil-based drilling muds.

Blue mussels have been collected from the platform "legs" and analyzed for petroleum hydrocarbons.

Water samples are collected at stations in the North Sea at intervals as part of the petroleum hydrocarbon monitoring.

Laboratory studies on the accumulation and metabolism of polycyclic aromatic hydrocarbons in different marine organisms have been carried out and the project will continue.

PORTUGAL

(prepared by the Rapporteur)

Instituto Nacional de Investigaçào das Pescas

Studies of trace metals in marine organisms and sediments are continuing and new work is beginning on the determination of organochlorines in marine samples.

SWEDEN

National Swedish Board of Fisheries, Institute of Hydrographic Research - Dr S Carlberg

Chemical work at this Institute is mainly carried out within two major projects. The first concerns long-term studies of the hydrographic conditions in the Skagerrak-Kattegat and the Baltic Sea areas, especially the stagnant conditions in the Baltic and their influence on the nutrient chemistry. The second activity is the undertaking within the national

monitoring programme, which is a part of the Baltic Monitoring Project of the Helsinki Commission. These two activities involve a great number of nutrient analyses, as well as determinations of oxygen, alkalinity, etc.

In addition to the main work, a number of complementary studies are carried out. Patchiness studies have been initiated. A pilot study was carried out in May 1981 and a joint study will be made in June 1982 in the BOSEX area of the Baltic Sea together with the Institut für Meereskunde in Kiel. Long time-series of alkalinity are available for the Baltic Sea area. A study is underway to compare old and new data to detect possible long-term trends in alkalinity. The preliminary results indicate that no trend can be detected.

The monitoring of petroleum-type hydrocarbons in sea water, using ultra-violet fluorescence spectrophotometry has been started again after a pause of about two years.

During 1982, we plan to begin analysis of heavy metals in water and, eventually, also in sediments and biological samples.

National Swedish Environment Protection Board (NSEPB) - Special Analytical Laboratory - Dr I Reutergerårdh

The laboratory's main task is to analyze organic chemicals which are of interest to the Board.

The following criteria could be applied to the chemicals:

- a) persistent
- b) bioaccumulating
- c) toxic, acute or long term.

One main interest is to handle the analysis within the national monitoring programmes and develop new methods that are applicable to series analysis, and methods for new contaminants that may be of interest for monitoring in the future.

This work has so far resulted in the conclusion that the levels of DDT compounds have decreased in herring and guillemot eggs since the beginning of the monitoring project (1970 for herring and 1968 for guillemot). A decrease has also been seen for PCBs in guillemot eggs.

New contaminants that have been found during this period (in biota) are polychlorinated terpenes (PCT) and polychlorinated camphenes (PCC), chlordanes components and the metabolites of those compounds.

This section of the laboratory is also responsible for the analysis of species which are near extinction, as birds of prey, or threatened by pollution, as seals and otters.

UNITED KINGDOM

MAFF Fisheries Laboratory, Burnham-on-Crouch - Mr R Law

Work has continued during the last year on the environmental impact of discharges of cuttings resulting from the use of oil-based drill muds in North Sea oil production areas. We now have a better idea of the scale of the problem, and discussions have begun with the Department of Energy on reduction of discharges by clean-up of cuttings, control of discharges,

and the use of alternative oils to diesel fuel. This work is carried out in conjunction with the DAFS Marine Laboratory, Aberdeen.

The Bermuda Biological Station's Marine and Atmospheric Program -
Dr A H Knap

The open-ocean work has revolved around the Panulirus hydrostation 'S' program, 15 miles SE of Bermuda. Sea water samples have been taken for the past 28 years with an average spacing of every 17 days. Normal physical oceanography measurements have been taken routinely to 2 600 m. Nutrient measurements were made in the 1950s and 1960s by Menzel and Ryther. Recently, we have expanded to monthly measurements of nutrients, some trace metals, and trace organics.

We have an atmospheric project involved with the transport and deposition of sulfur and nitrogen to the western North Atlantic by rainwater. This is being expanded in 1982 to include trace metals and trace organics in rain as well as vapor deposition for the organics.

We have been using ARL air mass trajectories to investigate the source, which appears to be anthropogenic sulfur emitted from North America.

We have been working on the methodology for chlorinated trace organics in sea water in conjunction with Dr Duinker's laboratory on Texel and Dr Palmork's laboratory in Bergen. We have also investigated the occurrence, uptake and possible depuration or metabolism of selected trace organics in marine organisms.

ANNEX 4

MEETING OF THE CO₂ SUB-GROUP OF THE JOINT PANEL ON OCEANOGRAPHIC TABLES AND STANDARDS, Miami, 21-23 September 1981, by Dr A Poisson

The aim of the meeting was to consider the information available on the thermodynamics of the CO₂ system in sea water. We have tried to determine the state of the art on:

1. the solubility of CO₂ in sea water
2. the dissociation constants K₁ and K₂ of carbonic acid
3. the dissociation constant K_B of boric acid
4. the solubility product of aragonite + calcite.

1. Solubility of CO₂ in sea water

After discussion, it was decided that the formula provided by R Weiss gives the best representation of CO₂ gas solubility as a function of temperature and salinity (Doc. 1974, "Carbon dioxide in water and sea water: the solubility of a non ideal gas". Mar.Chem., 2, 203-215).

2. The dissociation constants K₁ and K₂ of carbonic acid

Several data sets are available on K₁ and K₂. After discussion, it appeared clear that the more recent works of Mehrbach et al. (1973, Limnol.Oceanogr., 18, 897-907) and of Hansson (1973, Deep Sea Res., 20, 479-491) are more reliable than earlier works. So, a comparison of only these two sets was made.

These measurements have been made in two different pH scales:

Mehrbach = NBS pH scale

Hansson = total pH scale (Tris) (the concentration of H here is the total concentration of H ions, i.e., free ions + those combined with sulfate, fluoride and borate).

The link between the two scales is given through the evaluation of the total activity coefficient of the H ion (γ_t) and in taking into account the liquid junction potential changes which is in the NBS scale (when electrodes are transferred from buffers to sea water).

Appropriate corrections have been made to convert the two data sets to the same pH scale and intercomparisons of K₁ and K₂ have been made.

The conclusion of the Group has been that the two independent sets of data are in agreement to within the experimental error. But it was also agreed that further independent determinations of these constants would be appropriate before the Group makes a recommendation on what constants to use.

Effect of pressure on K₁ and K₂

Culberson and Pytkowicz (1978) studied the pressure effect over a range of temperatures. Their results agree well with previous work and with those obtained from partial molal volume data by Millero.

Millero has presented a formula that describes adequately this pressure dependence as a function of T and S (Millero, 1979,

Geochimica and Cosmochimica Acta, Vol.43, p.1651). No further work is needed concerning that effect.

3. The dissociation constants of boric acid

There is a discrepancy between the different constants that are found in the literature. The Sub-group has strongly recommended that this constant be determined as a function of temperature and salinity. It will be able to make a recommendation only after these measurements have been done.

4. The solubility product

Generally two forms of calcium carbonate are considered to be important in the ocean: aragonite and calcite.

Although many studies have been carried out on the solubilities of the two forms of CaCO_3 in sea water, there is some disagreement between the data sets, especially for the aragonite which is the unstable form of CaCO_3 . For calcite, the agreement is quite good, and the data on the pressure dependence of the calcite solubility product are considered to be reliable.

But there is a strong need for further measurements of the aragonite solubility product.

In conclusion, the Sub-group has reviewed the state-of-the-art of the different parameters governing the CO_2 system in sea water. It did not make a recommendation for the use of any of these parameters. The only recommendation which it made was to indicate the priority areas where further work is needed to lead to an acceptable description of the thermodynamics of the CO_2 system.

The complete report of the conclusions of the Sub-group will appear in the "UNESCO Technical Papers in Marine Science" series in 1982.

The next meeting of the Sub-group will not be held before 2 or 3 years. There is no need for another meeting before additional work has been done.

ANNEX 5

ASSESSMENT OF THE STATUS OF INTERCALIBRATIONS ON THE DETER-
MINATION OF CONTAMINANTS IN MARINE SAMPLES

	<u>Page</u>
TRACE ELEMENTS IN SEA WATER	32
ORGANOCHLORINES IN SEA WATER	35
TRACE METALS IN BIOLOGICAL TISSUE	35
ORGANOCHLORINE COMPOUNDS IN BIOLOGICAL TISSUE	39
PETROLEUM HYDROCARBONS IN MARINE SAMPLES	39
CONTAMINANTS IN SEDIMENTS	42

TRACE ELEMENTS IN SEA WATER

Members of the Sub-Group were: G Asmund, S Berman, M Bewers, F Koroleff, K Kremling, J Piuze and A Poisson.

Context

The present assessment should reflect the status of intercalibrations and intercomparisons of the different steps in the determination of trace elements in sea water, taken in the context of ensuring that the average laboratory in ICES and JMG member countries reaches a stage where it has the capability to conduct viable surveys in coastal and in open-ocean waters, with the possible exception of the nutrient-depleted surface waters of the open ocean. This does not preclude that certain laboratories might be at more advanced stages in some cases.

The sub-group considered the trace elements in sea water in two broad compartments: the dissolved phase and the particulate phase.

Dissolved phase

a) Sampling

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

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

b) Pre-treatment

The sub-group remarked that for open-ocean waters, filtration was unnecessary and, indeed, that it could very often become a possible source of contamination when working with very low levels.

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

c) Storage

The sub-group did not feel that there were major problems with storage. Acidification and storage in containers made of the proper clean material (depending on the elements considered) seem to be satisfactory over long periods (one or two years) for the elements listed as such in the table. The metals in parentheses have not been studied as fully, but are felt to be adequately preserved.

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

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

d) Analysis (including pre-concentration)

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

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

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

Particulate phase

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

Recommendations for High Priority Intercalibration Work

The following should be investigated during the 5th round intercalibration of trace metals in sea water in Nantes in September 1982:

sampling for Hg

sampling, filtration and measurement of particulates in coastal waters.

Other Remarks

It must be kept in mind that, in order to be really useful, any intercalibration or intercomparison should be run using samples which are as close as possible to natural samples both in terms of matrix and in terms of the range of concentrations.

The MCWG should consider ways and means of ensuring that laboratories from ICES and JMG countries benefit as much as possible from all the work going into the intercalibrations and that they actually follow suggested techniques when their own are not up to standard. The publication of methods in leaflets for the "Techniques in Marine Chemistry" series could be one possible option.

Depending on the requirements of other ICES Working Groups or even of other MCWG sub-groups on trace elements in biota or in sediments, it is possible that trace elements not presently included in the table should be added for various reasons (e.g., Be, Sb, Ag, etc.).

Table 1. Trace elements in sea water.

'DISSOLVED'					
	Satisfactory		Problematic		
		Status		Status	Priority
Sampling	Fe, Mn, Ni, Cu, Zn Cd (Al, Co, Mo, V, Cr)	V	Sn (As)	<input type="checkbox"/>	1
			Pb		5
			Se	<input type="checkbox"/>	5
			Hg	0	9
Pre-treatment	Open-ocean N/A	N/A	Filtration	0	9
Storage	Fe, Mn, Ni, Cu, Zn, Cd Hg (Al, Co, Cr, V, Mo)	V	Open-ocean Pb	<input type="checkbox"/>	1
			As, Sn	<input type="checkbox"/>	5
			Se	<input type="checkbox"/>	5
				<input type="checkbox"/>	
Analysis (incl. pre-concentration)	Fe, Mn, Ni, Cu, Zn, Cd Hg (Cr, Al)	V	Pb (<20 ng/l), Se	<input type="checkbox"/>	5
			As, Sn, Co, V, Mo	<input type="checkbox"/>	1

PARTICULATE (Coastal Waters)		
	Status	Priority
Sampling	0	9
Pre-treatment (phase separation)	0	9
Concentration measurement	0	9
Storage	<input type="checkbox"/>	1
Analysis	Total	<input type="checkbox"/>
	Fractions	<input type="checkbox"/>

Key:

- N/A = not applicable
- V = assessment completed
- 0 = assessment in planning stage
- = no proposals for the work at present

- Priority: 9 = high
5 = medium
1 = low

ORGANOCHLORINES IN SEA WATER

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

	<u>State of development</u>	<u>Further work</u>
Sampling	in progress	high priority
Phase separation	in progress	high priority for inshore waters
Extraction	in progress	high priority
Storage	not considered	} low priority
Sample clean-up	not considered	
Separation of fractions	not considered	
GLC separation and quantifi- cation	in progress	

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

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

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

TRACE METALS IN BIOLOGICAL TISSUE

Since 1971, the analysts and laboratories participating in the ICES Coordinated (now called Cooperative) Monitoring Programme have been involved in a series of intercomparison exercises to assess the comparability of analytical methods used for the measurement of trace metals in marine biota. These exercises have utilized a series of specially prepared reference samples (based on fish flesh, shellfish tissue and fish meal) containing different concentrations of the metals under examination. These exercises have shown that the majority of the participants in the monitoring programme have the capability to produce comparable data for the following metals at the given concentrations:

- Copper - all concentrations ≥ 0.3 mg/kg (dry weight basis)
- Zinc - all concentrations ≥ 5 mg/kg (dry weight basis)
- Mercury - all concentrations ≥ 0.05 mg/kg (dry weight basis)
- Lead - all concentrations ≥ 2 mg/kg (dry weight basis)
- Cadmium - all concentrations ≥ 0.8 mg/kg (dry weight basis).

More detailed information on the current status of trace metal measurements in marine biota is given in Table 2.

In anticipation of the proposed 1985 baseline study, to be organised and coordinated by the ICES Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic, the MCWG considers that a further intercalibration exercise for metals in biological tissue should be planned in 1983/1984 to compare the analytical methods used in this baseline study, particularly the methods employed by analysts/laboratories who have recently joined the ICES monitoring programme. A summary of the proposed plans for this intercalibration exercise is given in Table 3.

Table 2. Status of Trace Metal Determinations in Marine Biota.

<u>Criteria</u>	<u>Current Status</u>	<u>Future Plans</u>
Type of sample	∅ (fish and shellfish muscle)	0, (fish liver and representative shellfish homogenate)
Sampling	∅ - Contamination problems associated with Pb only. Work in progress to assess sample size required for trend monitoring	X, to continue present statistical work regarding sample size
Pre-treatment stage	∅ - work in progress to assess contamination problems during sample processing	X, to continue present work, particularly for lead analysis (MCWG Sub-group)
Storage	Information readily available (C.M.1981/E:19, Berlin Workshop 1981)	X, to assess stability of sample storage under deep-freeze conditions for short and long periods
Analysis		
(a) Digestion	∅ - outstanding problems apply only to Pb analysis	To continue present work (MCWG Sub-group)
(b) Matrix	∅ - problem recognized. Can be overcome by modification of digestion procedure and/or by extraction technique	
(c) Quantification	V	
Metals	V - Cd, Pb, Hg, Cu, Zn and As (completed during ICES intercalibration exercises)	To continue current work
Range of concentrations	∅ - complete coverage for Cu, Zn and Hg Limited coverage for Cd, Pb and As	0 - (see Table 3 for proposed intercalibration programme prior to 1985 baseline study)
Form of metal	∅ - total measurements made in relation to public health and trend monitoring programme	□ - No proposals to change present approach

Key: V - assessment completed
 ∅ - assessment partially completed
 X - assessment in progress
 0 - assessment in planning stage
 □ - no proposals for the work at present.

Table 3. Proposed Plans for the 7th ICES Intercalibration Exercise for Metals in Marine Biota.

<u>Metals</u>	<u>Tissues to be examined in monitoring programme</u>	<u>Concentrations of metals in materials¹⁾ employed in the intercalibration exercise mg/kg dry weight</u>
Cadmium	Fish liver, shellfish	<u>ca.</u> 0.1, 0.3 and 1.0
Lead	Fish liver, shellfish	<u>ca.</u> 0.3, 1.0 and 3.0
Mercury	Fish flesh, shellfish	<u>ca.</u> 0.05, 0.2, 0.5 and 1.0
Copper	Fish liver, shellfish	≥ 0.5
Zinc	Fish liver, shellfish	≥ 5.0
Arsenic	Fish flesh, shellfish	<u>ca.</u> 0.1, 1.0 and 10

- 1) In view of the need to cover the range of concentrations occurring in each of the tissues used in the monitoring programme, it may be necessary to have several types of reference materials. The minimum number will be three (i.e., a fish flesh sample, a fish liver sample and a shellfish sample); the maximum number should not be greater than 8 samples.

ORGANOCHLORINE COMPOUNDS IN BIOLOGICAL TISSUE

The sub-group considered the current status of knowledge regarding organochlorine compounds. Three groups of interest were identified:

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

PCBs have been subject to investigation as regards intercalibration work, as have some organochlorine pesticides but little, if any, investigation has been carried out in the case of polychlorinated camphenes (toxaphene) beyond identification in marine biotic tissues. It was stressed that intercalibration efforts would be needed with respect to these three groups prior to the 1985 Cooperative Baseline Study.

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

The sub-group agreed, therefore, that current customs with regard to these procedures (e.g., FAO, ICES) should be continued. Samples, other than oils, will have to be prepared with various organochlorine levels. Examples of such samples could be: (a) a low-fat, low-PCB fish tissue, (b) a high-fat, high-PCB fish tissue, and (c) a shellfish tissue.

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

Mia Kerkhoff agreed to investigate the preparation and suitability of fish tissue ground with Na₂SO₄ as an ambient temperature-stable material for intercalibration analysis.

Lars Reutergårdh will propose work concerning polychlorinated camphenes at the next meeting of the Working Group.

Members of the sub-group were as follows: K Vandamme, M Perttilä, L Reutergårdh, Mia Kerkhoff, M O'Sullivan and J F Uthe.

PETROLEUM HYDROCARBONS IN MARINE SAMPLES

The findings of the sub-group are summarized in the accompanying table (Table 4). For ease of discussion, the analytical section has been treated as one item because once extracted most samples, whether water, tissue or sediment, are analyzed by similar techniques.

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

There have been a few intercomparison exercises for analyses of petroleum hydrocarbons in tissue. The effects of type of sample, pre-treatment and storage methods have not been investigated adequately by past inter-calibrations. The extraction techniques were assessed to some extent by the ICES first round intercalibration, but the results indicated that this is a high priority item for further work. The concentration range for the total hydrocarbon content was 50 $\mu\text{g/g}$ wet weight and this concentration should be used for the next ICES round.

The sampling of sediments and sub-sampling is also a very high priority item. The question of storage has not been addressed, but the sub-group felt that sampling and extraction are high priority items. The results of the ICES first round show again that there has not been an adequate answer reached for interlaboratory variability.

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

Overall, the sub-group felt that the entire subject of petroleum hydrocarbon intercalibration should have a very high priority in all compartments.

Table 4. Status of intercalibrations of measurement of Petroleum hydrocarbons.

Type of sample	Sea water (<u>dissolved + particulate</u>)	Tissue (all high priority)	Sediment
Sampling	● IOC X Kiel (Brackish water)	<input type="checkbox"/>	<input type="checkbox"/> High priority
Pre-treatment	N/A	<input type="checkbox"/>	<input type="checkbox"/>
Storage	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
Extraction	● IOC X Kiel (Brackish water)	● ICES ● IDOE ● EPA	● ICES
Concentration range (Total HC by UVF)	up to 5 µg/l	~ 50 µg/g wet	~30 µg/g dry

Methods

Analysis (for all sample types)

Gravimetric	● ICES
IR	● ICES
UV	
UVF	● ICES ● IOC/WMO ● Kiel
GC	● ICES ● IDOE ● EPA
HPLC	● ICES
GC/MS	● ICES ● EPA
LC/MS	

Recommended Methods

For PAH analysis: capillary GC
GC/MS
LC/MS
HPLC

For THC (total hydrocarbon determinations):

Packed column and capillary GC
UV
UVF

Key

= no proposals for the work at present. X = assessment in progress
● = under consideration N/A = not applicable

CONTAMINANTS IN SEDIMENTS

The only international intercomparison exercise on sediments which has been performed has been organised by the Joint Monitoring Group of the Oslo and Paris Commissions. It focussed on three types of dry sediments and only heavy metal determinations were made; there was no analysis of chlorinated hydrocarbons or petroleum hydrocarbons. The conclusions drawn were that the participating laboratories were able to analyse most elements studied to a satisfactory degree in sediments which are polluted, whereas the results for non-contaminated sediments were unsatisfactory for some elements. A trial to estimate the bio-availability by a weak acid attack gave very unsatisfactory results.

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

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

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

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

There is also a need for international agreement on which basis the results should be expressed, e.g., on the basis of the total sample, or a fraction of the sample, organic content, etc., and how samples will be characterized physically and chemically.

Table 5. Results of the JMG intercalibration on trace elements in sediments.

Types of sediments:

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

Elements (30 participants) and Ranges in ppm

Hg	Cd	Pb	Zn	Cu	Fe
0.02-1.7	0.05-10	5-700	20-1700	2-110	4000-45,000
Mn	Cr	Ni	{ As }	Co	
150-700	4-25,000	3-40	{ 4-45 }	1-5	

Sampling 10 (high priority)

Pre-treatment

- drying: 0
- sieving: 0

Storage 1 (low priority)

Analysis

- total strong attack: V
- bioavailability: ∅ /

Key

V = assessment completed

∅ = assessment partially completed

0 = assessment in planning stage

= no proposals for the work at present

ANNEX 6

ICES FIFTH ROUND INTERCALIBRATION FOR TRACE METALS IN SEAWATER

Report of the Coordinating Group Meeting, Copenhagen, 1 February 1982

Following completion of the ICES Fourth Round Intercalibration for Trace Metals in Seawater, which was completed in 1979, it had been intended to conduct an assessment, or intercomparison, of seawater sampling devices for the collection of samples for trace metal analysis. However, due to delays in the identification of the vessels and laboratory facilities needed for the conduct of the next (fifth) intercalibration exercise, it was not possible to carry out the experiment in 1979, 1980 or 1981. Meanwhile, an intercomparison of seawater sampling devices has been carried out under the auspices of the Intergovernmental Oceanographic Commission (IOC) that dealt with many aspects of the original ICES Fifth Round experimental design that was formulated in 1977.

Now that laboratory facilities and a vessel for the conduct of the Fifth Round Intercalibration have been offered by ISTEP, Nantes, and the Netherlands North Sea Directorate, respectively, it is possible to plan the experiment for execution in September 1982. Planning for this experiment was started during earlier MCWG meetings and the following describes the present plans for the various components of the experiment and provides some logistical requirements.

The original design of the ICES Fifth Round Intercalibration for Trace Metals in Seawater has been revised to exclude attention to those factors that were specifically addressed during the IOC/WMO/UNEP Sampling Intercalibration that was conducted in Bermuda in January 1980. The major aspect of sample collection and pre-treatment that remains to be dealt with in further intercomparison exercises is sample treatment to separate the "dissolved" and particulate metal fractions in seawater. It is entirely appropriate that this aspect be dealt with as part of an ICES intercalibration since its application is most important in the case of coastal and continental shelf waters, which are important areas of concern within ICES.

Thus, the core of the revised Fifth Round Intercalibration for Trace Metals in Seawater will deal with the intercomparability of different procedures for the separation of the dissolved and particulate fractions. There are a number of combinations of filter types (Nuclepore, Millipore, etc.) and filter holders (Millipore, Swinnex and custom-built types) that are commonly used for this purpose. Equally, the various methods of filtering samples, e.g., pressure and vacuum filtration of aliquots drawn from sampling devices, and the use of different types of tubing also need to be compared. Attention will also need to be given to the measurement of suspended matter concentrations by different gravimetric techniques. These studies will form the core scientific program of the experiment and each would be conducted for waters containing different concentrations of suspended material.

There will obviously be a need for some measurements of the nature and variability of conditions in the area used for the collection of samples for the core scientific work. It is envisaged that a repeated transect from Nantes/St. Lazaire to an area some 50 to 100 km offshore would be made for the measurement of conditions and the selection of sampling locations. This work would be carried out by one or two expert laboratories in order to determine the distribution of metals and particulate matter on a series of stations along a transect normal to the coast from the Loire River/estuary.

The second component of the experiment would involve the provision of on-site training/advice in sampling and sample treatment. Demonstrations of seawater sampling, sample filtration, sample preservation and storage techniques could be provided and the opportunity given for participants to collect samples with their own equipment for later comparison with samples collected with a single common technique.

Finally, samples could be prepared for distribution and analysis by other laboratories who did not participate in the on-site work.

Number of Participants

For the core experiment:	4-8 laboratories of established reputation
For the baseline transect:	1-2 laboratories
For training on-site:	20-30 individuals
For receipt of samples:	up to 100 laboratories

Laboratory Requirements

The major requirements for laboratory facilities are space and equipment to conduct on-site analyses of samples for trace metals in filtered samples. This would require some 20 m² of clean laboratory space equipped with 2 metres of laminar flow bench space for sample extraction, plus a further 20 m² of clean laboratory space for the installation of atomic absorption spectrophotometers and voltammetric analysers. A maximum of 10 participants would expect to use these facilities during the exercise.

Further space (approx. 20 m²) would be required for the preparation of sampling and filtration equipment. This should be relatively clean space in which acids can be used to clean equipment prior to use.

Finally, some space would be required for the assembly and distribution of sample bottles and sampling equipment prior to, during and after the experiment.

Shipboard Facilities

The ship would be equipped with 300 metres of 3/16" diameter 3/19 construction, stainless-steel (type 302 unlubricated) aircraft cable on a suitable hydrographic winch (max. speed 200 m/min.). The winch drum should be clean or wrapped with a polyethylene sheet prior to loading the cable. Spooling guides should be either plastic or plastic sheathed (PVC or nylon) and the meter wheel block should contain a plastic wheel (PVC, nylon or similar material).

The ship should also have a CTD and winch assembly equipped with 300 m of conducting cable for salinity and temperature profiling.

A supply of filtered pure nitrogen (up to 20 cylinders) at 30-75 kPa pressure would be needed for pressurization of filtration assemblies.

The ship's laboratory should contain racks for 5 l, 12 l and 30 l GO-FLO bottles (up to 3 of each) and racks for 12 l Niskin bottles in case of a GO-FLO malfunction at high suspended sediment loads.

It would be desirable to equip the ship with the modular clean laboratory offered by the Chalmers Institute of Technology of the University at Göteborg. This

should, if possible, be mounted on the after deck, where reasonable protection from breaking seas might be provided.

The remaining laboratory space should be left clear for the installation of filtration equipment as and when needed during the course of the experiment.

Management

A strict time-table of activities would have to be closely adhered to if the experiment is to be successfully conducted.

It is recommended that further detailed planning, arrangements and organisation of the intercalibration be carried out by a Coordinating Team comprised of:-

Overall Coordinators:

M. C. Alzieu, representing ISTPM, Nantes
Dr. W. van Eyden, representing the Netherlands
North Sea Directorate

Scientific Advisers:

Dr. J. M. Bowers
Dr. J. C. Duinker
Dr. G. Topping
Dr. H. Windom

The Overall Coordinators will be fully responsible for the management and administrative aspects of the experiment.

ANNEX 7

"NEW CONTAMINANT" Overview Papers
(Section headings for 3-4 page reports)

A. INFORMATION OVERVIEW PAPERS FOR MARINE CHEMISTRY WORKING GROUP

1. Production and Discharges
2. Transport Mechanisms and Deposition to the Marine Environment
3. Movement and Fate within the Marine Environment
4. Distribution and Levels in Compartments (sea water, biota, marine sediments)

B. INFORMATION OVERVIEW PAPERS FOR WORKING GROUP ON MARINE POLLUTION
BASELINE AND MONITORING STUDIES IN THE NORTH ATLANTIC

1. Production and Discharges
2. Distribution and Concentrations in Marine Trophic Levels
3. General Toxicology
4. Implications and Public Health Aspects

The use of common formats by both Working Groups will allow for easier ranking of chemicals by both groups. The Marine Chemistry Working Group Chairman should consult with the Chairman of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic regarding the standardization of formats. Authors should be requested to prepare one or two papers on each chemical as they see fit.

ANNEX 8

ACTION LIST

The following activities were agreed to by the Working Group members listed. For items for which all members are requested to send information, null reports should be sent by members who have no information to present. Unless otherwise indicated, all written reports should be sent to the ICES Environment Officer to arrive no later than 15 November 1982 so that they may be circulated in good time before the next meeting.

1. All members are requested to prepare updated information on activities of interest to the Working Group, giving references and contact persons (Sec. 4).
2. Dr. Harms and members of his sub-group will continue their intersessional work on the analysis of lead in biological material and present a paper at the 1982 Statutory Meeting describing the work conducted and giving conclusions and recommendations (para. 5.2).
3. Dr. Uthe will coordinate the fifth intercomparison exercise on PCBs in biological tissue (5/OC/BT) and prepare a report on the results for the next meeting of the Working Group (if possible)(paras. 7.1.1 and 7.1.2).
4. Dr. Kerkhoff will investigate the preparation and stability of an Na_2SO_4 /tissue blend for use in intercomparison exercises concerning organochlorine extraction and analysis (para. 7.1.3).
5. Dr. A. Knap and Dr. G. Farrington should continue planning towards the design and conduct of an intercalibration exercise on petroleum hydrocarbons in biological tissues and sediments. In the event that further progress is made, they should submit a paper to the 1982 Statutory Meeting describing the design of and plans for the experiment (paras. 7.2.1 and 7.2.2).
6. Dr. Uthe should prepare a paper for the 1982 Statutory Meeting describing the design of an intercomparison exercise on analysis of polycyclic aromatic hydrocarbons (PAH) in biological tissue (para. 7.2.3).
7. Dr. van Eyden, M. C. Alzieu, Dr. H. L. Windom, Dr. Duinker, Dr. Bewers and Dr. Topping should carry out further design and planning for the ICES Fifth Round Intercalibration for Trace Metals in Sea Water. These persons will be responsible for the conduct and management of the experiment in September 1982. Dr. Knap will, at the request of the Coordinating Group, approach various instrument manufacturers for the provision of analytical equipment at ISTPM for this experiment (Sec. 7.3).
8. Dr. Topping, Dr. Uthe, Dr. Berman, Dr. Harms, Dr. Thibaud, Dr. Jensen, and Dr. Piuze will investigate the availability of suitable reference materials in relation to the proposed intercalibration exercise for metals in tissue, which will cover the range of concentrations of metals to be employed in this exercise (see Annex 5, Table 3). This work will be done prior to August 1982 and will form the basis of a report to the Marine Environmental Quality Committee at the 1982 Statutory Meeting (paras. 7.4.1 - 7.4.4).

9. Dr. Jensen will prepare a summary of the report on PCTs which is under preparation by the Danish National Agency of Environment Protection for discussion at the next MCWG meeting (Sec. 10.1).
10. Dr. M. O'Sullivan should prepare an overview paper on furans and dioxins in the marine environment for discussion at the next MCWG meeting (para. 10.2.3.).
11. The Chairman should bring the attention of the Chairman of WGMPNA to the section headings for overviews on new contaminants contained in Annex 7 (para. 10.2.4).
12. The Chairman should forward thanks to Dr. M. Waldichuk for his submission of the overview paper on lead, notify Dr. Waldichuk of the MCWG comments on the paper and request him to submit a revised version to the ICES Environment Officer before 29 March 1982 (paras. 11.1 - 11.3).
13. Mr. Law should revise his overview on PAHs in the marine environment that was presented at this meeting and submit it for discussion at the next MCWG meeting (paras. 11.4 and 11.5).
14. Dr. Palmork will gather information on the subject of photo-degradation products of petroleum hydrocarbons with a view to preparing an overview paper on this subject for discussion at the next meeting. All members should seek relevant information from colleagues for transmission to Dr. Palmork (para. 11.6).
15. Dr. Knap should contact Dr. Measures and Dr. Wrench and invite them to prepare a discussion paper on the geochemical and biochemical aspects of selenium in the marine environment (para. 11.7).
16. Dr. A. Poisson will prepare a paper on the subject of marine chemical aspects of the CO₂ problem for consideration at the next meeting (para. 11.8).
17. All members are encouraged to prepare one or more leaflets for "Techniques in Marine Chemistry" and to invite appropriate colleagues to contribute leaflets to this series (para. 13.4).
18. Each Editorial Board for "Techniques in Marine Chemistry" is requested to appoint one member to act as coordinator in order to facilitate the preparation of leaflets. The Editorial Board for Metals is requested to nominate an additional member with expertise on trace metals in sea water (para. 13.5).

ANNEX 9

RECOMMENDATIONS

Recommendation 1

The Marine Chemistry Working Group recommends that an intercomparison study on analyses of non-alkylated polycyclic aromatic hydrocarbons in shellfish tissue be carried out with Dr. J. Uthe as Coordinator. The exercise should utilize a sample of an acetone powder and the acetone-extractable, hexane-partitioned lipid phase, which should be analysed for a selected core group of compounds.

Recommendation 2

In preparation for the forthcoming baseline study of contaminant levels in marine organisms, the Marine Chemistry Working Group recommends that a seventh intercalibration exercise for trace metals in biological tissues (7/TM/BT) be carried out prior to 1984 according to details presented in a paper to the 1982 Statutory Meeting based on preliminary investigative work on the availability and stability of certain reference materials.

Recommendation 3

Recognizing the expertise in the analysis of metals, organochlorines and PAHs of the Canadian Dept. of Fisheries and Oceans, Fisheries Laboratory, Halifax, Nova Scotia, the Marine Chemistry Working Group recommends that this laboratory be nominated as an Intercalibration Coordination Center for biological tissue to facilitate continued attention to improvements in the determination of these compounds in marine biota and to facilitate the preparation of blind intercalibration sample material for continued testing of laboratories taking part in cooperative monitoring studies.

Recommendation 4

The Marine Chemistry Working Group recommends that the next meeting of the Group be held for 4 days in February 1983 consecutively with the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic meeting to consider, inter alia, the following items:-

- (1) preliminary results of the fifth round intercalibration of trace metal analysis in sea water,
- (2) a report on results of the fifth intercalibration exercise on organochlorines in biological tissues,
- (3) progress in plans and conduct of intercalibration exercises on trace metals in biological tissues,
- (4) overview papers on polynuclear aromatic hydrocarbons, PCTs, chlorinated dibenzofuran and -dioxins.



