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REPORT OF THE MARINE CHEMISTRY WORKING GROUP

Savannah, Georgia, USA

13 - 17 February 1989

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1 OPENING OF MEETING

The Chairman, Dr G. Topping, opened the meeting at 09.00 hrs on 13 February 1989 and welcomed the participants.

Dr David Menzel, Director of Skidaway Institute of Oceanography, then welcomed the participants to Savannah and gave a brief introduction of the work of his institute.

Each member, and the visitors from US institutes, then introduced him or herself, and described the main areas of research interest and responsibilities in marine chemistry.

2 ADOPTION OF AGENDA

The Working Group reviewed the draft and annotated agendas, which had been prepared and distributed by the Chairman before the meeting. The adopted agenda is attached at Annex 1 and the list of participants at Annex 2.

As in previous years, the Chairman drew the Group's attention to the large number of tasks that had to be addressed and their order of priority. He informed the Group that most of these tasks would have to be dealt with by the respective sub-groups prior to being discussed in plenary. Sub-groups would begin their discussions on the afternoon of the first day. Each day's session would begin with a plenary meeting to discuss the previous day's sub-groups' discussions. The reports from each sub-group would be dealt with in plenary on the final day. The reports would include any recommendations and action list for the forthcoming intersessional period.

The Chairman reminded members that the sessional chairman for each sub-group would be those who had been elected at the last meeting to serve as chairman of intersessional activities. Following discussion about the membership of sub-groups, the participants were grouped as follows:

Trace Metals:

G. Asmund, S. Berman, W.P. Cofino (Chairman), D. Cossa, J. Olafsson, B. Pedersen, D. Schmidt, J. Uthe, W. Vynke, H. Windom, and P.A. Yeats (Rapporteur).

Organics:

J.P. Boon, J. de Boer, M.G. Ehrhardt, J. Klungsøyr, R.J. Law (Rapporteur), T. Nunes, A. Thurén, and D. Wells (Chairman). C. Manen and R.M. Parris were visitors.

Chemical Oceanography:

A. Aminot, J. Calder (Rapporteur), S.R. Carlberg (Chairman), L. Føyn, D.S. Kirkwood, O. Vagn Olsen, M. Perttilä, and G. Weichart.

The Chairman informed the Group that he would be participating in each of the sub-group sessions to clarify any matters that arose

during discussions and to assist in the discussion and direction of tasks.

3 REPORT OF 75TH STATUTORY MEETING

The Chairman informed the Group that all of the tasks requested at the Statutory Meeting for attention by MCWG, from either the parent committee or ACMP, had been incorporated in the draft agenda.

4 REPORT OF RELATED ACTIVITIES

4.1 JMG of Oslo and Paris Commissions

The Chairman referred to the report of the 14th meeting of the Joint Monitoring Group (JMG) (Vigo, January 1989), which had been prepared for ICES by its representative (Dr J. Portmann, Chairman of ACMP).

He drew the Group's attention to the following items:

a) JMG had accepted that a repeat of the baseline study of trace metals in sea water was premature before the current study had been assessed and reported to ICES and JMG. As a result, JMG is proposing that the next baseline study should be scheduled for 1992.

b) Although JMG accepted ICES advice that a further baseline study of contaminants in marine organisms was not justified, it has proposed (following pressure from member states) that a limited study should be conducted to "fill gaps" left by the previous study. Planning for the next full-scale study will commence in late 1990 for the conduct of a baseline study in 1995.

c) Despite the ICES recommendation that trend studies of trace metals in sea water are unlikely to yield useful results, some members of JMG are still insisting on the use of such measurements for this purpose in areas they consider such an approach to be useful.

4.2 Intergovernmental Oceanographic Commission (IOC) Related Activities

The following items were brought to the attention of MCWG concerning intersessional activities under IOC's Group of Experts on Methods, Standards and Intercalibration (GEMSI), and the Group of Experts on Standards and Reference Materials (GESRM).

Dr Ehrhardt, referring to the organic analyses conducted at the IOC/UNEP sponsored Workshop on River Inputs held in Thailand in May 1986, reported that, in contrast to expectations, the fossil hydrocarbons were minor contaminants of the river water and that the principal contaminants were a suite of homologous phenoxy-tetradecanes of unknown origin. A paper describing these findings is to be published in Estuarine, Coastal, and Shelf Science.

He also informed the Group about the IOC/UNEP sponsored Workshop on Biological Effects, which was held in Bermuda in September/ October 1988, and which examined the impact of hydrocarbons, chlorinated hydrocarbons, and heavy metals on marine biota. The results of this Workshop, which involved measurements of the induction of mixed function oxidases and biosynthesis of stress proteins, are still being evaluated.

Dr Windom reported on the proposed IOC/UNEP Workshop on the Use of Marine Sediments for Pollution Monitoring, which is to be held in Dalian, People's Republic of China in September 1989. The Workshop will be attended by ca. 30 participants, 15 each for trace metals and organic contaminants and will involve intercalibration and methodological aspects and data interpretation.

The Chairman reported on the production of a document on Quality Assurance (QA) Practices in Relation to the Monitoring of Contaminants in Marine Organisms, for the IOC/UNEP reference method series. Following the distribution of this document to laboratories involved in IOC and UNEP regional activities, it was the intention of IOC/UNEP to organize a workshop on QA, for the coordinators of the regional programmes, to convince analysts of the need for such practices and to ensure that the quality of data was sufficient to meet the aims of the monitoring programmes. The second objective of this exercise was to commission the production of a monograph by specialists to provide more details on the content and application of QA practices.

4.3 ICES Working Groups

The Chairman informed the Group of the request from the Working Group on Environmental Assessments and Monitoring Strategies (WGEAMS) to assist it in the compilation of matrix tables for contaminants in the main phases of the marine environment in relation to the principal purposes of monitoring programmes (see Agenda Item 6).

5 REPORT ON PROJECTS AND ACTIVITIES IN ICES COUNTRIES

Two reports were tabled under this Agenda item. A paper by Dr Law (UK) on the Concentration of Organochlorine Compounds in the Blubber of Seals from East and Northeast England (Law *et al.*, 1989, Mar. Poll. Bull. 20, 110-115) and a report by Dr Berman on the Current Status of Canadian Marine Reference Materials.

6 REQUESTS FROM ACMP AND REGULATORY AGENCIES

The Chairman informed the Group that all requests made by ACMP at the Statutory Meeting in October 1988 had been incorporated in the circulated Draft Agenda. Since the distribution of this document, he had received additional requests for work from both the Chairman of ACMP and the Environment Officer in relation to ICES work and its role as advisor to the agencies:

- The need to assist WGEAMS in the production of the matrix tables for contaminants in monitoring programmes.

- To review and make recommendations on the Dutch paper on QA proposals which had been discussed at the 14th JMG meeting.

- To provide data on analytical and sampling variability particularly for trace metals in sea water, in relation to a request from JMG for guidance on what differences in contaminant levels are actually meaningful in trend and spatial studies.

- To discuss plans for phase 3 of the CBs intercomparison exercise for sediments.

The Chairman asked the respective sub-groups to deal with the first three items in their deliberations. Since the last item was considered more appropriate to WGMS, the Chairman asked Dr Calder, the Acting Chairman of the Working Group on Marine Sediments in Relation to Pollution (WGMS), to include this item in their discussions on the following week.

7 REPORTS OF SESSIONAL SUB-GROUP DISCUSSIONS

7.1 Trace Metals Sub-group

7.1.1 Baseline survey for trace metals in sea water

The Sub-group noted that a complete data set from the ICES data bank had been sent to the meeting by Simon Wilson (ICES).

Dr Schmidt described the German scientific project ZISCH (Circulation and Pollutant Processes in the North Sea) that will, in due course, produce several thousand measurements of trace metals in sea water that might be integrated with the ICES data.

It was noted that a good deal of data is available in the open literature and that they might be included with the baseline survey data. A small group (Wim Cofino, Shier Berman, Phil Yeats, Diether Schmidt, and Graham Topping) met twice to conduct a preliminary examination of these data and to develop a plan for the final analysis of the data and the preparation of a draft report.

In this examination the Sub-group used the criteria which had been agreed at the 1987 MCWG meeting:

a) Samples of sea water should have a salinity >20.

b) Only data from filtered samples would be considered unless SPM <1 mg/litre.

c) Participants should have been successful in the ICES intercalibration exercises for metals in sea water.

d) In the absence of (c), the results would be assessed by peer review.

The preliminary examination of the data revealed that for the five principal metals under investigation (Cd, Cu, Pb, Zn, and Hg) there are approximately 1,500 results for Cd, of which about 800 met the criteria for acceptance. Another 130 could not be screened because the laboratories were not intercalibrated and there was no

time to review these results. For copper, there were 1,400 results, of which 560 met the criteria and 200 could not be assessed. For lead, there were 120 acceptable results and 100 that could not be assessed. For zinc, the respective figures were 120 and 270. For mercury, only 12 results met the acceptance criteria because very few laboratories were intercalibrated. There are other Hg results that will have to be judged at a later date.

The Sub-group suggested that, in order to complete the assessment, the data would have to be entered into a PC-based spread-sheet program and screened according to MCWG criteria. The data would be interpreted by investigating geochemical features (relationships between dissolved metals and salinity, or the relationship between total metals and SPM, etc.) and preparing box-and-whisker plots. The data set would consist of ICES data, ZISCH data, and published data.

It was proposed that a small group of MCWG members should meet, intersessionally, to analyse the data and prepare a draft report for the 1990 MCWG meeting. This ad hoc group should consist of G. Topping (Chairman), W. Cofino, D. Schmidt, P. Yeats, and S. Berman. It was also proposed that Simon Wilson (ICES) should be asked to make ICES data available in a form for IBM compatible PCs. Dr Schmidt agreed to contact Simon Wilson to discuss how this might be done. A copy of this data set would be made available to each member of the ad hoc group. Dr Schmidt will endeavour to obtain the SPM (mg suspended matter/litre) and salinity data from ZISCH in order that all of his trace metal results could be incorporated into the final data set. If data on SPM were not available, then ZISCH data for filtered and unfiltered samples would not be evaluated. For the time being the ZISCH data will not be transferred to the ICES data bank.

Each member of the ad hoc group agreed to be responsible for one of the five metals under review: Mercury (Schmidt); Zinc (Topping); Copper (Cofino); Cadmium, and Lead (Yeats and Berman). The proposal required the data to be available from ICES and ZISCH by mid-April. The ad hoc group would meet in Hamburg at the DHI, 21-24 August 1989, in order to review the individual assessments of the data and to prepare a preliminary draft of the report, which would be reviewed at the 1990 MCWG meeting.

It was proposed that ICES should be asked to cover the travel and subsistence expenses associated with the Hamburg meeting since it was unlikely that the members of the ad hoc group would be able to obtain funds from their own institutes for this meeting.

7.1.2 Overview on metals in the marine environment

A revised version of the overview paper on Hg in the marine environment, presented at the 1988 MCWG meeting, was provided by Dr Cossa. A few minor corrections were suggested by the Sub-group. It was recommended that the paper should be published by ICES.

The Group accepted an offer from Dr Schmidt to prepare an overview on Cr. The first draft, which will be prepared in collaboration with one of his post-graduate students, will be submitted to the MCWG meeting in 1990. Unfortunately, no volunteer could be found to prepare an overview on Ni.

7.1.3 Reference materials

The Sub-group examined the role of various types of reference materials in assuring the quality of measurements made in the marine environment and suggested a variant of the recommendation proposed at the 1988 MCWG meeting with respect to the preparation of internal reference materials (IRMs).

It was recognised that for many laboratories the preparation of IRMs may present difficulties and could lead to more problems than were actually being resolved by the use of such materials. It was agreed that laboratories which feel confident in their ability to produce IRMs should do so; however, others, which lack the necessary experience in such preparations, should continue to use certified reference materials to ensure that their measurement processes are under control.

On the matter of uncompromised reference materials (URMs), the Sub-group emphasized the need for such materials to be produced in large quantities and for them to be supplied to the monitoring laboratories. URMs are essential to the successful execution of any planned exercise. It is clear from the discussions of the proposal for a quality assurance scheme for the 1992 JMG baseline study for trace metals in sea water that two URMs will have to be financed and prepared by OSPARCOM for this study.

The Sub-group noted that various agencies have reported contaminant results for biota based on a dry-weight or a fat (lipid) weight basis. It was also noted that the 1985 ICES Baseline Study showed instances in which highly variable lipid concentrations (replicate analyses) were reported by certain participants, especially when dealing with tissues containing low fat concentrations. The Sub-group referred ACMP to the previous discussion of this subject by the Organic Subgroup (1988 MCWG report, p.17) and its conclusions that for fat determinations in fish tissue the Bligh and Dyer method is preferred. When concentrations of contaminants are expressed on a fat basis, full details of the method must be given. The Sub-group noted that a recent paper by Dr de Boer (Chemosphere, 1988, 17, 1803-1810) discusses this matter.

7.1.4 Precision of analytical measurements

The Chairman of the Working Group on the Statistical Aspects of Trend Monitoring (WGSATM), Dr Uthe, repeated the request from his group for data on which statisticians could estimate the day-to-day analytical variance. This information is needed to (i) estimate the magnitude relative to the overall variance observed in trend studies and (ii) estimate the required sample sizes in relation to the level of expected change in contaminant concentrations.

Following a discussion on this topic, members from the Netherlands, Denmark, and France agreed to supply quality control results (analyses of duplicate samples) to WGSATM for its use.

7.1.5 Intercomparison exercises

The Sub-group did not have any proposals to make for the conduct of intercomparison exercises in the near future.

7.1.6 Any other business

The Sub-group was informed by the Chairman of MCWG that ACMP had asked it to review a proposal on quality assurance which had been presented to JMG by the Dutch delegation, in connection with the forthcoming JMP Baseline Study of Trace Metals in Sea Water.

The Sub-group noted that quality assurance is one of the items which would have to be addressed carefully in the Baseline Study and that the design of the whole programme must be critically assessed. It noted that the different components for the design of the study would have to be dealt with separately by the appropriate experts.

The Sub-group noted that the Dutch paper is in line with the general philosophy previously approved by MCWG regarding the design of monitoring programs. The proposal required a rigorous quality management procedure supervised by an expert laboratory or body. This approach contains a suite of activities which are all essential and laboratories, in order to participate, are obliged to follow the whole scheme or be excluded from the study.

The Sub-group welcomed the attention paid to the necessity of validating the sampling procedure in each participating laboratory and stressed the need for this in all exercises regardless of the material to be analyzed. It is obvious that if the sampling protocol in a particular laboratory is at fault, then the analytical results from that laboratory will have no meaning. In practice, several difficulties for validating individual methodologies for the sampling of sea water will have to be overcome. The Sub-group considered that the suggested approaches in the Dutch proposal could be satisfactory but would need to be elaborated in greater detail. Mr Cofino and Dr Berman agreed to prepare a paper on this subject during the intersessional period.

The procedure outlined for the validation of analytical methodologies in each participating laboratory specifically adheres to the basic principles discussed and elaborated in the past years by MCWG. That is, each laboratory must demonstrate that its analytical methods are under statistical control by replicate analyses of standard samples as well as a demonstration of accuracy by the analysis of reference materials.

The preparation of an internal sea water reference material by each laboratory was criticized by the Sub-group, owing to its potential contamination for the sub-samples as well as the possibility of contamination of individual sub-samples during their preparation. It is felt that the handling of sea water is still a task laden with potential pitfalls. The Sub-group suggested that certified reference materials could be used for this purpose with the additional advantage that accuracy and precision could be assessed in one procedure.

The Sub-group agreed that an intercalibration exercise following the validation stage was an essential external quality assessment measure for the participants. In addition, normal internal quality assessment measures would have to be maintained by the participants.

In respect of the dissemination of uncompromised reference materials to be analysed along with the actual samples, the Sub-group noted that this had been suggested earlier by the MCWG. The analyses of such materials represent a long-term intercalibration and appear to be a promising tool for quality assessment of data.

Finally, the Group considered that the proposed quality assessment programme together with a carefully designed baseline study were necessary prerequisites for success.

7.1.6.1 Monitoring of contaminants in relation to JMG's principal purposes: review of matrix tables prepared by WGEAMS

This item was discussed following a request from Dr Carlberg, the Chairman of WGEAMS, for MCWG to review the matrix tables produced by his Group. The Sub-group noted that these tables had subsequently been amended by ACMP at its last meeting (see page 21, 1988 ACMP report (Coop. Res. Rep. No. 160)).

In general, the Sub-group had reservations about the production of such generalized and simplified tables for monitoring purposes, particularly for programmes concerned with baseline studies and trend monitoring. On the basis of its collective experience, the Sub-group argued that a sampling strategy had to be devised for each programme of monitoring, taking into account the nature and aims of each programme and the characteristics of the sea area (hydrography, chemistry, biology, nature and quantity of inputs of contaminants) in which the investigation was to be conducted. These factors would largely determine the selection of contaminants and the matrix (or matrices) in which contaminants are to be measured, the location of sampling positions and the frequency of sampling. The Sub-group, therefore, considered that these matters could not be adequately and comprehensively dealt with by the production of sampling matrix tables for each monitoring purpose.

In concluding this discussion, the Sub-group noted that a paper on sampling strategies had been prepared by Dr Uthe and his co-workers and that the contents of this paper reflected their views on the approach to be taken in designing and conducting monitoring programmes (see discussion under Section 7.1.6.2).

7.1.6.2 Discussion of a paper by Dr Uthe and Canadian co-workers entitled "Sampling Strategies for Trend Monitoring Using Biota, Sediments or Sea water"

The outcome of the Sub-group's discussion was that a generalized monitoring strategy is difficult to establish. It was considered that a strategy would have to be devised for each case, taking into account the aims of the programme, the local environment, an understanding of geochemical processes for each area, etc.

The Sub-group considered that Sections 2.2.2 and 2.2.3 of this paper needed input from MCWG and noted that Dr Uthe had requested

help in developing protocols for sea water monitoring. In this context, Mr Cofino offered to contribute information on protocols being used in the Dutch programmes. The Sub-group stressed that, when sediments were considered for monitoring purposes, they should be used along guidelines previously provided by WGMS and accepted by ACMP. The Sub-group considered that this aspect of the paper should be reviewed by WGMS.

In considering this Agenda item, the request from WGEAMS about matrix tables (see Section 7.1.6.1), and the request from JMG to review the Dutch quality assurance paper, the Sub-group made the following remarks on monitoring strategies:

1) The design of monitoring programmes requires a multidisciplinary scientific effort, involving experts in biology, environmental and analytical chemistry, statistics, and hydrography, together with specific information on the area to be monitored. It is not possible to give a simple blueprint for the design of these programmes.

2) The objectives of the programme have to be defined qualitatively and quantitatively. Statistical model calculations, based upon realistic estimates of the overall variance, are a prerequisite in the design, to give insight on the differences in contaminant levels that can be determined. In most cases, a "pilot project" will be necessary in planning and designing a programme.

3) Any organisation supervising a monitoring programme should develop and maintain its own quality assurance scheme along the lines of widely accepted quality assurance practices (e.g., International Standards Organization, 9000-9004). This, in general, will comprise:

   - Procedures which enable the managers of monitoring programmes to establish and assess their programme objectives and determine whether the programmes are producing relevant data in relation to these objectives;

   - Appointment of a quality assurance manager to ensure that participating laboratories maintain adequate quality control (QC) and quality assurance (QA) protocols; and

   - Procedures to assess and govern the quality of data being produced by the participating laboratories. These procedures (supply of adequate quality assurance samples, intercomparison exercises) are in addition to mandatory QA and QC programmes in the individual laboratories.

4) Monitoring organisations are recommended to devise quality assurance manuals comprising:

   - the objectives of each monitoring programme,

   - technical and administrative procedures,

   - quality assessment/control measures for data.

5) Monitoring organisations are recommended to appoint an expert laboratory or body as quality manager, supervising a comprehensive quality assurance programme from sampling to data handling.

6) Participants in the monitoring programme should be obliged to follow the QA programme.

7.2 Organics Sub-group

Dr Wells opened the meeting and invited the participants to put forward any topics that they wished to be considered under item 7.2.7. Two topics were proposed, and the Sub-group then proceeded to the main items of the Agenda.

7.2.1 Intercomparison exercises for CBs and PAHs

Dr de Boer presented a progress report on the ICES/IOC/JMG intercomparison exercise concerning chlorobiphenyls (see Annex 3). The Sub-group noted with thanks the progress made intersessionally with this exercise and proceeded to a discussion of the conduct of subsequent stages of the exercise. A flow diagram was produced which summarized these discussions (see Annex 4). The following recommendations concerning this exercise were agreed:

1) If the degree of comparability achieved during stage 1 of the exercise is not acceptable, then stage 1 should be repeated with newly prepared standard solutions. Specific guidelines on how to improve performance would be given, highlighting areas where greater care should be taken. The performance and improvement shown by each laboratory would be reviewed on the basis of these analyses. Laboratories which failed to achieve satisfactory performance after repeating stage 1 would not be able to move forward to later stages of the exercise. The criteria for acceptability would be set by the coordinators, with assistance from WGSATM, in their report to MCWG, and would then be available for discussion by the Sub-group.

2) If possible, the same team of coordinators should be responsible for the repeat of the first stage of the exercise to maintain continuity.

3) The suitability of certain methods, and recommendations on techniques for additional stages in the analysis, should be made available to ICES, IOC and JMG laboratories participating in the exercise. The aim of the exercise is to encourage poor performers to improve.

4) Stage 2 of this exercise should be implemented as soon as stage 1 has been satisfactorily completed. This should be the subject of a recommendation to ACMP. Progress reports will be submitted to MCWG and the ICES Statutory Meeting, as appropriate. A progress report on the first iteration of stage 1 should be submitted to the Statutory Meeting in 1989.

Mr Law presented a progress report on the fourth round hydrocarbon intercomparison exercise (see Annex 5). The single solution prepared in acetonitrile was originally considered suitable for analysis by both HPLC and GC-MS techniques (see ICES, Doc. C.M. 1987/E:17). Subsequent work by the coordinator confirmed that acetonitrile gave good chromatography using automated on-column injection on a Hewlett-Packard GC system. However, reports from the analysts showed that a number of participants had experienced poor resolution and peak splitting with the prepared solution, and this, added to the problems of sealing the vials, suggested that it may prove necessary to re-run the first stage of the exercise. In this case separate solutions would have to be prepared for HPLC and GC-MS techniques. This could follow on directly after stage 1 and be completed in time for a report on both sets of analyses, to be prepared and submitted for discussion at MCWG 1990. A progress report will also be prepared for submission to the 1989 ICES Statutory Meeting.

7.2.2 Review of hydrocarbon analysis

There was extensive discussion of the three papers prepared by Drs Ehrhardt and Klungsøyr and Mr Law, concerning the analysis of hydrocarbons in sea water, biota and sediments, respectively. This centered on two main points:

1) The absence of the originally proposed complementary section concerning the atmosphere, to have been prepared by Dr A. Knap.

2) The organisation, areas of coverage and the intended readership of the finished document.

The Sub-group was informed that Dr Knap was unlikely to be able to prepare this section. Various alternative authors were considered but as no expertise existed within the group it was finally agreed to withdraw this aspect from the review. The remaining three sections would be structured as follows:

1) A common introduction, including discussion of the various aims for which such samples may be collected and analysed.

2) Three sections covering sample collection, extraction and clean-up for each of the sample matrices considered.

3) A common section on analytical measurement techniques, to include a discussion of the utility of the different techniques and guidance as to how each may be employed to meet the aims outlined in (1).

After completion, the paper will be submitted for review to Dr J. Farrington, and to Dr Hites (Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA), if he is willing to review it.

The final report is intended as a critical review of the available methodology, and will offer guidance to readers in the selection of methodology appropriate to the task in hand.

Another outcome of the discussion of these papers was that consideration is being given by sub-group members to the preparation, for MCWG 1990, of an information paper on the subject of metabolites of organic contaminants in bile. A short note concerning this topic is appended as Annex 6.

It was agreed that the three papers as they stand, with an executive summary (see Annex 7), should be passed to ACMP this year as a progress report. Dr Ehrhardt agreed to continue to act as coordinator of the intersessional work.

7.2.3 Overviews

7.2.3.1 Overview on planar chlorobiphenyls

This had been prepared by D Wells, P de Voogt and L Reutergårdh. In reviewing the paper, the first question considered was terminology, as the most commonly used description found in the literature is "coplanar", whereas planar was felt to be more accurate. It was agreed that the title of the paper should be amended to read: "Planar chlorinated biphenyl congeners and mono- and di-ortho congeners in the environment," and also that planar should be used throughout as the preferred description, with a footnote to the effect that the term "coplanar" is often also used. Dr Wells agreed to approach IUPAC, on behalf of MCWG, to confirm the nomenclature of this term. In addition, although only the non-ortho congeners are truly planar, there is some evidence that mono- and di-ortho congeners also exhibit the characteristics of planar molecules. Dr Boon illustrated the reasons with the following comments:

1) Although the non-ortho congeners can become planar most easily, there is evidence from studies on induction of cytochrome P450-dependent mono-oxygenase enzyme systems, that mono- and some di-ortho chlorine containing congeners also exhibit the characteristics of planar molecules. Such characteristics are always absent in tri- and tetra-ortho Cl containing congeners. Due to the obligatory overlap of atomic radii of ortho-chlorines, the energy requirement to reach a planar configuration is much greater for tri- and tetra-ortho Cl-substituted congeners.

2) It was noted in passing that there are only three highly toxic non-ortho-Cl planar chlorobiphenyls, numbers 77, 126, and 169. Minimal requirements for a high toxicity are the presence of Cl-substitution at both para-positions and at least at one meta-position of each ring. Toxicity decreases with increasing ortho-chlorine substitution.

If the minimum requirement for toxicity is taken into account (i.e., the presence of chlorine substitution at both para- and at least two meta-positions), then there are only three highly toxic planar CBs, IUPAC Nos. 77, 126, and 169. A number of suggested amendments were made; further comments are welcomed by the authors. A finalised text will be submitted to ACMP.

7.2.3.2 Hexachlorobenzene and lindane in the aquatic environment

The overview on these contaminants was prepared by Dr Wells. In general, concentrations of hexachlorobenzene (HCB) and lindane (γ-hexachlorocyclohexane; γ-HCH) in the environment, and particularly in the marine environment, are low with respect to the effect concentrations, except close to inputs. This had led to the consideration by some agencies (e.g., NOAA) of the withdrawal of these compounds from monitoring studies. The Sub-group felt this was a little premature since the analysis of samples for compounds from the CB and DDT groups could include results for HCB and lindane with little extra effort. Also, there are areas, such as the southern North Sea, where the concentrations in cod liver are higher than the baseline concentration observed elsewhere in areas remote from identical sources. In addition, lindane is used as a model compound in the study of processes relating to the measurement of K_d. (Distribution coefficient or sorption constant (K_d) is the ratio of the concentration of a solute adsorbed onto a solid ($\mu g\ g^{-1}$) and the concentration of the same solute ($\mu g\ ml^{-1}$) in equilibrium in the dissolved phase, such that $C_p = K_d\ C_s$.) There is transport of more soluble persistent contaminants and a lack of data on the breakdown products and metabolites of these compounds and their effects. Therefore, it was appropriate to recommend that determination of both HCB and γ-HCH should continue in conjunction with other organochlorine compounds. However, it should be emphasized that there is no justification to increase the effort in monitoring for HCB and lindane except in those few areas where there is a local source of these compounds. It was agreed that, after minor revision, the paper will be submitted to ACMP.

7.2.4 Polychlorinated dibenzo-p-dioxins and dibenzofurans - an update

This paper, requested by OSPARCOM via ACMP, was prepared by Dr Wells. It was first noted that the majority of the data reported related to fresh water, and to both PCDD and PCDF compounds, but that frequently only the 2,3,7,8-TCDD and -TCDF isomers were determined. If these two compounds were not found, then often this was taken to indicate that PCDD and PCDF in total were not present. This may well be an erroneous assumption in many cases.

It was agreed to submit this paper to ACMP following the incorporation of comments. Taking account of the similarity between planar CBs, PCDD and PCDF, the question was raised of a single combined review of all these planar molecules. However, this was felt to be premature since the Sub-group was informed of work to be published within the next year on interactions of planar molecules with DNA. It was, therefore, agreed to review the situation at MCWG 1990.

Dr Wells was thanked for his considerable efforts for the papers presented under this and the previous agenda items.

7.2.5 Precision of analytical measurements

Dr Uthe first clarified his requirements by addressing the following questions:

1) What is the long-term variance of the analytical measurements within a laboratory? (5-10 years).

2) What amount of the unexplained variance is due to the overall analytical variance? NB: Readers of this Section are encouraged to read the reports of WGSATM.

In response, the following guidelines were developed:

Guidelines for the Chromatographic Analysis of Organic Contaminants

I) Standard Solutions:

i) All solids used to prepare these solutions should be certified materials (if available).

ii) A purity check of standard materials is always necessary; for organochlorines, by GC-FID as well as GC-ECD.

iii) Results obtained using a newly prepared standard solution should not be significantly different from those of the previous standard solution. When such a comparison cannot be made, duplicate solutions should be prepared from the solid materials.

II) Instrument Performance

i) Linearity tests should be made on a regular basis. For CBs, at least 50 pg per injection for each congener is necessary. Different concentrations of the standard mixtures should not be prepared by serial dilution but by preparing standards from different weights of solids.

ii) A study of peak symmetry and the resolution of closely eluting individual compounds within chromatograms should be made as a check on chromatographic performance.

III) Quality Control of Preparative Procedures

i) Sample preparation (e.g., extraction, clean-up and isolation) should be checked to assess recovery of analyte.

ii) Procedural blanks should be made with each batch of samples.

iii) Internal standards should be added to the samples. Depending on different goals, they can be added at different stages of the analytical procedure.

iv) Standards, combining all compounds analysed, should be run at regular intervals (e.g., during each series of injections) to control the instrument performance.

IV) Sample Quantification

i) The concentrations of compounds analysed in the samples should be within the range of standards tested for linearity. One should never extrapolate beyond the range tested.

ii) Ideally, two aliquots of one homogenate should be analysed. A minimum of 5-10% of duplicate analyses is necessary. This allows an estimate of long-term variability to be made.

iii) Long-term analytical performance should be controlled by using an internal laboratory reference material to monitor the variance of the analysis on a continuous basis and the basis of the technique controlled by analysing an appropriate CRM. If no CRM is available, then an alternative RM should be selected which most closely reflects the nature of the matrix under investigation, e.g., use a fish oil CRM for CBs in seal blubber until a CRM for seal blubber is available.

iv) All data, including those for samples, blanks, standards and quality assurance procedures, should be recorded and stored in a secure place.

v) Mass spectrometric confirmation of the identity of compounds should be made for each set of samples. As samples analysed by GC-ECD do not usually contain enough material for individual confirmation by GC-MS, bulking of sample extracts and subsequent analysis of the bulked extract may be necessary.

7.2.6 Reference materials

Dr Parris informed about progress made during the past year by NIST, a note of which is attached as Annex 8. Dr Wells presented a paper on the need for organic reference materials. A number of additional RMs were proposed. For example, a large number of deaths of Atlantic bottlenose dolphins (Tursiops truncatus) on the east coast of the USA during 1988 had recently been attributed to brevetoxin. This pelagic toxin may be required as a reference material at a future date. NRC are to prepare a homogeneous mussel tissue contaminated with alkyltin compounds, which could be made available for use in an intercomparison exercise.

See:
Wells, D.E., de Boer, J., Tuinstra, L.G.M.T., Reutergårdh, L. and Griepink B. 1988. Frezenius Z. Anal. Chem., 332, 591-597.

Wells, D.E. (1988). Frezenius Z. Anal. Chem., 332, 583-590.

7.2.7 Any other business

Dr Wells was confirmed as the Chairman of the Sub-group for the intersessional period and for MCWG 1990. As no expert was available to prepare an overview of surface-active agents, it was with-

drawn from the programme. An overview on chlorophenols was considered, but no sub-group member felt he had the time to prepare such a paper. As this topic was felt to be a priority subject for an overview, it was agreed that members would bring information to MCWG 1990 with a view to preparing the paper at the meeting.

Dr de Boer informed the Sub-group that high concentrations (5 mg/kg) of tetrachlorobenzyltoluenes have been found in the tissue of eels from the Netherlands. These arise from a commercial hydraulic oil, Ugilec 141, manufactured in France and used in deep mining activities in the Federal Republic of Germany. Although these compounds are supposed to be used in "closed" systems, they have also been found in freshwater fish in the Federal Republic of Germany. It was reported that they are also on sale in the UK, although their purpose and use is not known, nor is the scale of manufacture. The presence of these compounds in samples may also be a problem in the determination of CBs by GC-ECD, as they co-elute with some congeners. GC-MS is needed to confirm the identity of each eluting compound. Laboratories which undertake CB analysis should be aware of this potential interference.

Dr Biscaya informed the Sub-group of a symposium, "Organic Micropollutants in Water", to be held in Lisbon in early 1990 under the EEC COST 641 programme. He will circulate further information to all sub-group members when available.

The Sub-group considered a paper by Dr Uthe entitled "Sampling Strategies for Trend Monitoring Using Biota, Sediments or Sea Water". It was noted that the major part of the paper concerned biota, and was in general targeted more towards nutrients and trace metals than organics. Some clarification of the use of specimen banking was agreed, to the effect that storage effects for real samples cannot be addressed using the results of analyses of CRMs, as these are designed to remain stable for the period of their shelf-life.

Finally, the Sub-group addressed the request from the Chairman of WGEAMS for assistance in redrafting a matrix table for monitoring purposes. Comments were made to the effect that, for purpose (a), the assessment of hazards to human health, for organics necessitates the analysis of the most lipid-rich edible tissues of the organism. For purposes (c) and (d) where sediments are to be used, some difficulties can be foreseen. Factors to be taken into account include knowledge of sedimentation rates and the erosion/deposition history of the areas, the degree of oxygenation of the sediment, bioturbation, sediment particle size structures and the need for fractionation prior to analysis. Also, the inadequacy of detection limits may present problems. The current requirements for organic analysis are limited to γ-HCH and PCBs. This may need to be reviewed with the objective of including those specific organic contaminants which are most likely to be an environmental concern. Where "PCB" are measured, the Sub-group supported the suggestion that those laboratories competent to perform CB analysis, on a congener basis, should over a period of time report results in both forms, with a view to eventual replacement of total PCB analysis on a formulation basis in all programmes. As a final point, the notes under purposes (c) and (d) regarding the use of sedentary species should not necessarily preclude the use of pelagic fish, since equilibrium partitioning between body

lipids and the ambient sea water appears to be the dominant process regulating organochlorine concentrations, as long as the first are representative of the area of capture (see, e.g., de Boer (1988), Chemosphere 17, 1811-1819).

7.3 Chemical Oceanography

7.3.1 The nutrient intercomparison exercise

Mr Kirkwood reviewed the history of a natural water sample collected near Greenland that appeared to be stable with regard to inorganic nutrient concentrations. To verify the suitability of this natural water as an intercalibration sample, 200 ml subsamples were sent to members of the Chemical Oceanography Subgroup in August 1988 for analysis. The results received by the end of January 1989 were tabulated for review by the Sub-group. The Sub-group concluded that the data supported the use of this sample in the Intercalibration Exercise for Nitrate, Phosphate, Total N and Total P.

Mr Aminot discussed the results of his studies to produce, from a natural water, a stable sample, artificially depleted in nitrate and phosphate. By exposing a 50 litre unfiltered sample to natural sunlight, phytoplankton growth occurred. After filtration, the nutrient-depleted water contained a low, and constant, level of nitrate and phosphate. Based on the data presented by Mr Aminot, the Sub-group concluded that this water would be suitable for the Intercalibration Exercise.

The Sub-group agreed that a third sample, of intermediate level, would be desirable for the planned exercise, but that it was undesirable to delay the exercise while investigating how to prepare such a sample. Mr Aminot suggested an approach that could provide a suitable sample in a short period of time. He proposed to heat-sterilize a natural water sample, thus stabilizing the sample from a biological standpoint. He would then perform sufficient analyses in his laboratory to determine short-term stability. If a positive result was obtained, subsamples would be sent to volunteers from the Sub-group who would provide analytical data to Mr Aminot within a short period. If these results are favourable, the sterilized water would be included in the exercise. Therefore, the exercise would consist of three or more water samples, each to be analysed for nitrate, phosphate, total N, total P, and, for samples not bottled in glass, silicate.

The Sub-group proposed that the samples should be analyzed using the participants' routine procedures. Following consideration of the statistical aspects and sample-size constraints it was agreed that participants should be asked to supply two replicate analyses for each determinand in each sample.

The coordinators for conducting the exercise will continue to be Messrs Aminot and Kirkwood and Dr Perttilä, who will perform the statistical evaluation of the returned data. The timetable for the exercise appears as Annex 9 to this report. Dr Perttilä will present a status report (not including any results or statistics) to the ICES Statutory Meeting in October 1989.

Mr Kirkwood proposed that a letter informing the participants of the timetable should be sent and that a questionnaire should be included asking for specific details of the phosphate analysis method to be used on samples by participants. This information could help to explain any observed variability in the returned data. Dr Carlberg stressed that details of methods used would be a required part of the response by the participants. The Sub-group concurred that a questionnaire should be included with the letter.

7.3.2 Review PEX chemical measurements

The Sub-group reviewed a letter of 2 January 1989 from Dr Dooley (ICES Hydrographer) in which he raised questions regarding the PEX nutrient data. The Sub-group members who were also PEX participants agreed with Dr Dooley that some nutrient analysis problems had been identified during the PEX exercise. Sub-group members who did not participate in PEX did not have firm views on this subject. Clearly, the PEX experience was a significant factor leading to the planned ICES nutrient intercalibration exercise coordinated by the MCWG. However, the Sub-group strongly disagreed with Dr Dooley's contention that PEX was simply an intercomparison exercise. The purpose of PEX was to develop a quantitative awareness of the distribution of patches of productivity and an appreciation of their formation and dissipation. Measurements of nitrate, phosphate, and chlorophyll were made for this purpose. Together, the three data sets provided a consistent view of the structure of patches. Thus, for the purpose intended, the nutrient data were satisfactory. It was never intended as part of PEX to acquire a high quality nutrient data set for inclusion in common data banks, such as the ICES data bank.

During PEX, three multi-ship nutrient intercalibration exercises were conducted. Results from the first exercise did illuminate some analytical problems. Some of these problems were traced to faulty nitrate reduction columns, and to high blanks in "nutrient-free" water and other reagents. Steps were immediately taken to rectify these problems; thus, the real data should be better than indicated by the first set of results. The "50 meter" exercise in fact showed much better agreement among the ships. Some of the observed variance here could well have been the result of use of water from 12 different Niskin bottles, rather than from a homogeneous sample. The Sub-group agreed that the correction factors applied by Dr Dooley, based on the "50 meter" data, although not being a perfect way of correcting, still offered an appropriate method for making a more comparable set of data. However, it would be wrong to use these correction factors on any other data. The biases observed during PEX cannot be assumed to apply to historical data and have no bearing on results reported by each PEX participant in their regular work. The pooled nutrient data from the Baltic Monitoring Programme have been evaluated and generally found reliable, even though unusual data have occasionally been found. Dr Perttilä was asked to discuss any outstanding details of the PEX data with Dr Dooley.

With regard to the proposed SKAGEX experiment, the Sub-group recommended that the participants should adhere to established principles of good laboratory practice, participate in intercomparison exercises, and make use of available reference materials, e.g.,

the Sagami nutrient standards. One member of the Sub-group (Dr Føyn), who is in charge of the chemical oceanography component of SKAGEX, will urge participants to take part in the ICES Intercalibration Exercise. Such participation should be a pre-requisite to reporting SKAGEX data to ICES for subsequent handling.

7.3.3 Problems associated with the determination of oxygen

In addition to the advice offered by the Sub-group in the 1988 MCWG report (Section 7.3.3), the following points were discussed in more detail at the request of ACMP.

1) In situ oxygen sensors. These sensors should preferably be used in conjunction with CTD-profiling instruments. In order to validate the oxygen profile two steps are essential. The first is to take water samples at different depths for traditional Winkler titration. The results of repeated calibrations in this way will show how many calibration samples are needed per profile and whether a calibration needs to be carried out for each profile.

   The second step is to evaluate the oxygen profile from an oceanographic viewpoint as regards stratification, etc. based on the CTD-profiles.

   Furthermore, if measurements are performed in areas with anoxic waters, it has to be established whether or not the oxygen sensor can recover from exposure to sulfide-bearing water, and the time required to produce meaningful oxygen data again. If the sensor recovers too slowly, or does not recover at all, two options are available: either cover the sensor when in anoxic waters or refrain from immersing the sensor at all in these waters.

2) In studies in which anoxic waters may be encountered, samples are sometimes taken for Winkler titration that contain hydrogen sulfide in very low concentrations. Such samples may yield erroneous positive values for oxygen. This problem can be addressed in different ways. One solution is to collect samples for both analysis of hydrogen sulfide and of oxygen. If the former samples give positive results, the latter samples are simply discarded.

   The second option is to accept the possibility of the coexistence of low concentrations of both oxygen and hydrogen sulfide, which may occur in rare cases in mixing zones. However, it is best to view the oxygen data with some reservation.

   The third approach when there is suspicion of hydrogen sulfide in the water is to perform the addition of Winkler reagents as usual, but after the precipitation has taken place, an aliquot of the supernatant is withdrawn and replaced with an exact amount of potassium iodate. Then the titration is performed in the normal way. The calculation of potential hydrogen sulfide is done according to Fonselius (in "Methods of Seawater Analysis", Editors Grasshoff et al., 1983, Verlag, Chemie).

7.3.4 Overview of nutrient measurements

Mr Kirkwood reported that no activity on this topic had taken place during the intersessional period. Mr Aminot reported that he has begun preparing some relevant data for transmission to Mr Kirkwood and promised to make the data available as soon as possible. It was pointed out that much of the data of interest to Mr Kirkwood resided in the ICES data bank and some have also been published in the open literature. Specifically Dr Weichart and Dr Vagn Olsen invited Mr Kirkwood to obtain their data directly from ICES. Mr Kirkwood agreed to proceed in that way and assured the Sub-group that any new data so obtained would not be made available to a third party and that all original data sources would be acknowledged.

It was pointed out by Dr Føyn that his paper to the 1988 Statutory Meeting (ICES Doc. C.M.1988/E:20) related directly to the topic of trend assessment of nutrient data. He agreed to send appropriate data to Mr Kirkwood. Mr Kirkwood agreed to prepare a report for the next meeting based on the data to be obtained from the various sources.

7.3.5 Any other business

1) The Sub-group reviewed the paper by Uthe *et al*. (Sampling Strategies for Trend Monitoring Using Biota, Sediments or Sea Water) and in general felt that the paper was sound and valid. However, the Sub-group took exception to the statement in Section 1.1.3 of the paper that stated "precision and accuracy of ±1% are routinely achieved" in the analysis of nutrients in sea water. It is generally agreed that statements like this must refer to a concentration level. In practice, precision and accuracy of ±1% are rarely achieved and only at high nutrient levels. At low nutrient levels, the Sub-group felt that ±10% was a very good achievement.

   Noting that Section 2.2.3 of the paper identified MCWG as the appropriate group for developing guidelines for the use of sea water in trend monitoring, the Sub-group discussed the merits of preparing a general protocol for sampling, storage and analysis of sea water for nutrients. Dr Perttilä agreed to compile the already published advice on the topic and to circulate a draft to other sub-group members for their comments and additions. Dr Føyn noted that as part of his SKAGEX responsibility, he would be able to provide substantial input on the sampling and storage aspects. Dr Perttilä will prepare a revised draft incorporating sub-group members' comments for consideration at the next MCWG meeting.

2) The Sub-group took note of the information provided by D Wells regarding the Third International Symposium on Biological Reference Materials.

3) Dr Føyn reminded the Sub-group that two years ago they had considered a new method for organic carbon and nitrogen in sea water, proposed by Japanese workers, that gave higher values than those using accepted techniques. At that time, the Sub-group felt that the Japanese method was unproven. More recent information lends support to the Japanese method and many scientists now believe that the earlier data are incorrect. The Sub-group agreed to follow this topic intersessionally and to discuss it again at the next meeting.

4) Dr Weichart considered that much of the historical data for phosphate, dating back to the 1930s, would in principle be reliable and useful for retrospective trend analysis. He agreed to prepare a paper, for the next meeting, that will evaluate more thoroughly the value of historical phosphate data.

5) The Sub-group considered the selection of a Chairman for the intersessional period and the next meeting. Members were unanimous in their appreciation of the efforts of the present Chairman, Dr Carlberg, and by acclamation endorsed his continuance in office. Dr Carlberg agreed to continue, noting that the energy put forward by the sub-group members made the job of Chairman relatively straightforward.

8 PLENARY DISCUSSIONS OF SUBGROUP REPORTS

The MCWG reviewed the reports prepared by the three Subgroups and the action lists and recommendations arising from each report.

Trace Metal Subgroup

The overview paper on mercury, and the recommendation that it should be published in the ICES Cooperative Research Report series, was endorsed by MCWG.

The recommendation that an ad hoc group of MCWG members should meet intersessionally to complete the assessment of data on trace metals in coastal waters was supported and endorsed by MCWG.

On quality assurance, MCWG noted and endorsed the recommendation that the preparation of IRMs should only be done by laboratories which were competent to make these materials and that less experienced laboratories should continue to use CRMs for in-house quality assurance work. MCWG supported the proposal that OSPARCOM should consider financing the preparation and distribution of two URMs for the forthcoming JMG Baseline Study of Trace Metals in Sea Water in 1992.

MCWG noted, and agreed with approval, the comments made on the monitoring strategies paper by Dr Uthe and his co-workers and agreed with the principle that a general protocol for monitoring should not be produced but that protocols should be drawn up on a case-by-case basis.

Organics Subgroup

MCWG noted the progress made on the Intercomparison Exercises for CBs and PAHs and agreed with the proposal that the first stages of these exercises should be repeated if the results from the first distribution of samples were unacceptable.

MCWG noted and welcomed the progress made on the review papers on hydrocarbon analyses, and agreed that the amended drafts of these papers, together with the Executive Summary in Annex 7, should be presented at the next meeting of ACMP.

MCWG noted with approval the preparation of the overview papers on planar CBs, HCB, HCH, dioxins, and furans and agreed that the amended versions of these papers should be submitted to ACMP for approval and publication in the ACMP report.

MCWG noted the advice given on guidelines for the chromatographic analysis of organic contaminants and agreed that this should be brought to the attention of JMG.

Chemical Oceanography Subgroup

MCWG agreed with the advice given on the precautions to be taken in the measurement of dissolved oxygen, using probes, and considered that this was suitable to be passed to the Working Group on the Baltic Marine Environment in response to their request for help in this matter.

MCWG noted with approval the progress made on the development of an Intercalibration Exercise for Nutrients in Sea Water. It considered, however, that the coordinators of this exercise should ensure that sufficient samples were prepared to allow for replicate analyses by participants to provide the necessary statistical data to judge laboratory analytical performance. This matter is to be considered further by the coordinators.

MCWG noted the intention of the Subgroup to prepare intersessionally a protocol for the sampling, storage, and analysis of nutrients in sea water.

In concluding the discussion, the Chairman thanked all of the Subgroup Chairmen and Rapporteurs for their efforts over the past few days, and those members who had been responsible for coordinating intersessional activities or preparing reports for the meeting. The intersessional activities are listed in Annex 10.

9 ANY OTHER BUSINESS

No matters were raised under this Agenda item.

10 RECOMMENDATIONS

MCWG then discussed the venue and time of its next meeting. It agreed that this should take place at ICES Headquarters, either in late February/early March or, if possible, back-to-back with the next meeting of WGSATM. A recommendation to this effect, together with a list of topics for consideration at this meeting, is given in Annex 11.

All other business being completed, the Chairman thanked all members for their hard work and constructive help during the meeting. On behalf of MCWG, he thanked Dr Windom and his colleagues for providing such an agreeable venue, comfortable and spacious working rooms, and good support services, which included an extremely helpful secretary (Dannah McCauley). He then closed the meeting at 12.15 hrs on 17 February 1989.

ANNEX 1

MARINE CHEMISTRY WORKING GROUP
Savannah, Georgia, USA
13-17 February 1989

AGENDA

1. OPENING OF MEETING

2. ADOPTION OF THE AGENDA

3. REPORT OF 76TH ICES STATUTORY MEETING

4. REPORTS ON RELATED ACTIVITIES

   4.1 JMG of OSPARCOM
   4.2 IOC
   4.3 ICES Working Groups
   4.4 Other activities

5. REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES

6. REQUESTS FROM ACMP AND REGULATORY AGENCIES

7. SUB-GROUP ACTIVITIES AND DISCUSSIONS

   7.1 Trace Metals

      7.1.1 Review of data for trace metals in coastal waters
      7.1.2 Overviews on Cr and Ni
      7.1.3 Reference materials
      7.1.4 Precision of analytical measurements
      7.1.5 Intercomparison exercises
      7.1.6 AOB raised by Sub-group

   7.2 Organics

      7.2.1 Review progress on CBs and PAHs I/C exercises
      7.2.2 Review of hydrocarbon analysis
      7.2.3 Review overviews on planar molecules, HCB and HCH
      7.2.4 Overview on dioxins
      7.2.5 Precision of analytical measurements
      7.2.6 Reference materials
      7.2.7 AOB raised by Sub-group

   7.3 Chemical Oceanography

      7.3.1 Review progress on nutrient I/C exercise
      7.3.2 Review PEX chemical measurements
      7.3.3 Dissolved oxygen measurements
      7.3.4 Overview on nutrient measurements
      7.3.5 AOB raised by the Sub-group

8. PLENARY DISCUSSION OF SUB-GROUP WORK

9. ANY OTHER BUSINESS

10. RECOMMENDATIONS

ANNEX 2

MARINE CHEMISTRY WORKING GROUP

Savannah, Georgia, USA

13-17 February 1989

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ANNEX 3

MARINE CHEMISTRY WORKING GROUP
Savannah, Georgia, USA
13 - 17 February 1989

PROGRESS REPORT OF THE JOINT ICES/IOC/JMG INTERCOMPARISON EXERCISE ON ANALYSES OF CHLOROBIPHENYLS IN MARINE MEDIA

At the meeting of the ICES Marine Chemistry Working Group in The Hague, 7-11 March 1988, it was decided that an intercomparison exercise on analyses of 10 individual chlorobiphenyls in marine mammals would be organised. This exercise would be a combined effort of the International Council for the Exploration of the Sea (ICES) and the Intergovernmental Oceanographic Commission (IOC). The exercise was to be conducted in three steps:

1) analysis of standard solutions

2) analysis of extracts

3) analysis of a sample of seal blubber

It was proposed, and accepted, that the first stage of the exercise could be a combined study with the laboratories of the Joint Monitoring Group of the Oslo and Paris Commissions. In June 1988, the participation of the JMG laboratories was confirmed at the 10th Joint Meeting of the Oslo and Paris Commissions in Lisbon. For the first step of the exercise, J. Duinker (Institut für Meereskunde an der Universität, Kiel) would act as coordinator on behalf of IOC and J. de Boer (Netherlands Institute for Fishery Investigations, IJmuiden) on behalf of ICES. J. Calder (National Oceanic and Atmospheric Administration, Washington) offered assistance for the evaluation of the data, which was accepted.

A few weeks after the MCWG meeting, provisional guidelines were designed by the two coordinators. The comments received from the ICES Working Group on Statistical Aspects of Trend Monitoring were considered thoroughly in the preparation.

D. Wells of the DAFS Marine Laboratory and J. de Boer met on 29 April in Aberdeen to evaluate the provisional guidelines and to examine if the ICES/IOC/JMG exercise could benefit from valuable experiences of a CB intercalibration exercise which was conducted by the Community Bureau of Reference of the European Communities.

Taking into account the different comments and advice, a definite design for the exercise was made by the two coordinators during June. Standards of individual chlorobiphenyls, ampoules and packing materials were ordered by the Institut für Meereskunde and tested for purity with GC/ECD and GC/FID. In November, the standard solutions were ampouled and some of them were sent to the Netherlands Institute for Fishery Investigations, where the solutions were tested with GC/ECD and GC/MS. It was concluded that the ampoules with the standard solutions were suitable for use in the exercise.

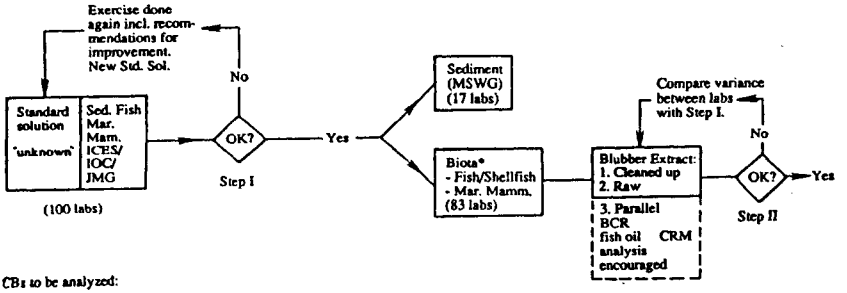
The last details in the guidelines were checked. A list of addresses of participants received from ICES was checked with the announcements received from the participants by the coordinators during the year. The total number of participating laboratories is estimated at around 100.

Theampoules and guidelines are currently ready for dispatch to the participants, who will be asked to return results before 30 June 1989. Evaluation of the results will take place during the second half of 1989 and the final report is scheduled to be ready around the end of 1989.

ANNEX 4

MARINE CHEMISTRY WORKING GROUP
Savannah, Georgia, USA,
13-17 February 1989

PROPOSED STAGES IN ICES/IOC/JMG INTERCOMPARISON EXERCISE FOR CBs



CBs to be analyzed:

28, 31, 52:] Closely eluting congeners on a SE-54 column.
101
105, 118, 138, 153:] * Priority will be given to supply labs concerned with analyses of
180
189 mar. mamm. tissues.

ANNEX 5

MARINE CHEMISTRY WORKING GROUP
Savannah, Georgia, USA,
13-17 February 1989

ICES 4TH ROUND HYDROCARBON INTERCOMPARISON

Exercise Stage 1 Progress Report

Eighteeen sets of samples have been distributed for this first stage of the exercise, 17 in November 1988 and one subsequent set in January 1989. One laboratory has since withdrawn from the exercise. The breakdown of participants by country is as follows:

Spain	1
Canada	2
Portugal	2
Finland	1
Netherlands	3
USSR	1
Federal Republic of Germany	2
Norway	1
USA	1
UK	3

To date, six sets of results have been received; three reporting results of HPLC, two of GC-MS and one of GC analyses. One laboratory reported problems of poor chromatography with the acetonitrile solvent and transferred the solutions to a hydrocarbon solvent prior to analysis.

One further problem encountered has been with the vials used for circulation of the standard solutions in the acetronrile solvent. Although it was originally intended to use flame-sealed ampoules, of 5 ml volume, these had not been delivered by November 1988. As it was hoped to obtain results from stage 1 in time for discussion at this MCWG meeting it was necessary to distribute the samples using 6 ml "hypo-vials" with crimp-seal caps. Although these vials have adequately contained the liquids it seems that there have been some losses of solvent vapour during transport and subsequent storage. If these losses have been large enough to cast doubts on the interpretation of the results of the first stage, then it may be necessary to repeat this part of the exercise utilising ampoules.

ANNEX 6

MARINE CHEMISTRY WORKING GROUP
Savannah, Georgia, USA
13-17 February 1989

HYDROCARBON METABOLITES IN BILE

An overview of the present state of research and information on the identification and quantification of the metabolites of lipophilic organic contaminants, such as the polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and "second generation" pesticides may be a useful piece of information. Metabolism of these compounds be exposed biota may make the detection of the parent compounds and any assessment of the effects of these compounds difficult, especially for the second generation chemicals. The use of metabolites as a measure of exposure is at present best advanced for the PAH. Determination of the metabolites of PAH in the bile of fish, birds and mammals is presently being used to indicate short term exposure to petrogenic and anthropogenic PAH. Long term exposure to PAH and PCB can be determined by the presence of the metabolites of these compounds in cellular DNA (DNA adducts). Both methodologies are still in a state of development and their roles in environmental assessment are only just beginning to be determined. Alternatively, the activity or induction of the metabolising systems, e.g., AHH oxidases, rather than the metabolites themselves, may be a useful contaminant measure as these systems may or will respond to mixtures of contaminants in additivie or synergistic fashion. Lastly, given the new classes of short-lived pesticides and herbicides being developed for general usage, the only way to identify their impact(s) on the environment may be through their metabolites and metabolising systems.

ANNEX 7

MARINE CHEMISTRY WORKING GROUP

Savannah, Georgia, USA,

13-17 February 1989

OVERVIEWS ON TECHNIQUES FOR ANALYSING HYDROCARBONS ASSOCIATED WITH DIFFERENT NATURAL MATRICES: AN EXECUTIVE SUMMARY

During the 1986 meeting of the Marine Chemistry Working Group (MCWG) it was suggested that overviews would be prepared on hydrocarbon analysis in:

a) sea water

b) organisms

c) sea water

d) atmosphere

Overviews (a) to (c) are in the advanced drafting stage, overview (d) was dropped from the list, because it was realised that the Working Group, as at present constituted, lacks the necessary expertise. The analytical hydrocarbon determination can be subdivided into stages:

1. Sample collection

   The influence of different methods of sample collection on the results obtained are largely unknown, but are believed to exercise the greatest effects in sediments, less so for water and atmospheric samples, and least of all in the case of organisms.

2. Isolation of hydrocarbons from the sample matrix

   Different extraction methods and solvent systems can yield large differences in the results of sea water analyses. Wide variations have also been noted in sediment analysis, where different extraction and clean-up techniques have been employed.

3. Quantitative analysis a) with, or b) without prior separation of individual hydrocarbons

   a) Analytical methods involving separation and individual determination of single hydrocarbons are highly developed (gas chromatography, high performance liquid chromatography, gas chromatography in combination with mass spectrometry). However, purchase of the instrumentation requires a larger financial outlay than for, e.g., UV fluorescence spectrometry, and the analyses are more time consuming. This has led to the widespread use of the simpler technique as a screening method, followed by the application of chromatographic methods to selected samples.

   b) The method for total fossil hydrocarbon analysis based on measuring the UV fluorescence of aromatic components has been shown to generate comparable results with sea water and sediments. The precision attainable with UV fluorescence analysis of fossil hydrocarbon residues accommodated in sea water is such that order of magnitude change in concentration by an order of magnitude can be detected at low levels of contamination (several tens of nanograms crude oil equivalents per litre) with a group of analysts using a common work-up procedure (Ehrhardt and Knap, Mar. Chem., in press). At somewhat el-evated levels of contamination precision improves to the point where approximately 20% changes in concentration become detectable.

      In the first ICES hydrocarbon intercomparison exercise a fine sandy intertidal sediment was analysed, no extraction or analytical method was specified. The best agreement was obtained for measurements by UV fluorescence.

Depending upon the question(s) to be addressed a selection can be made from a variety of methods. Guidelines will be developed intersessionally which would make it possible to judiciously select an appropriate method to analyse hydrocarbons in the most suitable matrix to answer a given question. These guidelines will critically evaluate the advantages and short comings of different methods and the type of information which they can or cannot provide. They will also discuss which matrix, eg water, particles, organisms, sediments, needs to be analysed for which purpose.

ANNEX 8

MARINE CHEMISTRY WORKING GROUP
Savannah, Georgia, USA,
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RECENT REFERENCE MATERIAL DEVELOPMENTS AT THE US NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY (NIST, FORMERLY NBS) OF USE IN MARINE CHEMISTRY ANALYSES

Recent reference material developments at the US National Institute of Standards and Technology (NIST, formerly NBS) of use in marine chemistry analyses.

Natural Matrix Reference Materials

Two SRMs are being developed which are representative of specimens for urban levels of moderate pollution levels. This work was supported by NOAA.

- SRM 1974, "Organics in Mussel Tissue (Mytilus edulis)". This material was collected in the Boston Harbour. The resulting shucked, "wet" (i.e., non-dried) mussel tissue (30 kg) was cryogenically homogenised in a teflon disk mill and bottled (15 g/jar). The SRM material is being stored at liquid nitrogen vapour temperature and will be shipped in dry ice to the purchaser. If the material is not thawed, it remains a free-flowing particulate homogenate. Projected availability: Fall 1989.

- SRM 1941, "Organics in Marine Sediment". This material was collected in the Baltimore Harbour, air-dried, pulverised, sieved (-150 mesh), homogenised and bottled (70 g/bottles). Projected availability: Summer 1989.

  For both SRM 1974 and 1941, concentrations of selected PAH are being certified. Information values will be reported for selected PCB congeners, chlorinated pesticides and trace elements.

Two additional SRMs are being developed.

- SRM 1588 "Organics in Cod Liver Oil" will also be available during the summer of 1989. Concentrations are certified for selected chlorinated pesticides, PCBs and for alpha-tocopherol. Information values are given for six PCDDs and OCDF which were added to the Norwegian pharmaceutical-grade cod liver oil. The material consists of [EQN "~~"] 1.2 g of material per sealed argon-filled ampoule.

- SRM 1939 is a river sediment material contaminated at levels simulating accidental spillage of PCBs. The material has been air-dried, sieved (-325 mesh) homogenised and bottled (50 g/bottle). Concentration will be certified for selected PCB congeners, and the SRM should be available by January 1990.

Calibration Solution Reference Materials

Solution SRMs of selected PCB congeners, of chlorinated pesticides, and or aromatic hydrocarbons have each been produced at two concentration levels to aid in the calibration of instrumentation used in the analyses of these compounds. This work was also supported by NOAA and is summarised below.

NIST	SRM	Solvent	Approximate concentration certified	Projected release date
1491	24 aromatic hydrocarbons	hexane/toulene (96/4 w/w/)	7 * *g/ml	Apr 1989
2260	same components as in SRM 1491	tolene	65 * *g/ml	Oct 1989
1492	15 chlorinated pesticides	hexane	200 ng/ml	Apr 1989
2261	same components as in SRM 1492	hexane	2 * *g/ml	Jun 1989
1493	20 chlorinated biphenyl congeners	2,2,4-trimethyl-pentane	200 ng/ml	May 1989
2262	28 chlorinated biphenyl congeners (20 CBs as in SRM 1493 plus 8 additional CBs)	2,2,4-trimethyl-pentane	2 * *g/ml	Jul 1989

ANNEX 9

MARINE CHEMISTRY WORKING GROUP
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ACTION LIST AND PROPOSED TIMETABLE FOR THE NUTRIENT INTERCOMPARISON EXERCISE

The coordinating group for this exercise consists of the following members of the Marine Chemistry Working Group (MCWG): Dr M. Perttilä, Mr A. Aminot and Mr D.S. Kirkwood.

Late February 1989

Mr Kirkwood to send a letter to prospective participants, informing them of the timetable.

Early March 1989

M Aminot to conduct the sterilisation of sea water experiment and to collate analytical data on samples circulated in January 1989 by end of March. If this sterilisation experiment is successful, samples of the sterilised sea water will be sent immediately to nominated members of the Sub-group of the MCWG.

Late April 1989

Deadline for receipt of data from sub-group members by M Aminot. The coordinating group to consider the suitability of the sterilised water for inclusion in the intercomparison exercise.

Early May 1989

M Aminot to prepare and distribute intercalibration kits to participants.

Late August 1989

Deadline for receipt of results of intercomparison exercise; results to be submitted to Dr Perttilä.

October 1989

Status report to be submitted to ICES Statutory Meeting.

Early November 1989

Dr Perttilä to circulate a draft report on the results of the exercise to the MCWG Sub-group for review.

Early December 1989

The coordinating group to meet in Brest to complete draft report.

Early January 1989

Dr Perttilä to finalise draft report for consideration by MCWG at its next meeting.

ANNEX 10

MARINE CHEMISTRY WORKING GROUP

Savannah, Georgia, USA,

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ACTION LIST FOR 1989

Trace Metal Sub-group

D. Cossa	to provide W. Cofino with a review paper on trace metals in sea water and to provide G. Topping with a report on organotin.
W. Cofino and B. Peterson	to supply quality control results to J. Uthe.
W. Cofino and D. Schmidt	to contribute information to J. Uthe on protocols used in their laboratory for sampling in relation to trend monitoring.
D. Schmidt	to contact Simon Wilson at ICES Headquarters in order to get the data base for trace metals in sea water in an appropriate format for analysis by the ad hoc Intersessional Group.
	to consider with the assistance of a post graduate student the preparation of an overview paper on chromium in the marine environment.
W. Cofino S. Berman	to prepare a paper on how to validate sampling methods dealing with sea water.
W. Cofino	to explore with colleagues the possibility of a review of surface active agents.

Organics Sub-group

J. de Boer R. Law	to prepare progress reports for MCWG 1990 on the conduct of the ICES CB and PAH intercalibration exercises, respectively.
M. Ehrhardt J. Klungsøyr R. Law	to submit to ACMP copies of their current draft texts on hydrocarbon methodology for information, and to finalise the critical review intersessionally.

D. Wells	to finalise the text of the papers on planar chlorobiphenyls; hexachlorobenzene and lindane; and polychlorinated dibenzo-p-dioxins and dibenzofurans for submission to ACMP.
	to approach IUPAC with a view to obtaining a ruling from their nomenclature group on the use of the terms planar/coplanar to describe flat organic molecules and to check which are the precise IUPAC rules for the notation of chlorobiphenyl congeners.
All sub-group members	to bring to the 1990 MCWG meeting any material of use in preparing in overview concerning chlorophenols, if no paper is prepared intersessionally, and also to provide information (as available intersessionally) on the production, use and presence in the environment of tetrachlorobenzyltoluenes and phenoxytetradecanes to J. de Boer and M. Ehrhardt, respectively.
	To supply any data which can be used for the comparison of individual chlorobiphenyl concentrations and total PCB concentrations to C. Manen.

Chemical Oceanography Sub-group

A. Aminot D. Kirkwood M. Perttilä	to conduct the nutrient intercalibration exercise according to the timetable presented in Annex 9 of this report.
A. Aminot L. Foyn	to submit North Sea nutrient data to D. Kirkwood by 1 May 1989.
D. Kirkwood	to prepare an overview on nutrients from the data supplied by A. Aminot and L. Foyn and the data obtained from the ICES data bank.
	to distribute this overview to the Sub-group in advance of the next MCWG meeting.
M. Perttilä	to draft a general protocol for sampling, storage and analysis of sea water for nutrients. This draft will be circulated for comment to the Sub-group by early June 1989.
	to contact ICES Hydrographer and discuss any outstanding questions on the quality of the PEX data.
G. Weichart	to prepare a paper for the next MCWG meeting evaluating from a chemical analytical standpoint the potential usefulness of historical phosphate data.

All sub-group members	to review the recent literature regarding the Japanese high temperature catalytic combustion method for organic carbon and nitrogen in sea water with a view to determining at the next MCWG meeting if this method should be recommended for use by ICES laboratories or if any further evaluation of this technique should be undertaken by the Sub-group.

ANNEX 11

MARINE CHEMISTRY WORKING GROUP

Savannah, Georgia, USA,

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RECOMMNDATIONS

Recommendation 1

The Marine Chemistry Working Group recommends that the overview paper on mercury in the marine environment by Dr. D Cossa, be published by ICES as an annex to the ACMP report.

Recommendation 2

The Marine Chemistry Working Group recommends that an ad hoc group of MCWG members should meet intersessionally to evaluate the data for the baseline study of trace metals in sea water and to prepare a draft report. This meeting should be convened for four days, 21-24 August in Hamburg at Deutches Hydrographisches Institut. The group should consist of Dr G. Topping (Chairman), Dr D. Schmidt, Mr W. Cofino, Dr P.A. Yeats and Dr S. Berman and travel and subsistence expenses should be borne by ICES.

Recommendation 3

The Marine Chemistry Working Group recommends that stage 2 of the ICES CB intercalibration should follow on immediately after the successful completion of stage 1 of the exercise (see Annex 4).

Recommendation 4

The Marine Chemistry Working Group recommends that the Coordinating Group (Mr D.S. Kirkwood, Dr M. Perttilä, M A. Aminot) for the Nutrient Intercalibration meet in Brest, France in late 1989 to finalise the draft report on this exercise (see Annex 9).

Recommendation 5

The Marine Chemistry Working Group recommends that organisations supervising monitoring programmes should incorporate quality assurance in the monitoring strategy in view of the fact that the control of data quality is an integral part of the overall management of the programme.

Recommendation 6

The Marine Chemistry Working Group recommends that the Working Group meet for five days in 1990 at ICES Headquarters to carry out the following tasks:

1. to review the report on the nutrient intercomparison exercise.

2. to review the report on trace metals in coastal waters prepared by an ad hoc intersessional group of MCWG.

3. to review progress on the intercomparison exercise of chlorobiphenyls and specific hydrocarbons.

4. to review the overview paper on chromium.

5. to review a paper on the validation of sampling methods for sea water studies.

6. to review a paper on the general protocol for sampling, storage and analysis of sea water for nutrient measurements.

7. to consider any other matters raised by the Hydrographic Committee and/or ACMP.