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REPORT OF THE MARINE CHEMISTRY WORKING GROUP

Copenhagen, 16 -20 February 1987

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REPORT OF THE MARINE CHEMISTRY WORKING GROUP

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1 OPENING OF THE MEETING

The Chairman, Dr G. Topping, opened the meeting at 9.30 hrs on 16 February 1987 and welcomed the participants. Each member then introduced him- or herself, indicating the main areas of research interest and responsibilities in marine chemistry and marine pollution studies.

2 ADOPTION OF AGENDA

The Working Group reviewed the draft agenda, prepared and distributed by the Chairman, and adopted it without change. The Agenda is attached as Annex 1 and the List of Participants at the meeting is given in Annex 2.

It was agreed that items 3-6 would be dealt with in plenary and item 7 - Sub-group Sessional Activities - would be dealt with in detail within the respective sub-groups, followed by a discussion of the reports of each sub-group in plenary. Items 9 and 10 would, as usual, be dealt with in plenary.

Membership of the respective sub-groups was as follows:

Chemical Oceanography

H. Dooley (part time), S.H. Fonselius (Chairman), L. Føyn, D. Kirkwood (Rapporteur), M. O'Sullivan, and O. Vagn Olsen.

Organics

J. de Armas, J.A. Biscaya, J. Calder, M.G. Ehrhardt, K. Granby, J. Klungsøyr, R. Law (Rapporteur), M. Marchand, E.L. Poutanen, L. Reutergårdh (Chairman), J. Uthe, and D. Wells.

Trace Metals

G. Asmund, S. Berman, W. Cofino (Chairman), U. Harms, J. Olafsson, S. Wilson, and P. Yeats (Rapporteur).

3 REPORT OF 74TH STATUTORY MEETING

The Chairman reported that the status of the Working Group was discussed at the 1986 Statutory Meeting and it was agreed that the MCWG should report to whichever Standing Committee was most appropriate for each issue, but the Hydrography Committee will remain the nominal parent.

The Working Group then reviewed the tasks assigned to it by the Council and decided which sub-group should handle each task in the first instance. The Working Group had also been requested to review several sections of a draft Irish Sea Status Report.

A list of 1986 Council Resolutions on environmentally related topics was presented and it was noted that several changes had been made in relation to working groups dealing with these topics (see Section 4.3, below).

4 REPORTS OF RELATED ACTIVITIES

4.1 JMG of the Oslo and Paris Commissions

The Environment Officer gave an overview of the meeting of the Joint Monitoring Group (JMG) that had taken place the previous month. The JMG had reviewed the draft report on the results of the Sixth Round Intercalibration on Trace Metals in Estuarine Water, which had been carried out at its request, and expressed disappointment at the fact that many JMP laboratories which had received samples had not returned results to the coordinator. The JMG was also disappointed that the results of the exercise had not shown improvement over the results achieved in 1982 in 5/TM/SW. The JMG discussed possible definitions of "good performance", but was not able to agree on a numerical definition. However, it was agreed to stress the use of good laboratory practice, including keeping analytical control charts and checking analytical procedures against certified reference materials.

The JMG took note of the ICES advice on the feasibility of conducting an intercalibration exercise on γ -HCH but decided that this should not be considered a priority activity. Similarly, the ICES advice on the feasibility of conducting an intercalibration exercise for petroleum hydrocarbons in sea water was considered and it was agreed that it was not necessary for such an exercise to be conducted. Finally, the ICES advice on the feasibility of conducting an intercalibration exercise on the analysis of PCBs in sediments was reviewed and the JMG agreed to recommend to the Commissions that they should financially sponsor such an intercalibration. ICES was requested to identify a suitable coordinator.

The JMG reviewed the results of the assessment of the JMP data on contaminants in fish and in sea water for temporal trends. The ICES advice on statistical models for assessing temporal trend data on contaminants in fish was accepted, but no statistical techniques were proposed for estimating temporal trends in sea water. The ICES advice on the determination of the lipid content of cod livers was accepted.

The JMG discussed monitoring nutrient concentrations in sea water, which will be conducted on a voluntary basis beginning in 1987. These measurements should be carried out in winter, at a minimum. The JMG agreed that all relevant nutrient data should be submitted to the JMP data center at ICES by 1 May each year, using either the Reporting Format for Contaminants in Sea Water or the ICES Hydrography/Hydrochemistry Data Format.

In the discussion of the topics from the JMG meeting, the MCWG noted that there is not enough information on the impact of the lipid content of tissues in conducting temporal trend assessments to be able to indicate the best type of lipid determinations.

This can only be answered by testing statistical models on appropriate raw data sets.

With regard to the discussion of 6/TM/SW, the MCWG expressed disappointment that the manpower costs of this intercalibration were not appreciated by the JMG, both in terms of the costs incurred by the Canadian government as well as those of the Netherlands government, who provided the ship used for sampling and some land-based facilities.

4.2 IOC

The MCWG was briefly informed about recent activities of relevant IOC groups of experts, including the Group of Experts on Methods, Standards and Intercalibration (GEMSI), the Group of Experts on the Effects of Pollutants (GEEP), and the new Group of Experts on Standards and Reference Materials for Marine Chemistry. The first meeting of this latter Group had been held the previous week and it was agreed that specific issues from that meeting should be addressed by the relevant MCWG sub-groups.

4.3 ICES Working Groups

The MCWG was informed that the following new Working Groups had been established at the 1986 Statutory Meeting, some of which had formerly been study groups or ad hoc groups: the Working Group on Environmental Assessments and Monitoring Strategies, the Working Group on the Biological Effects of Contaminants, the Working Group on the Statistical Aspects of Trend Monitoring, and the Working Group on the Baltic Marine Environment. This latter group represents a merger between two former groups, namely, the ICES/SCOR Working Group on the Study of the Pollution of the Baltic and the Working Group on the Coordination of Hydrographic Investigations in the Baltic.

Noting these new groups, the MCWG agreed that it was necessary to establish a good coordination between working groups to carry out certain activities, especially intercalibration exercises.

4.4 Other Relevant Activities

Dr Cofino informed the Group about the EUROTRAC programme, which is concerned with European research on the transport and transformation of environmentally relevant trace constituents in the troposphere. It includes:

- studies on wet and dry deposition and reaction processes;
- the development and application of numerical atmospheric models;
- the registration of emissions in Europe;
- the development of instruments for detection.

Dr Cofino also gave information on the EUROMAR project, which is a European marine research project with an emphasis on technology and methodologies. An international steering group coordinates this work, in which ten European countries participate.

Working groups have been established covering the following fields: (1) remote sensing, (2) models, (3) data systems, (4) mesocosms, (5) research vessels, (6) physical instrumentation, (7) biological and chemical instrumentation, and (8) atmospheric input.

The Working Group took note of this information with interest.

5 REPORTS ON PROJECTS AND ACTIVITIES IN ICES COUNTRIES

Dr Berman gave information on new certified reference materials that have been issued during the past year by the National Research Council of Canada. These include (a) trace metals in river water, (b) trace metals in dogfish muscle and liver, (c) trace metals in sea water (NASS-2, to replace NASS-1 which is depleted), and (d) 16 priority PAHs measured in four types of marine sediments. Tin values have now been certified in previously issued tissue and sediment reference materials. Several new materials are presently under preparation.

It was noted that the U.S. National Oceanic and Atmospheric Administration has prepared a looseleaf publication entitled "Standard and Reference Materials for Marine Science", which describes materials presently available. This book has a limited distribution as only 100 copies have been printed.

Dr Cossa informed the Group that a three-year monitoring programme was begun in 1986 to study contaminant concentrations in fish from the Bay of Biscay and the English Channel. The concentrations of As, Pb, Cd, Cu, Zn, Sn, Hg, methyl-Hg, and PCBs are measured in the muscle tissue and liver of 24 species of fish. A final report on the results will be available in 1989. This programme is conducted by IFREMER and supported by the French Department of the Environment.

6 REQUESTS FROM ACMP AND REGULATORY AGENCIES

The Working Group reviewed the relevant requests from the Oslo and Paris Commissions and agreed that all of them would be discussed under the most relevant agenda items. These requests had generally been reflected in the additional items added to the terms of reference for this MCWG meeting, as proposed by ACMP at the 1986 Statutory Meeting, except for a potential new request for a method to estimate net river inputs that had been raised at the recent JMG meeting.

7 SESSIONAL SUB-GROUP DISCUSSIONS

7.1 Trace Metals

7.1.1 ICES baseline studies of metals in fish, shellfish and coastal and shelf waters

Dr Harms presented a brief report on the outcome of the joint ICES/OSPARCOM/HELCOM meeting concerned with the results of the baseline study of metals in fish and shellfish. A more detailed report of this meeting, convened by Dr J. Portmann, is to be presented to the Statutory Meeting in 1987 and will be reviewed by the new ICES Working Group on Environmental Assessment and Monitoring Strategies.

Dr Harms stated that the aims of the meeting had been to assess geographical distribution of contaminants and to examine area to area variability. A large number of data sets for several types of biological materials had been reported, but there had not been enough data for good statistical analysis. The results of the intercalibration exercise for metals in tissue (7/TM/BT, Part 2) had been used to provide a basis for accepting or rejecting data, but a good deal of subjective assessment based on a common sense approach had also played a role in the evaluation of these data. The lessons learned from this exercise from an analytical chemistry viewpoint are presented under 7.1.2 by Dr Berman.

Dr Topping, the Convener of a Sub-group of MCWG which had recently carried out a preliminary review of the data on trace metals in coastal and shelf sea waters submitted to ICES, presented a brief report on the approach to and findings of this review. He stated that the aims of the review were to assess the spatial coverage and quality of these data. The Sub-group had used the following guidelines or information for the assessment: (a) data from reference stations, (b) data from intercalibration exercises, (c) the Sub-group's experience of these types of measurements, and (d) data from different laboratories for the same area. This preliminary, and to some extent subjective, review had shown that a number of laboratories had reported acceptable data for some of the coastal and estuarine areas of the NorthSea and adjacent waters. The data from other laboratories could well be acceptable but lack of information concerning (a) laboratory performance, i.e., intercalibration results, (b) reference station data, and (c) data on the salinity of sea water samples, prevented the Sub-group from assessing these data. A draft of the report on this review was examined by the trace metal Sub-group and suggestions were made for changes to the text and tables.

7.1.2 Intercalibration exercises for trace metals in tissue (7/TM/BT) and sea water (6/TM/SW)

Dr Berman, the coordinator of both exercises, presented a summary of the findings of these exercises. He spoke about the lessons learned, the implications for ICES and JMG, who were conducting monitoring programmes, and the future steps laboratories would have to take if they were to maintain and improve data quality.

An account of his analysis and recommendations is given in Annex 3.

The Sub-group agreed that laboratories should place more emphasis on quality assurance and adopt good laboratory practice, including the use of control charts to monitor laboratory performance. Improvement in contamination control was necessary and the use of reference materials for checking laboratory performance was stressed by the Sub-group. Checks on laboratory performance were only part of a sound quality assurance programme. It was equally important to ensure that sample collection, storage, and preparation were rigidly checked for sources of contamination and variability. Dr Harms agreed to prepare a note for the next meeting identifying sources of error in the handling of biological materials prior to analysis, e.g., collection of samples, pre-treatment, storage, etc. The Sub-group considered that data submitted to data banks should include the results of the analyses of reference materials and a realistic estimate of laboratory precision (mean values, standard deviation, and number of samples analysed) to assist future reviewers of data collected in monitoring programmes. The ICES reporting formats will have to be adjusted to take account of this new information.

7.1.3 Trend monitoring for trace metals in sea water

To begin work on a request from the Oslo and Paris Commissions, Dr L. Brüggmann had prepared a draft paper on the determination of temporal trends of trace metals in sea water at the MCWG meeting last year. Dr Brüggmann had continued his work on this topic interessionally and a new draft of a proposal for a programme of measurements for trend monitoring in sea water was available at the meeting. Dr Cossa also presented a paper giving his views on this topic.

Dr Brüggmann's paper provided a very detailed approach, which would be complicated and expensive to apply. Given the variance in analytical results as well as variances due to spatial and temporal inhomogeneity in conditions in sea water, the Sub-group felt that it could be very difficult to determine temporal trends in sea water. Accordingly, the Sub-group recommended that before considering such a sampling programme, an attempt should be made to estimate the likely impacts on the ocean of changing discharges of trace metals, and the likelihood of determining any associated temporal changes. The area of study must be well defined and the components of interest designated before any general strategy is adopted. Some calculations based on the known variability of metal concentrations in coastal waters and the estimated magnitudes of the changes in anthropogenic inputs, combined with an understanding of the hydrography, should permit us to determine if there is any hope of observing temporal changes due to changing anthropogenic activity (see, for example, Yeats, P.A., Bewers, J.M., and Walton, A., 1978. Sensitivity of coastal waters to anthropogenic trace metal emissions, Marine Pollution Bulletin 9, 264-268). In order to maximize the potential for success, the processes governing the variations must be understood and the sampling strategies designed such that the variance of the data is minimized.

It was the opinion of the Sub-group that calculations of this sort should be made and further discussion of potential sampling strategies should be postponed, and only reconsidered if the calculations suggest that the trend monitoring investigations are likely to succeed. It should be possible to determine on the basis of these calculations which open sea, coastal and estuarine regions are most likely to yield worthwhile investigations and results.

Several members agreed to do these calculations for their areas of interest and the Sub-group agreed to review Dr Brüggmann's paper next year on the basis of the results of this intersessional work.

7.1.4 Measurements of suspended matter in sea water

The Sub-group considered two papers on this topic which contained proposals from Drs Yeats and Brüggmann for an approach to determine the concentration of suspended matter in sea water. It agreed that these notes could form the basis for the preparation of a leaflet and Dr Yeats agreed to consider its production intersessionally. Dr Yeats also agreed to prepare a note on the feasibility of conducting an intercomparison exercise for this measurement.

7.1.5 Intercomparison exercise for methyl mercury in biological tissue

Dr Cossa presented the paper he and Dr Y. Thibaud had prepared for the meeting in which he gave the results of a questionnaire sent to laboratories involved in these measurements and his proposals for the conduct of an intercomparison exercise. The Sub-group felt that the exercise was worthwhile, in view of the responses received from potential participants, and that it should focus on measurements of methyl mercury in fish muscle and mussel tissue.

The Sub-group considered that this exercise should be restricted to laboratories who had experience with the analysis of methyl mercury and that it would be appropriate to use samples from the remaining stock of 7/TM/BT rather than prepare special samples, as proposed by Dr Cossa in his paper. This exercise will be coordinated by IFREMER, Nantes. Details of this exercise are given in Annex 4.

7.1.6 Overview papers

The Sub-group examined and discussed the papers on arsenic and mercury that had been prepared intersessionally by Dr P. Michel and Drs Cossa and Topping, respectively.

The overview on arsenic in the marine environment was considered by the Sub-group to be very valuable and they suggested a number of amendments which Dr Michel might consider before it was passed to ACMP. Dr Cossa agreed to discuss this with his colleague and to arrange for any amendments to be sent to the Environment

Officer by the middle of May. In discussing this item, the MCWG supported the Sub-group's recommendation that this paper should go to ACMP, subject to minor revision, and it expressed its appreciation to Dr Michel for preparing this document.

The draft paper on mercury was considered by the Sub-group to provide a good basis for updating the current overview paper on mercury in the marine environment. Some suggestions were made for improvements in the content and format. Drs Cossa and Topping agreed to prepare a second draft of this paper for consideration at the 1988 meeting of MCWG.

Drs Cofina and Topping reported that they had been unsuccessful in arranging for the preparation of overviews on copper and nickel, respectively. Further efforts would be made in this context.

7.1.7 Leaflets on sampling and analytical methods

Dr Berman informed the Sub-group that, owing to pressure of work, particularly associated with his role as Coordinator of the two intercalibration exercises during 1986, he had been unable to produce the leaflets dealing with trace metals in sea water. His colleagues considered that adequate details concerning these methodologies were available in published papers. Dr Yeats agreed to send a list of appropriate references which could be appended to the MCWG report (see Annex 5).

7.1.8 Atmospheric inputs of trace metals to the sea

A number of papers by Dr P. Buat-Ménard, covering methodology for the measurement of atmospheric deposition of trace metals, had been provided by Dr Cossa. Unfortunately, the Sub-group did not discuss these papers since they felt they did not have the necessary expertise. During plenary, the Chairman of MCWG informed the meeting that this matter would be taken up by ACMP at its June 1987 meeting. The ACMP had invited Dr T. Jickells (University of East Anglia, England) to attend its next meeting to advise them on this matter. Dr Topping agreed to report back at the next meeting of MCWG on ACMP's deliberations and recommendations.

7.1.9 Quality assurance and other intercalibration exercises

Dr Cofino presented a report on good laboratory practice (GLP) and quality assurance (QA) which he and his colleague had prepared intersessionally following a request from MCWG. The Sub-group considered that the booklet was a worthwhile contribution in that it brought together the range of procedures for GLP and QA. A number of suggestions were made to improve the format and contents, including an annex which contained a worked example of a control chart. It was agreed that the revised version should be submitted for publication in the ICES series Techniques in Marine Environmental Sciences. The Sub-group thanked Dr Cofino for his valuable contribution and the substantial time and effort he had allocated to this work on behalf of MCWG.

The papers on the rationale for an intercalibration of trace metal analyses in suspended matter, which had been prepared by Drs Yeats and Brüggmann, were not discussed by the Sub-group. This decision was taken by the Sub-group following a discussion between Dr Topping and Dr H. Windom (Chairman of the Working Group on Marine Sediments in Relation to Pollution) in which they had agreed that this matter should be addressed by WGMS at its meeting in late February.

Dr Yeats then reported on the topic of new certified reference materials, which had been discussed recently in Paris by the new IOC Group of Experts on Standards and Reference Materials. He stated that the Group had identified a need for the following new reference materials for trace metals: estuarine sea water, sea water specifically for mercury, and sea water for nutrients. Dr Berman reported on the plan of the National Research Council of Canada (NRCC) to develop an estuarine sea water reference material for trace metals and informed the Group of the recent additions to the list of certified reference materials for tissue and sediments prepared by NRCC.

The Sub-group then discussed the particular needs for reference materials by laboratories in relation to the monitoring of trace metals in sea water. Although NRCC will give serious consideration to the preparation of an estuarine reference material for trace metals, it will probably be based on samples collected from the St. Lawrence Estuary and this may not be an appropriate material for European laboratories, as the concentrations of trace metals and dissolved organic carbon would be lower than those in many European estuaries. NRCC could provide an additional certified estuarine sample based on a sample collected from an appropriate European river but they would need outside financial support for this project. The Sub-group suggested that this proposal be considered by the Oslo and Paris Commissions who might wish to provide the necessary funding for the collection and shipment of a sample of European water, plus the associated travel and subsistence costs of the staff involved in this work. Suitable ship time would have to be allocated and the JMG would need to identify the estuary from which the samples should be collected.

The Sub-group also identified the need for a certified reference material for mercury in sea water, but stated that investigative work was needed, prior to its preparation, to assess the stability of such a sample.

The Sub-group agreed that there are no requirements at this time for further intercalibration exercises for metals in biological tissues (except methyl mercury and possibly organotin compounds) or in sea water. Now that certified reference materials are being developed, it was felt that there would be less of a need for intercalibration exercises but, instead, checks could be made on the quality assurance programmes of laboratories by having them report on the results of analyses of reference materials. This would require a bank of homogeneous materials to be used as uncompromised reference materials. The Sub-group felt that in this context future business should address the following aspects: who should prepare such materials, how will they be distributed, who

will evaluate the results of the analyses of these materials, and how often should the results be submitted for this evaluation? In this context, Dr Berman agreed to consider the preparation of a position paper on quality assurance, particularly the role of working reference materials and 'uncompromised' reference materials, for the next meeting of MCWG.

7.2 Organics

Dr Reutergårdh opened discussions by conveying Dr A. Knap's apologies to the Sub-group for his absence.

7.2.1 Report on the ICES baseline study of organochlorines in fish and shellfish

In the assessment of results from the 1985 Baseline Study of Contaminants in Fish and Shellfish, an attempt had been made to estimate the quality of data for chlorobiphenyls, PCBs, p,p'-DDE and α - and γ -HCH in the absence of intercalibration information. This evaluation was, therefore, strictly intra-laboratory. No new hot-spot areas were identified, and it was apparent that for no species and for only very few samples were concentrations approaching those which would cause human health concern. The tentative conclusion regarding comparisons of data between 1975 and 1985 was that only for p,p'-DDE was the decrease in concentrations great enough to be an identifiable trend. Problems were identified with the data submitted; bias, errors in calculation and in basic parameters such as liver weight, were prevalent. A more detailed description of these problems is given in Annex 6.

It was noted that intercomparison exercises on this topic are currently in abeyance pending results of the BCR programme. A range of reference materials are currently being prepared by BCR (see Section 7.2.6).

It was also noted that analytical problems do not represent the whole problem and other important factors to be addressed include:

- 1) the adequate sampling of marine populations;
- 2) the changes in the form and distribution of contaminants following autopsy;
- 3) the assurance that all steps of the sampling, pretreatment and analysis are under statistical control.

Enquiries of the group members were made as to their participation in national intercalibration programmes, but in most cases no such programmes exist. It is apparent, therefore, that many countries depend upon intercalibration exercises run by international agencies.

The sampling and analytical techniques used in connection with the Baseline Study had not been given in sufficient detail for any conclusions to be drawn on the adequacy of the data with respect to precision and accuracy. The data could not, therefore,

be validated in any way. Nor was it possible to identify whether or not GLP or QA procedures were applied by laboratories or reference materials analyzed in conjunction with the analysis of Baseline Study samples.

An assessment of problems identified in the interpretation of pesticide Baseline Study data was presented by Dr Uthe; this is given in Annex 6.

Under this agenda item, the Sub-group also considered a proposal made by Dr Calder for WGMS, at the request of ACMP, for an inter-calibration exercise concerning chlorobiphenyls in marine sediments. The request had come originally from JMG, which has asked ICES to coordinate this exercise. No aims were specified for the exercise or for the programme that it supports. The Sub-group concluded that the plan was feasible, but could not identify a coordinator for the exercise as the aims were not apparent. The exercise could not, therefore, be accorded a high priority. Dr Calder will carry these comments to WGMS at their meeting next week.

The Sub-group did agree, however, that a paper should be prepared concerning the likely time-table for progress towards comparability in the analysis of organic contaminants, and this is outlined in Section 7.2.7 below.

7.2.2 Analysis of organochlorines in marine mammals

A draft report of the Joint Meeting of Biologists and Chemists concerned with Contaminants in Marine Mammals, held on 12 - 13 February 1987, was examined by the Sub-group. Dr Reutergårdh, who convened this meeting, gave a short resumé of the discussion.

He stated that the meeting did not have the required multi-national membership; 6 countries were represented (Sweden, Denmark, Norway, Federal Republic of Germany, Iceland, and the United Kingdom). Representatives from Canada and the Netherlands were unfortunately absent.

The analytical overview that had been prepared by Drs Reutergårdh and Knap concluded that it is difficult to compare the data in the literature because of the multiplicity of methods in use and the poor description of them in many papers. Dr Reutergårdh requested that, if anyone knew of data not included in the overview, they should send the information to him to allow inclusion in a revised version.

Many effects detrimental to the health and reproduction of seals have been noted in the Baltic Sea, though not elsewhere, other than in Beluga whales from the Gulf of St Lawrence. Skin lesions have been noted in most hot-spot areas, which include the Bay of Fundy, Firth of Clyde, Gulf of St Lawrence and the Wadden Sea in addition to the Baltic Sea.

At the meeting, a participant from Sweden volunteered to carry out analysis of samples of seal blubber from the crucial areas identified above for organochlorine compounds, if laboratories from the relevant countries will provide samples. Information on

the required sampling and preservation techniques will be supplied to the countries directly.

This study is justified by the lack of common and comparable methodology currently in use at the different laboratories undertaking such work. Long-term plans to overcome these difficulties were outlined, both with respect to standards and reference materials and intercomparison activities. An intercomparison exercise concerning chlorobiphenyls in seal tissue is proposed, to follow the stepwise approach recommended for improvement of comparability in other areas of analysis. The group felt that such an exercise was urgently required so as to provide answers to the intricate questions of seal pathology and contaminant concentrations, and that the exercise should proceed as quickly as possible. (See Recommendation 10, Annex 8.) No coordinator has yet been identified.

Planar molecules, especially planar CB molecules such as 3,4,3',4'-tetrachlorobiphenyl; 3,4,5,3',4'-pentachlorobiphenyl, and 3,4,5,3',4',5'-hexachlorobiphenyl, which produce toxic effects in a similar manner to 2,3,7,8-tetrachlorodibenzodioxin, have been suggested to be more toxic than the dioxins and furans as their concentrations in tissue are higher. This will be reviewed intersessionally.

During the meeting, the chemists placed most emphasis on the analytical difficulties, whereas the biologists emphasized the difficulties of defining and counting seal populations and deciding whether or not a population is declining. A second meeting was proposed for 1988, to include representatives from at least eight countries and a representative of the Working Group on the Statistical Aspects of Trend Monitoring (WGSATM). This meeting should address all the topics discussed above. This proposal was endorsed by the Sub-group and later by MCWG.

7.2.3 Analyses of specific hydrocarbons

A draft report of the Meeting on Hydrocarbon Intercalibration was available at the meeting and the Chairman (Mr R. Law) gave a short summary of the recommendations and discussion. The proposal made at the 1986 MCWG meeting for a step-wise approach over at least 3 years was confirmed, with a proposed first stage to concentrate on instrument calibration by analysis of standard solutions. These would preferably be obtained from organisations such as NRC (Canada) or NBS (USA), which have a proven expertise in the preparation and certification of standard materials. Techniques to be used in the exercise would be GC-MS, GC-FID and/or HPLC-UVF. If a total of 12 laboratories, who were prepared to provide firm statements of intent with regard to participation and completion of analysis, could not be found, then the recommendation would be not to proceed with the exercise as the base of data would be too small. In the absence of a coordinated monitoring effort for PAH, a primary list of 17 compounds for use in monitoring exercises was established, and a sub-set of 10 selected as the preferred compounds for use in the exercise.

Mr Law agreed to serve as coordinator for the first stage of this intercomparison exercise. The form of the second and subsequent

stages should be agreed by the participants at meetings following the completion of each stage. Samples will become successively more complicated than these standard solutions, possibly approaching real sample matrices after 3-5 years.

The Sub-group also considered under this agenda item the papers on hydrocarbon analysis in sea water, sediments and biota prepared by Drs Ehrhardt, Law and Klungsøyr, respectively. At the 1986 MCWG meeting, it was agreed that a critical review of analytical methodology for hydrocarbons should be prepared; Dr Ehrhardt had agreed to act as coordinator. These three papers represent three-quarters of the input, Dr Knap having unfortunately been unable to complete his section concerning the atmosphere by the time of the meeting. Comments, additions and corrections were made and noted.

It was agreed that Dr Ehrhardt would try to solicit Dr Knap's contribution (with assistance from Dr Reutergårdh) as soon as possible, with a view to:

- 1) combining the four contributions into a single review paper for publication in the open literature, and
- 2) preparing an executive summary paper (approximately 4 pages) for submission to ACMP.

7.2.4 Atmospheric input of organochlorines to the sea

Dr Reutergårdh reported that Dr Knap has collected most of the information to prepare an overview on methodology for the determination of atmospheric input of organochlorines to the sea, but has not yet completed writing it up. Hopefully, the paper will be available for discussion at the next MCWG meeting.

Work is under way in:

- 1) Sweden on the transfer of organochlorines to and from the atmosphere at locations around the Swedish coast.
- 2) the Federal Republic of Germany on organochlorines and other organics in both the atmospheric particulate and vapour phases in the vicinity of the Kiel lighthouse. So far, the study has shown that variations in composition occur and these are linked to the wind direction.

7.2.5 River Inputs

In the absence of Dr Knap, who had agreed to prepare a paper for discussion, Dr Reutergårdh stated there was nothing that the Sub-group could discuss on this topic. IOC is currently preparing guidelines and Dr Ehrhardt agreed to check on these and report back to MCWG.

7.2.6 Reference materials and standards

Following preliminary discussions of this item, the Sub-group agreed it would be appropriate to list the most recently available materials, and those either under preparation or being considered for preparation.

Available Certified Reference Materials for
Trace Organic Contaminants

(NRC = National Research Council; BCR = Community Bureau of Reference of the Commission of the European Community; EPA = Environmental Protection Agency; NBS = National Bureau of Standards.)

CLB-1	51 individual chlorobiphenyls in isooctane	NRC Canada
CRM 046-272	Individual purified polycyclic aromatic compounds	BCR
EO01-E996	Toxic and hazardous materials of varying form and purity	US EPA
SRM-1543	GC/MS system performance solutions	US NBS
SRM-1583	Chlorinated pesticides (5) in 2,2,4-trimethyl pentane ..	US NBS
SRM-1585	Chlorinated biphenyls (8) in 2,2,4-trimethyl pentane ...	US NBS
SRM-1586	Isotopically labelled (10) and unlabelled (10) priority pollutants in methanol	US NBS
SRM-1587	Nitrated polycyclic aromatic hydrocarbons (6) in methanol	US NBS
SRM-1614	Dioxin in isooctane	US NBS
SRM-1639	Halocarbons (7) in methanol	US NBS
SRM-1644	Generator columns for polynuclear aromatic hydrocarbons (3)	US NBS
SRM-1647	Priority pollutants polynuclear aromatic hydrocarbons (16) in acetonitrile	US NBS
SRM-1581	Polychlorinated biphenyls in oils (4)	US NBS
SRM-1582	Petroleum compounds (13) in crude oil	US NBS
CS-1	PCBs and individual CBs in coastal marine sediment	NRC Canada
HS-1, HS-2	PCBs and individual CBs in harbour marine sediment	NRC Canada
HS-3, HS-4, HS-5, HS-6	16 PAHs in harbour marine sediments	NRC Canada
	Individual CBs	BCR

New materials in preparation or under consideration:

NRC - Reference material and standards (in progress).

Marine fish oil for CBs, pesticides and PAH.

Lobster digestive gland for trace xenobiotic organics and trace metals.

A ¹³C-labelled CB (IUPAC No. 153).

6 to 10 toxaphene congeners.

CB metabolite compounds.

Nitro-PAH compounds.

IAEA - Intercomparison materials (in preparation).

Sediment and fish flesh for organochlorines (by mid-1987).

BCR - New material.

Two fish oils (mackerel and cod liver) for CBs (1987).

Sewage sludge for CBs (to begin in 1987).

Harbour sediment for pesticides, PAH and CBs (a group has begun work).

A seal blubber certified for CBs is under consideration.

NIES - Candidate reference materials.

Fish flesh for methyl mercury.

Marine organism for organic arsenic.

Marine sediments for organic tin compounds.

NBS - CRMs currently being prepared.

Marine sediment for CBs, PAH and pesticides.

Calibration solution in hexane containing 17 PAH.

20 pesticides and selected CBs.

The Sub-group considered the proposal put forward to GESRM (the IOC/UNEP Group of Experts on Standards and Reference Materials) by J. Farrington for the preparation of a certified reference material (CRM) for calibration of the UVF procedure for total hydrocarbons in sea water. Given that the primary use of this method is for screening purposes, and that its level of intercomparability is good, the Sub-group considered this to be of low priority and also felt that major problems may be encountered in both approaches put forward. The generator column approach would be preferable if a mixture of PAHs can be so prepared. It is not certain whether this is in fact feasible, so Dr Calder has agreed to contact NBS for information. The use of a contaminated harbour water sample may yield hydrocarbons which fluoresce at too low wavelengths (i.e., derived from diesel oil). Storage and shelf life problems may also occur and would need to be investigated. A third possible technique was suggested by Dr Ehrhardt, namely, that of producing a concentrate of lipophilic fluorescent material from sea water which could then be redissolved to produce the required concentrations.

With regard to the use of naturally contaminated or spiked material for CRM preparation, the Sub-group felt that the preferred choice is the use of naturally contaminated material collected in the field. Specific requirements may, however, dictate the use of other materials.

Some reservations were expressed over the use of freeze-dried material as CRMs as freeze-drying alters the surface chemistry of some materials making extraction characteristics different from those of fresh material. The preparation of acetone powders or "ice-cream" from biological tissue may be ways of yielding suitable material in terms of storage and extractability. All techniques have some advantages and disadvantages, however, and selection must be made with the particular purpose in mind.

The Sub-group could not address the question of CRMs for air, as it has no expertise in that area.

7.2.7 Overview papers

A paper is to be prepared on the likely timetable for improvements in comparability of results to be expected from current initiatives being pursued outside ICES in the area of chlorobiphenyl analysis, and the area of the analysis of organics generally. This should be presented to the 1987 Statutory Meeting and to ACMP for discussion at its one-day meeting in October in connection with the 1987 Statutory Meeting.

Other papers proposed for overviews were as follows:

- 1) Planar molecules with toxic effects, i.e., fitting the same or a similar receptor as 2,3,7,8-tetrachlorodibenzodioxin. This should be prepared by Drs Reutergårdh and Wells.
- 2) The compiled review of hydrocarbon analysis (see Section 7.2.3, above).
- 3) Surface-active agents. Dr Reutergårdh will try to arrange a paper.
- 4) The representative sampling of populations of marine mammals. This will be requested of the Marine Mammals Committee and of the Working Group on the Statistical Aspects of Trend Monitoring (WGSATM).
- 5) The representative sampling of marine sediments for organic contaminant analysis. This will be requested of WGMS and WGSATM.
- 6) Explore the feasibility of preparing guidance on sample handling from the time of collection to the time of analysis and the banking and preservation of samples.
- 7) Dr Ehrhardt agreed to prepare a short paper focussing attention on diphenylsulfone.

7.2.8 Intercomparison on hydrocarbons in sea water

The final report of the Oil Pollution Research Unit (England) intercalibration for hydrocarbons in marine sediment held in 1984 is still not available, but Mr Law presented a draft copy for discussion. Thirty laboratories received samples and, of these, 17 reported data. Seven of these were ICES laboratories. Measurements were made by gravimetry, UVF, capillary GC and GC-MS. A full evaluation of the data has not yet been made, but the coordinator, Dr S. Howells, has indicated that statistical treatment of the data will be difficult because of a shortfall in many of the results submitted. Variability in the data, particularly between, e.g., gravimetry and UVF for total hydrocarbons, gives cause for concern. The fact that a reference aromatic standard was not circulated for use in the GC-MS analyses is seen as a serious omission.

The final report is expected to be mailed to participants during 1987.

7.2.9 Good Laboratory Practice and Quality Assurance

The Sub-group recognised this paper as a good first step and recommends that analysts and managers should read it and avail themselves of the references therein.

7.2.10 Irish Sea Status Report

This had been submitted by Dr J. Portmann for comment and was introduced by Mr Law. Few comments were made except that "petroleum hydrocarbons" should be replaced by "hydrocarbons" as the hydrocarbons found are a mixture of natural and anthropogenically derived hydrocarbons.

7.2.11 Any other business

The Sub-group considered the matter of differing chemical nomenclature and agreed that IUPAC nomenclature should be used.

7.3 Chemical Oceanography

7.3.1 Review of nutrient measurements

The ICES Hydrographer introduced a paper entitled "Nutrient data in the Oslo-Paris Commission area", essentially a compendium of the twenty responses to Matti Perttilä's letter of 23.06.86 to MCWG members, and its enclosed questionnaire.

Attention was thereby drawn to ROSCOP (Reports on Scientific Cruises in Oceanographic Programmes) and the fact that this is the recognised vehicle for the tracking of data. A 'for instance' search of the data described on ROSCOP forms and limited to cruises providing nitrate data between 50° - 60° N and 10° E- 10° W (essentially UK coastal waters) from 1975 to 1986 identified 21,523 stations.

Detailed scrutiny, however, reveals that very little actual data are presently held by ICES and those organisations that have promised such data are again urged to fulfil this commitment in order that the maximum amount of data can be accessed for such purposes as the assessment of temporal trends, etc. The Hydrographer went on to outline the difficulties of identifying usable time-sets, as much of the currently available data were gathered adventitiously when the main objectives of the cruises were purposes other than nutrient determinations. An earlier Council resolution identified the International Young Fish Surveys as being potentially suitable occasions for the collection of samples but this generally precluded the possibility of on-board 'fresh' analyses. As yet only DAFS, Aberdeen and MAFF, Lowestoft have used such cruises to collect samples, despite commitments from other laboratories.

There appears to be a real problem concerning the use of data supplied to ICES. The Sub-group recommended that a way be found

of reassuring contributors that their data will not be used for any purposes other than those of ICES and that their expressed permission will be obtained before any release of data for whatever purpose.

The Sub-group then discussed preservation of samples and, in particular, gave detailed consideration to the paper C.M.1985/C:44 entitled "Chloroform as a preservative of deep sea water samples for reactive phosphate analysis" by I.M. Davies of DAFS, Aberdeen. This paper demonstrates conclusively that the addition of chloroform for sample preservative purposes can introduce turbidity due to the dispersal of the chloroform itself. This turbidity contributes a positive bias to the measured absorbance, the magnitude being dependent both on the quantity of chloroform used and on the agitation given to the sample at the time of the chloroform addition. After two weeks of storage subsequent to the initial agitation, the turbidity was surprisingly undiminished.

Biases of up to $0.5 \mu\text{g atom dm}^{-3}$ were demonstrated and this is clearly very serious.

It is worthy to note that item (i) (Nutrients) of the Executive Summary of the 1986 MCWG Report states "MCWG have concluded that turbidity measurements should always be done when nutrient concentrations are low", and it follows that it must now be considered necessary to correct each sample individually for potential turbidity introduced by this time-honoured method of sample preservation. By the same token, the producers and users of nutrient data must face and come to terms with the fact that every sample that has had chloroform added to it is thereby liable to a possibly serious positive bias from this source. The implications are, as usual, proportionately more serious the lower the actual nutrient concentration is in the sample.

7.3.2 Intercomparison of nutrient measurements

The Sub-group discussed at some length the paper entitled "Inter-calibration of Nutrients and Hydrographic determinands during PEX 86" prepared interessionally by Dr Perttilä. While the raw data are not fully available, this summary of the experiment leaves no doubt that in some respects the exercise posed more questions than it answered. It was an elegantly designed experiment that suffered such unforeseen misfortunes as a breakdown of the speed-boat that had been entrusted with the fast distribution of samples from the 'mother-ship' to the other participants. Many useful lessons seem to have been learned, not the least of which being that it is unlikely that research vessel time will be devoted on this scale to this kind of work outside the Baltic Sea area in the foreseeable future.

In noting the rather alarming (up to 60%) ship-to-ship differences in nutrient levels measured during the PEX intercalibration experiment, which is partly confirmed by the analysis of the field data, the Group considered that existing time series of nutrients should be re-examined to investigate the possibility that they too are affected by errors of large magnitude. This particularly applies to "international" time series, such as the HELCOM Baltic Monitoring Programme data set. The Group recommended that

further analysis on the nutrient data sets held by HELCOM should be postponed pending the outcome of this review, and the completion of a thorough analysis of the PEX field data. In drawing conclusions from the analysis of the PEX field data, attempts should be made to establish the representativeness of the errors identified in the data set from a particular ship/institute, including the time over which any correction factor is likely to be relevant.

The Chemical Oceanography Sub-group met jointly with the Trace Metals Sub-group to discuss the possibility of organizing some form of nutrient intercalibration exercise. The problem area of sample preservation was discussed in depth and it was generally agreed that there is probably no single recommendable method that is suitable for all of the determinations of interest.

It was agreed, however, that further use of synthetic standards (i.e., Sagami) will not be particularly helpful and that urgent consideration should be given to the allocation of resources for the development of a reference material based on 'real' sea water. The Sub-group was not presently in a position to make any recommendations for formal collaborative work in the near future. However, some proposals for informal collaborative work in small groups were considered (see Recommendation 1, Annex 8).

Interested parties will be invited to generate a 'phosphate-free' sample in their own laboratories by allowing a suitable volume of unpreserved sea water to stand for a prolonged period in a polythene container. It is assumed (or hoped) that the nitrate concentration will simultaneously 'settle-down' to a stable level. Aliquots of this sample will be sent to other laboratories for analysis. It is anticipated that each of 'n' participating laboratories will eventually receive and analyse a total of 'n' samples for nitrate, nitrite and phosphate. Results of this work will be collated by Dr Topping, DAFS, Aberdeen. Lars Føyn also offered to deliver replicate samples to Aberdeen during the course of a November 1987 cruise.

Although exercises of this kind are generally reckoned to represent a relatively small investment in time and materials, they could produce much useful data.

7.3.3 Temporal trends in nutrients in sea water

It follows from the discussion of analytical uncertainties in both Sections 7.3.1 and 7.3.2 that the identification of temporal trends in nutrients is rendered extremely difficult. However, Dr Kirkwood went on to describe the MAFF Lowestoft's attempts to collect and collate as much nutrient data as possible in a data file with appropriate search routines to aid in the identification of suitable time-sets, if any, for possible use in this context. Various aspects of the paper entitled "On long-term variations of nutrients in the Baltic Sea" (1969-1986) by Stig Fonselius (15th Conf. of Baltic Oceanographers, Copenhagen, Nov. 1986) were discussed and also "Nutrients in the German Bight, a Trend Analysis" (1936-1978) by Gunther Weichart (Dt. hydrog. Z. 39:197-206 (1986)).

The Sub-group was in general agreement that in the latter paper, the nutrient concentrations in samples of high salinity, i.e. open sea waters, showed no discernable increase over the time scale studied although values in nearshore areas of the German Bight have clearly increased over the periods in question.

Matters arising from 1986 Sub-group Report

The Sub-Group discussed the report entitled "Good Laboratory Practice and Quality Assurance" and considered that it meets the needs of those involved in nutrient determinations.

Noting the suggestion of ACMP that the Sub-Group should consider riverine and atmospheric inputs, the Sub-Group anticipates consideration of the work of Dr Knap in this area at next year's meeting.

Dr Koroleff's investigation of the causes of discrepancies between his and the method of Suzuki for the determination of total nitrogen in sea water will be considered at a future date.

8 PLENARY DISCUSSIONS OF SUB-GROUP REPORTS

The MCWG reviewed the reports of the three Sub-groups, and the action lists and recommendations arising from each report.

Trace Metals

The MCWG endorsed the proposal that there was no need for any further intercomparison exercise at present other than the one proposed for methyl mercury in biological tissue. The MCWG recommended that the intercomparison exercise on analyses of methyl mercury should be conducted (see Recommendation 6, Annex 8) and expressed its appreciation to Dr Cossa for his offer to coordinate this exercise. Similarly, the Group supported the view that quality assurance programmes in participating laboratories should be implemented and/or strengthened through the regular analyses of reference materials and these data should be reported when they submit data on monitoring programmes (see Recommendations 2 and 3, Annex 8).

The Group endorsed the proposal by the Sub-group that the overview on arsenic should be forwarded to ACMP once it had undergone minor alterations. It also endorsed the proposal that the report on GLP and QA should be forwarded to ACMP for its comments, and should thereafter be published in the Techniques in Marine Environmental Sciences series.

Organics

The Group endorsed the recommendations made by the Joint Meeting of Chemists and Biologists on the analyses of CBs in marine mammals, i.e., that laboratories in relevant countries should send samples of seal blubber from hot spot areas to Dr Reutergårdh for organochlorine analysis and that the Joint Group should hold a further meeting in 1988 to review progress in this work. The MCWG also endorsed the recommendation that an intercomparison exercise

on the analysis of organochlorine residues in seal blubber should be conducted (see Recommendation 7, Annex 8).

In addition, the MCWG endorsed the recommendation from the MCWG Sub-group on hydrocarbon analyses that an intercomparison programme be conducted along the lines given in its report (see Doc. C.M.1987/E:4).

Chemical Oceanography

The Group endorsed the proposal from the Sub-group that work on the improvement of nutrient measurements should be implemented as soon as possible by ICES and welcomed the measures proposed by members of the Sub-group for intersessional activity in this respect (see Recommendation 1, Annex 8).

9 ANY OTHER BUSINESS

The Chairman referred to the request from the Hydrography Committee for MCWG's assistance in preparing for the Water Quality Modelling Session to be held at the ICES Statutory Meeting in 1987. Specifically, the Chairman of the Committee wanted the Group to consider the production of simple models, in schematic form, which incorporate the biogeochemical aspects of selective contaminants in the marine ecosystem. An example of the type of simple model required had been sent to the Group based on information available for mercury. The Chairman reminded the Group that some of the contaminants listed by the Hydrography Committee (Cd, Hg, Pb, Cu, Zn, Cr, Ni, As, DDT, PCBs, HCH (α and γ isomers) and nutrients) had already been the subject of overviews carried out by MCWG members and their colleagues.

Members were then invited to volunteer to assist in this work by extracting the relevant information from these overviews and preparing a simple model along the lines suggested. A number of members agreed to consider this task intersessionally. It was agreed that the Chairman would coordinate any responses on this matter.

At the request of several members of the Group, the assessment chapter of the Quality Status Report on the North Sea, being prepared for the International Conference on the North Sea, was briefly reviewed. Several problems were identified in this document. In particular, it was felt that some of the statements made were too broad, some were without scientific basis and some were inconsistent. The report purports to cover the entire North Sea, whereas many statements really apply only to certain areas thereof; more precision is, therefore, required. A number of specific comments were given to the Environment Officer concerning amendments to this chapter and it was agreed that any additional comments should be sent to her as soon as possible. These will be made available to the ACMP, which will coordinate the final response of ICES to the Quality Status Report as a whole at its meeting in June. The Chairman reminded the Group that an additional avenue by which individual members from countries around the North Sea could express their concern over specific statements in this document was through their own country's representatives on the groups preparing for this conference.

The Group then reviewed the list of intersessional activities that should be carried out and agreed to them as given in Annex 7.

10 RECOMMENDATIONS

In addition to recommendations noted above, the MCWG recommended that the final reports on the results of the Seventh Intercalibration Exercise on Trace Metals in Biological Tissue (Part 2) and the Sixth Intercalibration Exercise on Trace Metals in Sea Water should be published in the Cooperative Research Report series (see Recommendations 4 and 5, Annex 8).

The MCWG also recommended that the ACMP explore the possibility of the Oslo and Paris Commissions providing funds for the preparation of a certified reference material for trace metals in estuarine water based on samples from a European estuary (see Recommendation 8, Annex 8).

The MCWG then discussed its next meeting and agreed it should be held for 5 days in February/March 1988.

The following topics should be considered:

- a) methyl mercury measurements in fish and shellfish;
- b) 1986 baseline data for trace metals in sea water;
- c) analysis of suspended matter in sea water;
- d) the role of reference materials in QA;
- e) measurements of nutrients in sea water;
- f) overview papers;
- g) measurements of hydrocarbons in marine samples;
- h) progress in measurements of organochlorines in biological tissue.

This is given as Recommendation 9 in Annex 8.

As all other business had been concluded, the Chairman thanked all members for their very constructive work during the week. He then closed the meeting at 16.30 hrs on 20 February 1987.

ANNEX 1

MARINE CHEMISTRY WORKING GROUP
Copenhagen, Denmark, 16 - 20 February 1987

Agenda

1. OPENING OF THE MEETING
2. ADOPTION OF THE AGENDA
3. REPORT OF 74TH STATUTORY MEETING
4. REPORTS OF RELATED ACTIVITIES
 - 4.1 JMG of the Oslo and Paris Commissions
 - 4.2 IOC
 - 4.3 ICES Working Groups
 - 4.4 Other relevant Activities
5. REPORTS ON PROJECTS AND ACTIVITIES IN ICES COUNTRIES
6. REQUESTS FROM ACMP AND REGULATING AGENCIES
7. SUB-GROUP ACTIVITIES AND DISCUSSIONS
 - 7.1 Trace Metals
 - 7.1.1 Reports on ICES baseline of metals in fish, shellfish and sea water
 - 7.1.2 Results of the I/C for trace metals in estuarine waters (6/TM/SW) and in biological tissue (7/TM/BT)
 - 7.1.3 Temporal trends of trace metals in sea water
 - 7.1.4 Measurements of concentrations of suspended matter in sea water
 - 7.1.5 I/C of mercury compounds in biological tissue
 - 7.1.6 Overview papers on metals in the marine environment
 - 7.1.7 Leaflets on sampling and analytical methods
 - 7.1.8 Atmospheric inputs of trace metals to the sea
 - 7.1.9 Other I/C exercises and QA activities
 - 7.2 Organics
 - 7.2.1 Report on ICES baseline study of organochlorines in fish and shellfish
 - 7.2.2 Analyses of organochlorines in marine mammals
 - 7.2.3 Analyses of specific hydrocarbons
 - 7.2.4 Atmospheric input of organochlorines to the sea
 - 7.2.5 River inputs
 - 7.2.6 Reference materials and standards
 - 7.2.7 Overview papers
 - 7.2.8 I/C of hydrocarbons in sea water
 - 7.3 Chemical Oceanography
 - 7.3.1 Review of nutrient measurements
 - 7.3.2 Intercomparison of nutrient measurements
 - 7.3.3 Temporal trends of nutrients in sea water
8. PLENARY DISCUSSIONS OF SUB-GROUP REPORTS
9. ANY OTHER BUSINESS
10. RECOMMENDATIONS

ANNEX 2

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ANNEX 3

ICES 7/TM/BT AND 6/TM/SW in Retrospect

These two intercomparison exercises for trace metals in marine biological tissues and sea water respectively were, in general, disappointing with regard to demonstrating the overall competence of the ICES community for trace metal analysis. The performance for tissue analysis is better than that for sea water analysis, but there are still a good number of laboratories who have not shown an ability to analyze trace metals in marine tissues at levels necessary for monitoring purposes.

There is only a small core of laboratories which show a consistent ability to perform error-free analysis. The number increases with every intercomparison exercise, but the rate of growth is painfully (and expensively) slow. However, there are conclusions to be drawn from these two exercises which may not have been evident at an earlier stage.

It is obvious that the analytical methodologies for the main metals of both studies are sufficiently developed such that competent laboratories can carry out confident analyses with respect to trace metals in the marine environment at levels necessary for present monitoring programs. If there are problems, they lie within the laboratory and are the result of improper practice, inadequate instrumentation, and a poor laboratory environment. While there is usually more than one way to carry out a successful analysis, there are some lessons to be learned from the performance of the ICES laboratories in these two studies.

For biological tissues, the probability of success increases if

- i) flame atomic absorption spectrometry is used for zinc, and especially for copper, when the analyte concentrations permit;
- ii) graphite furnace atomic absorption spectrometry is used for cadmium and lead measurements;
- iii) samples are decomposed with a mixture of acids rather than nitric acid alone when analyzing for arsenic.

For estuarine water, the probability of success increases if

- i) a chelation/extraction method is used to separate and concentrate copper, zinc, and cadmium prior to their determination by graphite furnace atomic absorption spectrometry;
- ii) a gold amalgam is used to concentrate mercury prior to atomization and atomic absorption measurement;
- iii) a scrupulous regime of cleanliness and blank control is maintained for all metals, but especially for lead;
- iv) those laboratories using electroanalytical methods are aware of the problems caused by the presence of dissolved organic carbon:

- v) those laboratories attempting direct determination of metal concentrations by GFAAS remember that precision degenerates swiftly as you approach the limit of detection.

For both materials, the probability of success increases if the limits of detection are at least a factor of 5 to 10 lower than the expected concentration of the analytes and if the arithmetic is checked prior to issuing a report.

While it was possible to assess the accuracy of the metal determinations in both studies, it would be a mistake to assume that the interlaboratory standard deviation represents the true precision of the laboratory for the analysis in question. If six replicates are analyzed, all that can be said (with 95% confidence) is that the true standard deviation is somewhere between 0.6 and 2.5 times the estimated value. The knowledge of a reliable estimate of a laboratory's variance for a particular analysis is essential to a monitoring program in order to determine the laboratory's ability to differentiate between analyte concentrations. This number can only be calculated from the experience of the laboratory with the repetitive analysis of a reference material of similar matrix and analyte concentration over a long term. If the laboratory has not implemented some quality assurance regime which can produce this number, then, even if it is an "accurate laboratory", its role in monitoring is severely restricted.

Also in relation to quality control it is clear that the use of certified reference materials is mandatory in a laboratory's self evaluation. These materials are now available for much of the marine tissue work, but the two available sea water certified reference materials would not have been of much use to the electroanalytical chemists for metal determinations in estuarine waters as they have low DOC contents.

It must be remembered that these intercalibration exercises are only valid with respect to sample digestion and metal measurement procedures for the tissues and with respect to the measurement processes for the estuarine waters. The sampling, preparation and preservation procedures of laboratories have not been assessed. These steps add to the variance of the overall analytical procedure, but an exercise to adequately intercompare laboratories for the complete process has yet to be devised.

There is probably no need for more intercalibration exercises of this nature with respect to these two media in the near future. One might consider specialized studies, such as an examination of digestion procedures when analyzing for arsenic in marine tissues, or the analysis of more esoteric constituents such as tri-butyl tin or methyl mercury.

Efforts must now be expended in ensuring that laboratories adopt good laboratory practice whereby they can demonstrate by the use of reference materials and some very elementary statistics that their analyses are under statistical control. In this way, those laboratories which have demonstrated poor performance in the intercalibration studies may be improved and those that performed well may continue to show their prowess.

Unless these improvements are made, the monitoring agencies will continue to risk the waste of considerable resources and the inclusion of misleading data in their monitoring reports.

ANNEX 4

INTERCOMPARISON EXERCISE FOR METHYL MERCURY IN BIOLOGICAL TISSUEBackground

At the 1986 MCWG Meeting, Dr. D Cossa (IFREMER, France) agreed to examine the need for, and feasibility of, an intercomparison exercise for organomercurials in biological tissue. In May 1986 he wrote to 27 laboratories seeking their views on this matter. Twelve responses were received, all supporting the idea and indicating that the exercise should focus on methyl mercury with accompanying measurements of total mercury. It was generally agreed that both fish muscle and mussel tissue should form the basis for this exercise.

These proposals were discussed by the trace metal sub-group of MCWG which recommended the following schedule:

- 1) Dr Cossa would send a circular in March 1987 to potential participants in ICES inviting them to join the intercomparison exercise.
- 2) In June 1987 the samples of fish muscle and mussel tissue (obtained from Dr Berman) would be distributed to participants who would be asked to provide the following data:
 - a) Six replicate analyses for methyl mercury, total mercury, and dry weight.
 - b) All mercury concentrations to be expressed on a dry weight basis.
 - c) Dry weight determinations are to be done on a separate sample.
 - d) Each participant must employ the analytical techniques in common use in their monitoring or research programme and a description of this method should be sent with the analytical data.
 - e) It would be desirable for each laboratory to use the AOAC method in addition to their own procedure for the measurement of methyl mercury.
 - f) Any measurements of other organomercurials made on these samples would be welcomed by the coordinator.
- 3) The deadline for the receipt of the results is September 1987.
- 4) A preliminary report on this exercise will be prepared by January 1988 for discussion in February 1988 by MCWG.

ANNEX 5

METHODS FOR TRACE METALS IN SEA WATER

The methods deemed to be best for the determination of trace metals in sea water are described in the following papers:

- 1) K.W. Bruland, R.P. Franks, G.A. Knauer, and J.H. Martin, 1979. Sampling and analytical methods for the determination of copper, cadmium, zinc and nickel at the nanogram per liter level in sea water, *Analytica Chimica Acta*, 105, 233-245.
- 2) L.-G. Danielsson, B. Magnusson, and S. Westerlund, 1978. An improved metal extraction procedure for the determination of trace metals in sea water by atomic absorption spectrophotometry with electrothermal atomization. *Analytica Chimica Acta*, 98, 47-57.
- 3) R.E. Sturgeon, S.S. Berman, S.N. Willie, and J.A.H. Desaulniers, 1981. Preconcentration of trace elements from sea water with silica-immobilized 8-hydroxyquinoline. *Analytical Chemistry*, 53, 2337-2340.

Two other methods that have been checked out for a smaller number of metals are:

- 4) E.A. Boyle and J.M. Edmond, 1977. Determination of copper, nickel and cadmium in seawater by APDC chelate coprecipitation and flameless atomic absorption spectrometry. *Analytica Chimica Acta*, 91, 189-197.
- 5) R.G. Smith and H.L. Windom, 1980. A solvent extraction technique for determining nanogram per litre concentrations of cadmium, copper, nickel, and zinc in sea water. *Analytica Chimica Acta*, 113, 39-46

ANNEX 6

Problems Identified in the Interpretation of
the Organochlorine (non-PCB) Baseline Data - 1985

In the assessment of the organochlorine results of the 1985 ICES Baseline Study of Contaminants in Fish and Shellfish, the interpretation of results submitted by the various participants was hampered due to the lack of current information on the intercomparability of data from these laboratories, i.e., there was no intercomparison exercise carried out during the 1985 Baseline Study. It had been known that intercomparability from past exercises was rather poor, with relative standard deviations of the order of 30% or greater.

However, in addition to this problem and problems with respect to sampling, i.e., all samples were not strictly comparable, with differences in sampling time, composition and numbers of individuals, a number of other problems relevant to the Marine Chemistry Working Group were identified. These are related to the generation and handling of numerical data sets and are applicable to all contaminants. The basic principle is to supply to statisticians or others charged with the interpretation of chemists' results data with known degrees of precision and complete enough to fit with a pre-selected statistical model or allow investigation of a variety of statistical models. It must be understood that any errors that occur sporadically or any misinterpretation cause severe statistical problems. It is also dangerous to assume anything about the magnitude of the variance associated with any step in the overall study.

With this in mind, two additional duties are suggested to be imposed upon the analyst:

- a) Careful completion of reports giving results of the analysis. In no instance should any result be entered more than once on a form and no derived information should ever be entered, e.g., the mean of N results. If one has any doubt about the exact information required, telephone the coordinator or data center.
- b) Careful and exact checking of computer printouts from the coordinator or data center to ensure that no misinterpretation or transcription errors are present. A wise coordinator will deliberately add a few errors to the printout prior to sending them to the data submitters.
 - 1) Determination of "dry" weight. Even with only a passing familiarity with techniques of determination of "dry" weight, chemists are generally aware that various methods (thermal drying, freeze drying, chemical drying) give somewhat different results, the problem being one of removing only and all water from the material without changing the other constituents. Obviously, dried material cannot be analysed for analytes (determinands) such as the organochlorines that are lost or altered by drying. Although few laboratories submitted duplicate determinations (in many instances apparently repli-

cate values were given, but since the figures were identical in all cases, these were not judged to be true duplicates), it was apparent that instances where true duplicates differed by substantial amounts and instances where values were only given to insignificant numbers of places, e.g., 1.00 and 2.00, is either sloppy chemistry or no significant figures were present.

The questions for the Marine Chemistry Working Group are "How does a chemist accurately determine dry weight? or What is the best way of estimating dry weight? and How good is this estimate?". To be useful, the variances associated with this measurement should be small compared with that of the analyte since variances tend to multiply.

2) Determination of "fat" percentage. The observations listed under (1), above, apply as well to this measurement. The standard method for fat involves acid digestion, generally HCl, to release fatty acids from glycoproteins, etc. The fat percentages listed in the raw Baseline Study data are apparently simply based on the weight of matter extracted by solvent from the tissue after chemical drying. The solvent is generally removed at low temperature, although sometimes a known portion of a measured extract volume is used. However, without washing (see Folch-pi *et al.*, 1957, Bligh and Dyer, 1961), this can contain substantial amounts of non-lipid material. The Group may recall the attempts by Dr Kerkhoff to obtain agreement on fat extraction and measurement procedures.

The data listings show that substantial differences are present in duplicate fat determinations. The questions to MCWG are the same as in (1), above. It should be noted that statistical modelling, e.g., the use of burden (tissue weight times contaminant concentration) can often circumvent the need for dry weight or lipid percent.

3) Completion of the data submission forms. It was obvious from the data printouts that various interpretations were used for certain items (e.g., analytical sample weight entered as tissue/organ weight), that inexact information was reported (e.g., ICES statistical rectangles are not specific enough for mussel watch type data), and that entry errors (e.g., double entries, too many significant figures) and addition errors (DDT added wrong) were present at an embarrassing frequency. This was after submitters had confirmed the information in the computer bank. Therefore, it is suggested that the input forms and information packages should be changed as follows:

- i) The sampling protocol must be re-written on an individual species/tissue matrix basis. This must be clear and exact. In certain instances contaminant must be included.
- ii) Geographical site designation must be given in latitude and longitude. Mid-trawl or mid-ICES designations can be used for spatially large samples. It is easy to generate ICES rectangle information from this and have the computer print-out sampling areas and other maps which were done by hand (3% error) in the initial evaluation of the Baseline Study data.

4) No derived inputs, e.g., DDT. Derived inputs are far more easily and accurately generated by computers than by chemists.

5) Use of a common base for information.

e.g., mg/kg using E power designation

e.g., 1.00 mg/kg = 1.00 E00
 0.001 mg/kg = 1.00 E-03
 0.286 mg/kg = 2.86 E-01

This avoids the significant figure problem to a degree and provides for correct averaging by the computer.

6) The importance of careful attention to detail must be communicated to the chemist, etc. Deviations from procedures only cause problems in comparing data unless the effect of the deviation can be statistically described (over the range, of course, not just at one level). It may be necessary to have a meeting of analysts prior to sampling to ensure consistency.

7) Copies of correctly filled-out forms should be included with the instructions.

It is necessary to ask the question of whether baseline or monitoring study should be carried out in the future. Given the present state of knowledge regarding the contaminants being studied in this program, the 1985 Baseline Study has shown that few species/tissue/contaminant samples had concentrations believed to pose a human health concern. Thus, it should be possible to designate those few combinations which require future study from a human health point of view. This will be considered by the Working Group on Environmental Assessments and Monitoring Strategies.

With respect to geographical distribution of contaminants, one must simply ask whether, given the problems currently apparent in the analysis of the contaminants and the overriding influence of biological factors, sea water monitoring using integrated samples would not be a superior approach?

With respect to time trends, it should be obvious that one must select those species for which sampling can be carried out satisfactorily to supply information for a rational statistical model for time trend analysis. Sample sites need selection based on the intention, i.e., background trends in selected fish stocks or monitoring of areas undergoing imposed change due to regulation of specific inputs.

All of the above should not be accepted as a final or even semi-final scientific approach to ICES coordinated monitoring, but rather as a catalyst to intensive scientific thought and planning for this difficult objective.

J.F. Uthe

ANNEX 7

MARINE CHEMISTRY WORKING GROUP

Action list for 1987TRACE METAL SUB-GROUP

- S. Berman
- to consider the preparation of a note on the role of reference materials and uncompromised reference materials in QA.
 - to prepare a note on NRC's progress with the production and consideration of new reference materials.
- P. Yeats
- to consider the preparation of a leaflet on the measurements of suspended matter in sea water and the feasibility of conducting an intercomparison exercise for this determination.
 - to send list of references on the sampling and analysis of trace metals in sea water to the Environment Officer.
 - to consider producing a simple biogeochemical model for zinc in the marine environment.
- W. Cofino
- to amend the manual of GLP and QA and send the amended version to the Environment Officer.
 - to explore the possibility with colleagues for the production of an overview on copper in the marine environment.
 - to consider with colleagues the preparation of simple biogeochemical models for trace metals in the marine environment.
- D. Cossa
- to coordinate the intercomparison exercise for methyl mercury in tissue.
 - to contact P. Michel regarding amendments to the overview on arsenic and send final version to the Environment Officer.
 - together with G. Topping to prepare second draft of the paper on mercury.

- U. Harms - to prepare a note identifying sources of error in the handling of biological materials prior to analysis.

ORGANICS SUB-GROUP

- L. Reutergårdh - to consider the preparation of a note on NONYL PHENOLS and ETHOXYLATES (J. Calder, M. Ehrhardt, and M. Marchand to send relevant toxicity data to L. Reutergårdh).
- to prepare a note on the outcome of the analysis of seal blubber samples from hot spot areas.
- to consider the preparation of a note on SURFACE ACTIVE AGENTS.
- and D. Wells - to consider the preparation of a paper outlining the expected timetable for improvements in the analysis of CB's and other organic compounds.
- to consider the preparation of an overview paper on planar molecules.
- Calder, Klungsøyr, Ehrhardt, Law, Granby, de Armas, Poutenan, Olafsson, and de Boer - to supply L. Reutergårdh with any relevant information on studies of organochlorines and pathology of marine mammals since 1967.

CHEMICAL OCEANOGRAPHY SUB-GROUP

- D. Kirkwood - to investigate the production of a blank reference material for nutrients in sea water and to consider its distribution to a number of ICES laboratories.
- L. Føyn - to deliver to DAFS, Marine Laboratory, Aberdeen, replicate samples of sea water collected in November 1987 for comparative analysis.

Chairman

- to prepare final version of MCWG report.
- to distribute Action List to members of MCWG.
- to raise with ACMP specific items from MCWG report and to prepare a report on any relevant ACMP discussions and recommendations.
- to prepare executive summary of MCWG report for Hydrography Committee.
- to finalize review paper on trace metals in sea water.

- to keep MCWG members informed intersessionally on any matters of concern to MCWG.
- Environment Officer
- to collate responses of MCWG members on North Sea Assessment paper and prepare note for ACMP.
 - to consider the need for revision of the reporting format forms for biota and sea water in light of discussions in MCWG.
 - to request all laboratories submitting data to ICES to send a full description of the methods used to the ICES Secretariat.

ANNEX 8

RECOMMENDATIONS

Recommendation 1

The Marine Chemistry Working Group recommends that, as there are considerable technical complexities in the analysis of nutrients, a systematic programme to optimize the determination of nutrients in marine samples should be initiated within ICES. In this connection, ICES should also explore the development of a suitable reference material for nutrients in sea water.

Recommendation 2

The Marine Chemistry Working Group recommends that ICES member countries encourage their laboratories that are participating in ICES monitoring programmes to ensure that the variances at all stages of their analyses are small. In this context, efforts must now be expended to ensure that laboratories adopt good laboratory practice whereby they can demonstrate by the use of reference materials and some very elementary statistics that their analyses (sampling, storage and measurements) are under statistical control.

Recommendation 3

The Marine Chemistry Working Group recommends that data submissions for monitoring and baseline studies should include

- a) the results from the analysis of suitable reference material and realistic estimates of laboratory precision for a particular determination; and
- b) results of periodic checks using certified reference materials.

Recommendation 4

The Marine Chemistry Working Group recommends that the final report on the results of the Seventh Intercalibration on Trace Metals in Biological Tissue (7/TM/BT) (Part 2), by Dr S. Berman and Dr V.J. Boyko, be published in the Cooperative Research Report series.

Recommendation 5

The Marine Chemistry Working Group recommends that the final report on the results of the Sixth Round Intercalibration on Trace Metals in Sea Water (6/TM/SW), by Dr S. Berman and Dr V.J. Boyko, be published in the Cooperative Research Report series.

Recommendation 6

The Marine Chemistry Working Group recommends that an intercomparison exercise on analyses for methyl mercury in biological tissues, under the coordination of Dr D. Cossa, IFREMER, Nantes, should be conducted according to the plans given in Annex 4.

Recommendation 7

The Marine Chemistry Working Group recommends that a stepwise intercomparison programme on the determination of organochlorine residues in seal blubber be conducted.

Recommendation 8

The Marine Chemistry Working Group recommends that the ACMP explore the possibility of the Oslo and Paris Commissions providing funds towards the preparation of a trace metal certified reference material based on European estuarine water.

Recommendation 9

The Marine Chemistry Working Group recommends that the Working Group meet for 5 days in February or March 1988 at a venue to be decided to carry out the following tasks:

- 1) to review the results of the intercomparison exercise for methyl mercury in biological tissue;
- 2) to review the 1986 data for the Baseline Study on Trace Metals in Coastal and Estuarine Waters;
- 3) to consider proposals for an intercomparison of the measurements of suspended matter in sea water and of the analysis of trace metals in suspended matter;
- 4) to consider the role of working reference materials in quality assurance work;
- 5) to assess progress in the measurement of nutrients in sea water and possibly to formulate plans for an intercalibration exercise on these determinations;
- 6) to review progress in the intercomparison of measurements of specific hydrocarbons;
- 7) to review progress in the measurement of organochlorine residues, particularly individual chlorobiphenyls.



