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SECOND REPORT OF THE MARINE CHEMISTRY WORKING GROUP

Copenhagen, 12-14 February 1980

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1. CHAIRMAN'S OPENING REMARKS

The Chairman, Dr M. de Barros, opened the meeting at 9.30 hrs on 12 February and welcomed the members. She noted with pleasure that this was the first working group meeting to take place at the new ICES Headquarters.

2. ADOPTION OF AGENDA AND APPOINTMENT OF RAPPORTEUR

The Chairman proposed the addition of two new points on the agenda: a new item 10 on sampling methodology for input studies of contaminants via rivers, and a new item 11 on composition of exhaust gases from incineration ships. The items on the draft agenda from former item 10 down were appropriately renumbered. The Working Group adopted the agenda with these changes and appointed the ICES Environment Officer as Rapporteur.

3. REPORT ON THE 67TH STATUTORY MEETING AND ACTIONS TAKEN BY THE COUNCIL RELEVANT TO THE WORK OF THE GROUP

- 3.1. The Environment Officer reported that the first report of the Working Group (Doc. C.M.1979/C:1) had been discussed at the Joint Session on Marine Chemistry at the 67th Statutory Meeting (Warsaw, 1-10 October 1979). The report had been favourably received and considerable interest had been expressed in the intercalibration programmes. All of the Working Group's recommendations (with some alteration to Recommendation 7) had been adopted by the Council. The publication of reports were approved as follows: a review of measurements of trace metals in sea water (C.Res. 1979/1:3), the results of recent intercalibration exercises on analyses of trace metals and organochlorines in biological materials (C.Res. 1979/1:4), and the results of the fourth intercalibration on trace metals in sea water (C.Res.1979/1:5). The intercalibration exercise on PCBs in fish oil was adopted in C.Res.1979/4:15 and the exercise on cadmium and lead analyses in shellfish tissue approved in C.Res.1979/4:16. By C.Res.1979/4:17, the Council approved the three-part intercomparison exercise for the analyses of petroleum hydrocarbons. Concerning the Working Group's Recommendation 7 on additions to the North Sea Nutrient Study, the Council approved (C.Res.1979/4:3) the portion concerning ad hoc intercalibrations and reaffirmed an earlier resolution (C.Res.1970/3:6,c) that Sagami nutrient standards be used as primary standards, but did not accept the inclusion of chlorophyll a and pH in the programme due to the fact that the Survey will be conducted in winter months. Finally, the Council approved the 1980 Working Group meeting in C.Res.1979/2:22.
- 3.2. The Environment Officer informed the Group that the Advisory Committee on Marine Pollution (ACMP) had also considered the Marine Chemistry Working Group report and had asked certain questions, especially concerning the intercalibration exercises. The Group agreed that these should be taken up under the relevant agenda items.

4. INTERNATIONAL ACTIVITIES OF INTEREST TO THE GROUP

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

- 4.1.1. The Environment Officer briefly mentioned the recent activities of this Group, including the final work-up of BOSEX results and the plans for a study of physical, chemical and biological patchiness in the Baltic Sea.
- 4.1.2. In this connection, it was pointed out that an intercalibration workshop on biological methods had taken place in Stralsund, German Democratic Republic, in August 1979 under the auspices of the Interim Baltic Marine Environment Protection Commission. The Group requested the Environment Officer to notify the members on how to obtain copies of the workshop report when they become available.

4.2. Joint Monitoring Group of Oslo and Paris Commissions

- 4.2.1. The Environment Officer reported that the Working Group's recommendations on sampling and sample preparation of marine organisms for pollution studies, including depuration of mussels, had been given informally to the Joint Monitoring Group (JMG) at its meeting in Dublin in June 1979. These recommendations had subsequently been accepted by the ACMP and were contained in the 1979 ACMP report. The Environment Officer informed the Group that the JMG had very much appreciated this advice and its members had generally agreed to follow it. Several participants at the JMG meeting had indicated that certain items in the sampling protocol could be difficult for them, but no details of these problems had been given in the JMG report.
- 4.2.2. The Working Group expressed interest in receiving details on the types and reasons for these objections to the sampling protocol and requested that the JMG provide more detailed feedback on the advice given by ICES.
- 4.2.3. In terms of the next JMG meeting, the Working Group noted that it was responsible for the initial review of three reports requested by the JMG: (a) the report on the results of the intercalibration of cadmium analyses in sea water (see Sec. 8.1 of this report), (b) the report on the results of the intercalibration of mercury analyses in sea water (see Sec. 8.2), and (c) an overview paper on fluxes and transport of mercury in coastal and estuarine environments (see Sec. 12.1).

4.3 Sediment Workshop

- 4.3.1 The Working Group had before it copies of the summary report of the ICES Sediment Workshop, published as Annex 6 to the 1979 ACMP report (Coop.Res. Rep.No. 92 (1980)). After briefly reminding the Group of the background to this Workshop held in Texel in September 1979, the Chairman invited Dr. Duinker to describe the outcome. Dr. Duinker reported that the Workshop had proposed the initiation of a two-phase international cooperative programme. In the first phase, a pilot survey should be conducted in several areas characterized by having fine-grained sediments. Several areas in the North Sea and on the North American Atlantic Shelf were identified as having the appropriate sediment characteristics. This phase should include intercalibration of sampling, preservation, and analytical techniques. The second phase would involve a study of pollutant dynamics in relation to bed, suspended sediment, and water properties. In this phase, processes of sedimentation and resuspension should be studied as well as processes of geochemical and biological transformation of pollutants in sediments.

- 4.3.2. The Working Group was informed that, in order to avoid delay in the initiation of the first of these studies, the Council had established a Coordinating Group to prepare detailed plans (see C.Res.1979/2:8). The resolution had not, however, clearly stated that an intercalibration/intercomparison of methods should be part of these plans. This Coordinating Group includes several experts in sedimentology and the Chairmen of the Hydrography Committee, the MCWG and the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic. The Chairman of MCWG had appointed Dr A. Jensen (Denmark) to represent her. The first Coordinating Group meeting would take place on 25-26 February 1980 in Texel.
- 4.3.3 In the general discussion of this subject, it was pointed out that although the Workshop had made two proposals for sediment studies, both of them were likely to be substantial undertakings with little possibility of an early conclusion. Several problems could be anticipated in these studies. There was general agreement in the Working Group that, although in many ways the Sediment Workshop had proved useful, several major questions had apparently not been discussed. Additionally, although others had been recognised, they had been the subject of such major disagreement that no conclusions had been reached. Topics falling into these categories were the importance of particle size, speciation and chemical partition in relation to overall fate and behaviour of pollutants as well as biological availability.
- 4.3.4 The Working Group felt that the question of intercomparison of chemical methodologies was one which required very early attention. In view of this, some dismay was expressed that neither the Workshop report nor the later Council deliberations had made any clear proposals regarding the conduct of an intercomparison exercise. Some concern was also expressed that there should be an attempt to stipulate methodologies without a clear understanding of their suitability and purpose.
- 4.3.5 In the course of the discussion on intercalibration, Dr. Jensen pointed out that the Joint Monitoring Group already had a sediment intercalibration exercise underway. He informed the Group that this intercalibration exercise involved analysis of several sediment materials, some of known composition, with each sample to be analysed by a number of methods including those of the analysts' own choice. The Working Group agreed that this intercalibration appeared to be very relevant to the work proposed by the Sediment Workshop and asked that more detailed information be obtained on the exercise and the availability of samples. Pending the outcome of this enquiry and that of the exercise itself, it was decided that there was little point in pursuing intercomparison of sediment analysis on an independent ICES basis.
- 4.3.6 Concerning the questions discussed at the Sediment Workshop, several members pointed out that the ICES interest in sediments had originally stemmed from a request by the ACMP in 1974 that the former North Sea Working Group should provide advice on the role of sediments in marine pollution studies. That Working Group had not felt able to answer the question adequately and as a result of its recommendation on the subject, a meeting of specialists had been held in 1975 later followed by the 1979 Workshop. Some members pointed out that the original question and intent appeared to have been overlooked and that ICES was still not in a position to answer questions related to the role of sediments in marine pollution monitoring activities. The Group generally agreed that this situation should not be allowed to persist, especially because since 1974 there had been a great deal of activity at the national level involving studies of sediments in a marine pollution context.
- 4.3.7 The Working Group agreed that a suitable starting point for the purpose of answering the outstanding questions would be to identify more precisely

what work is in progress in member countries on pollutants in sediments. In this context, the outcome of the 1975 ad hoc Meeting and some of the papers submitted at the 1979 Workshop could be used. In identifying what is going on, a clear need was recognised for ICES to note exactly why certain methods and investigations are being undertaken, as well as the more obvious question of how they are undertaken. Based on the outcome of this task, it was felt that it should be possible to identify the major limitations in those techniques which are currently being used and to make recommendations on the extent to which sediment studies can contribute effectively to marine monitoring activities and on which methods are suitable and for what purpose.

4.3.8 The Working Group concluded that it was for the Coordinating Group (meeting 25 - 26 February 1980) to undertake this task in the first instance. However, in view of the urgency of the matter, it was agreed that if the Coordinating Group did not take up the task or felt that it could not do so within the period leading up to the 1980 Statutory Meeting, the Marine Chemistry Working Group should undertake the work. To this end, a core group of members was identified who would be prepared to work by correspondence to answer the following questions:-

- 1) what is being done in relation to studies of pollutants and sediments;
- 2) why is it being done and how;
- 3) what are the limitations on this work and what can be recommended to the pollution regulatory commissions?

These persons also indicated that they would be willing to assist in any activity the Coordinating Group undertakes. The members agreeing to this work are Drs Duinker, Portmann, Jensen and Weichart. Dr D.H. Loring of the Bedford Institute was also nominated to assist in this project.

4.4 IOC/GEMSI

4.4.1 Dr. Bewers informed the Group that the third stage of the IOC intercalibration on analyses of trace elements in sea water had been conducted at the Bermuda Biological Station on 10 - 26 January 1980. He stated that the exercise had been successful and the results would be available in May 1980.

4.4.2 Dr. Palmork reported on the outcome of the IOC intercalibration on analyses of organohalogen residues in sea water, which had taken place on Bermuda at the same time as the metals exercise. He noted that, despite the excellent equipment and experienced people, not all the objectives of the exercise had been met. This was due to the very large problems encountered in attempting to measure organochlorines at the low concentrations found in open ocean waters. Dr. Palmork stated that the major conclusion to be drawn from this exercise so far is that more laboratory work is needed, followed eventually by a new intercalibration exercise which takes into account all relevant experience gained at sea and in the laboratory. He indicated that the final report of the IOC exercise should be available in September 1980.

4.5 Others

Dr. Bewers briefly informed the Group of discussions underway concerning the possible expansion of the IGOSS (Integrated Global Ocean Station System) Pilot Project on Marine Pollution (Petroleum) Monitoring to include trace metals and organochlorine residues.

5. PROGRESS IN INTERCALIBRATION ACTIVITIES

5.1 Cd and Pb in Biological Material

5.1.1 Dr. G. Topping, Coordinator of this intercalibration, reported that he had received requests for the reference samples for cadmium and lead from 26 scientists and that most of these participants had now been sent samples A (brown crabmeat/Cd) and B (fishmeal/Pb) prepared by the Marine Laboratory, Aberdeen. In due course, Dr J. Uthe would be sending sample C to each of the participants.

5.1.2 Although a deadline of 31 March 1980 had originally been set for the return of results in this exercise, in view of the delay encountered to date, it was considered that a deadline of 1 June 1980 would be more appropriate. This new deadline would permit laboratories who had not already requested samples to take part in this intercalibration programme. Dr. Topping stressed the need for all participants to submit their data by the agreed deadline so he can avoid delays and unnecessary work in producing the final report on this exercise.

5.1.3 The Group agreed that any data submitted after the 1 June deadline should not be included in the final report.

5.1.4 Dr. Topping reported that he still had enough of samples A and B to accommodate some additional participants. The Group therefore agreed that the Joint Monitoring Group of the Oslo and Paris Commissions should be informed that laboratories taking part in their programmes are welcome to participate in the intercalibration to the extent that samples are available.

5.1.5 Concerning the report on the results of the intercalibration, it was agreed that Dr. Topping would prepare a summary of the results for presentation at the 1980 Statutory Meeting. The full report should be prepared by 1 October 1980 for approval by the appropriate Committee(s), with simultaneous review via correspondence by intercalibration participants and MCWG members. The Group recommended (see Rec. 1) that this report be published in the Cooperative Research Report series, subject to possible amendments suggested by reviewers.

5.2 PCBs and other Organochlorines in Fish Oil

5.2.1 The Chairman briefly reminded the Group that as a result of the problems and poor performance which had been achieved in the previous intercalibration of PCB analyses in biological material, a further exercise was being undertaken. Because of the need to obtain Council approval for the exercise, invitations to participate had not been issued until October 1979. Dr. M. Bowers reported that to date Dr. Uthe, the Coordinator, had answered 18 requests for samples. The samples consist of kits containing a fish oil, the same fish oil spiked with a PCB formulation, and a PCB standard. Dr. Uthe had so far received no results and was seeking advice on what would be a reasonable deadline.

5.2.2 The Chairman drew attention to the fact that the ACMP had suggested that the exercise, which had originally been intended to include only PCBs, should be extended to include organochlorine pesticides. This was duly noted and the Chairman undertook to ensure that Dr. Uthe informed participants of this extension. Subject to the availability of samples, it was agreed that laboratories taking part in the Joint Monitoring Group programme should also be invited to participate.

5.2.3 Regarding the deadline for submission of results, the Group agreed that, in common with the metals exercise, an absolute deadline of 1 June 1980 would be set. Dr. Uthe was requested to produce a summary report for the 1980 Statutory Meeting and a full report by 1 October 1980, for a similar

review as for the report on the cadmium and lead exercise above. The Group recommended that the final report be published in the Cooperative Research Report series together with the report on the results of the cadmium and lead exercise (see Rec. 1).

5.3 Petroleum Hydrocarbons in Sediments and Biological Material

- 5.3.1 Dr. Portmann, Coordinator of this exercise, reminded the Group that at its first meeting it had been agreed that an initial attempt at an intercomparison exercise for analyses of petroleum hydrocarbons in marine samples should be undertaken using a crude oil, the same oil divided into two fractions, a sediment sample and a biological tissue sample. At that time, it had been felt that it would only be possible to make available a limited number of samples and, thus, that participation might have to be restricted. The Group had, therefore, agreed that preference should be given to those laboratories which were capable of using the more sophisticated techniques such as capillary GC and GC/MS. In the event, it had not proved necessary to restrict the availability of samples and in response to the concern expressed by ACMP and the Marine Environmental Quality and Hydrography Committees, complete freedom of choice was being given to participants on both analytical methods and components to be determined. The only stipulations made in distributing the samples were that participants should report their results in relation to the crude oil standard, although in addition they were free to use any other standard they may wish. Also, each participant was asked to analyse the samples by as wide a range of techniques as possible and for as many fractions or determinands as practicable. The basic objectives of the exercise were thus seen as establishing (a) the range of techniques in use and the range of capabilities among participating laboratories, (b) the variation in results produced by any one method and between methods, and (c) information useful to the development of firm recommendations on a more narrowly defined exercise in the future.
- 5.3.2 Several members mentioned that because the exercise was rather vague in its objectives and the number of restrictions on methods to be used were very few, some analysts were experiencing difficulties in understanding the real objectives of the exercise. After some discussion, it was generally agreed that although this was a very valid point, it was unavoidable if the exercise were to meet the ACMP and others' objections by not being restrictive. There was also general agreement that in any future exercise it may be necessary to place restrictions on methodologies and components to be determined.
- 5.3.3 Dr. Portmann drew attention to the fact that ample supplies of the crude oil, biological tissue and sediment samples were still available, together with limited supplies of a modified version of the originally proposed crude oil fraction, namely an aliphatic fraction and a solution containing a range of n-alkanes C₁₂-C₃₂, plus pristane and phytane. He also indicated that to date there were 24 participants from 11 countries, only one of whom had approached him for samples as a direct result of the General Secretary's invitation to Delegates and Committee members. In the light of this information, it was agreed that a further letter should be sent out by Dr. Portmann to national contacts for intercalibration exercises (as identified at the first MCWG meeting) and by the General Secretary to Delegates and Committee members, informing them of the further availability of samples and the fact that it now seemed unlikely that restrictions would be placed on their supply.
- 5.3.4 The Group agreed that, in common with the other on-going intercalibration exercises, the absolute deadline for submission of results should be set at 1 June 1980 and that a summary report on the outcome of the exercise should be available for the 1980 Statutory Meeting. The detailed report

should be prepared by 1 October 1980 for approval by the appropriate Committees, with review via correspondence by participants and MCWG members. The Working Group recommended that the final report be published in the Cooperative Research Report series (see Rec. 2).

6. FURTHER WORK ON PETROLEUM HYDROCARBONS

6.1 Questionnaire on Details of Sampling, Sample Preparation and Analytical Methods

6.1.1 The Chairman reminded the Group that it had been agreed at the first meeting that a questionnaire should be circulated as widely as possible with the objective of establishing exactly what methods of sampling and analysis were being used for petroleum hydrocarbons in marine substrates.

6.1.2 Dr. Portmann presented a draft of this questionnaire, which had been prepared jointly by Dr. de Lappe and his laboratory. A number of members made suggestions for further questions and improvements to the lay-out. However, in order to allow more detailed consideration and consultation with other colleagues, the Group agreed that more time should be allowed for comment. Accordingly, the Group set a deadline of 31 March 1980, by which time all further suggestions should be received by Dr. Portmann, and adopted the draft questionnaire, as modified by further comments.

6.1.3 The Group also agreed that the amended questionnaire should be circulated as widely as possible by the ICES Secretariat (Dr. Portmann to provide a list of proposed recipients) and that the deadline for responses should be set at 30 November 1980 to allow a report on the results to be made available to the MCWG at its next meeting.

6.2 Other Possibilities for Intercomparison/Intercalibration Studies

6.2.1 In relation to further intercalibration studies, the Chairman questioned the Group on whether it would be possible to plan the next phase of the petroleum hydrocarbon programme now in order to avoid a delay of one year until the 1981 Working Group meeting. Although there was some support for the view that a delay should be avoided, there was a general acceptance that no firm decisions could be taken on the plans for the next exercise until the results of the first exercise were available.

6.2.2 In this context, Dr. Palmork pointed out that procedures were now available to allow the preparation of sea water samples, spiked with oil or oil components, which could be extracted using XAD-2 resin. This would permit easy distribution of extracted sea water samples by ordinary air mail rather than special air freight, as presently required for solvent extracts. Dr. Palmork agreed to try to present a paper on the possible use of XAD-2 resin in petroleum hydrocarbon intercalibrations for presentation at the 1980 Statutory Meeting.

6.2.3 After some further discussion the Group agreed that in his summary report on the first intercomparison exercise for the 1980 Statutory Meeting, Dr. Portmann should attempt to include proposals on the future conduct of intercomparison exercises on petroleum hydrocarbons. This would allow the appropriate Committee(s) to formulate recommendations to the Council seeking approval to proceed with a second phase on the proposed basis. The detailed planning of this phase should be undertaken by the Marine Chemistry Working Group at its 1981 meeting. In this way, impetus would be maintained and a delay of at least one year would be avoided.

7. POSSIBILITY OF IMPROVING DETECTION LIMITS FOR Cd AND Pb
IN BIOLOGICAL MATERIAL

- 7.1 The Chairman, in introducing this item of the Agenda, indicated that the MEQC and the ACMP had expressed some concern that many laboratories which had participated in the fifth heavy metal intercalibration in biological material were not using methods of analysis which allowed them to measure the low concentrations of cadmium and lead in fish muscle tissue. She had, therefore, asked Dr. Harms to prepare a paper indicating what steps had to be taken in order to achieve the lower levels of detection which would be necessary to determine these concentrations.
- 7.2 Dr. Harms then introduced his paper on the methods needed to measure very low levels of cadmium and lead. After some comments on the details of the techniques, the Group unanimously agreed that it is possible to achieve the lower limits of detection needed in order to determine the true levels of lead and cadmium in fish muscle tissue.
- 7.3 Several members pointed out, however, that there is a large difference between what is possible and what is necessary in a given context. In a pure research context, it was generally felt that it is necessary to be able to analyse the natural concentrations of substances in biota and their environment. However, in a monitoring context, other factors are relevant which affect the decisions on the concentrations one needs to be able to measure as well as the organisms chosen for testing.
- 7.4 In the light of this discussion, the Group reviewed the proposal made at its first meeting that the requirement to analyse for cadmium and lead in fish muscle tissue be eliminated and considered whether or not this proposal was compatible with the aims of the coordinated monitoring programme identified by the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (see Doc. C.M.1979/E:36, para 5.2.4.). These aims are:-
- (a) to provide a continuing assurance of the quality of fish and shellfish for human consumption,
 - (b) to survey wide geographical areas on an intermittent basis, and
 - (c) to provide an analysis of trends for selected pollutants in selected species from selected areas.
- The MCWG generally agreed that there was no need to analyse fish muscle tissue for cadmium or lead in order to meet these objectives. Shellfish tissues or fish liver or kidney were considered more suitable because the concentrations of these metals are higher and the detection limit problem does not therefore arise.
- 7.5. In order to provide a clear answer to ACMP on this issue, the Group asked Dr Harms to expand on his paper on the analysis of low levels of cadmium and lead by giving a short summary and good bibliography of the techniques available, the detection limits achievable, and the drawbacks and problems encountered (e.g., the problem of obtaining good blanks for lead due to contamination). He was also asked to indicate the costs involved in these analyses in terms of special instrumentation required, time per analysis, etc. Dr Harms agreed to have an expanded version of his paper ready for the 1980 mid-term ACMP meeting. The Group expressed its appreciation to Dr Harms for his work on this subject.

8. REPORT ON INTERCALIBRATION EXERCISES FOR JMG

8.1 Cadmium in Sea Water

- 8.1.1 The Coordinator of this exercise, Dr. Thibaud, informed the Group that the intercalibration exercise for cadmium in sea water had proceeded according to the detailed plan he had presented at the first meeting of the MCWG. A draft of the complete report giving details on sample preparation, circulation of samples, analytical techniques and the results including statistical analysis was presented to the meeting and discussed.
- 8.1.2 Dr. Thibaud stated that 29 laboratories from 15 countries had participated in the exercise. The results of their analyses had been studied statistically in order to establish the mean values, standard deviations, percentage recoveries and also to compare the analytical techniques and the two preservation methods used on the samples - deep-freezing or acidification. The overall results showed a very good distribution of data for all the cases studied. The mean values obtained from the participants' results for the spiked samples were in very good agreement with the actual spikes. No statistically significant differences were found between the two preservation techniques used, nor between the two main analytical techniques employed - anodic stripping voltammetry and atomic absorption spectrometry. Dr. Thibaud reported that this study shows an improvement in the analytical capability of the laboratories involved and that within the framework of interlaboratory exercises on trace metals this exercise has resulted in the best distribution of results around the "true" values of the samples so far achieved. The exercise had further demonstrated that the reliability of the sea water sampling method and the sample preparation technique is just as important as the reliability of the analytical techniques involved.
- 8.1.3 In the discussion, it was pointed out by some of the members that the concentrations of certain metals in the unspiked sea water samples, including perhaps cadmium, were higher than might be expected in natural sea water. However, there was general agreement that whether or not this was the case the success of the exercise and the conclusions were unaffected.
- 8.1.4 The Group expressed its great appreciation to Dr. Thibaud for his efforts in coordinating this intercalibration and preparing the very fine report, which would now be transmitted to the ACMP. The Group recommended that the report be published in the Cooperative Research Report series (Rec. 3).
- 8.2 Mercury in Sea Water
- 8.2.1 Mr. Olafsson, Coordinator of this intercalibration, presented the preliminary report on the intercalibration of mercury analyses in sea water carried out for JMG. This report included results from 30 out of

37 participants. Mr. Olafsson considered that, although full statistical analysis of the results had not been possible in the time available before the Working Group meeting, the preliminary results demonstrated a marked improvement in performance compared to the previous ICES intercalibration of mercury analyses in sea water. Composite means of the results, after excluding outliers, showed large standard deviations for the natural sea water samples, but more acceptable standard deviations for the spiked samples. It was noted that the achievement of good spike recoveries did not seem to present a problem for most participants. For samples of natural sea water, 16 participants reported concentrations under 10 ng l^{-1} , but comparison of results from these laboratories on natural and spiked samples indicated a significant systematic bias. The preliminary report included observations showing that the unspiked sea water intercalibration samples had been representative of uncontaminated sea water. Also contained in the report was a brief review of the analytical methods employed by participants.

8.2.2 In the discussion, it was noted that only part of the procedure for the determination of mercury concentrations in sea water had been tested in this intercalibration, namely analytical methods. The other important steps of sampling and sample pretreatment, including oxidation, had not been included in the exercise. These other steps also influence the ultimate results.

8.2.3 The Group expressed its great appreciation to Mr. Olafsson for his work in coordinating the intercalibration exercise and preparing the draft report. Noting that the final report would be ready for the mid-term ACMP meeting, the Group recommended that this report be published in the Cooperative Research Report series together with the report on the cadmium exercise (see Rec. 3).

8.3 Second Draft of the Report of the Fourth Organochlorine Intercalibration

8.3.1 The Chairman reminded the Group that a draft of the report of the fourth organochlorine intercalibration exercise for biological material, prepared by the coordinator, Dr. A. V. Holden, had been presented to the first meeting of the MCWG. Following this meeting and in the process of revising the draft, Dr. Holden had found it necessary to add some supplementary information giving the results of his more detailed examination of the chromatograms and methods of analysis used by the participants. Since these new studies could introduce some substantial changes in the overall report, Dr. Holden had requested that the draft of the new paragraphs be presented to the Group for discussion and approval before inclusion in the previously approved report.

8.3.2 This supplementary report examined information on GLC columns, dimensions and temperature of operation as well as details of extraction, clean-up and pre-GLC separation techniques. The chromatograms provided as examples by the participants were studied and compared in order to identify general problems of analysis.

8.3.3 A total of 30 laboratories had submitted results. Most of them had employed packed columns and some form of pre-GLC separation, while several others used treatment with sulphuric acid as a clean-up procedure. A few laboratories employed capillary columns or wall-coated open tube columns in GLC analysis, thus obtaining a much greater degree of residue separation than is possible with the usual packed columns.

8.3.4 Separation of these laboratories was made into four groups - those using capillary or wall-coated open tube columns, those obtaining good chromatograms and those obtaining bad chromatograms using packed columns, and finally those using only the sulphuric acid technique. The analytical data from the four groups was subjected to variance analysis. Considering only the residues reported by all laboratories, it was seen that there was no significant difference between the four analytical groups with respect to the mean values of HCB, α -HCH, γ -HCH, DDE or TDE. The sulphuric acid treatment technique produced higher and much higher mean values, respectively, for DDT and PCBs, while the poorer quality chromatograms from the packed columns gave a value significantly higher at the 0.05 confidence level for PCBs. The much higher values for DDT and PCBs obtained by the sulphuric acid technique were the only anomalous results disclosed by the breakdown of analytical data, so the appropriateness of this technique may be in question.

8.3.5 In discussing this supplementary information, the Group felt that it would be useful to state in the report the criteria which were used to classify chromatograms as "good" or "bad" and to include examples of good and bad chromatograms as well as typical chromatograms obtained using the different columns and the sulphuric acid technique. The Group also requested a clarification of the conclusion on the use of the sulphuric acid pre-treatment method. Some members felt that it would be useful for Dr. Holden to consider whether or not the selection of different peaks from the PCB-containing extracts to estimate PCB residues could be a reason for the differences in the values reported. The Chairman agreed to inform Dr. Holden of these remarks to his report.

8.3.6 In conclusion, the Group felt that this supplementary information provided a valuable addition to the report of the fourth organochlorine intercalibration and approved its inclusion. The Group again expressed its appreciation to Dr. Holden for his excellent work in coordinating the exercise and evaluating the results.

8.4 Final Report on Fourth and Fifth Intercalibration Exercises on Trace Metals in Biological Tissues

8.4.1 Dr. Topping presented the second and final draft of his report on the fourth and fifth intercalibration exercises for analyses of trace metals in biological tissues. Forty-one laboratories out of a total of 56 which received the two samples of reference material had reported analytical data for some or all of the metals under examination. The standard analysis of these data, which included the 28 sets of data presented in the preliminary report and the 13 sets submitted before the revised deadline of 1 June 1979, showed that most of the participants had produced comparable data for copper, zinc, and mercury at the levels encountered in these samples. The analysis of the cadmium and lead data from the additional participants had not affected the conclusions drawn from the analysis of the data submitted by the first deadline (see C.M.1979/C:1, para 8A 1.1.3).

8.4.2 It was understood that Dr. Topping's report on the fourth and fifth trace metal intercalibration exercises would be combined with Dr. Holden's report on the fourth intercalibration exercise for organochlorine compounds and published as a Cooperative Research Report, as recommended at the last MCWG meeting and subsequently approved by the Council (C.Res.1979/1:4).

9. FIFTH ROUND INTERCALIBRATION FOR HEAVY METALS IN SEA WATER -
REPORT ON DEVELOPMENTS AND FUTURE PLANS

- 9.1 Dr. Windom, Chairman of the Coordinating Group planning this exercise, reminded the Working Group that at its previous meeting it had recommended that the ICES fifth round be carried out jointly with the IOC third stage intercalibration on trace metals in sea water on Bermuda in January 1980. For a number of reasons, this joint exercise had not been possible, but the IOC had carried out its exercise with Dr. Bewers as coordinator (see para 4.4.1). Dr. Windom reported that four out of the five members of the ICES Coordinating Group, and in all seven participants from the ICES fourth round intercalibration, had taken part in the IOC exercise on UNEP funds. The variables tested on Bermuda, which were chosen on the basis of the results of the ICES questionnaire survey conducted by Dr. Windom in 1978-79, consisted of the use of selected types of sampling bottles deployed on several kinds of hydrowires (see Annex V, part 2 for further details). Dr. Windom stated that the IOC exercise could not be considered a substitute for the ICES fifth round; only the sampling bottle types and hydrowires tested were the same as those to be used in the ICES exercise. No testing had been done on pre-treatment methods, storage bottles, nor any of the other variables envisaged for the ICES experiment. Furthermore, Dr. Windom felt that the experience gained in the planning and execution of the IOC exercise would be very valuable to the conduct of the ICES fifth round.
- 9.2 Dr. Windom further reported that the Coordinating Group had met on the evening of 12 February and had prepared expanded recommendations for the ICES fifth round intercalibration (see Annex V, part 3). The Coordinating Group recommended that the fifth round assume the character of a workshop, in which a core group of selected laboratories would be invited to carry out the central purpose of the intercalibration (as in the original plans for the exercise) and open participation would be invited for additional laboratories interested in gaining experience on the procedures being tested. The Coordinating Group further recommended that an effort now be made to find an institute or institutes willing to volunteer research vessel time and/or land-based laboratory facilities for the conduct of this exercise. The lead role in preparing further details of the exercise should then be assumed by the institute(s) providing these facilities, with assistance from the members of the Coordinating Group.
- 9.3 The Working Group agreed with these recommendations of the Coordinating Group. It was felt that the exercise should take place in European waters, including possibly the Baltic Sea. Although it was agreed that the plans should be designed for a one-ship exercise, they should be easily expandable for a multi-ship exercise if more than one ship becomes available.
- 9.4 The Working Group agreed that the first priority is to identify one or more institutes to provide research vessel time and/or appropriate land-based facilities where participants could carry out sample preparation steps and some analyses. The members agreed that, in the first instance, they would contact colleagues to try to find volunteers. If no offers were forthcoming by late summer, however, it was agreed that the Coordinating Group should prepare a paper on the issue for distribution to ICES Delegates asking their support. Inquiries on detailed requirements for vessels and land-based laboratories should be addressed to the Coordinating Group, whereas offers of vessels or facilities should be sent to the General Secretary of ICES.

- 9.5 In closing the discussion on this subject, the Working Group expressed its hope that the necessary offers would be made in adequate time so that concrete plans for the exercise would be ready for the next meeting of the Working Group.

10. SAMPLING METHODOLOGIES FOR MEASURING RIVER INPUTS
TO THE MARINE ENVIRONMENT

- 10.1 The Chairman informed the Group that a request had been received from the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic asking the MCWG to review the international work on sampling methodologies for measuring river inputs to the marine environment and advise on whether any initiatives should be taken by ICES on this subject.
- 10.2 After a short discussion, the MCWG agreed that a document should be prepared describing procedures by which river inputs of contaminants might be reliably measured. It was assumed that the information requested refers to both gross and net fluxes of riverborne contaminants to the ocean. However, the MCWG asked the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic to define their request for information in more detail and to decide whether their request refers only to gross river fluxes as determined at river mouths, or also to net fluxes of riverborne contaminants as measured at the outer coastal zone boundaries.
- 10.3 To carry out this work, Dr. Duinker agreed to prepare a draft paper in consultation with Drs. Windom and Bewers. It was agreed that this paper should be sent to the ICES Secretariat by 31 August for distribution to the other members of MCWG for review and comment.

11. COMPOSITION OF EXHAUST GASES FROM INCINERATION SHIPS

- 11.1 Giving the background for this agenda item, the Chairman explained that, at its October 1979 meeting, the Advisory Committee on Marine Pollution had considered a response to a request from the Oslo Commission concerning the selection of a common incineration site in the North Sea. This response had consisted mainly of advice on the fisheries aspects of the proposed sites, as prepared by the Advisory Committee on Fishery Management. The ACMP had felt that it would like information on the actual levels of pollutants resulting from shipboard incineration of toxic substances. Therefore, the ACMP had asked the MCWG to provide information on the chemical composition of exhaust gases from incineration ships.
- 11.2 Dr. Hoogweg agreed to prepare a report, in consultation with Dr. Weichart, on the composition of exhaust gases, especially the levels of non-combusted toxic substances, and the possible impact of these exhaust components on the marine environment. The Working Group agreed that this report should be presented at the October 1980 meeting of ACMP and asked Dr. Hoogweg to forward his report to the ICES Secretariat by 31 August for distribution to ACMP members.

12. FIRST DRAFTS OF OVERVIEW PAPERS ON FLUXES AND TRANSPORT OF
POLLUTANTS IN COASTAL ENVIRONMENTS

12.1 Mercury

12.1.1 It was recalled that at its first meeting, the MCWG had been informed of a Joint Monitoring Group request that ICES examine the physical, chemical, and biological processes which control the movement of contaminants between the various compartments of the marine environment from the point of input to the ultimate sink. The MCWG had decided to begin work on this project by preparing overview papers on the fluxes and transport of mercury and PCBs in the coastal environment.

12.1.2 The Chairman asked Dr. Topping to present the overview paper he and Dr. Windom had prepared on mercury. Dr. Topping explained that their draft paper only gave an overview of the main aspects of mercury transport. Among the processes covered, the report showed that biological activity does not play a significant role in the removal of mercury from the marine environment, as has been postulated. Nor were overall figures given on the quantities of mercury removed by sedimentation, as this varies greatly from estuary to estuary. In general, the authors stated, they had wanted to take a fresh approach to the estimation of the fluxes and transport of mercury, rather than merely summarizing the large body of literature on the subject.

12.1.3 The Group felt that the draft report presented an interesting overview of the subject but requested the authors to provide additional information on processes in inshore waters and a list of key references used to prepare the report. The Group agreed that this should be considered a trial exercise on the overall subject of the movement of contaminants in the marine environment and that it should be determined whether the ACMP (and possibly the JMG) is satisfied with this approach before additional overviews are prepared.

12.2 PCBs

12.2.1 The Chairman invited Dr. Portmann to describe the progress made by the sub-group which had been asked to prepare a PCB overview. Dr. Portmann apologised that his group had not been able to make very much progress. However, in consultation with the Chairman and Dr. Palmork, he had developed an outline of the intended coverage of this report. As presently proposed, the paper would be more of a review than an overview. This was because initially it had been felt that there was not much information available in a collated form on PCBs. However, it had become apparent that several review-type publications were already available. In the light of this information and the general approbation given to the mercury overview paper, Dr. Portmann questioned whether he should amend the proposed coverage of the PCB paper.

12.2.2 After a brief discussion, the Group agreed that, provided the mercury paper is well received by the ACMP and the Joint Monitoring Group, the proposed PCB paper should take a similar form. In this context, it was pointed out that attention should be paid to the fact that PCBs are degradable to a certain extent, making it difficult to identify and quantify formulations accurately. It was also pointed out that, in view of the probable incomplete knowledge on PCBs, there should be a concluding section in which gaps in understanding are identified.

13. REVIEW OF PAPER ON CADMIUM BY DR. SIMPSON

- 13.1 The Chairman reminded the Group that at its previous meeting it had been agreed that the preparation of an overview paper on the transport and fate of cadmium in the marine environment should be postponed until a review document on cadmium behaviour in the marine environment was published by the Institute of Oceanographic Sciences in Wormley, UK. This document, entitled "A Critical Review of Cadmium in the Marine Environment" by Dr. W. R. Simpson, had been studied by Dr. Bewers, who reported his findings to the Group. Dr. Bewers stated that this review, unlike previous reviews which have largely dealt with the effects of cadmium on man, focuses its attention on the aquatic chemistry and transport of cadmium in the marine environment, its global distribution in ocean waters and sediments, the cycles, fluxes and residence time of the metal in the oceans and the biochemical and physiological effects of cadmium on marine organisms.
- 13.2 Dr. Bewers said that the material in each of the substantive chapters is comprehensive and, in the main, well presented. He felt that this is as comprehensive a review as exists for other metals. Although much of the material is not strictly pertinent to the presumed needs of the Joint Monitoring Group, all the information required to prepare a brief overview of cadmium distribution, transport and behaviour in the marine environment is contained within the review. Thus, once an assessment of the suitability of the mercury overview for JMG purposes has been carried out, the Working Group agreed that it would be a relatively simple matter to prepare a cadmium overview to satisfy the JMG's request.
- 13.3. Dr Piuze and several other members indicated their willingness to consider similar overviews for other contaminants which have not been thoroughly studied in order to identify gaps in knowledge and information needs.
14. CARBON DIOXIDE CYCLING - POSSIBILITIES OF A WORK PROGRAMME
- 14.1 It was recalled that at the first meeting of the Group, Prof. K. Grasshoff had raised the question of whether ICES could usefully contribute to the study of carbon dioxide cycling in the oceans. At the request of the Group, he had prepared a paper for the 1979 Statutory Meeting (Doc. C.M.1979/C:28) which gave a background to the problem and some suggestions for coordinated research work. However, the paper was not discussed so there were no suggestions or comments from either the Hydrography or the Marine Environmental Quality Committees. With this background, the Chairman invited comments from the Working Group members.
- 14.2 Several members reported briefly on the type of research being conducted in their countries on CO₂ cycling. The Group felt that it would be useful to obtain information on the relevant work being conducted in all ICES countries and to have a critique prepared on this work and its focus and to identify further research needs, etc.
- 14.3 The Chairman reported that, although Prof. Grasshoff had been unable to attend the meeting, he had indicated his willingness to carry out further work on this subject. The Group accordingly asked Prof. Grasshoff to prepare the overview and critique of on-going research mentioned in the previous paragraph.

15. REPORT FROM STATISTICIANS ON TREND ANALYSIS STUDIES

- 15.1 In introducing this subject, the Chairman reminded the Working Group that at the first meeting it had been decided that little further progress on trend analysis studies could be made directly by the chemists and that the statisticians should be brought into the discussions in a more direct way. Accordingly, it had been agreed that Dr. J. Uthe should attempt to coordinate an exchange of ideas by correspondence, with a view to developing a concensus view on how to tackle trend analysis monitoring and the statistical approaches to be used.
- 15.2 In Dr. Uthe's absence, Dr. Bowers read out a brief progress report prepared by Dr. Uthe. Progress had not been very satisfactory and the exchange of views was far from complete. It was obvious that at present there was no concensus among the statisticians on which statistical techniques should be used in the regression analysis part of the investigations. Part of the reason for this was probably the fact that the individual statisticians were being asked somewhat different questions and were therefore taking somewhat different approaches to them.
- 15.3 As a result of the exchanges that had taken place so far and a careful appraisal of the analyses of the data which had been undertaken, it was Dr. Uthe's view that no further progress would be made until a more coordinated approach to the problem was achieved. In his view, the best way to achieve this would be to agree on the questions to be asked and to bring those involved together to have them work jointly on the raw data sets now available. To this end, he suggested that the three basic questions were:-
- 1) What method should be used to determine changes over time in pollution levels in a population within a discrete geographical area?
 - 2) What is the best way to determine relationships between a population and a contaminant level?
 - 3) What are the significant factors which control the levels of a contaminant within a population?
- 15.4 Several members agreed that part of the problem has been the lack of a coordinated approach to the issue or a general agreement on the questions asked. It was acknowledged that in some cases somewhat different questions or at least not all of those identified by Dr. Uthe were being raised. There was general acceptance that there should be a meeting of the statisticians, possibly with a representative from the Marine Chemistry Working Group present to ensure that the questions were fully understood.
- 15.5 However, there was an opinion in the Group that this trend analysis type of work is more relevant to the programmes of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA), especially as it requires the expertise of biologists as well as chemists and also a main interest in pollution. Thus, the MCWG agreed to ask the WGMPNA to take over the work on developing the appropriate methods to monitor trends in contaminant levels in biota. The MCWG further agreed

that it was prepared to offer any advice of a chemical nature to assist in the advancement of this work.

- 15.6 Returning to the issue of the meeting of statisticians, the MCWG recommended to the WGMPNA that a meeting should be held of statisticians involved or interested in the question of trend analysis in a pollution monitoring context. Prior to that meeting, each statistician should receive a copy of the three basic questions and selected raw sets of data from the chemists.
16. STATUS OF UPDATING OF NUTRIENT METHODS IN NEW BALTIC MANUAL
- 16.1 It was recalled that at its previous meeting, the Working Group had agreed to update the nutrient methods contained in the New Baltic Manual (Coop.Res.Rep.No. 29(1972)) so that they reflected improvements in methods as well as the approaches used in the entire ICES area. The question of intercalibration of nutrient methods had also been raised last year. The Chairman invited the opinion of the Group on these issues.
- 16.2 The discussion initially showed a great disagreement among members on both issues. Whereas some members felt that there were already enough authoritative manuals on nutrient methods available, others felt that an ICES manual on these methods could be very useful. After extensive discussion, the Group agreed that, instead of a bound manual of methods, a series of leaflets on methodologies would be very useful. Each leaflet could contain a description of the analytical method or methods which could be used to determine the concentration of a particular substance in a particular medium. Leaflets could also be prepared on sampling and sample preservation techniques. When any published method becomes outdated, a new leaflet would be published to supersede the earlier leaflet.
- 16.3 During the discussion, it became apparent that a series of leaflet publications on methods should have a much broader coverage than only nutrient determinations in sea water. The Group therefore recommended that a new series of leaflet publications be established in ICES with the title "Techniques in Marine Chemistry" (Rec. 4). The series should comprise descriptions of suggested techniques of sampling, preservation or analysis of substances occurring in the marine environment, i.e., in biota, sea water, or sediments. Each draft leaflet should be prepared by a person with special expertise in the subject and reviewed by the MCWG or selected representatives thereof. Following approval of the contents of a leaflet, it should be edited by the Environment Officer prior to publication.
- 16.4 Having agreed to this overall structure, the Group decided that the first leaflets in the series should describe nutrient methods. Dr. Fonselius agreed to coordinate their preparation.
- 16.5 The Group then reverted to the issue of intercalibration of nutrient methods. In agreement with the decision reached the previous year, the Group agreed that no overall intercalibration of nutrient methods should be conducted in the near future. It felt, however, that the conduct of intercalibrations on a regional basis, especially ad hoc intercalibrations among ships before beginning a multi-ship exercise, should be strongly encouraged. To provide broader access to the results of these intercalibrations, it was agreed that the results should be sent to the ICES Secretariat and later considered by the MCWG. A recommendation to this effect was agreed by the Group (Rec.5).

17. PROGRESS IN THE REVIEW OF STUDIES USING RADIONUCLIDE ANALOGUES IN THE MARINE ENVIRONMENT

- 17.1 The Chairman informed the Group that although Dr. P. G. W. Jones had agreed to prepare an overview document on this subject, he had been unable to do so in 1979 and he had further indicated that he might not be attending future meetings of the Working Group. The Chairman stated that Dr. Jones was still willing to carry out this work provided there was adequate interest in the issue.
- 17.2 In the discussion, it was apparent that many members felt that this was an important subject. Among the examples cited was the usefulness of radioactive tracers in studies of sediment processes and estuarine transport. However, it was also felt that persons with expertise in radiochemistry should be asked to assist in preparing this overview.
- 17.3 The Group ultimately decided that all members should be asked to collect information from their country on the use of radionuclide analogues in studies of the natural marine environment, e.g., studies of sedimentation and processes in the sediments, dispersion of dumped sewage sludge or other materials, mixing and transport in estuaries and coastal zones. They should contact key persons, if possible, to assist in collecting the material and preparing a review of the relevant studies. Dr. Jones was asked to collate and review the UK documents on this subject. It was further agreed that all reviews should be forwarded to the Environment Officer before 1 December 1980 so that she could summarize the overall information available. It was emphasized that the studies to be covered should be restricted to those in the natural environment; tank experiments were not to be included.

18. ANY OTHER BUSINESS

- 18.1 Dr. Bowers raised the issue of whether the Group should encourage the development of standard samples containing substances such as trace metals at their ambient concentrations in the environment. These standards could be particularly useful to laboratories who have not participated in the intercalibration exercises. The Group felt that discussion of this subject should be postponed until the 1981 meeting.
- 18.2 The Chairman proposed that in the future there be a standing agenda item for MCWG meetings in which members could report on the new issues they are working on and present ideas for new projects. The Group strongly endorsed this proposal, noting that this could provide a forum for the discussion of important topics in marine chemistry. It was agreed that this item should be handled early in the meeting and that at least one-half day should be allowed for discussion.

19. APPROVAL OF RECOMMENDATIONS AND DEADLINES

- 19.1 The Group approved the items in the Action List (Annex III) and the Recommendations (Annex IV). Concerning the recommendation on the next meeting of the Group (Rec. 6), it was agreed that the meeting should take place for four days in mid-February 1981. The Group strongly suggested that every other year it meet at a laboratory in a member country. The Group further expressed its interest in gaining the participation of scientists from the German Democratic Republic, Poland and USSR in its work and possibly holding a meeting at one of their laboratories.
- 19.2 With the business of the meeting completed, the Chairman thanked the members for their work and closed the meeting at 13.30 hours on 14 February.

MARINE CHEMISTRY WORKING GROUP

Second Meeting

12 - 14 February, 1980, 9.30 hours

ICES Headquarters, Palægade 2, Copenhagen

AGENDA

1. Chairman's opening remarks
2. Adoption of agenda and appointment of rapporteur
3. Report on 67th Statutory Meeting and actions taken by the Council relevant to the work of the Group
4. International activities of interest to the Group
 - a) ICES/SCOR Working Group on the Study of the Pollution of the Baltic
 - b) Joint Monitoring Group of Oslo and Paris Commissions
 - c) Sediment Workshop
 - d) IOC/GEMSI
 - e) Others
5. Progress in intercalibration activities
 - a) Cd and Pb in biological material
 - b) PCBs and other organochlorines in fish oil
 - c) Petroleum hydrocarbons in sediments and biological material
6. Further work on petroleum hydrocarbons
 - a) Questionnaire on details of sampling, sample preparation and analytical methods
 - b) Other possibilities for intercomparison/intercalibration studies
7. Possibilities of improving detection limits for Cd and Pb in biological material
8. Report on intercalibration exercises for JMG
 - a) Cadmium in sea water
 - b) Mercury in sea water
 - c) Second draft of the report of the fourth organochlorine intercalibration
 - d) Final report on fourth and fifth intercalibration exercises on trace metals in biological tissues
9. Fifth round intercalibration for heavy metals in sea water - Report on developments and future plans
10. Sampling methodologies for measuring river inputs to the marine environment
11. Composition of exhaust gases from incineration ships

12. First drafts of overview papers on fluxes and transport of pollutants in coastal environments
 - a) Mercury
 - b) PCBs
13. Review of paper on cadmium by Dr. Simpson (IOS, Wormley)
14. Carbon dioxide cycling - possibilities of a work programme
15. Report from statisticians on trend analysis studies
16. Status of updating of nutrient methods in New Baltic Manual
17. Progress in the review of studies using radionuclide analogues in the marine environment
18. Any other business
19. Approval of recommendations and deadlines

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ACTION LIST

1. Dr. Topping, as coordinator of the intercalibration exercise on cadmium and lead in biological tissues, to (a) notify participants that all results must be reported by 1 June 1980, (b) prepare summary of results for submission as a document for the 1980 Statutory Meeting, and (c) prepare draft of overall report for postal review by MCWG members and ACMP review at C.M.1980 (see para 5.1.5).
2. Dr. Uthe, as coordinator of the intercalibration exercise on PCBs in biological materials, to (a) notify participants that all results must be reported by 1 June 1980, (b) prepare summary of results for submission as a document for the 1980 Statutory Meeting, and (c) prepare draft of overall report for postal review by MCWG members and ACMP review at C.M.1980 (see para 5.2.3).
3. Dr. Portmann, as coordinator of the first intercalibration exercise on petroleum hydrocarbon analyses, to (a) inform national contacts for intercalibration exercises of further availability of samples, (b) notify participants that results must be reported by 1 June 1980, (c) prepare summary of results and proposals for future exercises for submission as a document for the 1980 Statutory Meeting, and (d) prepare draft of overall report for postal review by MCWG members and ACMP review at C.M.1980 (see paras 5.3.3, 5.3.4, 6.2.3).
4. All members to review draft questionnaire on petroleum hydrocarbon methods and send comments to Dr. Portmann by 31 March 1980. Dr. Portmann to forward final questionnaire and mailing list to ICES Secretariat thereafter (see paras 6.1.2 and 6.1.3).
5. Dr. Palmork to prepare paper for C.M.1980 on the possible use of XAD-2 resin in petroleum hydrocarbon intercalibrations (see para 6.2.2).
6. Dr. Jensen to report on the meeting of the Sediment Coordinating Group (25 - 26 February 1980) and the activities undertaken; the report should be sent as soon as possible after the meeting to the ICES Secretariat for distribution to MCWG members.
7. Dr. Harms to prepare an expanded paper on analyses of low levels of cadmium and lead for presentation at the mid-term meeting of ACMP (see para 7.5).
8. All members to explore the possibility that institutes in their country could provide ship time and/or land-based laboratory facilities for the fifth round intercalibration of trace metals in sea water (see para 9.4).
9. Dr. Duinker, in consultation with Drs. Windom and Bowers, to prepare a draft paper describing procedures by which river inputs might be reliably measured. The paper should be sent to the ICES Secretariat by 31 August for distribution to MCWG members (see paras 10.2, 10.3).
10. Dr. Hoogweg, in consultation with Dr. Weichart, to prepare a report on the composition of exhaust gases from incineration ships; the report should be sent to the ICES Secretariat by 31 August for distribution to ACMP members (see para 11.2).

11. The Chairman to determine when and how to proceed with the preparation of overview papers on the transport and fate of PCBs and cadmium in the marine environment. Drs. Portmann, Bowers, and Piuze to assist in the preparation of these overviews (see secs. 12.2 and 13).
12. Prof. Grasshoff to prepare a paper giving an overview and critique of the research being carried out on CO₂ cycling in the marine environment, for distribution to MCWG members at least one month before the next meeting. To assist in this work, all members should send the names and addresses of key scientists conducting work on this subject in their country to Prof. Grasshoff by 30 April 1980, Institut für Meereskunde an der Universität Kiel, Düsterbrookweg 20, D-2300 Kiel, Federal Republic of Germany (see paras 14.2, 14.3).
13. Dr. Fonselius to coordinate the preparation of draft leaflets on nutrient methods (see para. 16.4).
14. All members to prepare review documents on the use of radionuclide analogues in studies of the natural marine environment and send to the ICES Secretariat by 1 December 1980. The Environment Officer to summarize for the next meeting (see para 17.3).
15. All members are encouraged to prepare notes for discussion (1 - 3 pages) on new topics, new contaminants, new approaches to existing problems, etc.; They should be sent to the ICES Secretariat with a copy to the Chairman by 1 December 1980 for distribution (see para 18.2).
16. The Environment Officer to compile all reports on ad hoc nutrient intercalibrations and distribute to MCWG members one month before its next meeting (see para 16.5).
17. The Environment Officer to inform members about the availability of the report on the results of the Intercalibration Workshop on Biological Methods (Stralsund, August 1979).

RECOMMENDATIONS

Recommendation 1

It is recommended that the report on the results of the intercalibration of analyses of cadmium and lead in biological materials, prepared by Dr. G. Topping, and the report on the results of the intercalibration of PCB analyses in biological materials, prepared by Dr. J. Uthe, be published in a volume of the Cooperative Research Report series.

Recommendation 2

It is recommended that the report on the results of the first intercalibration exercise on petroleum hydrocarbon analyses in marine substrates, prepared by Dr. J. Portmann, be published in the Cooperative Research Report series.

Recommendation 3

It is recommended that the report on the results of the intercalibration of cadmium analyses in sea water, prepared by Dr. Y. Thibaud, and the report on the results of the intercalibration of mercury analyses in sea water, prepared by Mr. J. Olafsson, be published in a volume of the Cooperative Research Report Series.

Recommendation 4

It is recommended that a new series of leaflet publications be established in ICES entitled "Techniques in Marine Chemistry". The series should comprise descriptions of suggested techniques of sampling, preservation or analyses of substances occurring in the marine environment (biota, sea water, sediments). Each leaflet should be prepared by one or more experts on the technique to be covered, reviewed by the Marine Chemistry Working Group or representatives thereof, and edited by the ICES Environment Officer. The first leaflets in the series should describe nutrient methods and their preparation should be coordinated by Dr. S. Fonselius.

Recommendation 5

With reference to C.Res 1979/4:3, in which it is resolved that ad hoc intercalibrations of nutrient analyses be conducted between ships participating in the North Sea Nutrient Study, it is recommended that this be broadened to encourage the conduct of ad hoc nutrient intercalibrations on a regional basis, especially before beginning a multi-ship project. The results of these intercalibrations should be sent to the ICES Secretariat for compilation and consideration by the Marine Chemistry Working Group.

Recommendation 6

It is recommended that the next meeting of the Working Group be held for 4 days in mid-February 1981, at a place to be determined later, to consider the following items:

- a) progress in intercalibration exercises
- b) overview papers on transport of contaminants in the environment, and
- c) progress in petroleum hydrocarbon studies.

ANNEX V, part 1

REPORT ON DEVELOPMENTS AND FUTURE PLANS
FOR THE FIFTH ROUND INTERCALIBRATION FOR HEAVY METALS IN SEA WATER

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General plans for the 5th Round ICES Trace Metal intercalibration were formulated at the first meeting of the Marine Chemistry Working Group in Lisbon. A Coordinating Group was established and included M. Bowers, P. Jones, K. Kremling, J. Olafsson, G. Topping and myself. This Group recommended close cooperation between ICES and IOC since the latter was already committed to an intercalibration exercise in Bermuda during January 1980.

In view of the lack of funds and sufficient time for preparation, it was decided at the 1979 ICES Statutory Meeting in Warsaw to postpone the 5th round. In Council Resolution 1979/4:18 it was suggested that the Coordinating Group explore alternative means for carrying out this exercise.

The IOC exercise proceeded including a trace metal intercalibration coordinated by M. Bowers. The criteria for participation in this exercise was, of course, different from that of the proposed ICES 5th round. However, thanks to the efforts of Dr. Bowers, many of the laboratories proposed for participation in the ICES 5th round were included in the IOC exercise and were, in fact, designated as IOC laboratories. As it turned out most of the members of the 5th Round Coordinating Group participated (i.e., Bowers, Olafsson, Topping and Windom), and some aspects of the 5th round design were incorporated into the IOC exercise.

The IOC Bermuda exercise is briefly described in Part 2 prepared by Dr. Bowers. Because many of the scientific questions proposed in the 5th round were addressed in the IOC intercalibration, those of us who participated feel that the results will be extremely beneficial to the ICES exercise. We also feel that, based on this experience, certain logistical and management considerations should be made that did not occur to us previously. A meeting of the Coordinating Group was therefore convened on 12 February, 1980 to discuss these matters and future plans for the ICES 5th round. The results of this meeting and our recommendations to the Marine Chemistry Working Group are presented in Part 3.

IOC/UNEP/WMO INTERCALIBRATION OF SAMPLING PROCEDURES
FOR THE DETERMINATION OF TRACE METALS IN SEAWATER

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This intercalibration experiment took place at the Bermuda Biological Station between January 10th and 25th 1980 as part of the PANCAL-80 programme. Sampling operations were carried out on the National Oceanic and Atmospheric Administration vessel 'Kelez' temporarily based in St. George, Bermuda. The objectives of the experiment were to examine differences between commonly used procedures for seawater sampling. A comparison of different sampling bottles (GO-FLO, Hydro-Bios and Niskin) and different methods of deployment (on stainless steel, Kevlar and plastic-coated galvanised steel hydrowire) was therefore carried out. The experimental design consisted of deployment of the three types of sampling bottle together on a single hydrowire within a homogeneous body of water on Panulirus Station (Ocean Station S). Each participant is required to recover four duplicate samples from each type of sampling bottle in order to examine differences in the quality of samples recovered from them. Subsequent deployments of the same sampling devices on the other hydrowires in the same water mass would then be used to examine relative hydrowire influences through the collection of additional samples.

The chosen experimental design contains considerable inherent redundancy to allow for reductions in the available ship-time, equipment failure or other constraints. The design was in fact modified during the PANCAL-80 programme by reducing this redundancy but maintaining the validity of the intercomparisons. The actual sampling procedure carried out involves individual comparisons as outlined in the diagram below:

<u>Hydrowire Type</u>	<u>Bottle Type</u>			
	Hydro-Bios	Modified GO-FLO	Niskin	GO-FLO
Stainless Steel		X — — — — X		
Kevlar		X — — — — X		
Plastic-coated Galvanised Steel	X — — — —	X		
Stainless Steel		X — — — — — — — X		

Because of limitations in the winch handling capability aboard the 'Kelez' the original intention to deploy the sampling bottles at depths between 1 500 and 2 000 metres, where temporal and spatial gradients in temperature and salinity are small, had to be abandoned. As a result, the bottles were deployed in depths of 1 200 - 1 300 metres and it became desirable to check the assumption of homogeneity over depth and time scales utilized in the above comparison. A set of duplicate samples was therefore collected at the spatial and temporal extremities of a set of hydrowire casts to test the homogeneity assumption.

In addition, an examination of the effects of storage within sampling bottles was also carried out. A large volume of nearshore surface water was collected and used to fill different sampler types. Samples were then withdrawn from the sampling bottles at intervals up to 12 hours to see what influences on sample composition result from storage. Each participant was also encouraged to take samples of this surface water to provide additional intercalibration samples.

In most cases the participants took their samples to their home laboratories for analysis. They are expected to report their analytical data to the organizers by May 31, 1980. The analytical facilities provided by the Bermuda Biological Station and by Perkin-Elmer and Varian were extremely good and as a result a few participants carried out preliminary analyses or extractions on site.

Participants were drawn from Canada, the Federal Republic of Germany, the German Democratic Republic, Iceland, Japan, Korea, Malaysia, the Netherlands and the United States. Seven of these participants had previously participated in the ICES Fourth Round Intercalibration for Trace Metals in Sea water.

REPORT OF THE COORDINATING GROUP MEETING

12 February 1980

The Coordinating Group feels that the experience of the IOC Bermuda trace element intercalibration has provided a basis for the consideration of additions and modifications to the ICES 5th Round. These are given in the following recommendations:

1. The proposed ICES 5th Round can undertake to include a workshop for sea water sampling and analysis for all interested ICES laboratories. These laboratories would be in addition to those who would be invited under the criteria stated in section 8B.2.4 of the First Report of the Marine Chemistry Working Group, Doc. C.M.1979/C:1. The latter laboratories are essential to the conduct of the exercise as originally designed.
2. The Coordinating Group feels that plans cannot be carried further until there are commitments for the provision of the ships and laboratories necessary for the conduct of this exercise. It is therefore strongly recommended that members of the Marine Chemistry Working Group and other ICES representatives pursue the possibility of obtaining these commitments from agencies within their respective countries. These tentative commitments should be indicated directly to the ICES Secretariat who could then forward them to the Coordinating Group so that communications regarding such things as the availability and rating of facilities could be initiated.
3. Once available facilities are identified a new steering committee should be established with representatives of agencies providing these facilities assuming a lead role in the design and conduct of the 5th Round. The members of the present Coordinating Group are willing to assist in any capacity deemed appropriate or necessary by the new steering committee.
4. The design and conduct of the 5th Round trace metal intercalibration exercise will be necessarily dependent upon facilities* committed for this purpose. It is, however, strongly recommended that the following also be taken into consideration in the overall plan:-
 - a) the original design of the ICES 5th Round, and
 - b) the results of the trace metal portion of the IOC Bermuda exercise.

* It is presently thought that the basic facilities required for this exercise are:

- a) A research vessel of $\geq 1\ 000$ tonnes displacement for a period of ≥ 4 weeks.
- b) Land-based laboratory facilities including a clean lab large enough for four people to work simultaneously.