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the Exploration of the Sea

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REPORT OF THE MARINE CHEMISTRY WORKING GROUP

Copenhagen, 26 February - 1 March 1985

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* General Secretary
ICES
Palægade 2-4
DK-1261 Copenhagen K
Denmark

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REPORT OF THE MARINE CHEMISTRY WORKING GROUP

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1. OPENING OF MEETING

The Chairman, Dr. J M Bewers, opened the meeting at 9.30 hrs on 26 February 1985 and welcomed the participants.

Each participant introduced himself/herself, giving affiliation and main areas of scientific responsibility.

2. ADOPTION OF AGENDA

The Working Group considered the draft agenda and adopted it. The agenda is attached as Annex 1. The list of participants is attached as Annex 2. The ICES Environment Officer, Dr. J Pawlak, served as Rapporteur.

3. REPORT OF THE 72nd STATUTORY MEETING

The Environment Officer informed the Group about the relevant items of interest from the 1984 Statutory Meeting. In particular, it was pointed out that the publication policy for the Journal de Conseil has been changed such that it is intended that the Journal contain articles reflecting all the scientific subjects of interest to ICES. Accordingly, the submission of papers on pollution-related subjects and hydrography is actively being encouraged.

The Chairman informed the Group that an ad hoc Group of Chairmen has been set up under the Consultative Committee to examine the inter-relationships between the environmental Working Groups and prepare proposals for their future activities and structure. An important aspect of this review concerns the MCWG in terms of, among other things, how more attention can be given to issues related to chemical oceanography.

4. REPORTS OF RELATED ACTIVITIES

4.1 Joint Monitoring Group of the Oslo and Paris Commissions

Dr. Jensen summarised the outcome of the meeting of the Joint Monitoring Group (JMG) of the Oslo and Paris Commissions which was held in January 1985. He reported that the JMG had agreed to

recommend that the Joint Monitoring Programme be expanded to include analyses of copper, zinc, lead and γ -HCH (lindane) in organisms; copper and zinc in sea water; and mercury, cadmium, copper, zinc, lead, γ -HCH and, on a voluntary basis, PCBs in sediments. This expansion of the monitoring programme will depend on the successful intercalibration of the analyses of these substances.

Taking note of this information, it was agreed that requests made by JMG to ICES which were relevant to the MCWG should be considered under Agenda Item 6.

4.2 Intergovernmental Oceanographic Commission IOC/GIPME GEMSI/GEEP

Dr. Dawson, the representative from the IOC, summarised the activities that have taken place under the IOC Working Committee for the Global Investigation of Pollution in the Marine Environment (GIPME) during the past year. He reported that the GIPME Group of Experts on Methods, Standards and Intercalibration (GEMSI), which is now co-sponsored by the UNEP Regional Seas programme, has carried out a good deal of work to develop regional monitoring capability. GEMSI has working groups on the use of marine organisms in contaminant monitoring, the monitoring of contaminants in sediments, the estimation of riverine inputs, and the analysis of individual components of PCBs and PAHs. GIPME/GEMSI will coordinate a baseline survey of trace metals in the open ocean in 1986-1987. GEMSI has coordinated a number of intercalibration exercises in various regions, using materials remaining from ICES intercalibrations whenever possible. GEMSI is also concerned with the availability of standard reference materials and will propose a mechanism for the preparation and distribution of such materials. Concerning data exchange, Dr. Dawson reported that GEMSI and other bodies under IOC have reviewed and commented on the ICES data reporting formats for contaminants in various marine media. In concluding, Dr. Dawson stated that IOC and GEMSI are aware of the work being carried out by ICES and the need to avoid duplication. IOC appreciates the good working relations with ICES.

4.3 Relevant GESAMP Working Groups

The Chairman provided brief information on work being carried out under the IMO/FAO/UNESCO/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP). In particular, he noted the relevance of Working Group 22 on fluxes at the land-sea boundary, Working Group 23 on the assimilative capacity of the ocean, and Working Group 24 on global ocean monitoring.

4.4 Other relevant activities of Multilateral and International Agencies

Dr. Pertilla summarised the recent relevant activities carried out under the Baltic Marine Environment Protection Commission (Helsinki Commission). He reported that the hydrographic, hydrochemical and contaminant data from the Baltic Monitoring Programme will be organised according to the ICES system. Although the monitoring programme does not cover the coastal areas, compilations on results of studies in the coastal zone will be carried out. In terms of ICES work, the Helsinki Commission is supporting participation in the Baltic Sea component of the 1985 Baseline Study of Contaminants in Fish and Shellfish as well as the joint multiship experiment on patchiness in the Baltic Sea.

5. REPORTS ON PROJECTS AND ACTIVITIES IN ICES COUNTRIES

Dr. Law summarised a paper outlining the results of additional studies carried out in England on the effects of tributyl tin (TBT) - based antifouling paints, particularly on the oyster Ostrea edulis. The results of this work demonstrated effects of TBT on the reproductive capacity of the oyster. Work carried out elsewhere in the United Kingdom had shown similarly high toxicity to larvae of mussels (Mytilus edulis). Legislation has been prepared in the UK to ban the sale of TBT - based antifouling paints, both conventional and copolymer, for use on boats less than 12 m in length. This legislation should be in operation by July 1985.

Dr. Topping described work underway in Scotland to determine the effects of TBT used on salmon cages on the meat yields of scallops.

Dr. Calder described the Environmental Quality Monitoring Programme that will be carried out by the U.S. National Oceanic and Atmospheric Administration (NOAA). Reference materials to be used for the programme will include reference materials for trace metals prepared by the National Research Council (NRC) of Canada and samples for trace organics prepared by a NOAA laboratory. The Smithsonian Institute will host a working group to ensure a standard approach to histopathology and the diagnosis of fish diseases. The National Bureau of Standards (NBS) will host workshops on the analysis of trace metals and organics to promote a discussion of methods and the development of common methods where possible. NBS will also establish a specimen bank for the archival of samples of sediment, fish and mussels from important sites for future analysis. Statisticians will control experimental design and the quality of analytical data. A brief list of quality assurance guidelines has been prepared for analysts. A data base will be established for the data which will automatically present quality assurance data along with the results from the monitoring programme. Data will not be available until 1986.

Dr. Uthe presented a proposal for monitoring persistent contaminants in the North Atlantic and North Pacific by measuring contaminant levels in seabird eggs. The proposal specified the use of seabird eggs because seabirds are high in the food chain, they have a widespread pelagic distribution and relatively non-migratory habits and their eggs are easy to collect and store.

In discussing this proposal, it was noted that in Sweden there is 16 years of contaminant monitoring experience using guillemot eggs and that this has provided more useful information than the monitoring of contaminants in herring. In Denmark, the eggs of seabirds from Bornholm and the Faroe Islands have been analysed to show trends in concentrations of PCBs and DDT. In the UK, a document has been prepared which reviews the use of marine mammals and seabirds in the monitoring of marine pollution.

In closing the discussion of this topic, Dr. Reutergårdh offered to produce a paper for the 1986 MCWG meeting comparing the results obtained when monitoring organochlorines in herring and in guillemot eggs. Dr. Uthe also agreed to prepare an overview paper on the use of organisms for monitoring purposes based on Canadian experience.

6. REQUESTS FOR ASSISTANCE/ADVICE FROM REGULATORY COMMISSIONS

The MCWG noted that the following requests from the Joint Monitoring Group of the Oslo and Paris Commissions were relevant to its work:

- (a) to further advise on the methods of sampling to determine the the input of contaminants to the marine environment via rivers, with particular reference to net inputs;
- (b) to report routinely on all on-going and planned ICES intercalibration exercises preferably by means of a full report to JMG on the intercalibration exercise carried out; to plan an intercalibration exercise on Hg, Cd, Cu, Zn in estuarine waters;
- (c) to report on progress made in studies of sediments and pollution, by providing information on the progress of the various pilot surveys, the outcome of the relevant intercalibration exercises in which ICES is involved and to advise on the detailed methods of sampling and analysis which have been tried and tested and found to give satisfactory results;

- (d) to report on the progress towards the conduct of an intercalibration exercise on the measurement of petroleum hydrocarbons in seawater and the outcome of the work on intercalibration of petroleum hydrocarbons and PAHs in biological tissues;
- (e) to produce, as soon as practicable, a method for the calculation of the concentration of PCBs in environmental samples based on capillary gas chromatographic techniques. If necessary on an interim basis this advice could involve only a few selected PCB-congeners;
- (f) to consider the feasibility of conducting an intercalibration exercise for PCBs in sediments, and to advise accordingly. If such an exercise is feasible, to draw up plans for and conduct such an exercise, reporting on the results in due course.
- (g) taking account of the report of and the information available to the Working Group of the Paris Commission responsible for assessing the input of contaminants from the atmosphere to the sea, to review knowledge on the input of contaminants from the atmosphere to the sea and to advise on the most appropriate methodologies for quantifying inputs from this source;
- (h) to keep under review the question of new contaminants that may be of interest to JMG: this should be regarded as a current awareness exercise and implies an expectation that advice will be provided on those contaminants which ICES considers may give cause for concern in the future.
- (i) to advise on the extent to which the fat content of fish tissues is associated with the concentration of contaminants found in fish tissues and the most appropriate procedures for accommodating such variations in analysing data for trend monitoring purposes.

In addition, ICES has been requested to advise on which JMG laboratories have participated successfully in intercalibration exercises, so that data from the monitoring programme can be better evaluated.

Having taken note of these requests, the Working Group agreed that detailed consideration of each request should take place under the agenda item most relevant to it.

7. REQUESTS FOR ASSISTANCE IN HYDROGRAPHY

The Chairman opened the consideration of this subject by noting that concerns have been expressed that the Working Group has been too much involved with quality control of measurements of contaminants and not concerned enough with general chemical

oceanography and other issues in marine chemistry. He stated that under the Consultative Committee a review is being carried out of all environmental Working Groups under the Marine Environmental Quality Committee and the Hydrography Committee to determine whether there are overlaps between groups and whether the distribution of work should be reorganised. The future of the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic is also being reviewed in this context.

The Chairman then requested the ICES Hydrographer, Dr. H Dooley, to indicate to the Group: (1) the perceived criticism of MCWG by the hydrographers, (2) areas where MCWG could have an input, and (3) needs with regard to the patchiness study. Dr. Dooley stated that relevant activities within the Shelf Seas Hydrography Working Group have included a very detailed process-oriented experiment and an examination of ways to monitor the systems in shelf seas. A problem with process-oriented studies, e.g., JONSDAP'76, is that they concentrate on conditions at a particular time of the year, providing no information on within-year variations or on year-to-year changes.

Dr. Dooley then described the plans for the SCAPINS (Summer Circulation and Production in the North Sea) study, which aims to look on a regional scale at physical processes that affect chemical and biological processes. Six regions of the North Sea have been identified for study but very few concrete proposals have been made for implementing the programme.

The Group then discussed programmes to collect data on nutrients, particularly in the North Sea, and report these data to ICES. It was noted that, despite several Council Resolutions, e.g., C.Res. 1976/4:6, that data on nutrients in the North Sea should be obtained and reported to ICES, very few data have actually been received by the ICES Secretariat.

Dr. Dooley then informed the Group about the plans for a Joint Multiship International Investigation of Patchiness in the Baltic Sea which will take place in April-May 1986, preceded by a preliminary experiment in 1985. The investigations will be carried out in the central southern Baltic Sea and will involve intensive measurements of a number of physical, chemical and biological parameters. ICES will serve as the project center for these investigations, coordinating the data handling and the preparation of time series charts.

In the discussion of the views of the Working Group members as to the general subjects the Group should address, a wide range of views was expressed. Some members felt that the Group should concentrate more on studies of the sea itself. As an example was mentioned the use of nutrient measurements taken over cross-sections of the sea to demonstrate the occurrence of marine processes which may be very important for fisheries; traditional nutrient analyses should be used as a tool to understand how physical processes affect biological processes. Other members

felt that marine chemistry has developed into its own science, far beyond the original use of chemical oceanography as an auxiliary science to physical oceanography. These members felt that marine chemistry has developed into the science of substances in the marine environment, including the description of the chemical composition of the sea and the various changes in chemicals (degradation, etc.) which occur there. Many members felt that the Group should carry out more work to evaluate the actual significance of the chemical data produced for the marine environment, regardless of whether the data are for nutrients, trace metals, organohalogens or other chemical constituents of the sea. In terms of how to handle such a broad range of subjects, many members felt that it would not be advantageous to split into two Working Groups, one on chemical oceanography and the other on marine chemistry. Rather they felt that there should be a large parent Working Group with many sub-groups with very clear terms of reference. This would enable the detailed work to be carried out at sub-group level, with more general discussion and review of sub-group work taking place in plenary sessions of the full Working Group. In terms of the general division of the work, about 50% to 60% of the Working Group's efforts should be devoted to responding to requests for advice forwarded to the Group by ACMP or a Standing Committee and approximately 40% of the work should be concerned with discussion of developments in marine geochemical issues and activities the Group wishes to stimulate.

In closing the consideration of this topic, the Chairman stated that he would take this discussion into account in further consideration of the subject in the ad hoc group on environmental Working Groups of the Consultative Committee.

8. INTERCALIBRATION AND QUALITY CONTROL ACTIVITIES

8.1 Trace Metals

The discussion of the agenda items concerned with trace metals took place (a) in the ad hoc Sub-Group on Trace Metals Analysis which met on 25 February, and (b) in the Trace Metal Sub-group of MCWG, which met for parts of the days of 27 and 28 February. A summary of the report of the ad hoc Sub-group on Trace Metals is contained in the following paragraphs and the full report of the Trace Metal Sub-Group is contained in Section 8B, below.

Dr. Topping, Chairman of the ad hoc Sub-Group on Trace Metals Analysis, summarised the outcome of this meeting, which had been held primarily to review in detail the results of Part A of the Seventh Intercalibration Exercise on Trace Metals in Biological Tissue (7/TM/BT) in relation to the conduct of the 1985 Baseline Study of Contaminants in Fish and Shellfish. The full report of this meeting is contained in C.M.1985/E:8. Dr. Topping stated that

the overall conclusions of 7a/TM/BT were that a good majority of the participants had produced reproducible and comparable data on copper, zinc, mercury and cadmium. However, many laboratories still have problems with lead at the ppm level and, of the few laboratories analysing for arsenic, only half were able to produce good results. He stated that the exercise had generally been very good and much had been learned from it. Based on the results obtained, Dr. Berman, Coordinator of the intercalibration, would prepare summary charts showing the performance of the laboratories in terms of precision and accuracy of analysis (see also Section 8B.2, below).

Dr. Topping stated that the ad hoc Sub-Group had also discussed the future requirements for quality assurance of data and had agreed that, rather than conducting periodic intercalibration exercises, a supply of uncompromised materials should be made available for use in normal laboratory quality assurance work. This would provide for continuous QA checks. At the end of an agreed period, the results of these analyses should be sent to a coordinator for evaluation and preparation of a report. (This topic is further discussed in Section 8B.1, below).

The ad hoc Sub-Group had discussed the location of trace metal reference stations for use for intercalibration purposes in connection with the Baseline Study of Trace Metals in Coastal and Shelf Sea Waters. Four such stations were agreed and the exact positions identified.

8.2 Organics

8.2.1 Report of 5/OC/BT

The results of the Fifth Intercalibration Exercise on Organochlorines in Biological Tissue (5/OC/BT), coordinated by Dr Uthe, and of a subsequent study of PCB congener determinations, coordinated by Dr. Reutergårdh, were considered at the meeting of an ad hoc Sub-Group on Trace Organic Compounds which met on 24 and 25 February under the chairmanship of Dr Reutergårdh. The full report of that ad hoc Sub-Group is contained in C.M.1985/E:7 and was summarised at the MCWG meeting.

8.2.2 Report of 2/HC/BT

Dr. Farrington, coordinator of the Second Intercomparison Exercise on Hydrocarbons in Biological Tissues (2/HC/BT), reported on the outcome of this exercise. The exercise had been carried out as a joint ICES/IOC intercalibration. Fifty laboratories from 24 countries had requested samples and 80% of these had submitted the results of their analyses. Dr Farrington pointed out that, while he had originally intended that the mussel tissue samples

should be distributed as wet, frozen homogenates, he later decided to freeze-dry the frozen homogenates to minimize the problems of transport. The freeze-drying, however, proved to have a significant effect on the samples, resulting in the loss of several compounds that would have been measured if analysis had been made of the wet frozen material. Another effect occurred with the freeze-drying, namely, it appeared to activate a site which absorbed some of the materials, so that analysis of the wet samples gave concentrations of these materials 2 to 3 times higher than for the freeze-dried samples.

The results of the intercalibration showed that the analysis of n-alkanes, chrysene, and pristane in biota exposed to weathered oil is very difficult and is not more accurate than that permitted by the UVF method.

Dr. Farrington stated that, in the light of previous similar exercises, the results of this intercomparison were encouraging. Future intercalibration work should concentrate on a smaller number of specific PAH compounds and should be more limited in terms of the different types of laboratories that participate.

In the discussion of this report, the question was raised as to the value of the UVF method. Dr. Farrington stated that UVF is a good technique for screening large numbers of samples to identify which samples to explore in depth. It was pointed out that there are many problems associated with the determination of these compounds, from matrix effects, which can contribute about 20% to 30% variance, to poor software in the computers of the GC/MS systems. Reference materials are very much needed to assist in the development of better methods.

In conclusion, the MCWG thanked Dr. Farrington and his colleagues for the excellent work in coordinating this exercise. It was noted that the final report on the results will be available in July 1985. Recognizing the serious need for reference materials for PAHs in biological materials, the MCWG requested its Organics Sub-Group to prepare a status report on the analysis of PAHs in biological tissues, stating that reference materials are needed to enable individual laboratories to develop their methods to an acceptable level.

8.2.3 Report of 3/HC/BT

Dr. Uthe, Coordinator of the Third Intercomparison Exercise on PAHs in Biological Tissues (3/HC/BT), stated that intercalibration samples had been sent out to 25 laboratories but only ten laboratories had returned results. He stated that the results showed interlaboratory errors so great that no meaningful statistics could be done. Not even mean values could be reported owing to the very wide ranges in results. Dr. Uthe stated that for future studies one must be very specific as to what compounds should be determined and what methods should be used.

The MCWG thanked Dr. Uthe for his excellent work in coordinating this intercalibration exercise and endorsed his recommendation that the analysis of PAHs should not be included in the 1985 Baseline Study of Contaminants in Fish and Shellfish.

8.2.4 Report of IOC/GEMSI Hydrocarbon Intercalibration Workshop

Dr. Ehrhardt described the results of this Workshop, which demonstrated that UVF measurements in sea water intercalibrate well even in areas where the concentrations are low. Synchronous scanning must be used, however, in addition to single quantitative measurements at 310/360 nm or certain types of oil contamination may be missed. This was illustrated by the example of diesel oil contamination in Hamilton Harbour encountered during this exercise.

It was reported that in the ocean water off Bermuda, where fluorescence as measured at 310/360 nm was very low, 2000 liters of water were pumped through XAD-2 resin and aliquots of the extract were analysed by GC/MS in three laboratories by Drs. Ehrhardt, A Knap and K Palmork. No unsubstituted PAHs were found, but traces of anthraquinone and photo-decomposition products, along with a number of chlorine compounds of undetermined structure and 2,5-hexanedione were found in the pg.l⁻¹ concentration range. This analysis is ongoing; a report of the basic exercise will be available in 1985.

8.3 Additional intercalibration and quality control activities

Dr. Law presented a status report on a UK Oil Pollution Research Unit intercalibration exercise for hydrocarbons in sediments. This exercise was now underway and the deadline for receipt of the results was 28 February 1985. A number of laboratories in ICES member countries were taking part. Twenty-eight sets of samples had been distributed and nine sets of results had been received by mid-February. Eleven samples were included in the intercalibration kits: 9 sediment samples and two oil samples. Analyses were being conducted for total aliphatic and aromatic hydrocarbons by gravimetry and by UVF, for specific and total aliphatics by capillary GC, and for specific aromatics by GC/MS. Dr. Law stated that the results will be submitted to ICES for information at the 1986 MCWG meeting.

Dr. Berman described new research materials available from the National Research Council of Canada (see also Annex 4). New research materials include CASS-1, a nearshore sea water certified for ten trace metals, and four solutions of chlorobiphenyls (52 in all) in iso-octane. In preparation are dogfish liver and muscle to be certified for trace metals and a set of four sediment samples to be certified for specific PAHs. It is also planned that a sample of St. Lawrence River water will be taken for use as a reference material.

Dr. Calder informed the Group about a quality assurance scheme designed for NOAA by an external group of experts. This programme is now being implemented and the programme documentation is now complete (see also Section 5, paragraph 3).

8A. FORMATION OF SUB-GROUPS ON TRACE METALS, ORGANICS AND CHEMICAL OCEANOGRAPHY

The Working Group decided to form sub-groups for each of the major subject areas to consider in greater detail aspects of analytical techniques, quality control of data, requests from the Oslo and Paris Commissions and other relevant items. Three Sub-Groups were formed, as follows: (1) Trace Metals Sub-Group (Chairman: Dr. Topping), (2) Organics Sub-Group (Chairman: Dr. Reutergårdh), and Sub-Group on Hydrography/Chemical Oceanography (Chairman: Dr. Pertilla). The Sub-Groups met concurrently for parts of the days of 27 and 28 February and prepared written reports on the results of their work. These reports, beginning with the specific terms of reference for the Sub-Group, are contained in their entirety in the next three sections as follows:

- 8B. Report of the Trace Metals Sub-Group
- 8C. Report of the Organics Sub-Group
- 8D. Report of the Sub-Group on Hydrography/Chemical Oceanography.

8B. REPORT OF THE TRACE METALS SUB-GROUP

The Trace Metals Sub-Group was requested to address the following questions or issues:

- (1) What additional standards or reference materials would be valuable for the determination of trace metals in marine materials?
- (2) What are the criteria for satisfactory performance in an intercalibration exercise?
- (3) Review the draft leaflet on sampling methods for trace metals in sea water.

- (4) Prepare a proposal for the conduct of an intercalibration exercise on analyses of Hg, Cd, Cu and Zn in estuarine water for JMG.
- (5) Consider the results of an intercomparison exercise on the determination of trace metals in suspended particulate matter.
- (6) Discuss an approach to the evaluation of atmospheric fluxes of metals to the sea.
- (7) Consider approaches to the estimation of net riverine inputs of trace metal contaminants to the ocean.

The results of the Sub-Group's consideration of these issues are contained in the following paragraphs, with the sub-sections numbered according to the number of the corresponding term of reference.

8B.1

In considering the additional standards or reference materials that would be valuable for the determination of trace metals in marine materials, the Sub-Group agreed that both (a) certified reference materials (CRM) (i.e., reference materials containing trace metal concentrations certified by an expert laboratory), and (b) uncompromised reference materials (URM) (i.e., reference materials for which trace metal concentrations are unknown to all but the coordinator) were needed and that (c) compromised, uncertified reference materials (CURM) would be available in many cases, e.g., surplus materials after an intercalibration exercise has been carried out.

It was agreed that the uncompromised reference materials (URMs) should be available for a fixed period of about 2 to 3 years. When a laboratory has analysed a sample of these materials, the results should be sent to the coordinator, who will make a report on all the results reported to him by the end of the fixed period. The surplus of samples could thereafter be used as CURMs. The ideal use of URMs would be to analyse them as normal samples several times during the 2- to 3-year period, together with the monitoring and other samples. In this way, a true check of the general performance of a laboratory can be made.

It was noted that the production and storage costs for uncompromised reference materials are only a little less than those for certified reference materials; accordingly, the URMs cannot be delivered free of charge.

The Sub-Group then discussed the types of reference materials required for sea water and biological tissues. Sediments were not discussed, as they will be covered by the Working Group on Marine Sediments in Relation to Pollution.

Sea Water

The certified reference materials from the National Research Council of Canada (NRCC) include the following:

- (1) an open ocean sea water sample that is now available;
- (2) a sample of nearshore seawater that will be available late in 1985;
- (3) a sample of St. Lawrence River water that will be available in early 1986.

In addition, the Sub-Group agreed that there is a need for the following CRMs:

- (1) filtered estuarine sea water (salinity 5-15) certified for all trace metals;
- (2) open ocean sea water certified for all trace metals;
- (3) filtered estuarine sea water (salinity 5-15) certified for mercury;
- (4) open ocean sea water certified for mercury.

The following uncompromised research materials were suggested:

- (1) open ocean sea water
- (2) nearshore sea water
- (3) estuarine sea water (salinity 5-15) for all trace metals and mercury, respectively.

Marine Biological Materials

The following marine certified reference materials are presently available:

NBS oyster tissue
NIES Mytilus edulis (Japanese)

NRCC has the following CRMs in preparation:

dogfish muscle
dogfish liver
lobster hepatopancreas

These samples are spray dried and acetone extracted. A non-acetone-extracted lobster hepatopancreas sample with lipid content intact is under preparation, but it is difficult to stabilize with such a high fat content.

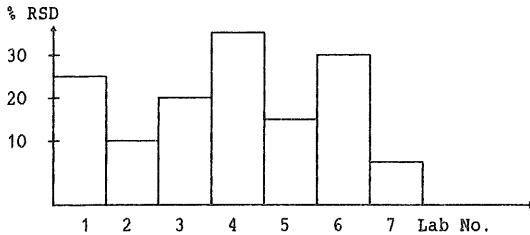
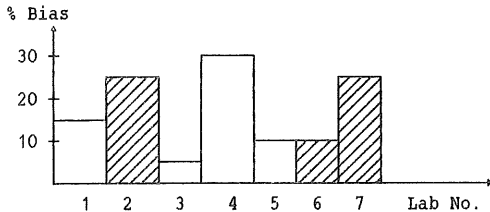
The following uncompromised research materials were proposed:

- mussel tissue
- fish muscle
- fish liver

All three samples should be prepared with both low and high concentrations of trace metals.

8B.2

It was noted that the Joint Monitoring Group had asked advice from ICES on the criteria for satisfactory performance in an intercalibration exercise. It was agreed that satisfactory performance must be based on deviation (bias) from the "true value" and the relative standard deviation (RSD) for each metal analysed in an intercalibration exercise. Several possibilities were suggested and discussed. It was ultimately agreed that the following figures demonstrate best the performance characteristics of the laboratories that have participated in an intercalibration:



The hatched columns indicate a negative bias. These two figures are required for every element, concentration level and matrix. Using the information contained in these figures, the persons evaluating the monitoring data will have to set the appropriate boundaries for adequate performance. It was felt that this must be done in relation to the actual purposes of the monitoring programme.

It must be realised that the performance indicated by these charts is only related to the types of materials and the

concentrations of metals studied, and that other matrices and concentrations can show a different level of performance by the same laboratory.

Dr. Berman agreed to produce charts similar to these on the basis of the results of ICES 7/TM/BT (Part A) and ICES 5/TM/SW (Fifth Round Intercalibration for Trace Metals in Sea Water).

8B.3

A draft leaflet on sampling methods for trace metals in sea water, which had been prepared by Dr. P A Yeats, was reviewed. The Sub-Group agreed that it was a relevant and useful leaflet which, after suggested amendments have been made, should be sent to ICES for publication in the Techniques in Marine Science series.

8B.4

It was noted that a request for the conduct of an intercalibration exercise on analyses of Hg, Cd, Cu and Zn in estuarine water had recently been made by the JMG to ICES. After some discussion, the Sub-Group agreed that the most experienced laboratory in this field is the Division of Chemistry of the National Research Council of Canada. Accordingly, it was proposed that Dr. Berman of this laboratory coordinate the exercise, including the preparation of samples, the evaluation of results and preparation of the final report. Dr. Cofino indicated that the Netherlands Rijkswaterstaat would probably offer to provide ship time for sampling and land-based laboratory facilities. Given that the JMG require relatively high concentrations of trace metals, it was agreed that sea water sampling should be carried out in an area such as the Western Scheldt Estuary. The JMG will be requested to indicate the ranges in concentrations of the trace metals that they wish to have and, on the basis of this and the knowledge of the river estuary, an appropriate sampling site will be selected. It was proposed that the sampling take place in April-May 1986 and that a preliminary report on the results be made available for discussion at the MCWG meeting in 1987. For this schedule to be followed, a proposal needs to be prepared for the joint meeting of the Oslo and Paris Commissions in June 1986 to approve appropriate funding for the exercise. As for previous intercalibration exercises carried out specifically for the Oslo and Paris Commissions, the financial arrangements should be made directly between the coordinating laboratory and the Commissions, while all scientific aspects, including the preparation of plans and the review of the report on the results, will go through the normal ICES review channels. A more detailed description of the proposed plans for this intercalibration is contained in Annex 3.

8B.5

Dr. Bowers orally presented a preliminary draft report of the results of the first intercomparison exercise on the analysis of trace metals in suspended particulate matter (SPM). This intercalibration had been carried out under the Working Group on Marine Sediments in Relation to Pollution with the participation of several members of MCWG. Samples of SPM had been analysed by eight experienced laboratories and very good results had been obtained. Coefficients of variation were generally in the 10% to 30% range. It was not, however, possible to distinguish between sampling and analytical variability. For this exercise, only ~1mg mg of SPM was obtained on each filter. If increased loads on the filters could be obtained, more laboratories would be able to take part in this work. It was noted that the good results obtained from this exercise indicate that the techniques have now advanced sufficiently to permit measurements to be made of contaminants associated with SPM in estuarine and coastal waters.

8B.6

It was noted that there has been a request from the Oslo and Paris Commissions for at least three years for ICES to prepare an approach to the evaluation of atmospheric fluxes of metals to the sea. Owing to other commitments of the persons who had promised to prepare a report on this subject, no report was available and the MCWG was not in a position to make any progress at this meeting. The MCWG was informed that the Paris Commission has established its own working group on atmospheric inputs, which has already met twice. Realising that sufficient expertise on this subject is not present among the members of MCWG, it was felt that this task should be handled in another forum. The most efficient way would be to convene a study group for this special project. Generally it was felt that if a request to a Working Group was beyond the terms of reference of that Group, the request should be handled by a more relevant group or a special study group should be convened.

8B.7

The Paris Commission has requested ICES to provide advice on methods for the estimation of net riverine inputs of trace metal contaminants to the ocean. The Sub-Group noted the statements contained in Annex 1 of the 1984 ACMP Report specifying three alternative approaches to the estimation of net river influxes. It felt that each of these approaches could usefully be applied and encouraged their application. The Sub-Group also noted that the metal/salinity relationships in the surface layer of the deep ocean were proving to be of interest in determining apparent zero-salinity end-member compositions and that this type of work fitted well with one of the approaches specified in the ACMP Report. Finally, it was again stressed that it is crucial that adequate information on gross riverine inputs be made available.

The Sub-Group urged ICES member countries to pay continued and increased attention to accurate measurements of river composition.

8C. REPORT OF THE ORGANICS SUB-GROUP

The Organics Sub-Group was requested to carry out the following:

- (1) Reconsider the selection of PCB congeners for primary attention in the determination of PCBs in marine biological tissues.
- (2) Specify the criteria which might make the selection of congeners for different marine materials different.
- (3) Propose how the preparation of replicates of a single batch of AROCLOR 1254 might be made available.
- (4) Determine if suitable numbers of frozen mussel homogenate samples might exist for interim quality control purposes.
- (5) Assess the situation with respect to PAH determinations
 - (a) in marine biological tissues
 - (b) in seawater
 - (c) in sediments.
- (6) Assess, to the extent possible, performance criteria for the measurement of PCBs and PAHs in marine materials.
- (7) Consider the relative importance of attention to lindane in contamination assessments.
- (8) Specify how a note on "good laboratory practice" might be prepared to provide information on how to implement routine quality assurance procedures in laboratories making determinations of organic contaminants.
- (9) In the light of the results of 2/HC/BT, 3/HC/BT and the IOC/GEMSI Bermuda Intercalibration on Hydrocarbons, determine whether it is possible to conduct an intercalibration for "petroleum" hydrocarbons in seawater, as requested by JMG. The Sub-Group should consider the proposal made by Brüggemann et al. in the June 1984 ACMP minutes.
- (10) Prepare a statement regarding the need for standards and reference materials for the measurement of PAHs in marine materials taking account of the concluding paragraph of the report of 2/HC/BT.
- (11) Consider "new" organic contaminants that might give rise to future environmental concerns, as requested by JMG.

- (12) Reconsider the previous ICES advice to JMG regarding the estimation of river discharge fluxes of organic contaminants and determine whether better or more specific advice on this topic can be provided by MCWG.

The full report of the Sub-Group's discussion of these issues is contained in the following sections.

8C.1

In response to the first two items, namely, to reconsider the selection of CBs for primary attention in the determination of PCBs in marine biological tissue and to specify the criteria where particular analytical attention may be required for different matrices, the Sub-Group reviewed the initial 7 chlorobiphenyls (CBs) proposed by M Kerckhoff (Doc. MCWG 1985/8.2) and other CBs included in the last two ICES intercalibration exercises and agreed to the following list, with the essential provisos concerning analytical criteria given thereafter:

Primary CBs which should be quantified

IUPAC Nos: 28, 52, 101, 118, 138, 153, 180

A further secondary list was proposed, depending on the sample source:

IUPAC Nos: 18, 31, 44, 66/95, 110, 149, 187, 170

Analytical criteria which should be observed

It was agreed that there were a number of CBs which could partially overlap in a normal linear temperature program CGC and that other CBs may be confounded by unknown co-eluting components. To minimise misidentification, the following information and guidelines should be observed.

<u>Peak Nr.</u>	<u>Potential overlapping peak</u>
28	31
118	149
153	105/132
18	15

These data are for an SE-54 stationary phase. Further information is available in Annex 4.

It was further recommended that for each batch additional analysis should be completed using two columns of different polarity. For confirmation in the critical regions of the chromatogram, a specific chromatographic program should be used to provide the necessary separation on a sub-sample from each batch. This may also be supported by GEMS, multiple ion monitoring where available.

Adequate column resolution should be checked on a regular basis using the accepted procedures of the laboratory concerned.

Examples of resolutions checks:

- (i) Separation of CB congeners 153/138 or 118/153
- (ii) Separation of homologous series, e.g. n-alkanes, n-trichloro-alkyl acetates, 2,6-dichlorobenzyl alkyl ethers.

The selection of criteria for particular CBs in different matrices is based primarily on individual/group expertise and cannot easily be expressed explicitly. The current literature is the best source of guidance, coupled with good chemical and analytical sense. When doubts cannot be resolved, then contact should be made with acknowledged experts in the appropriate field.

8C.2

In response to item 3, concerning the means by which a preparation of a single batch of Aroclor 1254 could be made available, the Sub-Group identified two sources of PCB technical mixtures:

1. A. Abarnou - Phenochlor DP⁵
2. J. Uthe - Aroclor 1254

It was agreed that individual batches should be warmed, mixed thoroughly and sub-sampled to provide 100 samples of 1g in a 5 ml glass vial with teflon seal. The whole batch prepared in Canada by Dr. Uthe should be shipped to Dr. Abarnou for distribution to laboratories who request these samples from ICES.

The ICES Secretariat should inform laboratories in ICES member countries when the material is available and thereafter transmit requests received to Dr. Abarnou.

8C.3

In response to item 4, to determine whether suitable numbers of frozen mussel homogenate samples could be made available for quality control purposes, the Sub-Group noted that according to the plans for the 1985 Baseline Study of Contaminants in Fish and Shellfish (contained in Annex 9 to the 1984 ACMP Report (Coop. Res. Rep. No. 132)) 20 laboratories have proposed to determine organochlorines, in tissues during 1985. If each of these 20 laboratories were to receive 5 packages of frozen mussel homogenate, a total of 100 packages would be required. This number of packages is presently available from the U.S. NOAA. The packages are in storage in Seattle, Washington in the laboratory of Dr. William MacLeod. To ensure that the packages remain frozen during transit, it is suggested that packages for European

laboratories be hand-carried to an ICES meeting at which most of the laboratories will be represented and then be transferred personally to the recipient laboratories. Laboratories must make a specific written request to ICES in order to receive the mussel homogenate samples. Accordingly, the ICES Secretariat should inform the laboratories participating in the organochlorine portion of the Baseline Study of the availability of this homogenate. The results of characterization analyses of the homogenate will be supplied with the samples.

8C.4

In response to item 7, to consider the relative importance of giving attention to lindane in contamination assessments, the Sub-group requested that any firm requirement by the Regulatory Commissions for analysis of lindane in any matrix be supported by a position paper clearly stating the background and justification for the request. This should include collated data currently available on levels in different environmental compartments, any known acute or chronic effects and measures to restrict usage and/or manufacture.

It was further suggested that such guidelines be adopted for any future requests on other contaminants.

8C.5

Concerning item 8, to specify how a note on "good laboratory practice" might be prepared to provide information on how to implement routine quality assurance procedures in laboratories making determinations of organic contaminants, it was felt that it was not the function of this group to educate laboratories on primary elements of good laboratory practice. Therefore, it was not recommended that MCWG become involved in preparing guidance papers on this topic, which is adequately covered in the literature. It was agreed that the following publications could be brought to the attention of laboratories involved in trace analysis and in any ICES intercomparison exercises. This list is merely a guide and is by no means exhaustive.

Keith, L H, Crummet, W, Deegan, J, Libby, R A, Taylor, J K, Wentler G. 1983. Principles of Environmental Analysis. Anal. Chem 55, 2210-2218.

Taylor, J K, 1984. Principles of Quality Assurance of Chemical Measurements (U.S. NOAA).

Griepink, B, 1984. Improving the Quality of Environmental Trace Analysis. Fresenius Z. Anal. Chem. 317, 210-212

Beyermann, K, 1984. Organic Trace Analysis. Ellis Horwood Ltd. (available in English and German). ISBN 0-85 312-638-0.

Additional references are listed in Annex 5.

8C.6

With regard to item 11, to consider "new" organic contaminants that might give rise to future environmental concerns, as requested by JMG, the Sub-Group recommended that any proposals on "new contaminants" to the MCWG for future consideration be supported by a position paper containing information currently available, either from the author's own studies or from the literature. This should be prepared and circulated before the appropriate MCWG meeting to facilitate a meaningful discussion.

8C.7

In response to item 12, to reconsider the previous ICES advice to the Paris Commission (TWG) regarding the estimation of river discharge fluxes of organic contaminants and then to determine whether better or more specific advice on this topic can be provided by MCWG, the Sub-Group felt that it had no direct information on this subject. It recommended that MCWG await the publication of the proceedings of the ICES/IOC/NOAA Symposium on Contaminant Fluxes Through the Coastal Zone (Nantes, May 1984). This question could also be addressed to other groups, e.g., GESAMP, GEMSI.

8C.8

The results of the Sub-Group's consideration of all items related to hydrocarbons (namely, items 5, 6, 9 and 10) were covered in a common statement addressing:

- (1) the current situation with respect to PAH determinations in marine biota, sediments and water.
- (2) the need for further intercalibrations on analyses of hydrocarbons in general and polycyclic aromatic hydrocarbons in particular.
- (3) the need for analytical standards for hydrocarbons and for research materials.

8C.8.1

In terms of the analysis of PAHs/hydrocarbons in biota and sediments, the Sub-Group agreed that the combined results of ICES 2/HC/BT and 3/HC/BT support the following recommendations and observations:

- (1) ICES should recognise that U.V. - fluorescence analyses of tissue extracts, sediments and sea water for hydrocarbons provide, at best, either (a) only general survey-type data identifying samples for more detailed analyses by more specific higher resolution methods, or (b) specific site monitoring for petroleum, e.g., a loading terminal or

production platform where the potential input source is well characterized periodically by more specific higher resolution methods, such as HPLC for PAHs or GC/MS (capillary column) for PAHs and other compounds.

- (2) ICES should recognise that analyses of individual alkanes (e.g., n-alkanes, pristane, phytane) provide reliable indications of contamination by petroleum only in limited cases of relatively freshly spilled oil input. Gas chromatographic analyses in the case of contamination of tissues by chronic, widely dispersed petroleum inputs and in the case of weathered spilled oil do not provide a quantitative indication of the degree of contamination by compounds of concern from the perspective of human health e.g., polynuclear aromatic hydrocarbons (PAH), or from the perspective of effects on organisms (e.g., mono- and di-aromatics).

ICES 2/HC/BT results showed that alkane measurements in a sample of tissue containing weathered/biodegraded petroleum are not very reproducible and are difficult to accomplish satisfactorily in the presence of the partially resolved and unresolved complex mixture of hydrocarbons in the sample. It is likely that this will be the case for many other species of organisms sampled in similar habitats. Due to the complex nature of the constituents in these extracts, the use of GC without MS cannot be recommended.

- (3) MCWG recognises that analysis of individual PAHs in tissues from marine organisms other than bivalve molluscs, and possibly selected crustacea and polychaetes, will not be an accurate measure of exposure to biologically available PAHs in the habitat because of the probability of induction of enzymes capable of metabolising PAHs.

From the perspective of human consumption of fish and shellfish, it is unclear at this time as to whether or not these metabolites produced by the enzyme metabolic activity are of concern from a human health perspective. In any case, the analytical methodology for quantification and identification of body burdens of metabolites is in a research and development stage.

- (4) Analytical methodology exists for precise measurements of selected individual PAHs in tissue samples, as demonstrated by the experience of the U.S.FDA (Food and Drug Administration) food analysis intercalibration for selected PAH compounds (using the method of Grimmev and Bohnke (J.Assoc. Off. Anal.Chem 38, 125-132)). Similarly, there is evidence (MacLeod et al., 1982, Anal.Chem. 54, 386-392) that the determination of PAHs in sediments can be improved by the use of a common analytical methodology.

- (5) There was a marked increase in the number of laboratories reporting PAH data for tissue analyses compared with the 1/HC/BT intercalibration (Law and Portman 1982, Cooperative Research Report No. 117). Thus, laboratories are willing to try these analyses. The poor comparability of results could be due to a number of factors such as: (a) inexperience with this type of analysis, (b) lack of standards and reference (research) materials, and (c) the pressure of other analytical work. While the results are disappointing in terms of not being satisfactory enough to include PAHs in coordinated monitoring studies, they are better in many respects compared with earlier published intercomparison exercises by the U.S. National Bureau of Standards (Wise et al. 1980. Anal. Chem. 52, 1828-1833). The results, unfortunately, represent the state of the art among the marine science/marine pollution monitoring laboratories.
- (6) Research materials analogous to those required for upgrading organochlorine analyses are also needed for PAH analyses. Such materials should contain, at a minimum, the list of PAHs requested for the 3/HC/BT exercise. The National Research Council of Canada is currently preparing four sediments as reference materials for PAH studies.
- (7) A fourth intercomparison exercise on PAHs should be considered for both a fish or shellfish oil matrix sample and a bivalve tissue homogenate, with the same reporting procedures requested as for the 3/HC/BT exercise or better. Participation should be open only to laboratories employing HPLC and/or GC/MS quantitation procedures. Qualification for participation in the exercise could be required in the form of satisfactory analysis of a standard solution of a suite of non-alkylated PAHs of unknown concentration and composition and submission of the required data and analytical methods for instrument operation. Only after achieving satisfactory ($\pm 10\%$) analysis of the PAH solution would a laboratory receive the more difficult fish or shellfish oil and tissue materials for analysis.

8C.8.2

Concerning the validity of UV-F analyses of organic seawater extracts the Sub-Group agreed that, based on the results of recent workshops on the intercalibration of measurements of oil residues dissolved/dispersed in seawater (Kiel 1981; Bermuda, 1984), it seems safe to conclude that such measurements can be made with a high degree of precision.

Except in cases of obvious contamination by petroleum residues, however, the nature of the fluorescent material may vary and frequently is unknown. Investigations on the chemical composition of lipophilic seawater extracts from the Baltic Sea have shown that pyrogenic PAHs account for most of the fluorescence signal observed in open waters. On the other hand, in seawater extracts

from off Bermuda showing a very weak fluorescence signal, no such compounds were found. Trace quantities of anthraquinone detected by GC/MS analyses of lipophilic material concentrated from large volumes (approx. 1600 litres) by adsorption onto Amberlite XAD-2 resin may have been responsible for the fluorescence signal.

That the fluorescence method as described in IOC Manuals and Guides No. 13 may have to be modified is suggested by another result of the Bermuda intercalibration exercise:

n-Hexane extracts of water from Hamilton Harbour, obviously contaminated with residues of fossil fuel, gave very weak fluorescence signals when excited with UV light at 310 nm as stipulated by the method. Synchronous scanning of excitation and emission wavelengths from 200 to 500 nm with a wavelength difference of 15 nm revealed that the excitation and emission maxima were shifted to shorter wavelengths and coincided with those of marine diesel fuel. Had chrysene been used as the reference material and emission been measured at 360 nm with 310 nm excitation wavelength, the erroneous conclusion would have been reached that the waters of Hamilton Harbour were practically free from contamination by oil residues.

It seems advisable, therefore, to extend UV-F measurements to include synchronous scanning of excitation and emission wavelengths. Certain information concerning the nature of the contaminating substances can thus be obtained with relative ease and reference materials can be chosen to reflect the actual situation.

8C.8.3

The Sub-Group had been requested to comment on the following proposed procedure that might enable a standard sample of hydrocarbons in water to be prepared and subdivided into replicate sub-samples for use in a round-robin intercalibration:

Gram quantities of oil energetically dispersed by ultra-sonic agitation and vortex mixing into litre quantities of seawater might be used to prepare a volume of water in which oil is present in both dissolved and dispersed (droplet) form. Subsequent high-speed centrifugation for extended periods could be used to remove excess dispersed oil fractions that are denser than water and repeated surface skimming should enable the removal of light fractions. With tight control of the conditions of mixing and separation of the light and heavy fractions, it might conceivably be possible to prepare duplicate standardized samples of oil/water mixtures from fixed volumes of oil and water. However, a better approach to the preparation of replicate samples would be to sub-sample a single resultant mixture into similar containers leaving enough space in each to allow the hydrocarbon extraction to be carried out within the sub-sample containers.

The Sub-Group felt that the approach taken in this proposal was not viable because:

- (a) the rate of and conditions for microbial decomposition of individual components of the oil standard are unknown. Thus, it is unclear whether or not the composition of the standard samples will change with time;
- (b) micro-droplets of the oil initially created by ultrasonication may coalesce to form a separate phase;
- (c) adsorption of the oil from the dispersed phase onto container walls and its time dependence are considered to introduce unpredictable changes in the concentration of the dispersed oil in the various sample vials.

The Sub-Group proposed, therefore, that large volumes (in the range of 10,000 litres) of sea water known to contain non-biogenic hydrocarbons, both aromatic and aliphatic, be passed through suitable filters for removing particles, and that the lipophilic constituents thus defined as dissolved and/or finely dispersed be adsorbed onto Amberlite XAD resin. The solvent eluate of the XAD resin column(s), representing a combination of natural and non-biogenic compounds found under normal environmental conditions, should be divided into the required number of portions which will be concentrated to less than 1 ml in a non-flammable solvent. The composition of the standard sample would have to be analyzed by the distributor and checked independently. Suitable compounds would be selected for intercomparison purposes. Flame-sealed into glass ampoules, these standard qualitative/quantitative samples would then be available for laboratories interested in an intercomparison exercise. The standard samples should be accompanied by a description of how to treat them before UV-F, GC and GC/MS analyses. The Sub-Group felt that this approach combined a number of desirable features:

- The material distributed for intercomparison reflects the composition of a natural seawater sample.
- The use of a non-aqueous solvent, possibly with antimicrobial properties, would prevent microbial decomposition. Chemical decomposition could be prevented by sealing under nitrogen in cold (-32^oC) amber vials.
- Small volume and weight of standard samples would facilitate shipment.
- The composition of the standard samples would ensure that intercalibrations are carried out under conditions to be expected in actual seawater analyses.
- The intercalibration exercise could be combined with basic research on the composition of lipophilic seawater extracts.

- The material could be used for trend analyses by eventual comparison with a similar sample taken at a later time at the same place under identical conditions.

8D. REPORT OF THE SUB-GROUP ON HYDROGRAPHY/CHEMICAL OCEANOGRAPHY

The Sub-Group on Hydrography/Chemical Oceanography was requested to carry out the following:

- (1) Consider progress in and new approaches to the estimation of net river inputs of nutrients to the ocean.
- (2) Assess the need for and role of nutrient measurements in patchiness studies.
- (3) Consider the relative importance of hydrography and chemical oceanography in the activities of MCWG.
- (4) Respond to the Oslo/Paris Commissions' request for advice on unusual plankton blooms.
- (5) Consider the proposed IAPSO intercalibration of total alkalinity standards.
- (6) Consider the need for improvement of nutrient analyses.

The report of the Sub-Group's consideration of these items is contained below, with sub-sections numbered according to the number of the corresponding term of reference.

8D.1

In terms of its first item, to consider progress in and new approaches to the estimation of net river inputs of nutrients to the oceans, the Sub-Group felt that MCWG was not competent on the topic of river inputs. This subject is usually studied by hydrologists, not by chemical oceanographers.

It realised, however, that river discharges are important for many reasons, e.g., mass balance calculations. For this reason, the Sub-Group expressed its concern about the fact that in many cases the analytical methods used by hydrologists are not wholly compatible with the methods used by oceanographers.

8D.2

In assessing the need for and role of nutrient measurements in patchiness studies, the Sub-Group noted that patchiness can be caused by biological or physical processes. In a patchiness study, physical processes, such as the influx of a new watermass to the study area, can be followed by means of frequent CTD controls. Since biological processes consume, and also produce, nutrients, nutrients, can be used as indicators of patchiness.

The following list of chemical parameters is recommended for determination in the context of a patchiness study:

Obligatory for all participants:

PO_4^{-3} , P_t , (NO_3^- and NO_2^-), pH, O_2 ,
chlorophyll, primary production

On a voluntary basis:

NO_2^- , NH_4^+ , SiO_4^{-4}

The reasons for this list are as follows. Phosphate, nitrate, nitrite and ammonium are all relevant to phytoplankton. Ammonium is readily consumed, but simultaneously excreted, by plankton thus making the changes in concentration difficult to detect. Since ammonium analyses on board ship are also easily affected by contamination, it is recommended that NH_4^+ should be included on a voluntary basis. Nitrate and nitrite are usually determined together by means of auto-analysers. Since the fraction of nitrite is generally negligible, and realising that analyses have to be carried out as quickly as possible, it is recommended that nitrite be included on a voluntary basis only.

Phosphate is the most important phosphorus nutrient and is easy to determine. Total phosphorus, together with phosphate, gives relevant information on the organically bound phosphorus. Most of the total nitrogen is very tightly organically bound in, e.g., humic substances, and cannot be used by plankton. The rest of N_t may exhibit patchiness variations, but because of its small fraction, the variations are difficult to detect. Silicate concentrations in the Baltic Sea are so high, ranging from about 30 μM in surface waters to 100 μM in deep waters, that the small variations due to plankton consumption are difficult to detect. For the first major patchiness study to be carried out in the Baltic Sea in 1986, it is not recommended that silicate or total nitrogen be determined.

In terms of the Patchiness Experiment in the Baltic Sea, the Baltic Monitoring Programme sampling depths should be followed at least through the halocline and, in addition, those depths at which primary production is measured. CTD runs should be carried out as often as practicable (possibly every hour) in order to detect changes in the water mass and changes in the halocline depth. The frequency of nutrient sampling depends on the capacities of the participating ships. If possible, sampling at 2-hour intervals is preferred.

Care has to be taken regarding the following pitfalls: artificial patchiness caused by diurnal variations (pH!), incoming watermasses, changes in halocline depth (for which reason the nutrient concentrations close to the halocline should be checked against salinity).

8D.3

In considering the relative importance of hydrography and chemical oceanography in the activities of MCWG, the Sub-Group noted that in the past, most of the official demands to MCWG have come from the ACMP or the Marine Environmental Quality Committee. However, it should be recognised that chemical parameters can be of help to hydrographers and physical oceanographers in following watermasses. Dissolved oxygen and elevated nutrient concentrations can be used to study the movements of stagnant conditions, which are difficult to follow otherwise. In 1984, a meeting sponsored by the Nordisk Kollegium of Physical Oceanographers was held in Reykjavik on chemical tracers and physical oceanography. The proceedings of this meeting will be published later this year. In addition, the study carried out by Prof. Ostlund, in which tritium was used to follow watermasses over long distances, highlights the possibilities of using chemical tracers. Biological oceanographers need hydrographical and chemical information to develop explanations for biological processes. The question of the amount of attention to be given to different aspects of chemical oceanography is for the whole of MCWG to consider, however, the Sub-Group felt that a more balanced distribution of efforts could be obtained by increasing the time spent in Sub-Group work.

8D.4

In discussing the Oslo/Paris Commissions' request for advice on unusual plankton blooms, the Sub-Group pointed out that this topic has been recognised as a problem of such importance that a Working Group on Exceptional Algal Blooms has been established to deal with certain aspects of the problem.

The Sub-Group noted that there seems to be some sedimentological evidence that these kinds of blooms have occurred in the geological time scale, and thus they may have both natural and man-induced causes. The need to predict such blooms is obvious. Normal conditions for a phytoplankton bloom are of course necessary, but in addition to that, one needs to know what triggers off the development of abnormal blooms. This triggering mechanism may be caused by even slight changes in physical, chemical and biological conditions during the bloom. These factors are still unknown to a large extent. This means that regular monitoring of chemical and hydrographical conditions is futile in predicting exceptional blooms, since it is not known what to look for. The Sub-Group supported the views expressed at the 1984 Statutory Meeting that extensive multidisciplinary scientific investigations should be carried out concerning the dynamics of plankton blooms. The Sub-Group also stressed the importance of including an adequate amount of chemical expertise in the Working Group on Exceptional Algal Blooms.

Concerning the role of MCWG, the Sub-Group felt that attention should be given to the analysis of toxins produced by species of toxic algae.

8D.5

In discussing the proposed IAPSO intercalibration of total alkalinity standards, the Sub-Group agreed that the IAPSO standard sea water was not suitable as a reference standard for alkalinity measurements. Thus, a new standard is needed, given that there are several reasons for requiring accurate alkalinity analyses, such as in studies of CO₂ processes and carbon fixation. According to the study by² Goyet *et al.*, a sodium carbonate solution, stored in glass ampoules, is stable enough to serve as an alkalinity standard, and the Sub-Group recommended its use.

The Sub-Group agreed that ICES should recommend that some laboratory, possibly that of Dr A Poisson, investigate the possibility (including financial cost) of preparing a set of sodium carbonate standards. This set could then be distributed among those laboratories that have shown an interest in alkalinity work, in order to carry out an interlaboratory check on the standard. An intercalibration exercise should only be carried out after this preliminary work has been completed.

8D.6

The Sub-Group then considered the need for improvement of nutrient analyses. Concerning nutrient standards, the Sub-Group was satisfied with the Sagami standards. It is normal for a laboratory to produce its own standards and to use the expensive Sagami nutrient standards only to check the laboratory standards.

With regard to nutrient analyses, the Sub-Group felt that the regular use of auto-analysers may weaken the accuracy of these analyses since the effects due to sample turbidity are no longer measured. A study should be carried out in order to evaluate the importance of the effect of turbidity on the results using auto-analysers. It was agreed that Mr Vagn Olsen (Danish Institute of Fisheries and Marine Research) should investigate the possibilities of carrying out such a study and report the results to the next meeting of the MCWG.

8E. CONSIDERATION OF SUB-GROUP REPORTS BY MCWG

The Chairman of each of the Sub-Groups reported on the results of the discussion of the items in the terms of reference, for consideration by the entire Working Group.

Concerning the report of the Trace Metals Sub-Group, the MCWG took note of the responses given to the various questions considered and approved the report for inclusion in the MCWG Report.

In the discussion of the Organics Sub-Group report by the MCWG, the question was raised as to whether a coordinating laboratory for the preparation of trace organic reference materials had been identified. The MCWG noted that such a laboratory had not been identified and that it may be difficult to find a laboratory to carry out this function, owing to the large amount of resources required to coordinate the preparation of reference materials. It was generally felt that the easiest way to have a near-term solution to this problem would be to use one of the existing standard organisations: National Research Council of Canada, U.S. National Bureau of Standards, Community Bureau of References (BCR) of the EEC, or the International Atomic Energy Agency. In this context, it was pointed out that a proposal has been made that IOC and UNEP coordinate a reference material programme. This topic is also being discussed in GEMSI, with the aim of providing a long-term solution to the problem.

The MCWG then discussed the issue of good laboratory practice. It was pointed out that this is a very basic problem in terms of obtaining reproducible and comparable results and that the problem begins at the very basic level of being able to weigh out small quantities of CBs reproducibly. The question was raised as to whether an intercalibration workshop could be useful to develop procedures of good laboratory practice, but it was generally felt that a workshop was not the right approach to gain better interlaboratory comparability at the level of the relatively good expertise involved here. The MCWG agreed that guidelines should be drawn up for quality assurance. The MCWG stressed that quality assurance procedures are costly; it may cost up to 20% of the analytical budget of a laboratory to carry out quality assurance, but this expenditure is necessary to ensure the appropriate quality of the data produced. It was also emphasized that there must be continuity in the analytical chemists, because of the length of time needed to train in the appropriate techniques.

In the discussion of the portion of the report regarding the problems associated with UV-F measurements of hydrocarbons in sea water, the question was raised as to whether a different fixed wavelength (e.g., 254 nm) could be used rather than the currently recommended 310 nm for excitation and 360 nm for reading. It was stated that a fixed wavelength could not be recommended; the use of synchronous excitation and reading is best. Another possibility would be to scan manually excitation wavelengths to find the area of maximum excitation because, while open water bodies have a maximum around 310 nm for excitation, closed water bodies will have a lower wavelength excitation maximum. When one scans excitation and absorption wavelengths synchronously, one can get a good idea of the types of hydrocarbons present in the sample before studying it in detail.

The question was raised as to why the Sub-Group did not deal with the term of reference on the estimation of river discharge fluxes of organic contaminants. While it was noted that some work has

been started on this subject, the general agreement was that the analytical problems associated with the determinations of organochlorine compounds must be solved before the study can begin of gross river water composition with respect to trace organics.

A question was then raised concerning the analysis of Lindane (γ -HCH) because the Joint Monitoring Group had recommended that Lindane be included in the Joint Monitoring Programme. In the discussion, it was noted that more complicated clean-up procedures are needed to separate Lindane during the clean-up step. While the identification is relatively easy, quantification is about as difficult as for PCBs. The use of Al/Si columns may cause an extra peak in the Lindane elution area. Dr. Uthe pointed out that the relative standard deviation for Lindane was 77% in 5/OC/BT and that the problems for measuring pesticides are as great as those for PCBs. The MCWG agreed that it could carry out work on the analysis of Lindane if the JMG so requests, but it might be preferable to finish the work on PCBs first.

The discussion of the report of the Sub-Group on Hydrography/Chemical Oceanography centered on the plans for the joint multi-ship investigation of patchiness in the Baltic Sea. It was noted that the selection of nutrients to be measured was particular for the Baltic Sea, owing to the fact that total nitrogen is tightly bound to the suspended particulate matter and cannot be used by plankton, and the concentration of silicate is so high that changes caused by its use by plankton are not detectable. In discussing possible studies of micro-patchiness, it was pointed out that different methods must be used to investigate inhomogeneity at smaller scales.

9. LEAFLETS AND OTHER PUBLICATIONS

9.1 Leaflets in Marine Science

The Environment Officer reported that the name of the leaflet series originally entitled "Techniques in Marine Chemistry" had been changed to "Techniques in Marine Science" to allow descriptions of biological methods to be included also. As was the case last year, there were still not enough manuscripts to begin the series. Only one manuscript, for a leaflet on analyses of low concentrations of lead and cadmium in biological tissues has been finalised, and two were under review: the leaflet on sampling methods for trace metals in sea water considered at this meeting and a leaflet on methods to measure primary productivity, prepared under the Biological Oceanography Committee.

The MCWG then discussed the value of these leaflets to the ICES community. Some members felt that they would be a poor duplication of better articles in the open literature. Others

felt that they could be useful to persons without easy access to this literature. After much discussion, it was finally agreed that the publication of leaflets should go forward on a trial basis. Methods should be described that have given good, intercomparable results and the value of the series would be assessed after a reasonable number of leaflets have been produced. The Working Group on Marine Sediments in Relation to Pollution should also be invited to contribute leaflets to this series. The leaflets should particularly deal with the sampling and analysis of trace metals in marine media.

Dr. Ehrhardt offered to prepare a leaflet on the cleaning and use of XAD resin for hydrocarbon analysis and Dr. Reutergårdh offered to submit a leaflet on the analysis of organochlorines. Dr. Berman agreed to continue efforts he had already started to have analysts with good methods for analysis of trace metals in sea water, as identified by 5/TM/SW, prepare detailed descriptions for inclusion in a leaflet. He also agreed to get descriptions of good methods for the analysis of trace metals in biological tissues, when 7/TM/BT has been completed. It was agreed that these draft leaflets should be submitted as soon as possible.

Dr. Dawson mentioned that IOC is also preparing descriptions of certain methods and suggested that the two Secretariats consult each other on the types of methods they are planning to publish.

9.2 ICES Data Reporting Formats - Contaminants in Sea Water

The Environment Officer stated that although a Draft Interim Reporting Format for Data on Contaminants in Sea Water had been prepared last year, it had been decided that this should only be used on an intermediate basis, pending a major review of the entire reporting system on hydrographic and hydrochemical data. The Environment Officer wished to identify a few MCWG members who would be willing to assist in this review procedure with the aim of developing an appropriate system for the reporting of data on contaminants in sea water. The following members agreed to provide assistance: Dr. Bewers, Dr. Carlberg, Dr. Jensen, Dr. Pertilla and Dr. Topping.

10. OVERVIEWS

10.1 Organosilicon Compounds

Dr. Kerckhoff stated that she had been unable to find a colleague who was willing to prepare an overview on organosilicons. She was uncertain as to whether she would be able to allocate time to prepare such a paper herself.

It was noted that GESAMP will review some information on this subject at its 1985 meeting.

10.2 Phthalate Esters

Dr. Law presented a paper he had prepared on "The Analysis and Occurrence of Phthalate Esters in the Marine Environment". This paper described the production and use of phthalate esters, the problems encountered in analysing for them, the mechanisms for their input to the marine environment, and the concentrations of some phthalate esters in various marine media.

After discussion of this paper, the MCWG accepted it for transmission to the ACMP, subject to the addition of several amendments. The MCWG expressed its appreciation to Dr Law for preparing this paper.

10.3 Phenols

Dr. Ehrhardt stated that it had not been possible for him to prepare an overview paper on phenols and he felt that work on this paper should be postponed owing to the difficulties of obtaining adequate data. He reported that current mass spectral libraries are inadequate for the identification of these compounds.

The MCWG then discussed the sources of these compounds and whether they really could be classed as contaminants. The question was raised as to whether they could be breakdown products of humic and fulvic acids and this was believed not to be impossible. It was noted that the great majority of data in the literature is for phenols in fresh water, with little or no marine data available.

10.4 Atmospheric deposition of metals

No paper on this topic was available for the MCWG.

10.5 Other overviews

Dr. Law reminded the Group that a paper on polynuclear aromatic hydrocarbons had been presented at the 1983 MCWG meeting and certain amendments had been requested. Subsequently the lead on the production of this paper had been taken over by Dr. A Moinet, but the paper produced by him was missing data specifically requested by MCWG. Dr. Law stated that he would prepare an appropriate paper on this subject, in collaboration with Drs. Farrington and Uthe, for discussion at the next meeting.

No additional overviews were presented.

11. NEW CONTAMINANTS

A report of the brief discussion of this topic, which took place in the Organics Sub-Group, is contained in Section 8C.6, above.

12. ANY OTHER BUSINESS

The Chairman asked for suggestions of topics to be discussed at the special Theme Session on Environmental Working Group Topics at the 1985 Statutory Meeting and a number of suggestions were given.

There was no other business.

13. RECOMMENDATIONS

The MCWG recommended that the reports on the results of 2/HC/BT and 3/HC/BT be published in the Cooperative Research Report series (Recommendation 1, Annex 7). Similarly, it recommended the publication of the results of Part A of 7/TM/BT in this series (Recommendation 2).

Referring back to the discussion of how to handle the request by the JMG for an intercalibration on analyses of mercury, cadmium, copper and zinc in estuarine waters (Section 8B.4, above, and Annex 3), the MCWG recommended that this exercise be carried out under the coordination of Dr S Berman, providing that satisfactory financial arrangements can be made with the Oslo and Paris Commissions (Recommendation 3).

The MCWG, recalling the discussion of the proposed IAPSO initiative for the development of a total alkalinity standard (Section 8D.5, above), recommended that ICES support this initiative and that an appropriate ICES-associated laboratory be included in the standardisation procedures for this material (Recommendation 4).

Taking note of the discussion of the need for organic reference materials reflecting the composition of lipophilic materials occurring in moderately contaminated sea water for the purposes of assessing hydrocarbon contamination (Section 8C.8.3) and of the offer of Dr. Ehrhardt to carry out the preparation of such materials, the MCWG recommended that Dr. Ehrhardt's laboratory be requested to undertake this work (Recommendation 5).

In addition, given the clear need for the preparation and distribution of (a) uncompromised research materials for use in the quality assurance programmes conducted by laboratories for analysis of trace metals in sea water and biological materials, and (b) certified reference materials for measurement of organic contaminants, especially chlorobiphenyls, in marine media, the MCWG recommended that ICES explore appropriate avenues for the

preparation and distribution of these materials, including financial support (Recommendation 6).

The Working Group then discussed its next meeting. Dr. Pertillä invited the Group to meet at the Institute of Marine Research in Helsinki and the Group accepted this kind invitation. It was agreed that the Group would meet for four days in February or early March, avoiding weeks 7 and 9, if possible. There was a discussion as to how much of the time should be spent meeting in sub-groups and it was generally agreed that two days should be spent in sub-groups, with the sub-group agendas sent out in advance.

In the discussion of topics to be covered, the questions regarding the reduction of coefficients of variation by monitoring contaminants at higher trophic levels to get a better signal to noise ratio was brought up. The MCWG agreed that this was a topic for the Working Group on Marine Pollution Baseline and Monitoring Studies in the North Atlantic (WGMPNA) and suggested that reviews of experience involving the use of avian as well as marine species should be prepared for the next WGMPNA meeting.

The MCWG agreed that for its 1986 meeting the following topics should be covered:

- (i) to consider what further progress may be made on the comparison of mass balance estimates for contaminant fluxes in the coastal zone following the results of the Symposium on Contaminant Fluxes Through the Coastal Zone;
- (ii) to review progress towards satisfying the need for reference materials in the marine chemistry community;
- (iii) to review the results of a study of the effects of turbidity on the measurement of nutrients using auto-analysers;
- (iv) to review and approve final plans for the conduct of an intercalibration of analyses of trace metals in estuarine waters for JMG; and
- (v) to evaluate the compatibility of marine chemical programmes in the ICES community with the broad objectives being formulated in such programmes as the Global Ocean Flux Study.

Another topic that could be considered was the preliminary results of the pilot study on patchiness in the Baltic Sea (PRE-PEX). It was suggested that the Hydrography Committee may also wish to request some work of the Group.

All business having been completed, the Chairman, Dr. Bewers, informed the Group that he will resign from the chair after this meeting. He stated that he had thoroughly enjoyed chairing the

Working Group and felt that it had done an enormous amount of work since it first met in 1979. He thanked all the members for their assistance during his term of office.

On behalf of the Group, Dr. Kerkhoff thanked the Chairman for his excellent work as Chairman. She noted that a good deal of progress has been made on work on trace metals and also on organics during his term of office and wished him good luck in his future work.

The Chairman then closed the meeting at 12.30 hrs on 1 March.

ANNEX 1

MARINE CHEMISTRY WORKING GROUP

Copenhagen, 26 February - 1 March 1985

AGENDA

1. Opening of Meeting
2. Adoption of Agenda
3. Report of the 72 Statutory Meeting
4. Reports of related activities
 - 4.1 Joint Monitoring Group of the Oslo and Paris Commissions
 - 4.2 Intergovernmental Oceanographic Commission
IOC/GIPME/GEMSI/GEEP
 - 4.3 Relevant GESAMP Working Groups
International Agencies
5. Reports on projects and activities in ICES countries
6. Requests for assistance/advice from regulatory commissions
7. Requests for assistance in hydrography
8. Intercalibration and quality control activities
 - 8.1 Trace metals
 - 8.1.1 Report of 5/TM/SW - mercury segment
 - 8.1.2 Report of 7a/TM/BT
 - 8.1.3 Plans for 7b/TM/BT
 - 8.1.4 Quality control in Baseline Programme
 - 8.1.4.1 Biological tissues
 - 8.1.4.2 Water
 - 8.1.5 Progress in 1/TM/SM
 - 8.1.6 Analysis of suspended particulate matter
for organics
 - 8.1.7 Progress in sediment intercalibrations
 - 8.1.8 Future needs/plans
 - 8.2 Organics
 - 8.2.1 Report of 5/OC/BT
 - 8.2.2 Report of 2/HC/BT

- 8.2.3 Report of 3/HC/BT
- 8.2.4 Report of 2/HC/MS
- 8.2.5 Report of IOC/GEMSI Hydrocarbon Inter-calibration Workshop
- 8.2.6 Proposal for intercalibration for hydrocarbons in water
- 8.2.7 Analysis of suspended particulate matter for organic substances
- 8.2.8 Future needs/plans
- 8.3 Additional intercalibration and quality control activities
- 8.4 Summary of short and long-range plans for future ICES quality control activities
- 9. Leaflets and other publications
 - 9.1 Leaflets in Marine Science
 - 9.2 ICES Data Reporting Formats - Contaminants in Seawater
- 10. Overviews
 - 10.1 Organosilicon compounds
 - 10.2 Phthalate Esters
 - 10.3 Phenols
 - 10.4 Atmospheric deposition of metals
 - 10.5 Other overviews
- 11. New contaminants
- 12. Any other business
- 13. Recommendations

ANNEX 2

LIST OF PARTICIPANTS

Abarnou A
IFREMER
Centre de Brest
BP 337 Brest
France

Asmund G
Geological Survey of
Greenland,
Østervoldgade 10
1350 Copenhagen K

Berman S
Div. of Chemistry
National Research Council
Ottawa, Ontario K1A 0R9
Canada

Bewers J M (Chairman)
Bedford Inst.of
Oceanography
Dartmouth, N.S. B42 4A2
Canada

Calder J
NOAA N/OMA 32
Ocean Assess.Division
Rockville, Maryland 20852
USA

Carlberg S. R.
Institute of Hydrographic
Research
National Board of Fisheries
Box 2566, S-40317 Gothenburg
Sweden

Cofino W
Govt. Inst. for Sewage &
Waster Water Treatment
P.O.Box 17
8200 AA Lelystad
The Netherlands

Dawson R
Intergovernmental Oceano-
graphic Commission UNESCO
7 Place de Fontenoy
75700 Paris
France

Dooley H
ICES
Palægade 2-4
DK-1261 Copenhagen K
Denmark

Duinker J C
Inst. für Meereskunde (Chemie)
Düsternbrooker Weg 20
2300 Kiel
Federal Republic of Germany

Ehrhardt M
Inst. für Meereskunde (Chemie)
Düsternbrooker Weg 20
2300 Kiel
Federal Republic of Germany

Farrington J W
Chemistry Dept.
Woods Hole Oceanographic Inst.
Woods Hole, MA 02543
U.S.A.

Fonselius S. H.
Institute of Hydrographic
Research
National Board of Fisheries
Box 2566, S-40317 Gothenburg
Sweden

Føyn L
Inst. of Marine Research
P.O.Box 1870
5011-Bergen-Nordnes
Norway

Gustavsson I
Swedish Environment
Protection Board
Laboratory for Coastal Research
S-17011 Drottningholm
Sweden

Huschenbeth E
Institut für Seefischerei
Palmaille 9
2000 Hamburg 50
Federal Republic of Germany

Jensen A
Marine Pollution Laboratory
Jægersborg Alle 1B
2920 Charlottenlund
Denmark

Kerkhoff M
Netherlands Inst. for
Fishery Investigations
P.O.Box 68, 1970 AB IJmuiden
The Netherlands

Law R
Fisheries Laboratory
Remembrance Avenue
Burnham-on-Crouch
Essex CMO 8HA
England

O'Sullivan M
Dept. of Fisheries & Forestry
Fisheries Res. Centre
Abbotstown, Castletknock
15 Dublin
Ireland

Olafsson J
Inst. of Marine Research
P.O.Box 390
Reykjavik
Iceland

Olsen O Vagn
Danish Inst. of Fisheries
and Marine Research
Charlottenlund Slot
2920 Charlottenlund
Denmark

Palmork K H
Inst. of Marine Research
P.O. Box 1870
5011 Bergen-Nordnes
Norway

Pawlak J (Rapporteur)
ICES
Palægade 2-4
DK-1261 Copenhagen K
Denmark

Perttilä M
Institute of Marine Research
P.O. Box 33
SF-00931 Helsinki
Finland

Reutergårdh L
The National Environmental
Protection Board (SNV)
The Special Analytical Section
Box 1302, S-171 25 Solna
Sweden

Tervo V
Institute of Marine Research
PB 33
SF-00931 Helsinki
Finland

Thibaud Y
IFREMER
B.P. 1049
Rue de l'Ile d'Yeu
44037 Nantes Cedex
France

Topping G
Marine Laboratory
P.O.Box 101, Victoria Road
Aberdeen AB9 8DB
Scotland

Uthe J F
Fisheries & Environmental
Sciences
Dept. of Fisheries & Oceans
POB 550, Halifax, N.S. B3J 2S7
Canada

Weichart G
Deutsches Hydrographisches
Institut
Bernhard-Nocht-Strasse 78
2000 Hamburg 40
Federal Republic of Germany

Wells D E
DAFS
Freshwater Fisheries Laboratory
Pitlochry, Perthshire
Scotland

ANNEX 3

INTERCALIBRATION EXERCISE ON THE DETERMINATION OF TRACE METALS IN ESTUARINE WATERS

Introduction

An intercalibration exercise for the analysis of trace metals in estuarine waters has been planned upon request of the Joint Monitoring Group of the Oslo/Paris Commissions (JMG). The request followed an evaluation of the results of the ICES Fifth Round Intercalibration for Trace Metals in Sea Water, during which it was suggested that the levels of metals in waters 30-40 km off St. Lazaire in the Bay of Biscay might be atypical of the levels prevailing at most of the JMP coastal and estuarine monitoring stations. The coordination has been delegated to Dr A Jensen (Marine Pollution Laboratory, Denmark) as representative of the JMG, Dr S Berman (National Research Council, Canada) on behalf of the performing laboratory and Dr W Cofino (Govt.Inst. for Sewage & Water Works, The Netherlands) representing the laboratory providing the research vessel.

The intercalibration exercise is intended for participation by all JMG laboratories as well as for other interested laboratories in ICES member countries. Additional participation by experienced laboratories with proven ability will be sought by the coordinators, in order to ensure that reliable estimates of the concentrations can be made for reference purposes.

Selection of Sampling Area and Trace Metals

The exercise will be performed on filtered and acidified water from the Scheldt or Rhine estuary. Analysis for Hg, Cu, Cd and Zn in the samples will be mandatory; the determination of other elements, in particular Pb, Ni and Cr, will be requested on a voluntary basis. The JMG meeting in January 1986 will be requested to indicate desired concentration ranges for Hg, Cu, Cd and Zn, and possibly to express a preference for the Rhine or Scheldt estuary as the sampling area. A suitable location for collection of the water will be determined with the aid of data on the characteristics of the water in the chosen estuary and a preliminary on-site survey.

Sampling

The National Research Council of Canada (NRCC) will provide sampling material, chemicals and containers, which all will be transported from Canada to the Netherlands. The collection of the samples will be performed by the NRCC with the assistance of the Rijkswaterstaat. This assistance comprises the providing of a ship for approximately one week, and laboratory facilities, including a clean working area with a laminar flow bench and an

AAS instrument with background correction. At least 400 litres of water will be collected and filtered through 0.45 µm filter membranes. Half of this will be required to prepare samples for the determination of mercury, the other half is needed for the samples for the analyses of the rest of the elements.

The water will be shipped in bulk to Canada. At the NRCC laboratories in Ottawa, the water will be blended and bottled in polyethylene (metals excluding Hg) and borosilicate containers (Hg). The interbottle homogeneity will be tested by NRCC prior to distribution.

It is intended to prepare 100 samples for the analyses of mercury and another 100 samples for the determination of the other elements. The latter will be supplied acidified in two-liter bottles. The samples for mercury will be contained in bottles with a smaller volume.

Sample Distribution and Data Manipulation

The samples will be distributed by NRCC, which will also undertake the receipt, compilation and evaluation of the results on behalf of ICES..

Time Schedule

A time table has been devised in order to make possible a discussion of the results and draft report at the MCWG meeting in February 1987. The following target dates are recommended:

June 1985	Approval by ACMP of the scientific design of the exercise.
June 1985	Approval by the Oslo and Paris Commissions of the proposal, including financial aspects.
October 1985	Determination of sampling period
January 1986	Indication by JMG of desired ranges for the concentrations of Hg, Cd, Cu and Zn; selection of the general location for sampling.
April/May 1986	Collection of water.
June 1986	Distribution of samples.
Aug./Sept. 1986	Deadline for providing results by participants.
February 1987	Presentation of a draft report at MCWG meeting for review and comment.

June 1987 Review of final report by ACMP, prior to transmission to the Oslo and Paris Commissions.

In order to be able to present a draft report at the 1987 MCWG meeting, it is imperative that the participants adhere strictly to the deadline for returning the results, which is presumably the end of August 1986.

Financial Aspects

It is anticipated that the National Research Council of Canada and the Rijkswaterstaat of the Netherlands will not charge for personnel costs. The NRCC will request reimbursement of the additional expenses, comprising bottles, chemicals, shipping, mailing, travelling and lodging. It is expected that four people from the NRCC will need to travel to the Netherlands for sampling. The total cost is estimated to be about 15,000 US dollars.

Summary of Activities

Dr. Jensen will handle the contacts with the Commissions.

Dr. Berman will coordinate the acquisition of chemicals and materials for the sampling, shipping, preparation and distribution of the samples, and for the receipt, compilation and evaluation of the results.

Dr. Cofino will arrange the ship and land-based laboratory facilities, provide a description of the ship to Dr Berman, and data from Rijkswaterstaat for the potential sampling areas.

It is stressed that this program is preliminary, and has to be approved by the Canadian and Dutch authorities.

ANNEX 4

CERTIFIED REFERENCE MATERIALS

Information on certified reference materials prepared by the Marine Analytical Chemistry Standards Program (MACSP) of the National Research Council of Canada (NRCC) is contained in this Annex.

A nearshore seawater certified for ten trace metals, designated as CASS-1, was issued in January 1985. A brief description of this material is given later in this Annex.

Mixtures of individually prepared chlorinated biphenyl (PCB) compounds in iso-octane will be offered in spring 1985. Designated as CLB-1, the materials consist of a total of fifty-one pure synthetic chlorinated biphenyl congeners divided into four mixtures, each compound having been characterized by proton nuclear magnetic resonance, mass spectrometry, and, where necessary, C-13 NMR.

The retention time and response factor of each PCB congener were established using capillary gas chromatography and electron capture detection. This information was used to select compounds suitable for each mixture, and to select concentrations to result in approximately equal response for each congener mixture.

A short description and information regarding the availability of CLB-1 is contained later in this Annex.

A sample of dogfish muscle and another of dogfish liver are in preparation as candidate marine biological tissue reference materials for trace metals. These are spray dried and acetone extracted samples. They will be bottled this spring and should be available by the end of the year.

A sample of St. Lawrence River water will be collected, filtered and bottled in the early summer. It should be certified with respect to trace metals content and available by next winter.

Attempts to produce a lobster hepatopancreas material with lipid content intact as a companion reference material to TORT-1 which had been acetone extracted have not been successful to date. The main problem is the inability to stabilize a material with such a high fat content. Work continues on this project because it is felt that such a material would more closely simulate samples analyzed in a marine laboratory.

A set of four harbour sediments and one estuarine sediment for determinations of polycyclic aromatic hydrocarbons (PAH) are scheduled to be issued later this year.

There are two new reports available in the MACSP report series: Available Standards for Use in the Analysis of Marine Materials by D.S. Russell (No.8) and The Analysis of Organic Compounds in Seawater, 1978 - 1983 by B.G. Whitehouse, C.C. Parrish and P.J. Wangersky (No. 9). The latter is an update of an earlier report (No.3) issued in 1977.

Two Canadian intercomparison exercises have been carried out over the past six months. These have involved the determination of trace metals in marine sediments and marine biological tissues, respectively. Forty-one laboratories participated in the sediment study, and forty-three in the biological material study. A preliminary report has been issued for the sediments and the report for the biological materials should appear before the end of March 1985. Copies of the final reports will be sent to members of this working group later this year.

Detailed description of CASS-1, a nearshore seawater reference material for trace metals:

The seawater is a nearshore sample gathered at the 15 metre level, 400 to 800 metres off the Nova Scotia shore about 10 kilometres south of Halifax harbour. The salinity is 31.8.

The seawater was filtered through 0.45 μm porosity filters, acidified immediately with nitric acid to pH 1.6, blended and bottled in 2-litre quantities in polyethylene.

The following table gives those elements for which reliable values have been established. Reliable values are based on the results of determinations by at least two independent methods of analysis. The uncertainties represent 95% tolerance limits for an individual subsample. That is, 95% of samples from any bottle would be expected to have concentrations within the specified range 95% of the time.

Micrograms per Litre

Arsenic	1.04	\pm	0.07
Cadmium	0.026	\pm	0.005
Chromium	0.118	\pm	0.021
Cobalt	0.023	\pm	0.004
Copper	0.291	\pm	0.027
Iron	0.873	\pm	0.076
Lead	0.251	\pm	0.027
Manganese	2.27	\pm	0.17
Nickel	0.290	\pm	0.031
Zinc	0.980	\pm	0.099

Samples are available from the

Marine Analytical Chemistry Standards Program
Division of Chemistry
National Research Council
Montreal Road
Ottawa, Canada K1A 0R9

The cost is \$109 for a 2-litre bottle or \$270 for three 2-litre bottles (Canadian funds for Canada, U.S. funds elsewhere), shipping costs included. Orders for three bottles may include any combination of CASS-1 and the open ocean seawater reference material NASS-1 at the same price.

For further information contact Dr. Shier Berman at the above address. Telephone: (613) 993 2043, TELEX: 053-3145.

Detailed description of CLB-1, mixtures in iso-octane of individually prepared chlorinated biphenyl (PCB) compounds:

CLB-1 is a set of four mixtures (CLB-1-A, -B, -C, -D) of pure, synthetic chlorinated biphenyls (PCB) in iso-octane. The set includes 51 synthetic, chlorinated biphenyls of established identity. The composition of each mixture was selected to assure easy chromatographic resolution of components. Each mixture in the set contains a group of 15 or 16 chlorinated biphenyls, including where possible the compounds with IUPAC nos. 15, 153 and 209. To help assess the resolution of the separation chromatography, each mixture contains a pair of congeners which elute closely.

Exactly 1.0 ml of iso-octane solution with PCB is contained in each glass ampoule. The concentrations of congeners range from 1.2 µg/ml (IUPAC no. 159) to 139 µg/ml (IUPAC no. 15). Dilution of the total contents of the ampoule to 100 ml yields a solution with concentration levels suitable for capillary column chromatography with electron capture detection. Without dilution, concentrations are suitable for GC/MS. The concentrations of congeners in each mixture have been selected so all components give responses of similar amplitude in an electron capture detector.

Mixture "D" contains the group of chlorinated biphenyls which were tentatively determined in reference marine sediments HS-1 and HS-2. Documentation included with CLB-1 predicts probable interferences from co-eluting congeners as a function of chromatographic resolution.

CLB-1 is available from:

Marine Analytical Chemistry Standards Program
Atlantic Research Laboratory
National Research Council Canada
1411 Oxford Street
Halifax, NS B3H 3Z1

The cost is \$100 for the set of 4 ampoules (CND \$ in Canada and US funds elsewhere). Requests for samples should be accompanied by either a money order in favour of the Receiver General for Canada (credit NRC), or an official purchase order.

For further technical information write to Dr. Roger Guevremont at the above address or telephone (902) 426-8280.

ANNEX 5

LIST OF PAPERS ON GOOD LABORATORY PRACTICE WITH REFERENCE TO
DETERMINATIONS OF TRACE ORGANIC COMPOUNDS

- Anon., 1976. Pesticides. G.C. analysis and standards. Supleco Inc. Bull. No. 758B, Bellefonte, PA. 12 p.
- Anon., 1976. Pyrossep S-1 Septum. Supelco Inc. Bull. No. 769A, Bellefonte, PA. 2 p.
- Anon., 1978. G.C. Septa. Supelco Inc. Bull. No. 780A. Bellefonte, P.A. 7 p.
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ANNEX 6
ACTION LIST

The following intersessional activities have been agreed by the Working Group:

1. Dr. Reutergårdh has agreed to produce a paper comparing the results obtained when monitoring organochlorines in herring and in guillemot eggs (see Section 5, para.6).
2. Dr. Uthe has offered to prepare an overview paper on the use of organisms for monitoring purposes based on the Canadian experience (see Section 5, para.6).
3. Mr. Vagn Olsen has agreed to coordinate a study on the effects of sample turbidity on the measurement of nutrients using auto-analysers (see Section 8D.6).
4. Dr. Berman has agreed to produce charts showing laboratory performance, in terms of relative standard deviation and relative bias, based on the results of the Fifth Round Intercalibration for Trace Metals in Sea Water (5/TM/SW) (see Section 8B.2, last paragraph).
5. Dr. Abarnou has agreed to distribute samples of Phenochlor DP5 and Aroclor 1254 to laboratories who request these samples (Section 8C.2).
6. Dr. Ehrhardt has agreed to prepare a leaflet on the cleaning and use of XAD resin for hydrocarbon analysis and Dr. Reutergårdh has offered to submit a leaflet on the analysis of organochlorines (Section 9.1, paragraph 3).
7. Dr. Berman has agreed to obtain detailed descriptions of several of the good methods identified on the basis of 5/TM/SW and 7/TM/BT for publication in the leaflet series (Section 9.1, paragraph 3).
8. Dr. Law has agreed to prepare, with the assistance of Dr. Farrington and Dr. Uthe, an overview paper on PAHs in the marine environment (Section 10.5).

ANNEX 7**RECOMMENDATIONS**Recommendation 1

The Marine Chemistry Working Group recommends that the reports on the results of the Second and Third Intercomparisons on Hydrocarbon Analysis in Biological Tissue, by Dr J W Farrington, Dr A Knap, Dr J F Uthe and co-authors, be published in the Cooperative Research Report series.

Recommendation 2

The Marine Chemistry Working Group recommends that the results of Part A of the Seventh Intercalibration on Trace Metals in Biological Tissue, by Dr S Berman, be published in the Cooperative Research Report series.

Recommendation 3

The Marine Chemistry Working Group recommends that ICES offer to conduct an intercalibration exercise on analyses of high concentrations of mercury, cadmium, copper and zinc in estuarine waters, as requested by the Joint Monitoring Group, to be coordinated by Dr S Berman (Canada), subject to suitable arrangements being made for the recovery of expenses incurred by the Coordinator.

Recommendation 4

The Marine Chemistry Working Group supports the IAPSO initiative for the development of a total alkalinity standard and recommends that an appropriate laboratory (Dr A Poisson, Université Pierre et Marie Curie) be included in the standardisation procedures for this material.

Recommendation 5

The Marine Chemistry Working Group, recognising the need for organic reference materials reflecting the composition of lipophilic material occurring in moderately contaminated sea water for the purposes of assessing hydrocarbon contamination and noting that the expertise required for preparing such standards is available at the Department of Marine Chemistry, Institut für Meereskunde, Kiel, recommends that this laboratory undertake the preparation of these reference materials.

Recommendation 6

The Marine Chemistry Working Group, having identified a clear need for the preparation and distribution of

- (i) uncompromised research materials for use in the quality assurance programmes conducted by laboratories for analysis of trace metals in sea water and biological tissues, and

- (ii) certified reference materials for measurement of organic contaminants, especially chlorobiphenyls, in marine materials,

recommends that ICES explore appropriate avenues for the preparation and distribution of these materials, including financial support.

Recommendation 7

The Marine Chemistry Working Group recommends that it meet for four days in February or early March 1986 in Helsinki with the following terms of reference:

- (i) to consider what further progress may be made on the comparison of mass balance estimates for contaminant fluxes in the coastal zone following the results of the Symposium on Contaminant Fluxes Through the Coastal Zone;
- (ii) to review progress towards satisfying the need for reference materials in the marine chemistry community;
- (iii) to review the results of a study of the effects of turbidity on the measurement of nutrients using auto-analysers;
- (iv) to review and approve final plans for the conduct of an intercalibration of analyses of trace metals in estuarine waters for JMG; and
- (v) to evaluate the compatibility of marine chemical programmes in the ICES community with the broad objectives being formulated in such programmes as the Global Ocean Flux Study.

The Environment Officer should take part in this meeting.