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**REPORT OF THE MARINE CHEMISTRY WORKING GROUP**

Copenhagen, 12 - 16 February 1990

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## 1 OPENING OF THE MEETING

The Chairman, Dr G. Topping, opened the meeting at 9.30 hrs on 12 February 1990 and welcomed the participants.

Working Group members, and visitors from Denmark, then introduced themselves and briefly described their main areas of research interests and responsibilities in the field of marine chemistry.

## 2 ADOPTION OF AGENDA

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

The Chairman informed the Group that most of the tasks would be dealt with by the respective sub-groups prior to being discussed in plenary. Sub-group sessions would begin in the afternoon of the first day and would be completed by the end of the third day. The reports from each sub-group would be dealt with in plenary on the fourth and fifth days. The reports would include any recommendations and action lists for the forthcoming intersessional period.

The Chairman reminded members that the sessional chairman for each sub-group would be: W. Cofino (trace metals), D. Wells (organics), and S. Carlberg (chemical oceanography). The remaining members and visitors were grouped as follows:

### Trace Metals:

D. de Armas, G. Asmund, S. Berman, U. Harms, T. Jensen, B. Pedersen, D. Schmidt, S. Westerlund and P.A. Yeats.

### Organics:

A. Abarnou, J. de Boer, J. Biscaya, J. Boon, M. Cleman, J. Klungsøyr, R. Law, T. Nunes, E.L. Poutanen, L. Reutergårdh, E. Stor-Hansen, U. Stefansson, and J. Tronczynski.

### Chemical Oceanography:

A. Aminot, L. Føyn, D.S. Kirkwood, K. Mäkelä and O. Vagn Olsen.

## 3 REPORT OF THE 77th STATUTORY MEETING

The Chairman informed the Group of the new role that ACMP would be playing in its tasks. In future, the report of MCWG would go directly to ACMP, who would be responsible for assigning tasks, and their priority, to MCWG and to the other working groups now reporting directly to ACMP. Questions and tasks from the Hydrography and Marine Environmental Quality Committees would continue to be put to MCWG, but these would now be passed via ACMP at the Statutory Meeting.

The Chairman repeated the statement made by ACMP at its June meeting, and subsequently by Dr J. Portmann (Chairman of ACMP), concerning the expectations of ACMP of its working groups, i.e., that in order for ACMP to complete its tasks for the Commissions, and to provide sound statements on marine environmental matters on behalf of ICES, its working groups should meet their assigned tasks within a reasonable timeframe. At the June 1989 meeting of ACMP, concern had been expressed over the lack of action by MCWG on the production of some overviews, particularly for Cr and Ni. The Chairman stated that so far such overviews had been dealt with by members on a voluntary basis, but that the absence of any volunteers in future would require him or one of the sub-group chairmen to identify a member for this intersessional task.

A number of members of the Group expressed concern over this new working practice; one member even proposed that certain tasks, such as overviews, which were quite time consuming and demanding for an individual member, might well be done on a consultancy basis.

#### 4 REPORTS ON RELATED ACTIVITIES

##### 4.1 JMG of OSPARCOM

Dr Pawlak provided a brief summary of matters arising at the last meeting of the Joint Monitoring Group (JMG) and the North Sea Task Force (NSTF) workshop in October 1989. She drew attention to the development of a five-year Monitoring Master Plan by NSTF which involves the collection of samples at fixed positions in inshore, intermediate, and offshore areas and the collection of data on contaminants in several marine matrices. Dr Wilson enlarged on this matter by specifically referring to the list of mandatory and voluntary substances in the various matrices targeted by NSTF. Some of the members who had attended the NSTF workshop referred to the current confusion amongst some scientists over the application of the matrix tables and felt that this matter should be resolved as quickly as possible. The Chairman expressed some sympathy with these remarks and said that this matter should be resolved by the Working Group on Environmental Assessments and Monitoring Strategies (WGEAMS). Dr Carlberg agreed to take this matter up with WGEAMS at its next meeting.

Dr Cofino, who had chaired the quality assurance (QA) discussions at the NSTF workshop and had been asked by NSTF to coordinate subsequent QA work, reported on progress since November 1989. He informed the Group that, following discussions with the EEC Bureau of Community Reference (BCR), he had contacted some members of MCWG (Wells, Topping, Aminot and Harms) to arrange a meeting on QA with BCR in December 1989. At this meeting, where unfortunately Drs Aminot and Harms were not present because of other commitments, BCR agreed to consider the funding of a three-year Pilot Programme on QA in relation to measurements of contaminants in marine samples as part of the NSTF/JMG monitoring programmes. Drs Wells and Topping had been asked to prepare the proposal for the three-year project for consideration by BCR by the end of May 1990. Dr Cofino then briefly referred to the plans for a workshop on QA which participants in the pilot programme would attend in May 1990.



The Chairman informed the Group that a paper documenting the outline of the pilot project was now available for members and that he and Drs Cofino and Wells needed constructive criticism from MCWG of this outline and the proposed workshop on QA before the end of the meeting.

The Chairman stated that the offer by BCR was most timely and that MCWG now had an opportunity to establish the type of comprehensive QA programme that it had been requesting for a number of years.

#### 4.2 Intergovernmental Oceanographic Commission (IOC)

The Chairman referred to a telefax received from Alex Bousoulengas (IOC), apologising for the absence of a member of the IOC Secretariat at MCWG, and requesting that the Chairman and Drs Yeats and Schmidt act as IOC spokesmen in his absence.

Dr Yeats gave a brief overview of the IOC/GESRM (Group of Experts on Standards and Reference Materials) meeting which he had attended in January 1990 in Halifax, Nova Scotia. He drew the attention of MCWG to the preparation of standards and conduct of intercalibration activities in relation to the IGOFS and WOCE programmes. There were developments for nutrients, dissolved oxygen, alkalinity and pigments. The emphasis was on a very high precision determination for "oceanographic" purposes. He referred to the preparation of an extensive catalogue of available standards and reference materials by Dr Adrianna Cantillo, NOAA, Maryland, USA (NOAA Technical Report No. NOSOMA 51), and stated that members interested in obtaining copies of this report should contact NOAA as soon as possible, as the available stock of this report was growing smaller daily. Dr Yeats also spoke about the initiative developed at that meeting to prepare a reference material for chlorinated organic substances in mussel tissue. Finally, he stated that GESRM's role was likely to be extended to dealing with QA in general, for laboratories associated with UNEP's regional seas programmes.

The Chairman concluded this item by giving an account of other IOC activities of interest to MCWG, namely:

The manual on determination of petroleum hydrocarbons in sediments had now been finalised by Dr Kathy Burns and would soon be published as an IOC/UNEP manual.

The manual on determination of organochlorines in sea water, prepared by Dr J. Duinker, had now been reviewed by GEMSI (Group of Experts on Methods, Standards and Intercalibration) and would be published as an IOC manual by June 1990.

The manual entitled "Contaminant monitoring programmes using marine organisms: Quality Assurance and Good Laboratory Practice. Reference Methods for Marine Pollution Studies No 57", UNEP 1989, prepared by Dr G. Topping, was now available for distribution.

The Planning Committee for the IOC/UNEP International Musselwatch Programme met in January 1990 in Jamaica and decided to carry out the pilot phase in the Caribbean and South American regions. If the pilot phase is successful, the programme will be expanded into a worldwide programme. Some of the samples from the pilot phase will be analysed by national and international laboratories for DDT and PCBs. The programme is expected to be funded by NOAA, IOC and UNEP.

Finally, a major intersessional GEMSI activity will be a workshop on the use of sediments in marine pollution research and monitoring, scheduled to take place in Dalina, China, in April 1990.

#### 4.3 ICES Working Groups

The Chairman drew the attention of the Group to the forthcoming Workshop on Biological Effects Techniques to be held in Bremerhaven in March 1990 and asked Dr Cofino, the coordinator of the chemical work, to provide a brief summary of this work. Dr Cofino stated that MCWG members from a number of ICES countries (France, Norway, UK (England and Scotland) and the Netherlands) had offered to collaborate with the biologists on this project. He stressed the need for MCWG, particularly the members from the above countries, to assist him in the establishment of guidelines for the collection and handling of samples, which would be done along two transects, one relating to a major river and the other to an oil platform. The Chairman agreed that an opportunity for this discussion should be made and this item was subsequently dealt with during a lunchtime session.

#### 4.4 Other Activities

The Chairman stated that no matters had been raised by members under this agenda item.

### 5 REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES

The Chairman informed the Group that only one report had been provided for this agenda item, namely, the annual progress report on Canadian reference materials by Dr S. Berman. This paper is attached as Annex 3.

### 6 REQUESTS FROM ACMP AND REGULATORY AGENCIES

The Chairman informed the Group that all such requests had been incorporated in the agenda, either at the time of the preparation of the draft agenda or during the adoption of the agenda at the beginning of the meeting.

## 7 REPORTS OF SESSIONAL SUB-GROUP DISCUSSIONS

### 7.1 Trace Metals Sub-group

#### 7.1.1 Baseline Study of Trace Metals in Coastal and Shelf Sea Waters

Dr Topping described the outcome of the meeting of the ad Hoc Group which had met during the previous week to prepare a report on this study. He reported that the Group had used a data management package provided by Dr Cofino to screen the individual data submitted by participants in this study. The Group had initially screened the data using the criteria agreed at the 1989 MCWG meeting. These were:

- a) Samples of sea water should have a salinity of > 20 psu.
- b) Only data for filtered samples would be considered unless the concentration of suspended particulate matter (SPM) in samples was < 1 mg/litre.
- c) Participants submitting data should have been successful in the recent ICES intercomparison exercises for metals in sea water (i.e., 5/TM/SW and 6/TM/SW).
- d) The comparability of participants' data collected at ICES reference stations.
- e) In the absence of (c) and (d), the data would be assessed by peer review, i.e., the members' knowledge of trace metal levels in various sea areas based on publications in recent research papers.

The ad Hoc Group felt, however, that the rigorous application of these criteria would automatically eliminate the data from some laboratories and almost all of that sub-set of the data from the ZISCH ('Zirculation und Schadstoffumsatz in der Nordsee') survey, since they were based on measurements on unfiltered samples for which there were no SPM measurements.

Since the ZISCH data set was one of two sets which covered a large number of offshore North Sea areas, there was some reluctance to eliminate it from the review. It was, therefore, decided to screen all measurements for unfiltered samples using SPM data which had been reported for the North Sea in 1986 by the ZISCH geology and mineralogy team. All measurements of metals in unfiltered samples in North Sea areas where mean depth-integrated SPM levels < 2 mg/litre were indicated would be included in the data selection procedure. Following an examination of the relevant contour maps for SPM, it was agreed that all data for samples from all the defined areas except NS3B, NS4 and NS5 would be used in the review. (NB. the defined areas used in the assessment correspond closely with, but are not identical to, the area sub-divisions of the North Sea Task Force).

Box-and-whisker diagrams were produced for each of the core group of metals (Cu, Cd, Zn, Pb and Hg) for each area and for three salinity ranges (20-25 psu, 25-30 psu and > 30 psu) with a fourth

plot covering sea areas of lower salinity waters (Kattegat, Belt Sea and Sound, and the southern Baltic). Each plot is based on all selected data for samples collected in the depth range 0-10 m. For selected areas and metals where there were sufficient data, plots of dissolved metal concentration against salinity were also produced.

The members of the Sub-group were then given an opportunity to examine the diagrams produced by the ad Hoc Group, and its main findings which are given in Annex 4.

Dr Topping informed the Sub-group that a preliminary report on this baseline study would be presented to ACMP in June 1990, following some further intersessional work by the members of the ad Hoc Group. Following this presentation, the ad Hoc Group would produce a final report on the study for publication in the ICES Cooperative Research Report series and a paper for the open literature. He stated that ACMP would probably include an account of the main findings of the study in its annual report and that JMG would receive a copy of the full report at its next meeting.

#### 7.1.2 Overview on Chromium

Dr Schmidt explained the background of this paper, which at this stage was only to be regarded as the first draft. The authors had used the overview on organic mercury as a model. The paper was not at this stage intended to be a critical review, but more a literature survey. Before the paper was discussed in detail, there was a discussion about the aim of this paper and other similar overviews. It was made clear that the paper had been a long-standing request from ACMP and also that overviews of scientific topics were a general request from different management organizations in the different countries.

The Sub-group suggested the following changes to the paper:

- 1) In the section 'Forms of chromium in the marine environment', more should be documented about the chemistry and especially the thermodynamics of Cr and, if possible, a model should be produced to explain the results.
- 2) The section 'Sources and emissions of chromium' should follow directly after the introduction. If possible, more data should be included, e.g., results from TiO<sub>2</sub>-waste dumping, river inputs, atmospheric inputs, and possibly a budget of the element, either in this section or elsewhere in the report. The members of the Sub-group promised to send any data on this topic and other relevant data to Dr Schmidt, as they were fully aware of the difficulties of getting good data within this field.
- 3) A section about analytical methods and their problems should be added, including a statement about the reliability of older data, e.g., pre-1980 values.

- 4) The general feeling after discussing the section entitled 'Distribution of chromium in the marine environment' was that there were not as many reliable data available for Cr as for, e.g., Cu, Zn, Pb, Hg, and Cd. This also holds for the next section 'Uptake of chromium by aquatic plants, invertebrates and fish', where the Sub-group considered that it would be valuable if some additional data could be included. For example, it was suggested that more information concerning the toxicity of Cr to fish should be included. This could be found in U.S. EPA guidelines for Cr-toxicity data. T. Jensen promised to send information about this and a literature search on metals in sediments, as well as some information about metals in biota to Dr Schmidt. It was also pointed out that the Sub-group felt that the subject was a matter of concern and that this should be pointed out in the paper.

Dr Schmidt agreed to amend the paper before the next meeting. The Sub-group recommended that a second version should be distributed during 1990 to the members of the Sub-group and all comments should be sent directly to Dr Schmidt. The paper could then be finally approved at the next MCWG meeting, before sending it to ACMP.

Unfortunately, the Sub-group Chairman was unable to find a volunteer to prepare an overview on nickel.

#### 7.1.3 BCR pilot programme on QA

Since this item was to be dealt with in plenary under agenda item 8, the Chairman only provided a brief description of the project and the proposed timetable for the preparation of the proposal.

#### 7.1.4 Validation of sampling methods for sea water studies

Dr Cofino introduced this paper. The aim of the paper was discussed and also whether the guidelines that could result from it were intended to be mandatory, e.g., for those laboratories that submit data to international organizations. The general feeling was that this would be the case.

The Sub-group felt that it was an important paper, as it was the first attempt to describe the quality assurance of sampling, which is taken to include all the activities prior to the work within the laboratory. The Sub-group did not have any comments on the first two sections, entitled 'Introduction' and 'A general discussion on quality assurance of sampling'.

The Sub-group suggested that the section entitled 'Validation of methodology in laboratory environment' should be removed, and that the text in the sections entitled 'Variability of data' and 'Assessment of statistical control of sampling' should be amended to clarify the message being presented. The Sub-group stressed the importance of assessing the statistical control of sampling.

The Sub-group also felt that the section entitled 'Sampling of an area with well-defined characteristics' needed some clarifying. It was suggested that the positions of the ICES reference

stations should also be included in the paper. The Sub-group recommended that a revised version of the paper should be presented at the next MCWG meeting before sending it to ACMP.

#### 7.1.5 Pooling of samples for monitoring purposes and analytical variance

Since this matter had been dealt with in plenary, there was no further discussion of this agenda item.

#### 7.1.6 Matrices for monitoring of contaminants

The Sub-group felt that the matrices proposed for the voluntary metals in the NSTF programme were the most appropriate ones.

#### 7.1.7 Trend monitoring

In view of the fact that the paper submitted by the Working Group on the Statistical Aspects of Trend Monitoring (WGSATM) entitled "Pooling may economise a sampling programme", which appears as Annex 10 in the 1989 report of WGSATM, had already been discussed in plenary, there was no further discussion of this agenda item.

#### 7.1.8 Bremerhaven Workshop

The Chairman informed the Sub-group that he had been appointed coordinator of the chemical aspects of this workshop and that during the course of the meeting he wanted to finalise the arrangements for sampling and analysis of the relevant biological samples. Since this matter required discussion with members of the Sub-group on Organics, it was agreed that the discussion of this agenda item should be deferred until a time when the relevant members from both Sub-groups could meet. This meeting was subsequently held, and the questions concerning how many samples should be collected and which laboratories would analyse the samples for metals and organics were resolved during a lunchtime discussion.

#### 7.1.9 Any Other Business

##### a) SPM intercalibration

Dr Yeats informed the Sub-group about the proposed phase 2 of the intercalibration exercise on analyses of trace metals in SPM, coordinated by the Working Group on Marine Sediments in Relation to Pollution (WGMS). The WGMS had requested advice on what to do next. The WGMS had put forward two proposals:

- 1) Distribute a bottle of water to which had been added a small quantity of suspended sediment to each laboratory and request both gravimetric and metal analyses of the sample;  
or

- 2) Distribute filters through which suspended matter had been filtered to provide a sample containing <1 mg SPM/filter.

According to Dr Yeats, it should be technically possible to distribute filters with an equal amount of SPM. He had experience with this on a small scale. The Sub-group felt that suggestion 1 could give storage problems. Several alternative possibilities were then discussed, namely:

- i) To distribute vials containing a small amount of sediment with a request that the analyst add this to a known volume of water which should then be mixed, filtered, and then analysed;
- ii) To conduct a practical workshop to evaluate the steps in the gravimetric and metal analyses; or
- iii) To prepare a slurry of sediment in water with instructions regarding dilution of the sample, and then proceed as in (i).

The common factor for all of these suggestions was that someone would have to investigate each of the procedures before they could be used. The Sub-group felt that it was important to assess the gravimetric and the quantitative metal determination procedures, preferably using samples containing natural SPM.

- b) Future work on marine chemistry of trace metals  
Dr Yeats presented a paper outlining his thoughts on this matter. He began by referring to the fact that considerable progress had been made on the measurement of metals in sea water by ICES laboratories over the past 5 - 10 years. We have now reached the stage, on the basis of the results of the recent review of trace metal measurements in the ICES baseline study, where a number of laboratories are capable of producing state-of-the-art measurements in their monitoring programmes. Given this progress, the question was raised as to what direction the Sub-group should take to further enhance our understanding of the marine chemistry of trace metals, particularly in coastal waters where the major inputs of trace metals take place.

Dr Yeats referred to the potential of the ICES data bank, to which both ICES and JMG laboratories supply data, as a possible source of data which might be used to provide a better understanding of the distribution and concentrations of metals in coastal water areas. He felt that there was more information to be gleaned from the existing data bank than that covered in the baseline study assessment (Section 7.1.1, above) and proposed that the ICES data bank be supplemented by additional data which laboratories had collected but not yet submitted to ICES. In particular, attempts might be made to use these data to gain a better understanding of the relationships between dissolved metals and salinity.

Dr Yeats considered that it was timely to begin a study of differences in estuarine behaviour of trace metals and the factors that influenced this behaviour. This study, which would provide useful information for the regulation and control of discharges of wastes containing metals, could be done as a collaborative venture between scientists working in different types of estuaries.

Given our ability to accurately measure metals in sea water, Dr Yeats felt that we could now use this expertise to collaborate with biologists on the assessment of the biological impact of trace metals on biota, i.e., extend marine contamination work to marine pollution studies.

In general, the members of the Sub-group were supportive of the proposals made in the paper by Dr Yeats, and it was agreed that members would consider the matter interessionally with a view to providing some firm proposals for collaborative and other work at the next meeting of MCWG.

## 7.2 Organics Sub-group

### 7.2.1 Progress in Intercomparison Exercises

#### 7.2.1.1 Chlorobiphenyl Intercomparison Exercise

The report of phase 1 of the ICES/IOC/OSPARCOM Intercomparison Exercise on Analysis of Chlorobiphenyls (CBs) was introduced by one of the principal authors, J. de Boer.

The choice of the CB congeners included in the intercomparison exercise was made at the 1988 MCWG meeting. A total of 60 out of 90 laboratories returned their results by the deadline of 30 June 1989. The response from ICES/JMG laboratories (50 out of 73=79%) was far better than that from the IOC laboratories (2 out of 17=12%).

Mr J. van der Meer (NIOZ) performed the statistical treatment of the data, including a principal component analysis. Ten outlying laboratories were identified by this means. One set of results was not included in the statistical treatment because the data submitted were in great error.

Some of the major conclusions of the report were as follows:

The results for CB-52 had the highest variance of all congeners. It is likely that this was caused by the difficulty of working in the linear range of the ECD-detector, as CB-52 was present at a concentration which was 10 times higher than that of the other CBs.

The separation of CB-118 from CB-149 was made more difficult because of the relatively high concentration of CB-149.



The separation of CB-153 and CB-105 was often very good, but this will become more difficult in environmental samples because of the large differences in concentration between the congeners (CB-153 > CB-105) and the additional presence of CB-132.

In addition to the the 10 CBs formally considered during the exercise, some 'unknown' CBs were added to the samples: CB-49, CB-149 and CBs-110 + 77 (co-elution on SE-54 type columns). The number of laboratories which identified/quantified these congeners were:

CB-No.	49	77	110	149
Identified	24	15	15	23
Quantified	11	2	4	9

Of the participants, 46 used splitless injection, while 11 used on-column injection. No significant differences between injection types were observed.

Quantification of the CBs based on peak-height was better than that based on peak-area. This is in contrast with the theoretical expectation, but may be explained by the use of integrators which may not define the peak as accurately as necessary.

The separation obtained by a 50 m x 0.15 mm column was much better than that on 25 m x 0.32 mm column.

Obtaining clean blank chromatograms was a problem throughout the exercise.

Many laboratories worked outside the linearity ranges which they had established as a first part of the exercise, i.e., < 50 pg on column per congener. Improvement can be achieved by either concentration of the sample (evaporation of the solvent) or by working with a series of standards of differing concentrations (bracketing standards or multi-level calibration).

The Chairman and members of the Sub-group gratefully acknowledged the work of the coordinators and authors of the report (J. de Boer, J.C. Duinker, J. Calder, and J. van der Meer). The report has shown good agreement on the analysis of standard solutions between laboratories, but at the same time has identified some important problem areas.

Those laboratories which were outliers in the first step will need to demonstrate that they have optimized their systems and produced acceptable results for Step 1 before their results for Step 2 can be accepted. A detailed procedure will be prepared by the coordinators of the second stage.

The names of the ICES and JMG laboratories which have committed themselves to complete the exercise and have received samples, but did not respond, will be added to the report on the first step and identified as not complying with their own agreement. They will be excluded from the rest of the exercise.

Following the discussion of the report on the results of the intercomparison exercise on CBs, the Chairman gave a resumé of the three areas to be discussed:

- 1) The arrangements for the next steps of the CB intercomparison exercise;
- 2) The determination of planar CBs; and
- 3) The analysis of seal tissue samples.

#### CB intercomparison: next steps

Initially it had been decided to create two groups of participants after the first step of the exercise, namely, sediment laboratories for JMG and marine mammals laboratories for ICES and IOC. The possibility was discussed of keeping these two activities linked in the same exercise, but since J. Calder had offered to coordinate the second step of the exercise for JMG laboratories, it was appropriate to inform him of the suggested change in the management of the project.

The future steps of the exercise were outlined as follows:

- a) Standard solution(s) to check the preparation of calibrated standards + unknown standard solutions;
- b) Cleaned-up extracts of sediment and/or marine mammal blubber;
- c) Raw extracts of sediment and/or marine mammal blubber.

#### Standard solution(s) and unknown solutions

This first point was critically evaluated. Each participating laboratory should use its own standard solutions prepared from pure reference compounds. Laboratories will also receive from the coordinator(s) an unknown solution containing the determinands to check the validity of their prepared standard solutions. The choice of the compounds to be determined was also discussed. The following list of congeners, determined during the first step, was modified to replace CB-189 with CB-156.

IUPAC No.	CB
28	2,4,4' trichlorobiphenyl
31	2,4',5 trichlorobiphenyl
52	2,2',5,5' tetrachlorobiphenyl
101	2,2',4,5,5' pentachlorobiphenyl
105	2,3,3',4,4' pentachlorobiphenyl
118	2,3',4,4',5 pentachlorobiphenyl
138	2,2',3,4,4',5 hexachlorobiphenyl
153	2,2',4,4',5,5' hexachlorobiphenyl
156	2,3,3',4,4',5 hexachlorobiphenyl
180	2,2',3,4,4',5,5' heptachlorobiphenyl

Most of these compounds are available as certified reference compounds (BCR-EEC) or commercially (CB-31, CB-105). CB-189 is not commercially available and is only present in a very low concentration in biota; thus, it was replaced by CB-156.

J. Boon had also argued for the inclusion of CB-156 (2,3,3',4,4',5) on this list as a third mono-ortho substituted component. L. Reutergårdh explained the difficulties in the inclusion of toxic planar congeners on the list. Recent studies have shown that a combination of non-ortho and mono-ortho congeners is possibly more toxic than individual groups. Any increase in this list to include other compounds would be more appropriate in an additional exercise for a limited number of more experienced laboratories. This would be conducted informally as a completely separate venture (see 7.2.4).

#### The choice of the matrix

The choice of matrices was discussed, as was the link between the activities in determination of CBs in sediment and marine mammals.

J. Boon presented the relative distribution of the congeners in these two matrices, as follows:

CB No.	28	52	101	105	(132)	118	138	153	180
Sediment	++	+++	+++	++	++	+++	+++	+++	+++
Seal	+	+	+	+	+	+	+++	+++	+++

+ low  
 ++ intermediate  
 +++ high, relative concentration

Both matrices present a different range of CBs at different concentrations so that linearity and separation of each determinand should be looked at more critically by the participants. An exercise where participants are invited to determine CBs in sediment and seal blubber will be more informative than two separate exercises for each of these two matrices with respect to the improvement of the measurement of CBs in the marine environment.

The following proposals were made for the second step of the exercise:

- i) Preparation of standard solution and check with an unknown solution; and
- ii) The analysis of a cleaned-up extract of sediment and/or marine mammal blubber.

The next step, to cover the analysis of raw extracts of the same material, will be undertaken at a later stage.

J. de Boer drew the attention of the Sub-group to the fact that both of these tasks would represent considerably more work for the coordinator(s) than that done by them during the first round of the programme.

#### Organisation of the work and time schedule

The coordination of this work has been divided into three distinctive parts:

- the preparation of a standard unknown solution by J. de Boer, after discussion with J.C. Duinker.
- the preparation of a cleaned-up sediment extract by D. Wells. This could be done in Aberdeen in conjunction with the PAH intercomparison exercise. Some information exists for a sediment from the Clyde Estuary.
- the preparation of a cleaned-up seal blubber extract, carried out by L. Reutergårdh and his colleagues. Approximately 0.5 kg of seal blubber seems to be sufficient for this task.

The time schedule for this work was set up as follows:

- By mid-March 1990 the participants in the first step of the intercomparison exercise will receive the report and the discussion, and information on the next steps. It was emphasized that they should be clearly informed of the necessity to have pure reference compounds to prepare their own standard solutions. They should also be informed of the deadline to submit their results, to enable them to reserve the required time for the task.
- In June the coordinators (J. de Boer, D. Wells, L. Reutergårdh) will meet in Brussels to coordinate their efforts for the preparation of the work.
- The material and detailed protocols should be ready for distribution to the participants by 1 July 1990.
- The results should be returned to the coordinators by 1 November 1990.

These requirements appeared to be the most suitable for carrying out the task in 1990, so that the report of the results could be presented at the 1991 MCWG meeting.

The last point discussed was the participation in this second step of laboratories which were "outliers" in the first round. They will receive extra ampoules of standard solutions to demonstrate that they have improved their ability to analyse CBs since the first step (resolution and/or linearity problems) before proceeding to the next step. This arrangement will also apply to any new participants in this exercise. (Action: de Boer, Reutergårdh and Wells).

#### 7.2.1.2 Review of Progress in PAH Intercomparison Exercise

A preliminary report of the ad hoc meeting of analysts to discuss the results of the ICES fourth round hydrocarbon intercomparison programme (Stage 1) was presented by the coordinator, R. Law (see Annex 5). This report covers the details of both phases of Stage 1 and summaries of the data submitted by the participants. It also includes some preliminary overview comments and conclusions of the ad hoc Working Group, and the proposals for the design, implementation and timetable for Stage 2. New participants in this exercise would be afforded the same arrangement as that proposed for new participants in the CBs exercise.

J. de Boer proposed that advice on optimisation procedures, where available, be given. R. Law plans to prepare a full report of both phases of Stage 1 which will be available during 1990.

R. Law considered that the second stage of the PAH exercise will require the same amount of finance as that agreed for the first stage. The cost of the second phase of the CBs exercise will be presented to ICES either just before, or just after, the 1990 ACMP meeting. (Action: Law, Wells)

#### 7.2.2 BCR Quality Assurance Programme

The intention of this programme is to provide a basis for ensuring that data collected by laboratories participating in JMG and NSTF monitoring programmes are of the required quality for these purposes. By developing a QA programme for participants with limited experience in this work and by assessment of the long-term variability observed in analyses at all laboratories, valuable information relating to the ability of laboratories to determine/observe trends in contaminant levels will be obtained. Such an approach was felt to be very valuable.

The possibility that other activities, such as intercomparison exercises and the preparation of laboratory reference materials could, at a later date, also be taken under this umbrella was seen as an advantage in the longer term.

#### 7.2.3 Pooling of samples for monitoring purposes and analytical variance

Since this matter had been dealt with in plenary, there was no further discussion of this agenda item.

#### 7.2.4 Overviews

The overview on HCB and  $\gamma$ -HCH (lindane) was reviewed. A number of minor amendments were suggested. L. Reutergårdh agreed to provide a brief section on "Production and Usage" and some additional references would be forwarded to the author for inclusion in time for presentation to ACMP in 1990. (Action: Wells, Reutergårdh)

It is clear that there is some potential misunderstanding regarding the requests for specific overviews which are made without any explanation. It would be encouraging and enlightening if ACMP could, as a matter of routine, present a short supporting statement on the reasons for the selection and, in the case of multiple requests, a reasoned order of priority. This has been requested in previous years by MCWG.

#### PBBs

The Organic Sub-group considered that PBBs were not the main source of brominated organic contaminants and recommended that the overview be expanded to account for these compounds and also other, equally toxic, organobromine compounds. The overview proposed will cover "Brominated Fire Retardants". This overview will be prepared by L. Reutergårdh, J. de Boer and J. Boon. (Action: Reutergårdh, de Boer, Boon)

#### Triazines

The triazines form a wide group of compounds, many of which have no significant presence or influence in the marine environment. The Sub-group recommended that this overview be tailored to the specific needs of the NSTF/JMG requirements, namely, an overview on Simazine and Atrazine. J. Tronczynski has agreed to prepare this. (Action: Tronczynski, Reutergårdh or colleague)

#### Octachlorostyrene

This overview will be prepared by R. Law and J. Klungsøyr. (Action: Law, Klungsøyr)

#### Surface active agents and chlorinated water discharges into the marine environment

A. Abarnou informed the Organics Sub-group of two recent reviews prepared at IFREMER in an important research project on urban wastes.

The first review, concerning surface active agents, has been prepared by G. Thoumelin. It deals with the properties, use, and production of these compounds. The analytical techniques for these compounds and, in particular, for anionic and non-ionic surface-active agents, have been critically evaluated. Some data on the concentrations of these compounds in aquatic environments (sewage, river, estuaries and coastal marine) are given. This report also includes information on the fate of these compounds in the aquatic environment, e.g., by degradation, and will be completed with data on the effects of the surface-active agents on marine life. This last part is to be prepared by a colleague from IFREMER in Nantes.

The second review deals with the chlorination of urban sewage before it is discharged into the coastal marine environment. Chlorine is very efficient against various micro-organisms which are abundant in urban waste. Due to its low cost, the chlorination of waste-waters is very common in order to preserve the normal uses of coastal waters, such as shellfish farming or

recreational activities. Therefore, such a treatment might create undesirable effects on marine life due to residual oxidants and/or undesirable chlorinated or brominated organic by-products.cp,6;

The report is divided into three parts. The first chapter presents the basic chemistry of chlorine in water and in wastewater. The second deals with the disinfection process. The last part deals with the effects of the residual oxidants and some of the by-products on marine life.

These two reviews are now completed and could be presented as an overview to the next MCWG meeting. (Action: Abarnou)

During the discussions, J. Pawlak informed the Sub-group that the problem of surface-active agents had been addressed by ACMP some years ago and an overview would probably be well received. After discussion with R. Law, it was thought that M. Waldock (MAFF, Burnham-on-Crouch) could also be associated with this overview because he has measured some of these compounds in British waters. Moreover, a large amount of chlorine is released into the marine environment, either as an anti-fouling agent, for cooling sea water in power plants, or for the treatment of wood pulp in the paper industry. These aspects should be included in the overview on chlorination. (Action: Law and Waldock)

Any comments on these proposals are welcomed, as is any information relevant to the chemistry and the formation of chloro- (bromo-) organo-compounds in the wood industry. This last point is in particular addressed to our Scandinavian colleagues.

#### 7.2.5 Selection of matrices for new contaminants of interest to NSTF

The Sub-group scrutinised the NSTF matrix tables for mandatory and voluntary determinands.

A revised table for voluntary determinands is given in Annex 6. Fish liver and muscle have been included, since it was generally felt that it was important to include biota in the monitoring of temporal and/or spatial trends. Polybrominated diphenylethers used as flame retardants were considered to be so important that they should replace the brominated biphenyls (PBBs). Analyses of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are very costly and complicated; they are performed by only a few laboratories. The cost effectiveness of such analyses on sediments was questioned by the Sub-group. If carried out, the Sub-group felt that they should preferably be done on fish liver.

It was suggested that some additional compounds should be included on the list of PAHs to be analysed. These are given in the notes to the Tables (see Annex 6) and constitute PAHs introduced into the marine environment from combustion sources and oil inputs. Those PAHs, which were selected for the ICES intercomparison exercise, were chosen for analytical rather than monitoring purposes.

The seven CBs have been put on the list of mandatory determinands in sediments. The Sub-group suggests that all ten congeners included in the on-going ICES/IOC/OSPARCOM intercomparison exercise should be included. THE ANALYSIS OF CBs OTHER THAN AS INDIVIDUAL CONGENERS IS STRONGLY DISCOURAGED, SINCE THIS WILL REPRESENT A STEP BACKWARDS IN QUALITY ASSURANCE. The Sub-group felt that this approach ought to be possible, given the current resources in the participating laboratories, provided that participants are prepared to put the necessary effort into the analytical work. The option to analyse total PCB instead of individual CBs is, therefore, taken out of the Table notes.

The analysis of planar CBs is of special environmental concern and has been added to the list of voluntary determinands. Their analysis is strongly encouraged by the Sub-group.

Additional measurements of contaminants in biota on the mandatory list should be considered by the NSTF, since the existing data were obtained without a strict QA programme being in operation. These earlier data are very difficult to validate and assess.

#### Important statements

- 1) The Sub-group strongly endorses a previous proposal that all of the organic determinand analyses in sediment matrices should be accompanied by:
  - a) total organic carbon (TOC) analysis;
  - b) size fractionation <63 µm; and
  - c) description of sediment type.
- 2) The Sub-group feels that sampling stations were not selected properly for observations of accumulation of contaminants in the sediments. These sites are not all situated in accumulating and stable sedimentary regions.

#### General comments brought up during discussion

There is a general lack of common standards for some chemicals. Dioxin analyses may be performed properly in only a few specialized laboratories. Analytical schemes are complex and sophisticated equipment, such as high resolution mass spectrometry, as well as qualified technical staff are necessary.

A list of specific isomers (congeners) of dioxins in biota should be prepared. The lack of standards, and the high cost of those that are available, was again mentioned.

Some laboratories analyse dioxins according to in-house standards and these analyses are translated into toxicity equivalents.



Various options on the utilisation of fish liver for trend assessment were noted. The large variability in contaminant concentrations was underlined. This variability may be due to metabolic or physiological activities, or seasonal variations. Against this, successful studies on trend assessments in cod liver had been carried out.

The use of samples of shellfish and polychaete worms for CB determinations was discussed. Cultured shellfish may be important biota for survey and health considerations, but they are less important from a monitoring standpoint. CB concentrations in polychaete worms may depend on a dynamic equilibrium in the distribution of these compounds between sediments, pore water, and dissolved organic carbon (DOC). (Action: Abarnou)

#### 7.2.6 Trend monitoring

This matter was dealt with in plenary.

#### 7.2.7 New contaminants

Various studies underway in Sweden on chloronaphthalenes, chlorinated paraffins, and metabolites of PCBs were reported by Dr Reutergårdh for information.

Dr Wells described work at DAFS on haemolytic anemia in salmon, related to resin acids discharged from paper and pulp mills into the River Don.

Dr Wells has written to IUPAC regarding the use of the term "coplanar" for toxic chlorobiphenyls and in reply they confirmed that "planar" was the preferred nomenclature. Although this is the opinion of the nomenclature group, it is not a published statement.

#### 7.2.8 Bremerhaven workshop

This matter was dealt with by an ad hoc group of the Trace Metals and Organics Sub-groups during a lunchtime session.

#### 7.2.9 OPRU Hydrocarbon Intercomparison

This exercise was undertaken in 1984 with participation from some ICES-related laboratories. The report is now available and should have been distributed to participants. If not, please contact R. Law, who will contact the coordinator.

#### 7.2.10 Analysis of seal blubber samples by a single laboratory

In the ICES 1987 Council Resolutions (C.Res. 1987/3:4 and C.Res. 1987/4:8) it was mentioned that ICES laboratories were encouraged to analyse CB contents in seal blubber samples. The same samples could be sent to the Special Analytical Laboratory in Solna,

Sweden. This laboratory would also analyse these samples to identify a spatial distribution and any possible systematic error. Although this action was not carried out, it is still of interest, and the MCWG proposes that this exercise should take place during 1990. The number of samples per laboratory is restricted to 2. The seals should be juvenile seals. L. Reutergårdh was appointed coordinator for this exercise. The participants in the joint meeting of the Working Group on Baltic Seals and the Study Group on the Effects of Contaminants on Marine Mammals, in Stockholm in May 1990, will be asked to obtain the seal blubber samples and to carry these samples to Stockholm at the time of their meeting.

#### Planar chlorobiphenyls

In addition to the list of 10 CBs proposed for the second step of the ICES/IOC/OSPARCOM intercomparison exercise on CBs (see Section 7.2.1), there is an interest at some laboratories to analyze the planar CBs 77, 126 and 169. The Special Analytical Laboratory in Solna, Sweden, will be conducting an intercomparison exercise on these planar CBs during 1990. The MCWG proposes that laboratories which are interested in this matter should contact L. Reutergårdh. In principle, they will be welcome to join this exercise. To be included in the statistical evaluation of this exercise, it will be necessary to analyse 5 replicates. In the letter with the report on the first step of the ICES/IOC/OSPARCOM CB intercomparison exercise, laboratories will be invited to join this exercise on planar CBs. The time schedule is as follows: the ampoules will be dispatched at the end of March 1990 and the deadline for returning results is 1 October 1990. Possibilities for a separate ICES intercomparison exercise on planar CBs will be considered during the MCWG meeting in 1991 in relation to the success of the Swedish exercise and the performance of participants in the second step of the ICES/IOC/OSPARCOM intercomparison exercise on CBs.

#### 7.2.11 Any Other Business

Dr Wells was confirmed as Chairman for next year's meeting of the Sub-group, and for the coordination of intersessional activities.

#### 7.3 Sub-Group on Chemical Oceanography

##### 7.3.1 ICES (Fourth Round) Intercomparison Exercise for Nutrients in Sea Water

The Sub-group reviewed the preliminary report on the results of the Intercomparison Exercise on Nutrients in Sea Water and congratulated the authors on their work; they noted especially that the preliminary report was presented within one year, as agreed upon at the MCWG meeting in 1989.

The Sub-group agreed that there would not be time at this meeting to work through the document in detail in order to do final editing. The members, therefore, confined their comments to certain parts which needed changes.

D. Kirkwood had prepared a new list for Annex 2 of the report in order to correctly reflect the results as they were reported by the respondents.

It was agreed to rewrite, and expand, the introductory part of the preliminary report in order to describe the background and to explain how the results had been treated.

The new introductory pages should also mention more clearly the purpose of the intercomparison exercise and the limited amount of water available for distribution, since MCWG at its last meeting had identified the need for replicate analyses as a necessity for a proper statistical treatment of the results.

The new introductory pages should also mention the silicate and ammonia values. Sea water stored in glass bottles will give high silicate values depending on the storage time, while samples for ammonia determinations are not likely to be stored at all. The purpose of analysing for silicate was to gain information on silicate interference in the phosphate analysis. Ammonia was determined by the participating laboratories which routinely made measurements of this parameter.

Ammonia determinations were requested as a means of identifying biases. The use of statistics in the preparation of the report is limited to the purpose of identifying laboratory performance.

The Sub-group considered that the final report should be attached to the MCWG report. [SECRETARIAT NOTE: Large reports intended for subsequent publication are not attached as annexes to Working Group reports. Accordingly, this report has not been annexed.] The Sub-group also recommended that the final report should be published in the ICES Cooperative Research Report series. The need for regular intercomparison exercises was stressed and, in view of this, the Sub-group recommended that ICES, through MCWG, should organize this every second year or on some other regular basis.

#### Further Activities in the Field of Intercomparison of Nutrient Determinations

D. Kirkwood referred to the forthcoming intercomparison exercise, financed by the EEC, to be organised by the Fisheries Research Centre, Dublin, Republic of Ireland, in which Aminot and Kirkwood had been asked to act as coordinators. The samples will be available before summer 1990 and participants are welcomed from SKAGEX and from any other ICES laboratories that were unable to participate in the ICES exercise.

#### 7.3.2 Protocol for sampling and storage of nutrient samples

This subject was first raised at the Sub-group meeting in 1989 when a paper by Uthe et al., entitled "Sampling strategies for trend monitoring using biota, sediments or seawater", identified the MCWG as the appropriate group to develop guidelines for the use of sea water in trend monitoring. Based on this, the Sub-group discussed the merits of preparing a general protocol for

the sampling and storage of sea water for nutrient analysis. Dr Perttilä had agreed to prepare a draft to be circulated to the Sub-group members.

Subsequently, the ACMP requested MCWG to prepare a protocol on sampling, storage and analysis of seawater samples for nutrients to meet the needs of NSTF. This request produced considerable discussion in the Sub-group, since it was not clear whether the protocol was aimed at institutes participating in the NSTF work or if it was to serve as a documentation of recommended procedures for NSTF.

The ICES Oceanic Hydrography Working Group, at its meeting in 1989, requested MCWG to establish guidelines for the conditions under which nutrient samples should be stored, which storage conditions should be used, and what accuracies could be obtained under different conditions.

Furthermore, it should be noted that the Sub-group had not previously agreed to develop a protocol on analysis of nutrients. The recent ICES nutrient intercomparison exercise has clearly shown that the intercomparison of the actual performance of the analysis is far more important than deciding on exact descriptions of common analytical methods.

Following the discussions at the 1989 MCWG meeting, Dr Perttilä prepared a draft protocol for sampling and storage of samples. In reviewing this draft, the Sub-group discussed the difficulties of arranging a programme specifically for trend monitoring of nutrients in an area with the oceanographic characteristics of the North Sea, and also how detailed or general a protocol would have to be to cater for the needs of NSTF, given the rather non-specific request. After some considerable discussion, Mr Carlberg agreed to amend the draft to reflect this discussion and the views of the Nutrients Working Group of the Paris Commission at its fourth meeting in Oslo, 26-29 September 1989. The points to be considered are the benefit of using a profiling fluorometer to optimise the sampling programme for chlorophyll and phytoplankton, as well as a clear statement that at present there is no single method for the preservation and storage of nutrient samples that can be recommended for general use in all sea areas and for all seasons. It was also stressed that any trend monitoring programme has to be based on the oceanographic knowledge of the area and, for maximum benefit, has to take account of ongoing programmes concerning station networks, etc.

The revised text by Mr Carlberg was subsequently considered by the Sub-group. Later discussions in plenary led to the MCWG Chairman agreeing to contact Dr J. Portmann (Chairman of ACMP) to clarify exactly what form the protocol should take to meet the needs of NSTF. Amendments to the re-draft will take place by correspondence during the intersessional period.

The Sub-group then examined the paper entitled "Quality assurance and sampling", prepared by Dr Cofino and colleagues. The Sub-group agreed that the paper was quite comprehensive and argued the need for a properly designed sampling programme. It was agreed that the paper would form a useful annex to the nutrient protocol for NSTF.

Finally, the Sub-group reviewed the paper, distributed by J. Biscaya, on the storage of samples for nutrient analysis. Although the Sub-group considered that the results were of great interest, and that other institutes had made progress in the examination of this problem, it could not at this stage recommend a general preservation and storage procedure to cover all sampling programmes.

### 7.3.3 BCR pilot programme for QA

The Sub-group agreed that QA activities need to be encouraged in all marine laboratories and, as such, welcomed this initiative by BCR. Although there were many practical questions to be resolved before the programme got underway, the eventual programme would be of considerable value to participants and the Sub-group gave the proposal its full support. However, it was pointed out that participation should not be limited strictly to the categories of laboratories listed, and that every step should be taken to offer participation to all interested marine institutes.

### 7.3.4 Design of an intercomparison exercise for dissolved oxygen in Baltic waters

The Sub-group noted that ICES had been asked by HELCOM, through its 1989 meeting of the Scientific-Technological Committee, to organise an intercomparison exercise for the measurement of dissolved oxygen in sea water. In its response, ICES had suggested that this exercise be done in cooperation with the Swedish organisers of the Third Biological Intercalibration Workshop (BIW III), scheduled for 27-31 August 1990 in Visby. The Sub-group noted that a preliminary proposal for this exercise had been drafted at ACMP by Drs Topping and J.M. Bowers.

The Sub-group was asked to review this preliminary proposal and make any amendments it considered to be appropriate. The following scheme was proposed by the Sub-group for consideration by the workshop organisers:

The entire exercise will be carried out aboard one ship in order to minimise the effects of patchiness. The design assumes that repeated sampling can be done from a homogeneous water mass. The following parts of the exercise are designed to assess the variability associated with the measurement procedure:

#### Step 1: Variability caused by sampling equipment

Each type of sampling bottle to be used by laboratories in the Baltic studies is to be tested. Each bottle will be used to collect a sample of water from a pre-determined depth. These collections will be made by one person who will subsequently use one of the sampling bottles to collect additional samples to assess the variability of the water mass during the collection period. One person will then withdraw samples from each bottle and perform all subsequent steps of the analysis.

This entire procedure will be repeated for a different water mass with a lower level of oxygen.

Step 2: Variability caused by sampling staff

As for Step 1, except that every participant will operate his/her own sampling bottle.

Step 3: Variability related to the analysis of samples

Every participant will withdraw a set of sub-samples from a bulk sample of sea water and will take the samples through the entire procedure of analysis. This sub-sampling process is carried out three times, so that every participant obtains three sets of samples from the beginning, middle, and end of the process. The entire step is then repeated with a different bulk sample of lower oxygen content.

Finally, the Sub-group noted that BIW III is organised by an international steering group plus conveners for the different parameters to be intercompared. Analyses for dissolved oxygen and nutrients will be intercompared within one parameter group. After discussion of the organisational details, the Sub-group concluded that the steering group fulfilled the requirements of a management group as requested by ICES.

7.3.5 High precision measurements of dissolved oxygen

The Sub-group was informed by the Chairman that the ICES Oceanic Hydrography WG had asked MCWG to review a proposed method for high precision determinations of dissolved oxygen. Following an examination of this proposed method, the Sub-group concluded that the method seemed well suited for its purpose with one important addition, namely, that the fixation reagents have to be added as exact volumes. The accuracy of the total reagent volume should be within  $\pm 0.02$  ml. Other points were made to improve the method for high accuracy determinations:

- a) the sample bottle should be gravimetrically calibrated at 20<sup>0</sup>C to the nearest 0.01 g;
- b) the original Carrit and Carpenter reagents should be used. This involves the use of NaI instead of KI in order to obtain sufficiently high concentrations of I after dissolution of the precipitate; and
- c) it is recommended that burettes be calibrated, particularly automatic burettes with rubber membrane back-flush valves.

### 7.3.6 Historical review on the comparability of phosphate determinations: paper prepared by G. Weichert

The Sub-group felt that the conclusions of the paper were in agreement with the general opinion of the use of old phosphate data: "Old phosphate data can be considered reliable from 1923 onward, if a certain number of qualifiers were met", i.e., if

- the phosphomolybdenum blue method was used;
- the analyses were made immediately after sampling;
- the general guidelines for good laboratory practice were used; and
- the analyses were done carefully by a trained technician or experienced scientist.

All the qualifiers, in the opinion of the Sub-group, again underlined the caution that has to be exercised when examining nutrient data.

Historical phosphate data have a better chance of being comparable than nitrate data, since the changes in analytical methods for the latter have been much more fundamental from a chemical viewpoint.

### 7.3.7 Nutrient Data Comparison and Trend Evaluations

The Sub-group examined the paper presented by the ICES Hydrographer at the 1989 ACMP meeting. The purpose of this paper was to show how difficult it is to achieve reliable data for trend monitoring purposes.

The PEX nutrient data had an overall discrepancy of over 50%. A discrepancy of the same magnitude seems to occur in the BOSEX data ten years prior to PEX. The same discrepancy seems also to exist in the BMP (Baltic Monitoring Programme) data.

The Sub-group discussed the problem of comparing nutrient data from different sources and possible ways of normalizing data in order to assist in this comparison. A successful approach of this kind had recently been applied by the ICES Hydrographer for the evaluation of the PEX data set. However, it was agreed that such normalization is likely to be done in relation to the specific needs of the task in question. In such circumstances, normalized data cannot be stored in the general ICES hydrographic data base, but must be stored as separate data sets.

The discussion pointed to the need for good quality assurance practices for nutrient analysis both at the analytical and the sampling level. In this context, it was stressed that greater effort has to be placed on the production of good nutrient data for the scheduled SKAGEX (May-June 1990) and other programmes, as well as in the evaluation of existing data sets.

The SKAGEX multi-ship engagement will provide an opportunity to conduct an intercomparison of "real" samples, from parts of cross sections representing different water masses, when the ships meet in harbour for two days during this exercise.

The Sub-group reviewed the statement of the 1989 Hydrography Committee meeting on trend determinations of nutrients (see Annex 7). The Sub-group felt that the statement made by the Hydrography Committee on this issue was in full agreement with the view of the Sub-group.

#### 7.3.8 Any Other Business

The Sub-group nominated Stig Carlberg to act as Chairman of the Sub-group for the next session and for coordinating intersessional activities.

### 8 PLENARY DISCUSSIONS OF THE SUB-GROUP REPORTS

The MCWG reviewed the reports prepared by the three Sub-groups, and the action list and recommendations arising from each report. Trace Metals Sub-group

The members were informed that the Sub-group had examined the preliminary report of the ad Hoc Group reviewing the results of the Baseline Study of Trace Metals in Coastal and Shelf Sea Waters and had agreed with the findings. Members noted that the main findings of the review will be presented to ACMCP in June 1990 and that a full report will be sent to JMG in December 1990. The recommendation that the final report should be published in the ICES Cooperative Research Report series was supported and endorsed by MCWG.

The MCWG noted that the overview on chromium and the QA paper on sampling sea water for trace metal analysis were to be amended during the intersessional period for presentation to MCWG in 1991.

On the matter of the SPM intercomparison exercise, the MCWG was informed that Dr Yeats was to prepare a note on the advantages and disadvantages of different methods and send it to Dr Calder, Chairman of WGMS.

Dr Cofino reported on the outcome of a sessional meeting to discuss the arrangements for chemical analysis at the Bremerhaven Workshop. Six MCWG members had agreed to collaborate on this work which was to be done at 6 stations in the vicinity of the Elbe estuary. Measurements of metals and CBs are to be carried out in samples of sediment, soft tissue of shellfish, and fish liver. Members expressed approval of this input to this important piece of collaborative work, but expressed some concern about the lack of planning which had resulted in Dr Cofino being brought in at a late stage of the operation to organise the chemical aspects of this work. In the event that a similar collaborative project takes place in the future, the members strongly advised the respective working group to approach MCWG at the start of the



discussions so that the logistical aspects of the chemical work could be arranged with less haste and therefore more effectively.

#### Organics Sub-group

Members were informed by Dr Law, coordinator of the PAH intercomparison exercise, that a final report on this exercise would be prepared for submission to ACMP once the statistical aspects of the report had been revised and the data in the preliminary tables had been checked for accuracy. The MCWG noted that the second stage of this exercise would begin in 1990 and would be based on extracts of sediments rather than biota. Dr Law agreed to prepare a note on this decision for the Chairman in case this matter was raised at ACMP. The proposal to hold a two-day meeting prior to the next meeting of MCWG, to discuss the results of stage 2, was endorsed by MCWG.

Dr de Boer informed the members that the report on the first step of the CB intercomparison exercise would be finalised in the near future. Several members questioned the statistical approach taken by his co-worker, Dr van der Meer. After discussing this matter at length, members concluded that there was a need to take a standard approach to the statistical appraisal of results from intercomparison exercises and recommended that an intersessional group be established to prepare proposals on this topic. This group should consist of representatives from MCWG, particularly those currently responsible for organising these exercises, and representatives of WGSATM. In relation to the next step of this exercise, members asked Dr de Boer to ensure that the lessons learned from the first step (e.g., problems identified with the response of the detector on the GC system caused by oxygen leaks, and problems of severe contamination) should be conveyed to the participants as soon as possible. The MCWG noted and approved the recommendation that the second stage consist of a further check on standards in addition to the analysis of cleaned-up and raw extracts of both sediments and marine mammal tissue. The MCWG endorsed the proposal to publish the report of the first step of the exercise in the Cooperative Research Report series, following amendments made on the basis of comments by members. It also supported the request to ICES for finances to fund the second step of this exercise.

The MCWG noted and approved the following work by the Sub-group:

- the proposed intersessional work on overviews on brominated compounds, triazine and octachlorostyrene;
- the comments and advice given on the proposed voluntary determinands for the NSTF monitoring programme; and
- the proposal by Dr Reutergårdh to coordinate measurements of planar CBs in seal blubber samples.

In relation to overviews, the MCWG supported the request by the Chairman of the Sub-group that ACMP confirm which of the two sets of guidelines should be used by MCWG in the preparation of these documents.

Dr Topping subsequently discussed this matter with Dr Portmann, Chairman of ACMP. Dr Portmann considered that the model preferred by ACMP would be one based on the overview for organo-tin compounds (see Annex 5, 1984 ACMP report (Coop.Res.Rep. No.132)). This covers all the key issues required by ACMP, namely:

Natural occurrence, production and uses, physico-chemical properties, routes into the environment, methods of analysis, levels in the environment, fate in the environment, bioaccumulation, effects on marine biota and man, and conclusions as to present and future environmental significance.

If possible a budget, as in the earlier reports on mercury and lead, etc., would be useful.

#### Chemical Oceanography Sub-group

The MCWG discussed the report of the intercomparison exercise for nutrients, particularly the statistical approach used by the coordinators to analyse the data sets for each determinand. Mr Kirkwood agreed to raise this matter with his colleague Mr M. Nicholson, a member of WGSATM, and to re-analyse the data using a more acceptable statistical method before the final report is sent to ACMP. The MCWG endorsed the recommendation that the report be published in the ICES Cooperative Research Report series.

In discussing the Sub-group's re-draft of Dr Perttilä's paper on a protocol for sampling and storage of water samples for nutrient measurements, a number of members felt that the NSTF's request for such a protocol should have been supported by a clear statement on what exactly it wanted and how it was to be used. Since this matter could not be clarified by either MCWG members or the ICES Environment Officer, it was agreed that the Chairman of MCWG should prepare the re-draft following consultation with Dr Portmann. Several members offered to review the amended paper before it was submitted to ACMP.

The MCWG noted and approved the advice offered by the Sub-group with respect to high precision measurements of dissolved oxygen and the intercomparison exercise for dissolved oxygen in Baltic waters.

The MCWG noted with some concern that the systematic interlaboratory differences, evident in the intercomparison exercise for nutrients, may have persisted for some years. As a specific example, the intercomparison exercise demonstrated a 20% difference in nitrate levels measured by the Institut für Meereskunde (Rostock) and SMHI (Gothenburg), a difference that was evident in BOSEX (1977) and PEX (1986). Although it was gratifying that the observed differences appeared constant over time, it was clear that normalization of the data was necessary where joint programmes required the merging of data (e.g., NSTF, BMP, PEX). However, given the high level of internal consistency within an institute, it was important that national data sets should not be normalized, in order to preserve long time series. The ICES data centre recognized this fact following PEX, and sought to ensure that data going through traditional data centre routes should not be normalized. Thus, data collected during PEX exist in two

forms: one normalized for the purposes of PEX, the other remaining as reported by the institute concerned. As a corollary to this, it was also important that an awareness of these differences should not encourage institutes to change their procedures without first ensuring the integrity of their own time series.

#### 9 ANY OTHER BUSINESS

The MCWG discussed the proposal by the Trace Metals Sub-group regarding the future work of that Sub-group. There was general agreement that it was now timely to consider joint studies on estuarine systems to investigate the factors which influence the concentration, distribution, and speciation of trace metals in estuarine and coastal waters. MCWG also agreed that biological effects work done in collaboration with biologists was worthy of support.

The MCWG was informed about the HELCOM assessment of the Baltic marine environment, to be completed by the Group of Experts for the Second Periodic Assessment (GESPA) in April 1990. Drs Schmidt and Harms were to be the reviewer and convener, respectively, for the evaluation of data on trace metals. Dr Schmidt requested that ICES examine the Baltic data held by ICES in its data bank. Dr Pawlak saw no reason why this request should not be met, since it only involved a small data set, and agreed to respond on this matter.

The MCWG agreed that for future meetings, agenda items 3-6 inclusive, which are generally items of information for the members, would be dealt with by the preparation and distribution of written reports before the meeting. If no submissions for these items are received, they will not be dealt with at the meeting. Any papers for these agenda items will be deemed to have been read by the members before the meeting, so that discussion of them will be kept to points of clarification and any matters arising.

#### 10 RECOMMENDATIONS

The Chairman informed the Group that all recommendations arising from the Sub-groups, together with any arising from the plenary discussions, would be appended in Annex 9. A list of intersessional tasks would be given in Annex 8.

The MCWG then discussed the venue and time of its next meeting. The Chairman reminded the Group of the offer by Professor R. Wollast to host the next meeting in Brussels. It was agreed that the Chairman would try and arrange for the meeting to take place during the week beginning 8 April.

All other business having been completed, the Chairman thanked the members for their hard work and constructive help during the meeting and closed the meeting at 14.00 hrs on 16 February 1990.

**ANNEX 1****ICES MARINE CHEMISTRY WORKING GROUP  
COPENHAGEN, 12- 16 FEBRUARY 1990****AGENDA**

1. Opening of meeting
2. Adoption of the agenda
3. Report of 77th 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 regulating agencies
7. Subgroup activities and discussions
  - 7.1 Trace metals
    - 7.1.1 Review the report on trace metals in coastal waters prepared by the *ad hoc* group of MCWG
    - 7.1.2 Overview on Cr
    - 7.1.3 Validation of sampling methods for sea water studies
    - 7.1.4 Variance of analytical measurements and the effects of pooling of samples for monitoring purposes
    - 7.1.5 Selection of matrices for new contaminants of interest to NSTF.
    - 7.1.6 Review WGSATM's paper on statistical aspects of trend monitoring
    - 7.1.7 AOB raised by subgroup

## 7.2 Organics

- 7.2.1 Review progress on CBs and PAHs I/C exercises
- 7.2.2 Variance of analytical measurements and the effects of pooling of samples for monitoring purposes
- 7.2.3 Review updated overview on HCB and HCH and identify author(s) for overviews on PBBs, triazines and octachlorostyrene.
- 7.2.4 Selection of matrices for new contaminants of interest to NSTF
- 7.2.5 Review WGSATM's paper on statistical aspects of trend monitoring.
- 7.2.6 Identification of new contaminants
- 7.2.7 AOB raised by subgroup

## 7.3 Chemical oceanography

- 7.3.1 Review report on nutrient I/C exercise and identify future intercomparison work
- 7.3.2 Sampling, storage and analysis of sea water for nutrient measurements
- 7.3.3 Intercomparison exercise for dissolved oxygen measurements in Baltic Sea
- 7.3.4 AOB raised by the subgroup

- 8. Plenary discussion of subgroup work
- 9. AOB
- 10. Recommendations and Action List
- 11. Date and venue of next meeting
- 12. Closure of meeting

## ANNEX 2

## MEETING OF THE MARINE CHEMISTRY WORKING GROUP

Copenhagen, 12 - 16 February 1990

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## ANNEX 3

NATIONAL RESEARCH COUNCIL OF CANADA  
MARINE ANALYTICAL CHEMISTRY STANDARDS PROGRAM

The past year has again been very productive, both in terms of reference materials and new methodologies for the analysis of marine samples. The provision of data regarding the chemical speciation of metals as well as their total concentrations in environmental samples has become of increasing importance and the Ottawa laboratory is devoting a major part of its research efforts toward this goal. The Atlantic Research Laboratory (ARL) in Halifax has become very interested in shellfish toxin problems and is now moving more in a biological direction.

Reference Materials

The non-defatted lobster hepatopancreas "second generation" reference material for trace metals, LUTS-1, was certified for 17 trace metals plus methylmercury and issued last June (see attached sheet). The material, which has a 55% lipid content, has been homogenized and stabilized following the addition of only a small quantity of water and closely resembles the type of sample normally analyzed in many laboratories. It is not freeze or spray dried. It is too early yet to determine what the response will be to this new type of reference material.

The successful production of the Mytilus edulis reference material, MUS-1, for domoic acid by ARL (see attached sheet) in a manner similar to the production of LUTS-1 leads us to consider the feasibility of preparing a second generation Mytilus edulis sample for trace metals. Such a material may be quite attractive to monitoring laboratories, especially those involved in mussel watch programs.

Certified values for monobutyl, dibutyl and tributyltin were issued in June for the harbour sediment reference material PACS-1. These numbers are the first certified alkyltin values for any reference material. They represent the culmination of a short, but intense, cooperative research program in our laboratory and corroborative analyses from five external expert laboratories: Texas A & M University, the U.S. Department of the Navy, Canada Centre for Inland Waters, Battelle Northwest, and Battelle Ocean Sciences.

## Milligrams/kilogram (as Sn)

Tributyltin	$1.27 \pm 0.22$
Dibutyltin	$1.16 \pm 0.18$
Monobutyltin	$0.28 \pm 0.17$

Work is under way which we hope will lead to the certification of a biological reference material, probably Mytilus edulis, with respect to alkyltins. The alkyltin contents of our present biological tissue reference materials are all too low to enable reliable certification.

SLRS-2, the replacement for the riverine reference material, SLRS-1, is now in the certification process and will be ready for distribution when stocks of SLRS-1 are depleted within the next few months. Another river water sample has been gathered to produce a natural water reference material for trace mercury. All going well, the latter should be in distribution by summer. The sample will be bottled in borosilicate glass, which will obviate the certification of the material for other trace metals.

ARL has also issued a domoic acid calibration solution and a sample of  $^{13}\text{C}-\text{Cl}_6$ -biphenyl for use as an internal standard in mass spectrometric determination of organochlorines.

#### Methodologies

There are several continuing research projects under way concerning the determination of total and/or speciated metals in marine samples. Most of these are motivated by our need to have relatively independent methods for these analyses to use in the certification of the reference materials. Also, we are continually searching for simple and reliable procedures which may be transferred to laboratories involved in marine monitoring activities.

The analytical chemistry regarding the analysis of marine samples for total trace metals of environmental interest at environmental levels is now under good control for most metals. Much effort has also been devoted to speciated metals such as organomercury and alkyltins. Problems caused during the certification of the riverine waters SLRS-1 by arsenic species have resulted in work with this element.

#### a) Tin speciation in marine sediments, biological tissues and waters

The HPLC-ICP-MS method for the determination of tributyltin (TBT) and dibutyltin (DBT) in sediments reported last year has been refined to yield more accurate and precise results. Thermostatting of the nebulizer spray chamber at 0°C has greatly reduced problems of fluctuating sensitivity, and a slight modification of the extraction procedure has greatly improved the precision of replicate analyses. A new set of results for TBT and DBT in PACS-1 are in excellent agreement with data obtained by gas chromatography with flame photometric detection and by ion spray tandem mass spectrometry.

Work continues on the application of methods developed for butyltins in sediments involving chromatographic and ion spray tandem mass spectrometric procedures to marine biological tissues. Progress is slow mainly because the concentrations of tin are less than 1 microgram per gram (dry weight) even in contaminated samples.

Attempts are also under way to employ liquid chromatographic mass spectrometric methods for metal speciation in natural waters.

b) Arsenic speciation in river water

A method for chemical speciation of arsenic in the river water reference material SLRS-1 was developed based on cation exchange techniques coupled with direct analysis and hydride generation graphite furnace atomic absorption spectrometric procedures. Besides As(III), As(V) and dimethylarsinic acid, a large (22%) unidentified inert fraction, which is believed to be related to arsenobetaine, was isolated.

c) Determination of aluminum in biological materials

We have never been able to certify any of our biological materials for aluminum in spite of the relatively high concentrations of this metal in the materials. Results generated in this and in collaborating laboratories working with our samples have never been in sufficient agreement. An effort to produce a new independent procedure using a gas chromatographic separation of aluminum after chelation with beta-diketones is being made.

d) Oxide reduction in inductively coupled plasma mass spectrometry (ICP-MS)

A series of experiments has been carried out in an effort to find a practical means to reduce the levels of certain polyatomic species, in particular, oxides, which can interfere with the ICP-MS determination of some elements because of isobaric interference. One approach which has been studied involves reduction of the amount of water (the major source of oxygen) reaching the ICP, either by cooling the nebulizer spray chamber to reduce the water vapour pressure, or by partial desolvation of the sample aerosol. Another approach involves the addition of nitrogen to the argon plasma gas. In addition to raising the temperature of the plasma, the nitrogen may also act as an oxygen "scavenger", effectively competing with other elements for available oxygen. For example, the addition of nitrogen has been found to reduce the signal for  $^{40}\text{ArO}$ , which is isobaric with the major isotope of iron, by 2 orders of magnitude, greatly improving the detection limit for this element. Iron can now be directly determined in freshwater samples such as the St. Lawrence River water SLRS-1.

e) Determination of trace lead by graphite furnace atomic absorption spectrometry

A method was developed for the determination of lead using the in situ preconcentration of the lead as  $Pb(C_2H_5)_4$  by reacting lead with sodium tetraethylboron. This technique is simple and very sensitive. The detection limit achieved (1 pg/ml) is, to our knowledge, the lowest reported for inorganic lead. The sodium tetraethylboron is now commercially available from Strem Chemicals.

f) Graphite furnace microwave induced plasma (GF-MIP)

Studies are continuing in order to characterize the analytical use of a graphite furnace interfaced to a helium microwave induced plasma in order to assess the potential of the technique for multi-element analysis. This will be done in conjunction with simultaneous in situ hydride generation and preconcentration for those elements which lend themselves to this technique.

g) Atomic fluorescence determination of mercury

Work has started on the construction of a simple cold vapour mercury detection system based on atomic fluorescence. The technique should offer a 10-fold improvement in detection capability over the present atomic absorption spectrometric scheme.

h) Furnace atomization plasma emission spectrometer (FAPES)

A novel plasma emission source, FAPES, has been built and evaluated. The workhead consists of a graphite furnace with an axial graphite electrode to permit the establishment of an atmospheric pressure helium radio frequency plasma. Samples are vaporized from the tube wall and excited in the plasma. This offers an emission alternative for the graphite furnace and opens up a new field of analytical possibilities.

Research Papers

The following MACSP related papers have been published by the Ottawa laboratory or have been accepted for publication over the past couple of years.

- 1) Acid Digestion of Marine Samples for Trace Element Analysis Using Microwave Heating.  
S. Nakashima, R.E. Sturgeon, S.N. Willie and S.S. Berman.  
Analyst, 113, 159-163 (1988).
- 2) Atomic Absorption Determination of Tin Using in Situ Concentration of Stannane in a Graphite Furnace.  
R.E. Sturgeon, S.N. Willie and S.S. Berman.  
Anal. Chem. 59, 2441-2444 (1987).
- 3) Trace Element Analysis and Graphite Furnace Atomic Absorption.  
R.E. Sturgeon.  
Can. J. Spectrosc. 32, 79 (1987).

- 4) Sampling and Storage of Natural Waters for Trace Metals.  
R.E. Sturgeon and S.S. Berman.  
C.R.C. Crit. Rev. Anal. Chem. 18, 209-244 (1987).
- 5) The Marine Environment.  
K.W.M. Siu and S.S. Berman.  
Chapter 11 in Occurrence and Distribution of Selenium, M. Ihnat, Ed., CRC Press, 1989, pp 263-293.
- 6) Reference Materials in Assurance of Quality in Analysis of Seawater, Marine Sediments, and Biological Tissues.  
M. Waldichuk, W.D. Jamieson and S.S. Berman.  
Marine Poll. Bull. 18, 477-481 (1987).
- 7) Sorption and Atomization of Metallic Hydrides in a Graphite Furnace.  
R.E. Sturgeon, S.N. Willie, I. Sproule and S.S. Berman.  
J. Anal. At. Spectrom., 2, 719-722 (1987).
- 8) Reference Materials and Analytical Techniques for Marine Trace Metal Analysis.  
R.E. Sturgeon, S.S. Berman.  
Ann. Chim. (Rome), 78, 1-13 (1987).
- 9) New Marine Biological Reference Material for Trace Metals.  
S.S. Berman and R.E. Sturgeon.  
Fresenius' Z. Anal. Chem., 326, 712-715 (1987).
- 10) Environmental Applications of ICP-AES.  
J.W. McLaren.  
Chapter 3 in "Inductively Coupled Plasma Emission Spectroscopy, Part II, Applications and Fundamentals", P.W.J.M. Boumans, Editor. "Chemical Analysis" Series, Vol. 90, John Wiley and Sons, 1987.
- 11) Determination of Trace Metals in Seawater by Graphite Furnace Atomic Absorption Spectrometry with Preconcentration on Silica Immobilized 8-Hydroxyquinoline in a Flow System.  
S. Nakashima, R. Sturgeon, S. Willie and S.S. Berman.  
Fresenius' Z. Anal. Chem. 330, 592-595 (1988).
- 12) Determination of Trace Metals in Seawater by Graphite Furnace Atomic Absorption Spectrometry after Preconcentration by Tetrahydroborate Reductive Precipitation.  
S. Nakashima, R. Sturgeon, S. Willie and S.S. Berman.  
Anal. Chim. Acta 207, 291-299 (1988).
- 13) Determination of Trace Metals in an Open Ocean Water Reference Material by Inductively Coupled Plasma Mass Spectrometry.  
D. Beauchemin, J.W. McLaren, A.P. Mykytiuk and S.S. Berman.  
J. Anal. Atom. Spectrom. 3, 305-308 (1988).
- 14) Analysis of the Marine Sediment Reference Material PACS-1 by Inductively Coupled Plasma Mass Spectrometry.  
J.W. McLaren, D. Beauchemin and S.S. Berman.  
Spectrochimica Acta, Part B 43B, 413-420 (1988).

- 15) Atmospheric Pressure Chemical Ionization and Electrospray Mass Spectrometry of Some Organoarsenic Species.  
K.W.M. Siu, G.J. Gardner and S.S. Berman.  
Rapid Commun. Mass Spectrom. 2, 69-71 (1988).
- 16) Sediment Reference Materials and the Canadian Marine Analytical Chemistry Standards Program.  
P.G. Sim, W.D. Jamieson, S.S. Berman and V.J. Boyko.  
In: Chemical and Biological Characterization of Sludges, Sediments, Dredge Spoils and Drilling Huds, ASTM STP 976, American Society for Testing Materials, Philadelphia, 1988, pp. 27-34.
- 17) Acid Digestion of Marine Samples for Trace Element Analysis Using Microwave Heating.  
S. Nakashima, R.E. Sturgeon, S.N. Willie and S.S. Berman.  
Analyst 113, 159-163 (1988).
- 18) Identification and Quantitation of Arsenic Species in a Dogfish Muscle Reference Material for Trace Elements.  
D. Beauchemin, M.E. Bednas, S.S. Berman, J.W. McLaren, K.W.M. Siu and R.E. Sturgeon.  
Anal. Chem. 60, 2209-2212 (1988).
- 19) Atmospheric Pressure Chemical Ionization and Ion Spray Mass Spectrometry of Some Organotin Species.  
K.W.M. Siu, G.J. Gardner and S.S. Berman.  
Rapid Commun. Mass Spectrom. 2, 201-204 (1988).
- 20) Determination of Organomercury in Biological Reference Materials by Inductively Coupled Plasma Mass Spectrometry using Flow Injection Analysis.  
D. Beauchemin, K.W.M. Siu and S.S. Berman.  
Anal. Chem. 60, 2587-2590, (1988).
- 21) Determination of Arsenic Species by High Performance Liquid Chromatography - Inductively Coupled Plasma Mass Spectrometry.  
D. Beauchemin, K.W.M. Siu, J.W. McLaren and S.S. Berman.  
J. Anal. Atom. Spectrom. 4, 285-289 (1989).
- 22) Use of External Calibration for the Determination of Trace Metals in Biological Materials by Inductively Coupled Plasma Mass Spectrometry.  
Diane Beauchemin, James W. McLaren and Shier S. Berman.  
J. Anal. At. Spectrosc. 3, 775-780 (1988).
- 23) Determination of Trace Metals in Marine Biological Reference Materials by Inductively Coupled Plasma Mass Spectrometry.  
D. Beauchemin, J.W. McLaren, S.N. Willie, and S.S. Berman.  
Anal. Chem. 60, 687-691 (1988).
- 24) A New Approach to the Preparation of Biological Reference Materials for Trace Metals.  
S.S. Berman and R.E. Sturgeon.  
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marine

## LUTS-1

### Non Defatted Lobster Hepatopancreas Reference Material for Trace Metals

LUTS-1 is a second generation reference material. The material has not been defatted or dried during its preparation like the lobster hepatopancreas reference material TORT-1. Except for the addition of some water and a small quantity of antioxidant the sample is a natural biological material containing 55 percent lipids on a dry weight basis.

The material was prepared from edible grade lobster tomalley. It was homogenized by comminution and an antioxidant was added at this stage. The water content was increased and the slurry was processed through a high pressure homogenizer. The homogenate was bottled in 10 ml polypropylene vials which were then heat sealed, sterilized and individually packed in tritamine pouches. (See Berman, S.S. and Sturgeon, R.E., *Fresenius Z. Anal. Chem.* 332, 546-548 (1988).)

Certified values are available for 17 metals (Ag, As, Ca, Cd, Cr, Co, Cu, Fe, Hg, K, Mg, Mn, Ni, Pb, Se, Sr and Zn) and methylmercury.

LUTS-1 is distributed in a package of 6 vials, each containing  $10.30 \pm 0.05$  g of reference material. The moisture content of the bottled material is  $85.10 \pm 0.07$  percent. The rigid control afforded to the mass of material per vial and the moisture content enables the analyst to quantitatively prepare a slurry from any vial and immediately utilize it for reference purposes without the need to establish a dry weight on the sample.

#### To order this material, or for further technical information, contact:

Marine Analytical Chemistry Standards Program  
Division of Chemistry  
National Research Council  
Montreal Road  
Ottawa, Ontario, Canada K1A 0R6

Telephone (613) 993-2359  
Facsimile (613) 993-2451  
Telex 053-3145

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

**Trace Metal Concentrations – (milligrams/kilogram)**

	<b>As Bottled</b>		<b>Dry Weight</b>	
Arsenic	2.83	± 0.13	19.0	± 0.9
Cadmium	2.12	± 0.15	14.2	± 1.0
Calcium	203	± 33	1360	± 220
Chromium	0.079	± 0.012	0.53	± 0.08
Cobalt	0.051	± 0.006	0.34	± 0.04
Copper	15.9	± 1.2	107	± 8
Iron	11.6	± 0.9	77.8	± 6.0
Lead	0.010	± 0.002	0.069	± 0.011
Magnesium	89.5	± 4.1	601	± 28
Manganese	1.20	± 0.13	8.02	± 0.86
Mercury	0.0167	± 0.0022	0.112	± 0.015
Methylmercury (as Hg)	0.0094	± 0.0006	0.063	± 0.004
Nickel	0.200	± 0.034	1.34	± 0.23
Potassium	948	± 72	6360	± 480
Silver	0.580	± 0.049	3.89	± 0.33
Selenium	0.641	± 0.054	4.30	± 0.36
Strontium	2.46	± 0.28	16.5	± 1.9
Zinc	12.4	± 0.8	82.9	± 5.4



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Programme de standards  
de chimie analytique  
marine

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### DACS-1

#### Domoic Acid Calibration Solution

DACS-1 is available as a set of 4 ampoules containing a solution of domoic acid. It has been prepared as an instrument calibration solution to aid the analyst in the determination of domoic acid.

Each glass ampoule contains 0.5 mL of a solution of domoic acid dissolved in acetonitrile/water (1:9, v/v) at a concentration of 89 µg/mL. This concentration is suitable for determination by high performance liquid chromatography (HPLC) with UV detection.

To order these materials, or for further technical information, contact:

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

Telephone: (902) 426-8280  
Facsimile: (902) 426-9413  
Telex: 019-21653



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## MUS-1

### Mussel Tissue Reference Material for Domoic Acid

MUS-1 has been prepared as a shelf-stable slurry of mussel tissue (*Mytilus edulis* L.) containing domoic acid. Batches of contaminated and clean pre-cooked mussel tissues were blended to obtain a target level of domoic acid. After addition of an antioxidant (0.02% ethoxyquin) and adjustment of the moisture content to 87%, the homogenate was bottled in 15-mL polypropylene containers. The bottles were heat sealed, thermally sterilized and individually packed in trilaminate pouches.

MUS-1 is distributed as a set of 4 bottles, each containing 15 g of mussel homogenate. The domoic acid level, 126 µg/g, is suitable for determination by high performance liquid chromatography or by gas chromatography combined with mass spectrometry after sample extraction and work-up. This level is also suitable as a reference for the AOAC mouse bioassay for shellfish toxins.

To order this material, or for further technical information, contact:

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

Telephone (902) 426-8280  
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## ANNEX 4

### ICES BASELINE STUDY OF TRACE METALS IN COASTAL AND SHELF SEA WATERS: A REVIEW OF MEASUREMENTS MADE BY ICES AND JMG LABORATORIES DURING 1985-1987

Report of an ad Hoc Group of the ICES Marine Chemistry Working  
Group (MCWG) convened at ICES Headquarters 5-9 February 1990

#### SUMMARY OF FINDINGS

##### All metals

- a) baseline levels can now be established for most of the areas covered in this study.
- b) A number of ICES/JMG laboratories which were not considered by MCWG in 1984 as sufficiently experienced in trace metal measurements in sea water, have now achieved the capability to produce state-of-the-art data.
- c) Concentrations of Cu, Zn, Hg, Cd, and Pb for the salinity range >30 psu are remarkably similar throughout the North Sea and other adjacent coastal waters.

##### Cadmium

- a) Concentrations of dissolved Cd are higher in inshore waters; levels reported by participants for offshore areas are similar to those reported by experienced investigators (i.e., those identified in the 1984 MCWG report).
- b) The highest values for Cd in inshore areas are found off the western coast of the UK.
- c) Inverse relationships exist between dissolved Cd and salinity for a number of areas; the slope of the regression varies from area to area.
- d) The behaviour of cadmium (like Zn) is non-conservative; maximum values are observed in the third range of salinity values.
- e) Measurements by the same laboratory at one location over the period of the baseline study suggest that there were no obvious trends in concentration during this time.

Copper

- a) Highest values for salinities > 30 psu are found in inshore areas; the highest value recorded in area NS5 must be viewed with caution.
- b) In general, the baseline levels for areas at salinities >30 psu are similar to those reported in the recent literature for these areas.
- c) Levels in surface waters in offshore areas are higher (x 2) than those for surface waters off the continental shelf.
- d) Dissolved Cu versus salinity relationships were defined for most of the areas covered; the slopes of the regressions varied from -0.01 (Kattegat) to -0.18 (Severn Estuary). The relationships based on results from two laboratories reporting data from the Skagerrak/Belt area were essentially the same (similar values for slope and intercept).

Lead

- a) In the salinity range >30 psu, the highest values are found in offshore areas of the North Sea.
- b) Offshore values of dissolved lead are similar to values for surface waters of the oceanic NE Atlantic.
- c) Although an inverse relationship between dissolved lead and salinity appears to exist, there are insufficient data to compare this relationship for different areas.

Mercury

- a) Median values for the salinity range >30 psu for all areas lie within a very small concentration range (i.e., ca. 3 ng/l).
- b) No strong relationships between dissolved mercury and salinity could be defined.

Zinc

- a) There is a strong relationship between salinity and dissolved Zn for the waters in the vicinity of the Forth and Rhine rivers.
- b) Zinc does not behave conservatively throughout the salinity range 0-35 psu, so extrapolation of metal concentrations to zero salinity should be done with caution.

Other points to be noted

- a) Many of the data were collected without adherence to the guidelines. Some of the data submitted, therefore, come from surveys undertaken by particular laboratories into specific discharges. Such data were inappropriate to the baseline survey and were, as far as possible, excluded.

- b) Many of the data submitted were from locations close inshore; this should be emphasized. Thus, comparison with the literature data is rather difficult since such data are generally for offshore (even oceanic) waters.
- c) The extent of agreement between the areas covered in the baseline survey appears to be quite good, however, there is a tendency to feel that at very low concentrations things must be "about right", e.g., Hg < 2-3 ng/l, Pb 10-20 ng/l. It is likely that such data are imprecise and that further improvements are necessary. Fine structure is likely to be revealed with improved techniques.
- d) There is a tendency to correlate high concentrations and contamination. This is rather simplistic and cannot be taken for granted; we should be careful not to assume it.
- e) The results indicate that we are not really in a position to monitor trends of metals in sea water since we do not fully understand the hydrographic and seasonal controls on concentration. It is likely that, at present, analytical uncertainties are larger than any trend which could be anticipated. Within estuaries, concentrations will be influenced by tide, season, freshwater discharge, etc.

Matters to be considered in relation to future sea water monitoring/baseline studies

In 1984, it was generally agreed that there were a sufficient number of European laboratories with the capability to carry out accurate and precise measurements of trace metals in sea water to participate in a baseline study of metals in coastal and shelf sea waters of ICES member states. In view of this, and the request from ACMP to do this task as soon as it was practicable, the MCWG drew up proposals for a baseline study [see 1984 MCWG report (ICES, Doc. C.M.1984/C:2) and paper by Topping and Bewers (1984) (ICES, Doc. C.M.1984/E:39)]. These proposals included a quality control mechanism (sampling at reference stations) and identified the need to measure other parameters: S (psu), T ( $^{\circ}$ C), SPM (mg/l), dissolved oxygen, nitrate, phosphate, and silicate, in samples collected for trace metal analysis to assist the assessment of baseline data.

It was assumed that the adoption of these guidelines by participants would lead to a reasonably comparable data set and that the task of assessing such a data set, in relation to the main aims of the work, would be straightforward.

Unfortunately, for a number of reasons which will be outlined and discussed below, the task of assessing the baseline data was both difficult and time consuming.

- a) The majority of participants in the baseline study were inexperienced in the collection and analysis of trace metals in sea water; of the six core institutes and eight reasonably experienced institutes listed by MCWG (ICES, Doc. C.M.1984/C:2) as potential participants, only two of the first group and two of the second group took part in the baseline study.

- b) Only a few participants (4) conducted measurements on samples collected at one or more of the ICES reference stations; thus, in the absence of other quality control data (e.g., successful participation in ICES intercomparison exercises), the assessment of data from the majority of the participants had to be based on the knowledge and experience of the assessment group. A summary of data reported from the reference stations is available in the report of this review.
- c) Participants were asked to conduct measurements on filtered samples and, where relevant, to collect such samples along a salinity gradient. A proportion of the participating laboratories did not carry out these requests, with the result that a large proportion of results submitted were from analysis of unfiltered samples with no accompanying data on SPM. Despite the absence of SPM measurements, the assessment group felt that it should review some of these data which appeared from the preliminary screening to be sensible. In order to judge whether data on unfiltered samples could be included in the assessments, the group spent considerable time examining the data sets for each individual area, and had to introduce pragmatic criteria such as using SPM information derived from published reports on other studies (e.g., the ZISCH sub-project on suspended sediments).



## ANNEX 5

### REPORT OF THE AD HOC MEETING OF ANALYSTS HELD TO DISCUSS THE RESULTS OF THE ICES 4TH ROUND HYDROCARBON INTERCOMPARISON PROGRAMME (STAGE 1)

Copenhagen, 9 and 10 February 1990

#### Participants

R. Law (Chairman), A. Abarnou, J. Biscaya, J. Boon, M. Ehrhardt, U. Kirso, J. Klungsøyr, N. Theobald, J. Tronczynski, D. Wells.

#### Agenda

The meeting was held to discuss the results of the first stage of the exercise (held in 2 phases) and to make proposals for the future structure of the programme in the light of experience so far.

The original proposals for this programme and a summary of the first phase are given in two ICES papers, C.M.1987/E:17 and C.M.1989/E:15, respectively.

#### Phase 1

Two problems were identified by participants in phase 1; firstly, a measurable and continuing weight loss from the sample containers (Pierce hypo-vials) on storage; secondly, a number of laboratories reported problems with gas chromatographic analysis of the acetonitrile solution. For these reasons, phase 2 of the exercise was conducted. The results of the first phase, however, suggest that neither of these difficulties seriously compromised the laboratories' overall performance.

#### Phase 2

Phase 2 was broadly similar to phase 1, except that:

- 1) Solutions were flame-sealed into glass ampoules.
- 2) Separate sets of solutions were prepared for GC and HPLC analyses, the solvents used being hexane and acetonitrile, respectively.

Three ampoules were supplied for each type of analysis, containing pure solvent and 2 standard solutions. These standard solutions were identified as G1 and G2 (GC), and H1 and H2 (HPLC). Solution 1 in each case contained the 10 PAH at declared concentrations, and solution 2 the same 10 PAH at concentrations known only to the coordinator. Each ampoule was weighed after sealing and the weights recorded on a return slip enclosed with the samples. All samples were distributed by post in October 1989, with a deadline for return of the results of 1 January 1990. The final set of results was received on 20 January 1990.

Samples were distributed to 18 laboratories and results were received from 17, a return rate of 94%. The remaining laboratory gave instrumental failure as the reason for non-participation in the exercise.

There were 15 sets of results submitted for standard solution G2 (in hexane), 7 analyzed by GC/FID, 7 by GC/MS and 1 by low temperature (Shpol'skii) fluorescence. Eight sets of results were reported for standard solution H2 (in acetonitrile), 5 by HPLC with fluorescence detection and 3 with detection by UV absorption.

A list of participants, identified by laboratory number, is given as an appendix to this report.

### Results of Phase 2

Despite the improved sealing of ampoules and the optimization of solvents used for each method, the results generally show a greater variance compared with the data for phase 1.

Laboratory 16 reported very low and very variable results for all determinands analyzed by GC/MS, associated with an instrumental problem. This laboratory intends to rerun the stage 1 analyses when the problem has been rectified.

### GC/MS analyses

The results of laboratories 4 and 8 were consistently rather high, and those of laboratory 12 were consistently low. In the latter case, this was caused by falling MS sensitivity when the samples were run, but no explanation has yet been found in the former. Laboratory 14 reported anomalously high values for indeno-[123-cd]pyrene by GC/FID, and both HPLC methods yielded low results for benzo[ghi]perylene.

### Design of Stage 2

The proposed intercomparison programme agreed at MCWG in 1987 was designed to improve comparability for all matrices routinely analyzed (water, sediment, and biota). Initially, it was agreed to concentrate on the determination of PAH in biota. It was agreed at this meeting that the most appropriate species was *Mytilus edulis*. However, it was the unanimous view of the meeting that a sediment should be the first matrix to be studied, for the following reasons:

- a) A sediment sample is more readily stabilized.
- b) The North Sea Task Force included PAH in sediment for baseline monitoring purposes.
- c) There is an urgent need to demonstrate competence in these analyses.
- d) The next stages of the exercise will be significantly easier to prepare if the matrix selected is a sediment.

Figure 1 shows in diagrammatic form the proposed plan of stages 2 to 4 of this exercise.

A natural sediment extract would be distributed for stage 2 of the programme. Stages 3 and 4 would require additional sediment, and it was agreed to propose that these materials be prepared as part of the EC/ICES/JMG Pilot Programme. There is a need for a sediment to be prepared as a Laboratory Reference Material, which should include these 10 PAHs.

It was agreed that these 10 PAHs should be purchased as CRMs for stages 2 to 4, and that in advance of the preparation for stages 3 and 4, it will be necessary to request (via MCWG) that further funds be set aside by ICES to cover costs to be incurred.

Mr Law agreed to act as coordinator for stage 2, but requested that, in view of the scale of preparatory work needed, a second laboratory volunteer to assist. Dr Wells agreed to prepare the sediment extract. A provisional timetable was then agreed for stage 2, constrained by the need to report progress to MCWG in 1991. This was:

Collection, preparation, and testing of sediment February - July 1990

Distribution of samples ..... 1 Aug 1990

Deadline for receipt of results ..... mid-Nov 1990

Preliminary report by ..... Feb 1991

Although the laboratories represented by Drs Boon and Tronczynski did not partake in stage 1, it was agreed that they could participate in stage 2 provided they first completed stage 1 (phase 2) to the satisfaction of the coordinator.

Three laboratories will analyze the stage 1 solutions prior to stage 2 of the programme.

#### Acknowledgements

A substantial amount of work has been put in by all involved in this exercise and the coordinator would like to thank each laboratory for their efforts. The participants in this meeting recorded their thanks to Mr Law for his work as coordinator.

## ANNEX 6

PROPOSED MODIFICATIONS TO PAGE 1 OF ANNEX 1 OF REPORT OF A WORKSHOP ON  
MONITORING PROGRAMMES IN THE NORTH SEA AND NORTH EAST ATLANTIC WATER IN 1990-1991

	MeHg	TBT	Chlor- danes	Planar CBs	PCDDs+ PCDFs	DDTs	Diel- drin	PAHs	PCCs	Tria- zines	PBDEs
Estuaries and nearshore waters										S	
Offshore waters											
Sediment		S/T (nearshore)	S/T			S/T	S/T	S	S/T		S&T
Shellfish	h	h						S			
Fish (cod/dab):											
Liver			S/T	S	S	S/T	S/T		S/T		S/T
Muscle			S/T			S/T	S/T		S/T		

H = Human health assessment.  
h = animal health assessment.  
T = Time trend.  
S = Spatial distribution.

Notes to Tables:

- 1) Mandatory CBs on an individual basis: CB nrs -28, -31, -52, -101, -105, -118, -138, -153, -156 and -180. This list is the same as that of the ICES intercalibration exercise and involves all three mono-ortho-Cl substituted CBs considered to be of environmental concern.
- 2) (Changes to be decided by the chemical oceanography subgroup of the MCWG).
- 3) Chlordanes: Cis-chlordane, trans-nonachlor, trans-chlordane oxychlordane.
- 4) Planar chlorobiphenyls; CBs-77, -126, and -169.
- 5) Polychlorinated dibenzodioxins and dibenzofurans to be selected by expert laboratories, bearing in mind that a full lateral chlorine substitution of the molecules increases toxicity and resistance to biotransformation.
- 6) Only the laterally (4,4') substituted forms of DDE, DDD (=TDE) and DDT.
- 7) Dieldrin is the only representative of the group of "drin-insectides" considered to be important in the marine environmental concern.
- 8) PAHs selected: Naphthalene and C1-, C2- and C3-alkyl derivatives; Phenanthrene and C1- and C2-alkyl derivatives; Anthracene; Dibenzothiophene and C1- and C2-alkyl derivatives; Fluoranthene; Pyrene; Benz[a]anthracene; Chrysene (+tri-phenylene); Benzo[fluoranthene]; Benzo[e]pyrene, Benzo[a]pyrene; Perylene; Benzo[g,h,i]perylene; Indeno[1,2,3-cd] pyrene and Dibenzo[a,h]anthracene.
- 9) Polychlorinated camphenes = Toxaphene. For quantification purposes it has to be borne in mind that this extremely complex mixture can only be quantified on the basis of technical mixture equivalents at the present time.
- 10) Simazine and Atrazine are the major compounds of importance. 2,4,2',4'-tetrabromodiphenylether (TBDE) and 2,4,5,2',4'-pentabromodiphenylether (PBDE) as representatives of the brominated fire retardants.

Main recommendations brought up:

Voluntary Determinands (Annex 1, p.1)

- 1) Triazine should be removed from the NSTF table as it is not a specific organic chemical. Triazine is the generic name of a specific class of organic compounds which are unlikely to be found in the wider marine environments.
- 2) Atrazine and simazine are two representative compounds of the triazine class which might be measurable in estuarine waters. However, there is little information on their occurrence in marine waters. It was agreed that atrazine and simazine should be removed if no additional data on their concentrations is provided.
- 3) The PBBs should be replaced by two brominated diphenyl ethers, namely: 2,4,5,2',4'-pentabromodiphenylether (PBDE) and 2,4,2',4' tetrabromodiphenylether TBDE.

There is little information on the occurrence of PBBs in the marine environment. PBDE and TBDE are more specific chemicals and some information already exists on their presence in marine biota.

- 4) The name toxaphene should be changed to polychlorinated camphenes (PCC).
- 5) PAHs: A new list of these determinands is proposed. Many important environmental PAHs are omitted in the NSTF list. The latter included only the PAHs used for intercomparison with analytical objectives.

However, it was noted that PAHs in shellfish may indicate very small "hot spot" areas in nearshore samples, integrating local inputs.

- 6) TBT is proposed for nearshore sediments and molluscs, considering the high toxicity of this compound on these species (malfunctioning, lethal effects).

It was noted that the half life of TBT is of the order of three (3) years in poorly oxygenated sediments.

NOTE:

The following codes for matrix annotations were proposed:

H = health assessment

T = Trend assessment

S = Spatial assessment

These codes refer not only to specific determinands and their matrices, but also to specific assessment objectives.

## ANNEX 7

EXTRACT FROM THE 1989 REPORT OF THE HYDROGRAPHY COMMITTEE,  
PROCES-VERBAL DE LA REUNION 1989, PP. 75-76

6. Before the discussion of Working Group on Marine Chemistry matters, it was noted that this Working Group in future will report directly to ACMP, although the Hydrography Committee will be free to assign relevant problems on chemical oceanography to this Working Group as previously. Furthermore, the Committee was informed of the status of the ICES Intercomparison Exercise on Analyses of Nutrients in Sea Water. In relation to this intercomparison exercise, the Committee was informed of the present state of the following special investigations:

- a sterilization experiment on sea water in order to prepare stable intercomparison samples,
- preparation of reference samples by aging sea water, with the outcome that it is not yet possible because a real stability of the sample is not developed,
- ongoing work on the use of natural sea water for use as a standard reference.

The general problem of quality assurance was stressed once more, again having in mind the implications for ongoing projects like SKAGEX et al.

Four papers were concerned with aspects of nutrient measurements in the North Sea, which were prompted by the topical issue of whether nutrient trends can be identified from amongst the natural environmental noise in the area. In February of each year, many stations (more than 400) are worked during the ICES International Young Fish Survey (IYFS) and the issue of whether participants in this survey could collect nutrient samples for later analysis without any loss of accuracy was addressed by Doc. C:30. This document proposed a procedure that had been developed through the Chemical Oceanography Sub-Group of the Working Group on Marine Chemistry and concluded that it was acceptable to collect nutrient samples during this survey only if the preservation procedures described in this report are followed. Consequently, the Hydrography Committee encourages all participants of the IYFS to include nutrients in their sampling programme, as was requested in 1983. Participation in this survey provides the opportunity annually to ensure that their nutrient data can benefit from quality control at the ICES Secretariat as well as providing a detailed annual picture of the distribution of the different nutrients throughout the North Sea.

A small ad hoc group comprising Drs L. Otto, R. Dickson, F. Føyn, and H. Dooley was formed to bring back a concise statement on the problems concerning the identification of nutrient trends in the North Sea. The outcome of this special discussion is summarized as follows:

A number of papers presented the results of nutrient trend analysis. In the subsequent discussion, the Hydrography Committee focussed on the question whether ACMF could be provided with a critical review of those papers, as well as those presented earlier, while they come to different conclusions with respect to a nutrient trend.

It first has to be noted that a clear distinction should be made between different nutrients that have different discharge histories and for which the chemical problems of data set homogeneity are different. Phosphate, for which the methodology has not changed much over time, may be more suitable than nitrate. It is furthermore not certain that there is a common general trend, considering the widely differing inputs and the hydrographic differences. In addition the identification of more regional or local trends is being frustrated by the fact that the majority of data have not been collected for trend analysis purposes. Consequently, there are complications arising from natural processes, in particular the variability in the distribution of water masses and by the fact that it is rarely possible to obtain data sets that are unaffected by production processes in the sea. Even in January, this possibility is not negligible. Furthermore, also in view of the differences in sampling, preservation, and analysis, vigorous trend analysis often appears not to result in more than "indications", hinting at trends or suggesting their absence. Therefore, the situation does not permit one to obtain a single general answer along these lines.

The nutrient trends that have been found in specific areas where the effect of river discharge is large enough or where better quality data sets are available cannot be extrapolated to the open North Sea. Non-conservative substances are being dealt with, and different areas of the North Sea may react differently. It is believed that, unless the number of available, good quality historical data increases considerably, allowing for new statistical studies to discover possible marginal signals, the discussion of increased discharges should be based more on the outcome of process-oriented research. It is concluded that the quality of the available historical data and the regional differences of the North Sea environment as a whole do not permit a statistically sound answer concerning a general trend. Results of local or regional studies may be affected by the same problem and should be considered carefully. They may not be representative for the entire North Sea. The answer to questions regarding possible general increases cannot be given solely upon the basis of statistical evidence of existing data sets.

Concerning a North Sea monitoring programme, the Committee was advised to take the opportunity to carefully review the results of the ongoing work on monitoring within the North Sea Task Force.

7. The Chairman of the Biological Oceanography Committee presented details of a proposed ICES Symposium on the Measurement of Primary Production for 1992 or later. Discussion in the Committee centered on measurements, assessment of errors and the spatial and temporal variability.



## ANNEX 8

## ACTION LIST

Trace Metals Sub-group

- D. Schmidt           to amend the overview paper on Cr and distribute a copy to subgroup members before 1991 meeting.
- T. Jensen            to send information on the toxicity of Cr to D. Schmidt in relation to the above overview.
- W. Cofino and  
P. Yeats            to consider the amendments required for the QA paper on sampling and prepare an a new draft before the next meeting.
- Ad Hoc Group  
on metals in  
sea water           to prepare discussion sections of report along the lines of that given by Dr Yeats and to send their amended versions to Dr Topping for incorporation in the final report for ACMP.
- All members         to send any relevant data on inputs of Cr to the marine environment to D Schmidt.
- to consider the preparation of proposals for collaborative studies on trace metals in coastal and shelf sea waters.

Organics Sub-group

- J. de Boer           to prepare a standard unknown solution for CBs for the second stage of the CBs intercomparison exercise, after discussion with J.C. Duinker.
- to send copy of report on the first stage of the CBs intercomparison exercise following the incorporation of any statistical amendments, and proposals for the second stage, to all participants in the first stage.
- D. Wells            to prepare a cleaned-up sediment extract for both the CBs and PAHs intercomparison exercises.
- to complete the overview on HCH and HCB and submit it via the chairman to ACMP in June 1990.
- L. Reutergårdh      to provide, with the assistance of colleagues, section "production and usage" to D. Wells for overview paper.
- D. Wells and  
J. de Boer           to meet in Brussels to finalise plans for the CBs intercomparison exercise
- J. de Boer and  
J. Boon             to consider the preparation of an overview on brominated fire retardants for 1991 MCWG meeting.

- J. Tronczynski to consider the preparation of an overview on simazine and atrazine.
- R. Law to finalise report on first stage of PAHs inter-comparison exercise and send copy to all participants.
- to discuss with his colleague, Dr Waldock, the preparation of an overview on surface active agents.
- D. Wells to prepare costs for the second stages of the CBs and PAHs intercomparison exercise.
- J. Klungsøyr to consider the preparation of an overview on octachlorostyrene.
- A. Abarnou to present IFREMER reports on surface active agents and on chlorinated compounds associated with chlorination of domestic waste at 1991 MCWG meeting.
- All members to forward information on the chemistry and the formation of chlorobromo compounds in the paper and pulp industry to the chairman of the sub-group.
- to contact L. Reutergårdh if they are interested in participating in the intercomparison exercise for planar CBs 77, 126 and 169; the samples will be distributed by the end of March 1990 with 1st October as the deadline for reporting results.
- Participants to contact R. Law if they have not received a copy of 1984 OPRU intercomparison report.

#### Chemical Oceanography Sub-group

- S Carlberg to clarify the monitoring proposals of NSTF with his colleagues in WGEAMS
- D. Kirkwood, A. Aminot and M. Perttilä to finalize the report on the nutrient intercomparison exercise, following the inclusion of the amendments agreed at 1990 MCWG meeting, and to send a copy of the final version to ICES for presentation at 1990 ACMP meeting.
- General item to prepare guidelines regarding the preferred statistical approach to the analysis of data from intercomparison exercises. This work will be done by a subgroup of MCWG and WGSATM; MCWG members are those currently responsible for organizing intercomparison exercises:
- A. Aminot, W. Cofino, S. Berman, J. de Boer, R. Law, D. Kirkwood, M. Perttilä.

The Chairman of WGSATM might consider nominating the following members of his group in view of their interest in such matters:

M. Nicholson, J. van de Meer and R. Fryer.

Environment  
Officer

to arrange for Dr S. Wilson to review the trace metal data sets held on the ICES computer in order to identify those which might be useful for:

the establishment of baseline levels in coastal waters, and

the identification of processes which influence levels in estuarine areas.

The Chairman

to prepare a re-draft of the Ad Hoc Group's report on trace metals in coastal waters for submission to ACMP in June 1990.

to finalize the 1990 MCWG report and send it to the chairman of the sub-groups for final comment prior to its submission to the ICES Environment Officer.

to prepare an executive summary of 1990 MCWG report and circulate a copy to all members together with a copy of the action list and recommendations.

to liaise with Dr Carlberg on the re-drafting of his sub-group's paper on sampling and storage of sea water for nutrient analysis

to discuss the following matters with Dr Portmann (Chairman of ACMP):

- guidelines for overviews
- NSTF request for protocol on sampling and storage
- finance for I/C exercises for CBs and PAHs.

All members  
of MCWG

to read any papers sent to them prior to the next meeting of MCWG and to ensure that any items they want to present under agenda items 3-6 inclusive at 1991 meeting are submitted as written items before the meeting to all members.

## ANNEX 9

### RECOMMENDATIONS

#### Recommendation 1

The MCWG recommends that the final reports on the following be published in the ICES Cooperative Research Report series:

Intercomparison exercises for nutrients in seawater and  
CBs and PAHs in standard solutions

Baseline study of trace metals in coastal and shelf sea  
waters

#### Recommendation 2

In relation to the second stage of the PAH intercomparison exercise, the MCWG recommends that a 2- day meeting of participants be convened immediately prior to 1991 meeting of MCWG, at national expense, to prepare a report on the results from stage 2.

#### Recommendation 3

The MCWG recommends that ICES finances the second stages of the intercomparison exercises for CBs and PAHs.

#### Recommendation 4

In the light of the need to adopt a common approach to the statistical analysis of data from future intercomparison exercises, the MCWG recommends that a group drawing expertise from MCWG and WGSATM prepare, by correspondence during the intersessional period, a paper outlining the preferred statistical approach for such data.

#### Recommendation 5

The MCWG recommends that ICES sets aside sufficient funds for the financing of 3rd and 4th stages of the PAH exercise and the 2nd stage of the CBs exercise.

#### Recommendation 6

In the light of MCWG's experience with the organisation of the chemical aspects of the Bremerhaven workshop, the MCWG recommends that such future multidisciplinary activities should have a multidisciplinary steering group in order to facilitate the exchange of information and to improve the planning of logistical aspects of such exercises.

#### Recommendation 7

In the light of the review of trace metal data, the MCWG recommends that a subgroup of MCWG periodically reviews the trace metal data held in the ICES data bank in order to consolidate the baseline levels produced in the first review.

#### Recommendation 8

The MCWG recommends that ICES give serious consideration to the organization an intercomparison exercise for nutrient measurements on a regular basis, e.g., every two years.

#### Recommendation 9

The MCWG recommends that the Working Group should accept the offer made by Professor R. Wollast to host the next meeting of MCWG in Brussels and that this meeting should be held for five days commencing 8th April 1991 to carry out the following tasks:

1. to review the final report on the baseline study of metals in coastal and shelf sea waters;
2. to review and finalize the reports on the second stages of the intercomparison exercises for CBs and PAHs;
3. to finalize the overview document on Cr and review the overview documents prepared during the intersessional period;
4. to finalize the QA document on sampling and the protocol on sampling and storage of sea water;
5. to review the overviews on PBBs, atrazine and simazine, and octachlorostyrene;
6. to review and finalise the document on guidelines for the conduct of intercomparison exercises;
7. to review progress on the analysis of seal tissue for CBs;
8. to review the results of the ad hoc intercomparison exercise on planar CBs;
9. to review any intersessional work on nutrient studies, particularly the comparability of nutrient data;
10. to examine the report on the Baltic intercomparison exercise for dissolved oxygen and nutrients;
11. to consider any proposals for collaborative work on trace metal studies in estuarine waters;
12. to examine the results of the chemical aspects of the Bremerhaven workshop on biological effects;
13. to review progress on QA work carried out under the proposed BCR programme; and
14. to consider any other matters raised by ACMP.

