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# *REPORT OF THE MARINE CHEMISTRY WORKING GROUP*

The Hague, Netherlands, 7 - 11 March 1988



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## 1 OPENING OF MEETING

The Chairman, Dr G. Topping, opened the meeting at 09.30 hrs on 7 March 1988 and welcomed the participants. Each member then introduced him- or herself, indicating the main areas of research interest and responsibility in marine chemistry and pollution.

## 2 ADOPTION OF THE AGENDA

The Working Group reviewed the draft agenda, which had been prepared and distributed earlier by the Chairman, and adopted it without change. The agenda is attached as Annex 1 and the list of participants at the meeting is given in Annex 2.

In view of the large number of items on the agenda, the Chairman informed the Group that items 3-6 would be considered in plenary and item 7, the Sub-group sessional activities, would be dealt with by the respective Sub-groups, followed by a discussion of their respective reports in plenary. As usual items 9 and 10 would be dealt with in plenary on the last day of the meeting.

Membership of the Sub-groups was as follows:

Trace Metals

| | |
|---|---|
| T. Anderson | A. Jensen |
| G. Asmund | V. Tervo |
| S. Berman | W. Vyncke |
| W. Cofino (Chairman) | P. Yeats (Rapporteur) |
| D. Cossa | S. Westerlund |

Organics

| | |
|---|---|
| J. de Armas | J. Klungsöyr |
| J. de Boer | R. Law (Rapporteur) |
| J. Boon | L. Reutergårdh (Chairman) |
| J. Calder | R. Ritsema |
| J.C. Duinker | J.F. Uthe |
| H. Hofstraat | D. Wells |
| M. Kerkoff | |

Chemical Oceanography

| | |
|---|---|
| A. Aminot | T. Nunes |
| S. Carlberg (Chairman) | M. O'Sullivan |
| L. Føyn | W. Schreurs |
| D.S. Kirkwood (Rapporteur) | O. Vagn Olsen |

The Chairman informed the Group that he would be participating in each of these groups throughout the Sub-group discussions and that Simon Wilson had requested that he attends the meetings of the first two groups since there were a number of items on which he had to report back to J. Pawlak who was attending a meeting of the Technical Working Group of the Paris Commission at that time.

## 3 REPORT OF THE 75th STATUTORY MEETING

In the absence of a report from the Environment Officer, the Chairman gave a brief presentation of matters relevant to the group which had arisen at either the Statutory Meeting or during the intersessional period. He informed the Group that all of the items, on which the Group had been requested to comment, had been incorporated into the draft agenda.

## 4 REPORTS OF RELATED ACTIVITIES

### 4.1 JMG of the Oslo and Paris Commissions

In the absence of the ICES Environment Officer who normally presented this report, the Chairman reviewed the items which were of relevance to the Group. He referred to the report of the 13th meeting of the Joint Monitoring Group (JMG), which was available for members of MCWG, particularly to Annex 6 which listed the tasks for ICES for 1989. The relevant items for MCWG had already been incorporated into the agenda, i.e., nutrient intercomparison, methods for assessing river inputs to the sea. The Group was informed that JMG had accepted MCWG's advice, given in the 1987 ACMP Report, on a number of topics, e.g., that there was no need for intercomparison exercises for trace metals in tissue and sea water in the near future and that analytical data for reference materials should be submitted with the fish and shellfish data to the coordinators of monitoring programmes to provide evidence of data quality throughout the period of the analysis of these samples. The Working Group was also informed that its advice on the approach to the monitoring of trace metals in sea water had been used by JMG in the design of its monitoring programme.

### 4.2 IOC Activities

Dr Duinker informed the Group on IOC activities which are relevant to MCWG. IOC will be involved in the Joint Ocean Global Flux Studies (JGOFS) through a formal agreement with the SCOR Scientific Planning Committee for JGOFS.

The activities of the three groups of experts within the GIPME programme were summarised. The Group of Experts on Effects of Pollutants (GEEP) is planning workshops on biological effects studies (Bermuda, China and seagoing activities together with ICES). The report of the first workshop (Oslo) is ready for printing.

The Group of Experts on Standards and Reference Materials (GESREM) had its first meeting in February 1987. Users and producers discussed the availability and needs and possible distribution systems for these materials. The Group of Experts on Methods, Standards and Intercalibration (GEMSI) had its eighth meeting in Paris in July 1987. The Group adopted documents on the use of marine sediments in contaminant monitoring, analysis of PCBs by capillary GC-ECD and the Intercalibration Workshop on Riverine Inputs (Thailand).

Intersessional work will be carried out on photodegradation of organics, preparation of standards of individual CBs, preparation for the open ocean baseline study for trace metals and organics, and on drafting and reviewing Reference Manuals for UNEP Regional Seas Programmes and IOC Guides and Manuals.

4.3 ICES Working Groups

No requests had been received from any of the other environmental working groups within ICES. The Chairman reminded the Group that the draft report of MCWG would be sent to the Working Group on Statistical Aspects of Trend Monitoring and the Working Group on Environmental Assessments and Monitoring Strategies for consideration at their respective meetings this year.

4.4 Other Relevant Activities

No matters were tabled under this agenda item.

5 REPORTS ON PROJECTS AND ACTIVITIES IN ICES MEMBER COUNTRIES

Dr Berman reported that six new reference materials were issued in 1987. These included marine sediment reference materials PACS-1, certified with respect to trace metal contents, produced from a sediment gathered from a Canadian west coast harbour and which contains relatively high trace metal concentrations.

There were four harbour sediment research materials (HS-3, HS-4, HS-5, HS-6) with reliable concentrations for 16 PAHs and an estuarine sediment research material (SES-1) specified with 15 PAHs. These are designated as research materials rather than certified reference materials because the certifying procedures for the organic constituents are not nearly as reliable as those for trace metals.

Certified values for tin were assigned to the sediment materials BCSS-1 and MESS-1 and the biological tissue TORT-1 already in distribution. These are the only known environmental samples certified with respect to tin.

An estuarine water, SLEW-1, was collected in the St Lawrence estuary in August 1987. The certification for trace metals is nearly complete and the reference material should be available in June 1988.

Certification of the three biological reference materials TORT-1, DORM-1 and DOLT-1 for methyl mercury is in progress. Concentration values should be available late this year. The possibility of certifying the sediment and biological reference materials for alkyl tins is under study.

A new approach for the preparation of biological reference materials has been developed. It has been found possible to prepare a wet tissue homogenate which can be stabilised, stored and reproducibly sampled. A lobster hepatopancreas sample, akin to TORT-1 but with no lipids or water removed, is now in prepara-

tion. Certification should be complete by the end of 1988. If this product is successful, a range of materials closely resembling samples analysed in the laboratories will be considered for preparation. A similar approach is under study for organic contaminants in marine tissues.

## 6 REQUESTS FROM ACMP AND REGULATORY AGENCIES

The Chairman informed the Working Group that he had incorporated all requests from ACMP and the agencies into the agenda for this session. Some of these items would be considered by all Sub-groups and some by individual Sub-groups. As in the previous year, the Chairman had requested that these items be given a priority rating and this had been done in consultation with the Chairmen of ACMP and the Hydrography Committee.

## 7 REPORTS OF SESSIONAL SUB-GROUP DISCUSSIONS

### 7.1 Trace Metals Sub-group Report

The trace metals Sub-group began its work at 14.00 on 7 March under the Chairmanship of Wim Cofino.

#### 7.1.1 Assessment of net river inputs

GESAMP Reports and Studies No. 32 on Land/Sea Boundary Flux of Contaminants: Contributions from Rivers and the PARCOM *ad hoc* Working Group on Input Data report were briefly outlined by Dr Yeats. Discussion of the GESAMP report generated the following comments:

1) Net input methods only agree within an order of magnitude, so they cannot be used for trend monitoring.

2) The report does not describe direct inputs to estuaries and their effect on estuarine distributions.

3) Redox effects on estuarine behaviour have not been considered.

4) $K_d$s for estuaries may not be as useful as suggested because equilibrium may not be established in estuaries.

5) Some discrepancies, such as DTI (dissolved transport index) for Hg, were identified.

6) The limitation of some procedures, e.g., scaling river data to the global situation, have not been adequately described. Also, there are serious limitations on the accuracy of estimates of effective river concentrations that are based on extrapolation of metal/salinity relationships to zero salinity.

However, in general the Sub-group considered that the report was a valuable document, the review had been well done and represented a good synopsis of the state of the art.

The Sub-group then addressed the report of the ad hoc Working Group on Input Data (Paris Commission document INPUT 3/9/1) and suggested some amendments to the text for the estimation of gross riverine inputs given in Annex 5 of that report, as follows:

| Section | Comment |
|---|---|
| 1.1 | All gross river and direct inputs of selected pollutants to Convention waters. |
| 2.1 | The following parameters will be monitored whenever possible in solution and in suspended solids. |
| 6.3.3 | Delete this paragraph entirely. |
| 6.6 | Delete entirely chapter 6.6. |
| 8.1 | Replace by: "It is recommended to have limits of detection which are at least five times lower than the expected concentrations". |
| 8.2 | Replace by: "Concentrations of contaminants should be measured separately in solution and in particulate matter." |
| 9. | The monitoring programme should be planned and performed adhering to the principles of Good Laboratory Practice (GLP) and Quality Assurance (QA). GLP and QA are outlined in report No. 6 in the ICES series "Techniques in Marine Environmental Sciences" and are also discussed in the JMG guidelines for the sampling and analysis of trace metals in sea water (revised, January 1988). |

Following the discussion of the above documents, the Sub-group prepared a brief note which presented their views on the approach to be used for estimating net river inputs to coastal and open sea areas. This is attached as Annex 3.

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

Dr Wilson opened the discussion on this item by describing the programme and referring to the report on the 1985 data. Dr Topping then reminded the Sub-group that the objective of the exercise was to assess data on metals in coastal waters that were collected from 1985 to 1987 as part of the ICES 1985/1987 Baseline Study of Trace Metals in Coastal and Shelf Sea Waters.

The Sub-group then reviewed the criteria developed by the MCWG ad hoc Group in 1987 and agreed the following guidelines on the basis of the discussion of the preliminary report on the 1986 data which had been prepared by Dr Wilson.

Selection of data to be included in the review

1) The period of sampling was to be confined to 1985-1987.

2) All coastal water samples were to be included, using a salinity cut off of 20 for estuarine data and only using lower salinity estuarine data to help decide on the quality of the data.

3) It was acceptable to use data on unfiltered samples unless samples are classified as estuarine by geography or contain SPM (suspended particulate matter) >1mg/l, in which case one would use the data from filtered samples.

4) The geograhical basis for selecting data would be decided by the Chairman of the review group in consultation with appropriate national representatives in sufficient time to allow Simon Wilson to do necessary computing before the final assessment meeting.

Quality assessment of data

It was agreed that there was no need to change the protocol used for the assessment of the 1985 data. It was noted that the use of reference stations has not been as extensive as requested and there is a need to emphasise the importance of occupying these stations whenever possible.

Source of data

In addition to those data specifically collected by ICES laboratories for this purpose, it was agreed to include selected JMP data marked for use by ICES, bearing in mind the need to ignore some data from estuarine areas, and any other relevant data collected by competent laboratories (e.g., the survey work done by Dr D. Schmidt, German Hydrograhic Institute).

Data treatment

1) It was suggested that metal/salinity relationships should be investigated and it was noted that these would have to be area specific.

2) The Chairman should consult national representatives on whether data should be averaged for one year over all three years.

3) The statistical treatment and presentation of data should include box-and-whisker plots for each salinity range in each geographical area.

Although the Sub-group had decided not to examine the 1985 and 1986 reports in detail, it was noted that in Table 1 of the 1985 report, river values for Hg and Zn are too high. A value of 0.005 µg/l for Hg was suggested in this context.

The Sub-group recommended that a coordinator should be identified to consult with national representatives on how to treat their data and to liaise with Dr Wilson so that he could provide the

necessary computer software to deal with the data analyses. It was agreed to recommend Dr Cofino for this role.

The Sub-group also recommended that a two-day meeting should be arranged in order to complete the final assessment of the data. Assuming that the necessary data are in hand, this meeting should take place immediately before the 1989 MCWG meeting, and Dr Cofino was nominated to chair it.

### 7.1.3 Intercomparisons of measurements of SPM and trace metals in SPM

Dr Calder introduced the paper describing the results of the suspended particulate matter (SPM) questionnaire and outlined the background to this work. Responses had been received from 73 scientists who conduct studies on SPM. He concluded from this exercise that many people are doing SPM analyses and most are experiencing some problems. The biggest problem was the inability to collect large enough samples for chemical analysis. He considered that an intercalibration exercise at present would be premature.

The Sub-group agreed that an intercalibration will be required in the future because measurements of SPM are consistent with its recommendations in relation to inputs of metals to the sea and this work would require an intercalibration to be conducted in the next few years. The group agreed, however, that an intercalibration exercise for analytical procedures for trace metals should be tackled before considering an intercalibration exercise for sampling procedures. Although several possible approaches to an intercalibration were identified by the Sub-group, it felt that the details should be decided intersessionally by those coordinating the exercise. It was pointed out that the Working Group on Statistical Aspects of Trend Monitoring will address some of the generalised aspects of intercalibration exercises and should, therefore, be consulted on this matter.

The Sub-group agreed that the lead for this exercise should be taken by the Working Group on Marine Sediments in Relation to Pollution (WGMS) and suggested that WGMS should consider submitting a paper to the Statutory Meeting describing the background and plans for such an exercise.

The Sub-group then discussed the paper prepared by Dr Yeats on methods for the collection of SPM samples for gravimetric and trace metal analysis. Dr Yeats described the background to this paper, referring to the contribution made by Dr L. Brügmann (Institut für Meereskunde, Rostock, German Democratic Republic). Following discussion of this paper, some small changes were suggested. The Sub-group recommended that the paper should be submitted for publication in the Techniques in Marine Environmental Sciences series, following any comments and amendments suggested by WGMS.

### 7.1.4 Intercomparison of analyses of methyl mercury in biological tissue

Dr Cossa described the organomercury intercalibration exercise, that he and Dr Y. Thibaud had coordinated, and presented the preliminary report. Two sets of samples (fish muscle tissue and mussel soft tissue), provided by Dr Berman, had been distributed in August 1987 to 20 laboratories that had requested to participate in the exercise. Thirteen laboratories had reported their results by 15 February 1988 and one additional set of data had been received since preparation of the report on the results. Dr Cossa concluded that the exercise had shown that: (a) methyl Hg intercomparison can be conducted for biological tissue, (b) a good performance had been achieved by the participants, and (c) there was no difference between results for the analysis of methyl Hg and organo Hg.

Dr Berman referred to the uniqueness of this work, i.e., it was the first intercomparison exercise on analyses of organomercury in marine biological tissue. However, he cautioned Dr Cossa from putting too much emphasis on variances on the basis of such a small data set. He suggested that the t-test would be better for this small number of samples, and that using this test the data for lab no. 19 for sample E would have been excluded.

Dr Jensen suggested that a table summarising all of the data would be helpful, and that an explanation was needed for the figure in this report. Dr Cofino referred to the consistency of the water content reported by lab no. 8 and the apparent high results for this lab. Drs Cossa and Berman referred to methods of drying samples and the need for standardisation for this measurement. Dr Berman questioned the use of the Dixon test for rejecting outliers.

The Sub-group recognised that this exercise represented a significant advance in the ICES intercalibrations and illustrated a good example of progress that could be made among MCWG members. The Sub-group noted that the report needed only minor modification to deal with the above comments and recommended that the modified report should be submitted to ACMP and thereafter to ICES for publication in the Cooperative Research Report Series. On discussing this item, the Sub-group felt that authors of such reports should be sent copies of published reports as soon as they were available and they recommended that all participants in MCWG intercalibration exercises should get copies of reports free of charge.

### 7.1.5 Trend monitoring of metals in sea water

Dr Cofino introduced this item by informing the group that the ad hoc Working Group on Monitoring under the JMG had recently reduced its emphasis on temporal trend monitoring of metals in sea water and, therefore, this item was of a low priority for MCWG.

The Sub-group noted with interest that many of the ideas incorporated in the JMG guidelines for sampling and analysis of trace metals in sea water were based on the proposals contained in Dr Brügmann's paper but that the JMG report did not recognise this

input by Dr Brügmann and MCWG. One of the concepts developed in Brügmann's paper was the potential use of integrating in situ extractors (e.g., Seastar System). The Sub-group discussed the applicability of this type of system to monitoring purposes, but felt that there was not yet enough information available to assess the usefulness of these systems.

The JMG report on guidelines for the sampling and analysis of trace metals in sea water was then discussed. The group concluded that this was a good document and needed little modification. The group agreed that the detection limit should be defined as three times the standard deviation of the blank.

7.1.6 Overview on Mercury

Following the presentation of his paper "An Overview of Mercury in the Marine Environment" by Dr Cossa, the Sub-Group had the following comments to make: (a) the comparison to Pb should be removed from the summary section, (b) the section on human health was too brief and should be expanded, and (c) a figure or a table showing ranges of concentrations would be helpful since it was noted that concentrations varied over nine decades.

The Sub-group recommended that a revised version of this paper should be submitted in due course to ACMP. The final version of this paper, which would include any written comments sent to Dr Cossa, would be submitted to ACMP after the report on the intercomparison exercise on methyl mercury, which had first priority, had been finalised by Dr Cossa.

7.1.7 Reference materials and quality assurance

Following a statement made by Dr Topping on the need for clear advice for JMG from MCWG on this topic, it was agreed that Dr Berman would update his paper on quality assurance which he had prepared for 1987 MCWG meeting. The revised version is given in Annex 4. This paper reflects the views of the Sub-group on such matters as the role of intercomparison exercises, good laboratory practice, the need for and role of different types of reference materials, the financing of the preparation of these materials and the conduct of intercomparison exercises. Dr Griepink was present for the discussion of this item.

7.1.8 Water quality modelling

Dr Yeats explained the purpose of the water quality modelling session at the 1988 Statutory Meeting and encouraged Sub-group members to submit papers or consult with other colleagues who may be willing to do so. Several potential contributors were identified by the group.

7.1.9 Any other business

A document on Cd in Mytilus species prepared by Dr Cossa was presented to the group. In this paper, Dr Cossa reviewed the inven-

tory of information on Cd in mussels and compared Cd levels in mussels to those in water. The Sub-group identified additional data that could be included in this paper. This paper is to be submitted to Marine Environmental Research and was presented here for information and comment.

Dr Jensen then presented his paper on the determination of organic and total tin in sea water to the Sub-group with a request that members send any comments on this paper to him by 11 April. The paper is presently being reviewed by Dr M. Waldock (UK). The Sub-group recommended that this paper should be submitted for publication in the Techniques in Marine Environmental Sciences series.

## 7.2 Organics Sub-group

Dr Reutergårdh opened the meeting, and invited the participants to put forward any items that they wished to be considered under item 7.2.8 (Any other business). Following this, the Sub-group proceeded to the main Agenda items.

### 7.2.1 GESAMP report on net river inputs

Dr Duinker gave a short introduction to this substantial document (Land/Sea Boundary Flux of Contaminants: Contributions from Rivers (GESAMP Reports and Studies No.32)), and it was then opened for discussion. The Sub-group agreed that this was an important document containing essential information, and something which had been lacking for many years. They then discussed the practical and theoretical aspects of such studies, and tried to identify the types of organic contaminants which should be measured in the dissolved and particulate phases. It was agreed that, to be of use, all data must be collected within a framework of solid hydrographic data, and that water soluble compounds were of little interest, since for these compounds the gross flux is equal to the net flux. Data are required for a range of individual lipophilic compounds with varying physical-chemical properties, and with log $K_{ow}$ values in the range 3 to 9, that is, those compounds that are likely to be found in association with particulate materials as well as in the dissolved phase, the relative contributions depending on log $K_{ow}$ and suspended matter concentration and composition. In the first instance, chlorobiphenyls would be a suitable class of compounds for study. They are chemically similar; good background data are available for them; they are ecologically relevant, exerting toxic effects because of diffuse inputs rather than point sources; they are relatively persistent, and exhibit a range of vapour pressures and water/lipid solubilities. Complex and largely undefined technical mixtures, such as toxaphene, are not considered to be suitable for this work yet, because, unlike chlorobiphenyls, they cannot be analysed as well-defined compounds.

It was recognized that temporal variance was an aspect often absent from data sets, and the importance of sampling during storm events could not be stressed too highly. Studies in pristine areas are inappropriate for organic contaminants because in such areas no synthetic chemicals would be present. Two questions were referred to the plenary group:

1) Should ACMP be asked to consider the formation of a Sub-group which could, over a longer period than a few days, consider the GESAMP report and its implications in the detail it deserves?

2) A problem that remains to be addressed in future is that of exchange of organic contaminants with the atmosphere, and whether influxes/effluxes are significant in terms of net riverine flux measurements.

In general, the Sub-group urged that more work be conducted on flux measurements as a measure of the amount of contamination entering the seas and the exposure to marine biota. This was seen as especially important in the North Sea in the context of the ongoing series of Ministerial conferences. A further recommendation was made that when estimates are made of riverine fluxes, the importance should be recognised of determining the reliability of such estimates and the confidence limits that can be placed upon them, for two reasons:

1) to show the range within which the best estimates lie, and

2) to identify those factors contributing most of the uncertainty in order to focus research on those areas and to reduce the overall variability of the estimates.

### 7.2.2 Intercomparison of measurements of specific hydrocarbons

Mr Law presented a short progress report on the intercomparison exercise on measurements of specific hydrocarbons, that he is coordinating. Due to instrumental problems with the GC-MS system, the start of the exercise has been delayed to April/May 1988. Participants have been informed by letter. A further participating laboratory was identified in the Netherlands. Some discussion took place on the important matrices to be considered for the later stages of the programme; mussels/oysters, SPM and sediments were identified. The analysis of PAH-metabolites, as the carcinogenic agents, rather than the parent PAH was discussed. The importance and relevance of this was agreed, but as methodology is not commonly agreed upon, it was considered to be beyond the scope of the current exercise. It was also emphasised that the analytical step is only one link in the chain from sample collection to result - and often not the weakest.

On the question of coordination of later stages of the programme, Mr Law advised the Sub-group that he could give no commitments beyond the first stage, but personally would like to remain involved throughout the work.

7.2.3 Measurements of individual organochlorine residues

Discussion centred on the ICES/IOC intercomparison exercise concerning chlorobiphenyls in seal blubber (ref MCWG 1988/7.2.3/2). Dr Reutergårdh informed the Group that, as he may not be a member of MCWG for the next two years, he would have to step down as co-coordinator (ICES) of this exercise (with Dr Duinker (IOC)). He informed the members that Dr de Boer will take his place.

Dr Duinker stressed that SE-54 must be the stationary phase used by all participants in the exercise, because for only that phase were retention data available for all 209 CB congeners (Mullin et al.) and the application of multi-dimensioned GC-ECD shows which congeners actually contribute to each peak in commercial mixtures and environmental samples. This was agreed, as was the proposal that a second phase could be used for confirmatory purposes as required. There followed considerable discussion on two points:

1) Which congeners can be analysed accurately by GC-ECD, and

2) which criteria should be applied in the selection of CBs to be included in the marine mammal and other intercomparison exercises.

Eventually a list of CBs was agreed, based on the following criteria:

1) Toxicity concerns (e.g., to mammals);

2) Environmental occurrence;

3) Analytical capability. Either the CBs yield single, resolvable peaks, or have been specifically chosen to give a test of column resolving power and to solve controversies on analytical capabilities;

4) Pure, certified reference CBs are readily available.

The CBs proposed are: 28, 31, 52, 101, 105, 118, 138, 153, 180, 189. These can be compared to the list of congeners previously selected by BCR, ICES and IOC and for the sediment intercalibration, as given in Table 1. Information on the known toxicity of some CBs is also given in Table 1.

On the basis of Table 1, and the considerations discussed above, ten CBs were selected for inclusion, as listed in Table 2. In the second column of Table 2, possible interferences in the GC-ECD analyses are indicated on the basis of the chromatographic properties of all 209 congeners on SE-54 (Mullin et al.) and multidimensional GC-ECD on SE-54 (Duinker et al.).

TABLE 1

CB congeners chosen by various groups

| IUPAC No. | BCR | ICES 1 | ICES 2 | IOC | Sediment | I/C Toxicity[1] | Selection by the group |
|---|---|---|---|---|---|---|---|
| 8 | | | | | X | | |
| 18 | | | X | X | X | | |
| 26 | | | | X | | | |
| 28 | X | X | | | X | | X |
| 31 | | | X | | | | X |
| 44 | | | X | X | X | | |
| 49 | | | X | X | | | |
| 52 | X | X | | X | X | | X |
| 66 | | | X | | X | | |
| 77 | | | | | X | X | |
| 95 | | | X | | | | |
| 101 | X | X | | X | X | | X |
| 105 | | | | | X | X | X |
| 118 | X | X | | X | X | X | X |
| 126 | | | | | X | X | |
| 128 | | | | X | X | X | |
| 138 | X | X | | X | X | X | X |
| 149 | | | X | X | | | |
| 151 | | | | X | | | |
| 153 | X | X | | | X | | X |
| 156 | | | | | | X | |
| 169 | | | | | | X | |
| 170 | | | | X | X | X | |
| 180 | X | X | | X | X | | X |
| 183 | | | | X | | | |
| 187 | | | X | X | X | | |
| 189 | | | | | | | X |
| 194 | | | | X | | | |
| 195 | | | | | X | | |
| 206 | | | | | X | | |
| 209 | | | | | X | | |

[1] Affinity for (aryl hydrocarbon) AH-receptor (3-methyl cholanthrene and mixed type MFO-induction).

TABLE 2

List of congeners selected

| IUPAC No. | Possible interference |
|---|---|
| 28 | 31, 50 |
| 31 | 28, 50 |
| 52 | - |
| 101 | 90 |
| 105 | 153, 132 |
| 118 | 149, 123 |
| 138 | 163, 160 |
| 153 | 132, 105 |
| 180 | - |
| 189 | - |

In accordance with the requests of ICES for specific information regarding the intercomparison exercise, the following was agreed:

Individual CBs will be used to prepare standard solutions for circulation.

The potential number of participants involved in analyses of seal blubber was 19. By country this was:

| | | | |
|---|---|---|---|
| Canada | 1 (?) | Poland | 1 (?) |
| Denmark | 1 | Portugal | 1 |
| Finland | 1 | Spain | 1 |
| France | 1 | Sweden | 1 |
| Germany, Fed. Rep. | 3 | UK | 1 |
| Netherlands | 4 | USA | 1 (?) |
| Norway | 1 | USSR | 1 (?) |

(?) indicates a degree of speculation.

The samples will consist of synthetic mixtures in which the selected CBs are present as well as some other possibly interfering CBs.

The use of the stationary phase SE-54 will be mandatory for both the ICES and IOC laboratories; ICES laboratories should also use a second confirmatory column.

As a first stage intercomparison exercise to assess analytical capabilities using standard solutions, this is an opportunity to broaden the participation in the exercise to laboratories involved in the fish and shellfish monitoring programme and to laboratories carrying out sediment analyses, using the same solutions.

Drs de Boer and Duinker, as ICES/IOC coordinators for the marine mammal exercise, will prepare the samples. Evaluation of the data will be carried out by:

Dr Duinker IOC participants

Dr de Boer ICES marine mammals and fish and shellfish laboratories

Dr Calder sediment laboratories

Depending on the results of the first stage, the follow-up stages would probably be separate for each matrix.

It is recommended that MCWG request WGSATM to provide statistical assistance in the interpretative stage of the exercise.

If agreed by the Oslo and Paris Commissions, laboratories participating in the JMP can join this exercise on the basis of the Commissions sharing the costs with ICES.

The provisional timetable for the exercise is given in Annex 5.

As this will be a stepwise collaborative exercise, it must be made clear to laboratories that a firm commitment to the pro-

gramme must be made and it will not be possible for others to join the exercise only for the later stages. Experience from the BCR and other similar exercises will be incorporated, good communications and feedback to laboratories will be essential.

Under this agenda item, the Sub-group also discussed the intercomparison exercise on the determination of chlorobiphenyl congeners in Baltic herring oil, that was coordinated by Drs Reutergårdh and Litzen. This report had been considered by the Sub-group in 1985, but not mentioned in the report. The Sub-group considered that publication of the report would be worthwhile as a record of the improvements made during successive exercises. The exercise would be numbered 6/OC/BT.

### 7.2.4 Methodology for total organochlorine residues

The Sub-group considered a paper by Dr C. Grøn (Technical University of Denmark), entitled "Determination of Organic Halogens: Group Parameters in Investigations on Marine Pollution", and agreed that the AOX procedure could be recommended as a suitable method for screening industrial effluents from pulp mills to the adjacent receiving waters, if the composition of the effluent remains essentially unchanged. Before the recommended method is forwarded to the Helsinki Commission, however, they felt that it should also be considered and approved by the Working Group on the Biological Effects of Contaminants.

### 7.2.5 Overviews

Mr Law presented Dr M. Ehrhardt's paper on diphenyl sulfone in Baltic Sea water. The Sub-group noted his work with interest, but felt that they currently had little background information on this compound. Its environmental toxicity is unknown, and it was also noted that it could be a natural product and, thus, could occur naturally in the marine environment at low levels. Mr Law indicated that diphenyl sulfone does not seem to be registered for use as a pesticide in the UK.

For the 1989 meeting of MCWG, overviews are to be prepared on:

1) Planar molecules. Drs Reutergårdh and Wells. This paper is in preparation but is not yet finished.

2) The compiled review of hydrocarbon analysis, being coordinated by Dr Ehrhardt.

3) HCB and the HCHs. Drs Reutergårdh and Wells.

4) Surface active agents. Dr A. Granmo (Sweden).

### 7.2.6 Reference materials/QA

The Sub-group were pleased to welcome Dr Griepink, Bureau of Community References (BCR) of the European Community, who gave a short introduction to their current work programme and their mode

of work. It was apparent that one of the goals was to enhance the performance level of Community laboratories and that the production of reference materials was one aspect of this education. Discussion of quality assurance (QA) followed, during which it was agreed that, in order to encourage laboratories participating in the Cooperative ICES Monitoring Studies Programme to embrace QA philosophy, a recommendation should be made to ICES concerning such laboratories. In future, all laboratories should participate successfully at least annually in a relevant intercomparison exercise, and submit to ICES a copy of the report of the exercise identifying their own results along with their monitoring data. Data validated in this way should be flagged as such in the ICES database.

Dr Calder advised the Sub-group of new reference materials currently in preparation by the U.S. National Bureau of Standards (NBS). During 1988, two reference materials will become available:

1) a solution of chlorobiphenyls in iso-octane; and

2) an air-dried, homogenised marine sediment certified for 20+ PAH compounds, and with information values for several chlorobiphenyls and oganochlorine pesticides.

A mussel tissue certified for organochlorines and PAHs is also being prepared.

Dr Wells gave a progress report (paper 7.2.6/1) on the BCR chlorobiphenyl intercalibration exercise, which has culminated in the certification of two fish oil samples, that are now available. Materials currently being prepared include a dried sewage sludge (to be available during 1988), a dried milk powder, a dried mussel homogenate and a lubricating oil. Dr Calder then described an intercomparison exercise that had been carried out in the USA concerning CBs in sediment. The results were encouraging and suggested that CVs of $\pm$ 20% had been achieved. Intralaboratory and interlaboratory variability were very similar. Control materials were analysed with each batch of samples, and results were variable for different CB congeners. An HPLC clean-up technique improved the blank values and general data quality, and this procedure can be automated. Details of this technique were also presented by request of the Sub-group.

### 7.2.7 Water quality modelling

There is a lack of good quality data sets for synthetic organic contaminants related to firm hydrographic data, as was identified during discussions of the estimation of riverine fluxes. Hydrophobic contaminants are well suited to modelling studies because of their interactions with particles. The modelling of chemical and physico-chemical transitions could however lead to very useful predictions, for instance, of the effect of adsorption processes on the concentrations in the dissolved phase of contaminants derived from point source inputs. Dr Kerkhoff agreed to consult some of her colleagues with a view to having them prepare a paper for the Theme Session at the 1988 Statutory Meeting.

7.2.8 Any other business

The National Research Council of Canada (NRC) are considering the preparation of up to four pure toxaphene congeners, and asked for suggestions as to which were the most appropriate other than Toxicant A & B. The subgroup, however, had only limited information on which of 8500 congeners were of higher environmental concern, but welcomed the effort and recommended NRC to contact Dr Cassida who might contribute.

Dr Duinker will contribute to the 1989 MCWG meeting a paper, currently in preparation, concerning the input to the sea of CBs from the atmosphere, which occurs primarily by wet deposition.

Dr de Boer presented his two papers 7.2.8/1 and /2, and Dr Uthe his paper 7.2.8/3, all concerning the extraction of fatty tissues for chlorobiphenyl analysis, and the associated determinations of fat content. These papers were felt to be useful to the ICES laboratories. Saponification generally yields the highest CB concentrations, but cannot be used if organochlorine pesticides are to be analysed as some are destroyed by this procedure; additionally, yields of some of the higher CBs, such as No.180, are reduced.

A mixture of 50% pentane/dichloromethane seemed to yield the best compromise. Following much discussion, it was agreed that when results are reported on a lipid basis, or when lipid concentrations are reported along with concentrations based on wet weights, the full details of the method(s) used for extraction and lipid determination should be described and documented. It was also urged that the "organ weight" of liver be recorded and submitted with data for monitoring programmes to allow the estimation of body burdens.

The Sub-group also agreed that all papers considered by them should be appended as annexes to the subgroup report. Information was passed to the group by correspondence from Dr A. Abarnou on an intercomparison exercise concerning organochlorine compounds and CBs in dredged spoil, to be run by IFREMER. Dr Calder agreed to contact IFREMER, and to circulate details of the protocol for the exercise to subgroup members. They could then consider both their own laboratories' participation, and whether it was appropriate to encourage the participation of other ICES laboratories.

7.3 Chemical Oceanography Sub-group

The Chairman, Dr Carlberg, commenced the meeting by listing the various documents that would form the basis of discussion:

1) Notes on Chemical Oceanographic Activities at the ICES Secretariat. MCWG 1988.

2) Hydrochemical conditions in the North Sea during IYFS 1987. H. Dooley. ICES Doc. C.M.1987/C:11.

3) On the management of the PEX dataset. H. Dooley and K. Jancke. ICES Doc. C.M.1987/C:12.

4) Nitrate trend analysis in the North Sea, west of $3^0$E (discussion document). R. Dickson and D. Kirkwood.

5) Intersessional Activities on Nutrient Preservation, etc. (discussion documents). D. Kirkwood.

6) Determination of Inorganic Phosphate in the presence of Hydrogen Sulphide in Anoxic Waters. S. Carlberg and T. Nunes. MCWG 1988.

The Chairman then reminded the Sub-group of the specific tasks that had been set and the order of priorities.

7.3.1 Measurements of nutrients in sea water

In the absence of the ICES Hydrographer, Dr Topping attended the initial part of this meeting, together with Dr Wilson of the ICES Secretariat, who gave a brief presentation of the work described in Doc. C.M.1987/C:12. The Sub-group then discussed several aspects of the PEX experiment and, while agreeing that there were many lessons to be learned from this work, felt that they were unable to discuss and comment fully on the finer details, particularly those concerning the proposed normalisation treatment, in the absence of the Hydrographer. There exists a strong current of opinion within the Sub-group that although the PEX results are, to some extent, disappointing, there may be problems of sample stability, contamination, etc. complicating the situation and there is no reason to suspect the analytical chemistry used. However, there was general agreement that while some kind of normalisation was necessary to the PEX data, this approach cannot be recommended for routine handling of oceanographic data.

Mr Kirkwood gave an account of the intersessional activity he had coordinated, including an informal workshop at Aberdeen in November 1987. Freshly taken samples from the North Sea were first analysed by Dr Føyn's group on board the Norwegian R/V "G O Sars" and replicate samples were delivered to the Marine Laboratory, where soon afterwards both Aberdeen and Lowestoft staff analysed these and other samples by their own methods and equipment. Briefly, the entire exercise was characterised by remarkably good agreement between the participating laboratories.

It is clear that when the samples under test are demonstrably stable, there is no difficulty securing the levels of agreement that the Sub-group believes should be attainable purely from a consideration of the underlying analytical chemistry.

Also described was work on the stability of samples taken off Greenland in June 1987. Samples from several depths showed various degrees of instability in the presence of added chloroform; but, surprisingly, without added chloroform and in the complete absence of any recognised preservative measures, unfiltered samples stored in clear glass bottles at room temperature showed remarkably good stability in respect of nitrate and phosphate. Concentration levels have been confirmed by two other laboratories and it is suggested that additional supplies of water from this source should be considered as a candidate reference material.

The response to M Perttilä's questionnaire on the proposed intercalibration was considered in detail. After considerable discussion of technical problems, it was agreed that it was now appropriate to proceed with an intercalibration exercise (see proposed timetable in Annex 6) and the following were identified as priority determinands: nitrate, nitrite, phosphate, silicate, ammonia, total P and total N.

Sample materials will be based on real sea water and will include: a) an (approx.) 1200 m depth sample from off Greenland as described earlier, and b) a set of samples based on estuarine and coastal waters covering an appropriate concentration range (to be prepared by A. Aminot).

The Group decided that oxygen should not be included in the intercalibration because of the difficulty in the distribution of uncompromised samples to a great number of participants in several countries. The Group considered that the distribution of a standard iodate solution for the standardisation of thiosulphate solutions should not offer any solution to this intercalibration need, as has been demonstrated by the PEX-intercalibrations.

T. Nunes described the work on determination of phosphate in the presence of $H_2S$ in anoxic waters carried out jointly by Dr Carlberg and herself. Problems of maximum absorbance wavelength shift, sulphide precipitation, varying reaction rates, etc., were encountered. The outcome is that traditional colourimetric methods as they stand are insufficiently robust to give reliable results in anoxic situations.

The submission of nutrient data to ICES continues to present a problem for some laboratories. Certain laboratories have voiced their fears that their data, if submitted to ICES, could be made available to outside organisations without their knowledge or approval. It is recognised that some laboratories are required to operate in a more commercially sensitive manner than was formerly the case and they see their data as having some considerable market value. These laboratories are reluctant to submit data in the absence of assurances that the data will not be used to the advantage of any organisation that could be described as being in any way a commercial competitor.

The Sub-group supports any measures that can be implemented to safeguard the confidentiality of such data and suggested that, in addition to identifying the responsible research vessel, it would be helpful if individual workers could be identified so that a potential user would have a specific contact for questions of this kind. After similar discussions took place at the 1987 MCWG meeting, it is understood that a significant amount of additional data were submitted; but the greater part of the potentially available data, as indicated by ROSCOP, is still in the hands of the originating laboratories.

### 7.3.2 River inputs

The Sub-group pointed to the fact that mathematical models are being developed for the description and prediction of the con-

centrations of chemical substances in river water. These models will provide useful tools in the assessment of riverine inputs.

### 7.3.3 Measurement of dissolved oxygen at low concentrations

The Chairman explained that the background to the request to consider this item stemmed from the PEX experiment. After some discussion, the Sub-group concluded that its only recourse was to restate familiar caveats on the use of oxygen probes, particularly:

1) that these devices invariably possess appreciable response time, thus necessitating proper timing when the signal from the oxygen sensor is combined with those from depth, salinity and temperature sensors;

2) that they continue to require calibration against the traditional titrimetric chemical method;

3) when towed, they can at best give only an indication of gross changes.

In response to the request from HELCOM concerning procedures for oxygen determination, the group concluded that laboratories which had experienced difficulties in intercalibrations (e.g., PEX) should review their procedures for sampling and analysis and compare them to the well-known procedures published in recognised handbooks.

### 7.3.4 Water quality modelling

D. Kirkwood presented the discussion paper, that Dr R. Dickson and he had prepared, showing the preliminary results of a statistical treatment recently applied to a data set consisting mainly of data from the Aberdeen and Lowestoft laboratories for the western part of the North Sea from 1960 onwards. While recognising that there are many gaps in the time series and geographical coverage, it is an attempt to handle data for nitrate in a way that takes salinity into account. The treatment does not show a continuous upward trend in nitrate concentrations, as might have been expected from what is known of river input data.

Members were invited to help to fill the gaps with contributions from their own data, where appropriate. Several constructive suggestions concerning the statistical treatment were gratefully acknowledged.

It was recommended that, in order to meet the request from JMG, the ICES Hydrographer, in consultation with the Hydrography Committee, should identify two sets of nutrient data covering a period of at least 10 years which would be suitable for temporal trend analysis. The trends that may emerge should be identified without further correction or normalisation of the data. The techniques used for the preliminary analysis of nitrate trends, as reported to MCWG, could be valuable in the analysis of these data.

## 8 PLENARY DISCUSSIONS OF SUB-GROUP REPORTS

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

### Trace Metals Sub-Group

The MCWG endorsed the paper prepared on gross and net river inputs assessment and noted that the views of the Organics Sub-group are reflected in the first three paragraphs of this paper.

The MCWG supported the recommendation of the Sub-group that a two-day meeting was required to complete the assessment of data on trace metals in coastal waters and that Dr Cofino should chair this meeting and liaise with Dr Wilson on this matter prior to this meeting.

The MCWG endorsed the expansion of the paper by Dr Yeats and Dr Brügmann on the measurement of particulate trace metals in sea water and supported the recommendation that the revised paper be submitted to ICES for inclusion in the Techniques in Marine Environmental Sciences series. It noted the need for an intercomparison exercise for the analytical component of this measurement and agreed that the WGMS was the appropriate group to plan this exercise and identify a coordinator.

The MCWG supported the recommendation of the Sub-group that the overview paper on mercury should be submitted to ACMP for publication in its report and the report on the intercomparison of methyl mercury analyses in biological tissue should be submitted to ICES for publication in the Cooperative Research Report series.

The MCWG noted with approval that the Sub-group had revised the paper on QA and intercomparison exercises and that this advice would be brought to the attention of JMG via ACMP. It endorsed the needs identified for additional reference materials and the recommendation that ACMP seek a means to provide financial arrangements for the preparation of these materials and the conduct of any subsequent intercomparison exercises for trace metals in marine samples. It also noted that the Sub-group would consider the preparation of guidelines for the production of internal reference materials (IRMs) by individual laboratories. The Group was informed by Dr Uthe (Chairman of WGSATM) that his group has prepared a paper on sampling aspects of QA and in due course this paper will be passed to MCWG for information and comment.

### Organics Sub-Group

The MCWG noted the points made, and advice given, by the Sub-group on net river input measurements. The Chairman agreed to raise the question of the need for a special meeting to discuss this topic further at ACMP.

The MCWG noted the progress made with the intercomparison of measurements of specific hydrocarbons and looked forward to receiving a report on the first stage of this exercise at its next meeting.

The MCWG noted with approval the progress made with the development of the programme for the ICES/IOC intercomparison exercise for CBs in marine samples, particularly marine mammals, and endorsed the proposed timetable and plans for the coordination and reporting on the first stage of this exercise. It endorsed the recommendation that plans for this exercise be considered by the WGSATM.

The MCWG noted that members of the Sub-group would be preparing a number of overview papers for the 1989 meeting.

Chemical Oceanography Sub-Group

The MCWG noted with approval the progress made by Sub-group members on the measurement of nutrients in sea water and endorsed the recommendation that an intercomparison exercise be conducted for these measurements and the proposed plans for this exercise.

In concluding the discussion, the Chairman thanked all of the Sub-group Chairmen and rapporteurs for their efforts over the past few days and those members of the sub-groups who had been responsible during the intersessional period for the conduct of exercises and preparation of reports for the Sub-group sessions.

## 9 ANY OTHER BUSINESS

The Chairman informed the members that, having served as chairman for a period of three years, he was obliged to conduct an election for a new chairman under the new guidelines laid down by the parent committee. Before handing over the chair for this election to a non-member of MCWG, he explained the procedure for conducting the election. He then invited Dr Kerkoff, as a non-member of MCWG, to take the chair for this election.

Dr Kerkoff then invited nominations from the floor. Three were received - Drs Calder, Cofino and Topping. Dr Cofino declined to be nominated. A ballot was then held for the remaining two nominees. Dr Topping, receiving a majority number of votes from the members of MCWG, was then re-elected for a further three years. Dr Topping resumed the chair for the meeting and thanked Dr Kerkoff for her help in chairing the election.

The Group then reviewed the intersessional activities of the three subgroups. An action list is given in Annex 7.

## 10 RECOMMENDATIONS

Each of the sub-groups had made a number of recommendations in their respective reports. These were discussed by the group and a list drawn up for inclusion in Annex 8.

The MCWG then discussed its next meeting and agreed it should be held in February/March 1989 for a period of five days at either the Skidaway Institute of Oceanography, Savannah, Georgia, USA (to be hosted by Dr H L Windom) or ICES headquarters, in the event of the former venue being unacceptable by the Delegates or if this location would preclude a significant number of the group

attending the next meeting. A recommendation to this effect, including a list of topics for consideration at the next meeting, is given in Annex 8.

All other business being concluded, the Chairman thanked all members for their hard work and constructive help during the week. He then closed the meeting at 16.00 hrs on 11 March 1988.

## ANNEX 1

MARINE CHEMISTRY WORKING GROUP

The Hague, Netherlands, 7-11 March 1988

## AGENDA

1 OPENING OF THE MEETING

2 ADOPTION OF THE AGENDA

3 REPORT OF 75TH 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 SUB-GROUP ACTIVITIES AND DISCUSSIONS

7.1 Trace Metals (in Order of Priority)
7.1.1 GESAMP report on net river inputs
7.1.2 Review of 1986 data for trace metals in coastal waters
7.1.3 Intercomparison of measurements of suspended matter in seawater and measurements of trace metals in suspended matter
7.1.4 Intercomparison exercise for methylmercury in tissue
7.1.5 Trend monitoring of metals in seawater
7.1.6 Overviews on Cr and Ni
7.1.7 Reference materials/QA
7.1.8 Water quality modelling
7.1.9 AOB raised by subgroup
7.2 Organics (in Order of Priority)
7.2.1 GESAMP report on net river inputs
7.2.2 Intercomparison of measurements of specific hydrocarbons
7.2.3 Measurements of individual organochlorine residues
7.2.4 Methodology for total organochlorine residue
7.2.5 Overviews
7.2.6 Reference materials/QA
7.2.7 Water quality modelling
7.2.8 AOB raised by subgroup
7.3 Chemical Oceanography (in Order of Priority)
7.3.1 Measurements of nutrients in seawater
7.3.2 GESAMP report on net river inputs
7.3.3 Measurements of dissolved oxygen at low levels
7.3.4 Water quality modelling
7.3.5 AOB raised by subgroup

8. PLENARY DISCUSSION OF SUB-GROUP ACTIVITIES AND DISCUSSIONS

9. ANY OTHER BUSINESS

10. RECOMMENDATIONS

ANNEX 2

MARINE CHEMISTRY WORKING GROUP
The Hague, Netherlands, 7 - 11 March 1988

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## ANNEX 3

## ESTIMATION OF NET RIVER INPUT OF METALS TO COASTAL WATERS

Before the net river flux of metals to coastal waters can be estimated, gross river flux must first be measured, since this is the fundamental piece of data that is required to study inputs from rivers. Details of the sampling procedures to estimate this input are given in Appendix 7 to GESAMP Reports and Studies No. 32, Land/Sea Boundary Flux of Contaminants: Contributions from Rivers. Although complex, these procedures would appear to be the best way to collect river samples. However, it is noted that under the Paris Commission, laboratories are presently conducting extensive measurements of river concentrations and fluxes, and if they can be convinced to adopt good sampling practices (as outlined by the GESAMP Report, Appendix 7) with good quality control (as outlined by ICES Techniques in Marine Environmental Sciences No.6) and the revised procedures suggested for the PARCOM ad hoc Working Group on Input Data (see para 7.1.1), then they should be able to produce good estimates of gross river inputs for all the rivers in the PARCOM region.

Based on the information in GESAMP Reports and Studies No.32, it would appear that the best way to estimate net river inputs to the deep ocean is to use the zero salinity intercept extrapolation method based on samples collected from the outer part of the coastal zone to oceanic surface waters. However, this will not always be successful because it depends on obtaining good relationships between metals and salinity and these will not always be observed. Also, the errors resulting from extrapolations of metal/ salinity relationships to S = 0 mean that the error associated with the apparent river concentration will be large, resulting in at best only an imprecise estimate of net input to deep sea waters. In the opinion of MCWG, however, this method provides a rough estimate of net inputs to the deep sea.

Net fluxes from estuaries to offshore areas can be estimated by conducting surveys of metal distributions/behaviour in the major estuaries. The GESAMP report 32 reviews the subject of the study of metal geochemistry in estuaries. The PARCOM guidelines for sampling and analyses of trace metals in sea water also describe assessment of trace metal behaviour in estuaries but details of surveys would depend on characteristics of each estuary. These surveys would have to be conducted at least seasonally and probably more frequently. It would be important to measure dissolved metal concentrations, particulate metal concentrations, and suspended particulate matter concentrations (SPM) on samples from the whole salinity range from fresh water to offshore coastal waters. These data can be used to calculate net fluxes of dissolved and particulate metals from the estuaries, usually by determining the relationships between metals and salinity in the outer part of the estuary and the coastal waters. The situation will generally be clearest for dissolved metals, for which reasonably clear relationships with salinity should be observed. Particulate metal (in µg/l of water) relationships with salinity may be less clear because of variability in SPM concentrations. Studies of SPM budgets are required for the determination of

particulate metal fluxes. In many cases, extrapolations of these particulate metal relationships to zero salinity will give effective river concentrations which, when multiplied by river water flux, will give net river input. It is important to measure both dissolved and particulate metals rather than just total metals because these measurements greatly increase the ability to understand the metal geochemistry in the estuary.

The metal/salinity relationships for samples from the outer parts of estuaries and the coastal zone provide a river to coastal zone analog for the metal/salinity relationships for the outer coastal zone to the deep sea. If these relationships for different regions and different seasons are consistent, it may be possible to reduce the number of surveys and only use "average" relationships. However, it must be recognised that such a simplification would degrade the precision of any estimate of net flux because of the problems of magnifying the uncertainty when extrapolating to zero salinity from data that are clustered at high salinity values.

In summary, it is considered that gross river fluxes can be determined if the improved guidelines outlined above are followed. Since estuarine behaviour will vary greatly from estuary to estuary, studies of net river inputs will have to be designed by scientists who have a good understanding of the physical characteristics of each estuary, i.e., sediment transport and hydrology. The actual strategy for determining processes and fluxes in individual estuaries will thus be designed for each estuary. In this context, one important consideration in many estuaries will be the need to determine direct inputs to the estuary from pipeline discharges. Finally, it should be emphasised that, whereas gross fluxes can be estimated with some level of certainty, estimates of net fluxes will be imprecise and will only be rough (order of magnitude) corrections on the gross fluxes.

## ANNEX 4

## QUALITY ASSURANCE

There have been, to date, 15 intercalibration exercises sponsored by ICES regarding trace metals in marine samples; eight related to biological materials, six related to marine waters, and one for marine sediments. The results, discouraging in the early exercises, have in the later exercises shown marked improvements in the abilities of many ICES laboratories to analyse marine samples with respect to their trace metal contents. This is a result of two factors. Firstly, there has been a general improvement in analytical chemistry technology over the last decade, whereby instrumentation and procedures are now available so that trace metals may be readily and reliably determined at environmental levels. Secondly, many marine laboratories, aware of these developments, have upgraded their facilities, techniques and personnel in order to improve their performance. However, there remains a significant number of laboratories which have not demonstrated an ability to analyse trace metals in marine samples at the levels necessary for monitoring purposes.

The intercalibration exercises were invaluable in focusing attention on the analytical problems and provided a means of assessing performance, improvements and intercomparibility. But is must be remembered that these exercises were only valid with respect to sample digestion and/or metal measurement procedures. The sampling, preparation and preservation procedures of the laboratories have never been assessed. These steps add to the variance of the overall data, but a study to intercompare laboratories adequately for the complete process has yet to be devised. Intercomparison exercises will have to be conducted in the future for ICES, JMP, and BMP laboratories, but not necessarily at the same frequency as in the past. Furthermore, intercalibration exercises on the scale of 7/TM/BT, 6/TM/SW or 1/TM/MS will not be possible without significant financial support.

For the forseeable future, efforts must be expended to ensure that ICES laboratories adopt good laboratory practices whereby they can demonstrate both to themselves and the monitoring agencies, through the use of various reference materials and some very elementary statistics that their analyses are accurate and are under statistical control. The information in the recently published ICES pamphlet on good laboratory practice and quality assurance (Vijverberg and Cofino 1987) can be readily used to establish an adequate QA programme.

The role of reference materials within good laboratory practice is well established. There is now available a range of certified reference materials covering various concentrations of trace metals in marine biological tissues, waters and sediments. More are in production and work is in progress to produce reference materials which resemble more closely the samples analysed in the laboratories. Apart from certified reference materials, which enable the accurate testing of procedures and instruments, there is a need for two other types of reference materials.

The first material, which may be called an internal reference material (IRM), is a homogeneous material similar in nature to the sample analysed and is used in the quality control process. The concentration of the analytes in the IRM need not be accurately known and the material can be prepared within the laboratory. Repeated analyses of the IRM will provide a quality control record and a good assessment of the true laboratory variance for a particular procedure. Knowledge of the variance is essential in a monitoring programme in order to determine the laboratory's ability to differentiate between different concentrations of the analyte in samples.

The second material, which may be called an uncompromised reference material (URM), is a large quantity of homogeneous material prepared by a central laboratory on behalf of the monitoring agency and distributed to the monitoring laboratories. This material should be analysed alongside the samples collected in the monitoring programme or baseline study. The results of the analyses of the URMs, preferably combined with data from the intralaboratory quality assurance programme (IRMs and CRMs), should be sent to a coordinator to allow an assessment of accuracy and intercomparability. Once the URM is "compromised", i.e., values for the concentrations of analytes have been established and are well known by the users, it will become a very valuable quality assurance reference material.

It is recommended that guidelines be prepared for the laboratories indicating reliable procedures for the preparation of internal reference materials.

It is recommended that the monitoring agencies be approached regarding their financing the preparation and distribution of uncompromised reference materials to the monitoring laboratories.

REFERENCE

Vijverberg, F.A.J.M. and Cofino, W.P. 1987. Control Procedures: Good laboratory practice and quality assurance. ICES Doc. Techniques in Marine Environmental Sciences No.6.

## ANNEX 5

## PROVISIONAL TIME SCHEDULE FOR THE ICES INTERCOMPARISON PROGRAMME ON CHLOROBIPHENYLS IN SEALS (FIRST STAGE)

April 1988

- contact J. Duinker/J. de Boer/D. Wells about the details of setting up the first step of the intercalibration including preparing instructions and advice to the participants about GC parameters, dimensions of columns, linearity tests, etc., choice of internal standards, preparation of the standards, etc.

- proposal (if ready in time) to be sent to J. Uthe to be discussed in the ICES WG on the Statistical Aspects of Trend Monitoring

- requests to be sent out by ICES/IOC to the participating laboratories to make a commitment for the different steps of the exercise

- start of the preparation of the standard solutions and testing using GC/ECD and GC/FID by J. Duinker

June 1988

- testing of the standard solutions using GC/MS by J. de Boer

July 1988

- requests to be sent to the JMP laboratories (if it is decided that they will participate) to make a commitment for the different steps of the exercise

September 1988

- dispatch of the samples to the participants (J. Duinker to the IOC laboratories, J. de Boer to the ICES and JMP laboratories)

December 1988

- receiving results of IOC laboratories by J. Duinker, of ICES laboratories by J. de Boer and of JMP laboratories by J. Calder

January 1989

- evaluation of the results by the three coordinators

February 1989

- first impression of the three coordinators to be presented at the ICES MCWG meeting

- results of the intercalibration exercise to be sent to J. Uthe for statistical evaluation

## ANNEX 6

## PROPOSED SCHEDULE FOR THE INTERCALIBRATION EXERCISE FOR NUTRIENTS IN SEA WATER

Phase 1

- Laboratories will be approached and invited to indicate their willingness to participate in this exercise and to supply details of their analytical methods.

Phase 2

- Preparation of sample materials by D. Kirkwood and A. Aminot with a preliminary limited distribution for stability assessment. These results will be discussed at the 1989 MCWG meeting.

Phase 3

- Distribution of samples to all participants (Spring 1989).

Phase 4

- Analysis and reporting of results (Summer 1989).

Phase 5

- Review and documentation of the exercise by the coordinators (summer/autumn 1989).

Phase 6

- Submission of preliminary report at the 1989 Statutory Meeting and at the 1990 MCWG meeting.

ANNEX 7

MARINE CHEMISTRY WORKING GROUP, ACTION LIST FOR 1988

Trace Metals Sub-group

S Berman:

- to consider the preparation of a note on guidelines for the preparation of reference materials by laboratories involved in monitoring programmes

- to prepare a note on NRC's progress with the development and production of certified reference materials.

D. Cossa

- to finalise the overview paper on mercury and the report on the intercomparison exercise for methyl mercury and to submit them to ACMP for consideration at its meeting in June 1988.

P. Yeats

- to finalise the paper on methods for the collection of SPM and send it to the ICES Environment Officer.

W. Confino

- to liaise with S. Wilson (ICES) on the Baseline Study of Trace Metals in Coastal Waters.

- to act as a contact for the Chairman for matters connected with the Trace Metal Sub-group before the next meeting of MCWG.

S. Wilson

- to contact D. Schmidt in connection with the trace metal data he is compiling for the North Sea coastal areas.

- to update the Chairman on the progress of the review of the trace metal baseline data.

Organics Sub-group

R. Law

- to prepare a progress report on the specific hydrocarbon I/C exercise.

J. de Boer

- to liaise with J. Duinker and J. Calder on the CBs I/C exercise and, in collaboration with them, prepare a report on the progress of this work for the next meeting of MCWG.

J. Calder

- to contact IFREMER and circulate details of the proposed I/C exercise for CBs in dredged spoil.

J. Duinker

- to consider the preparation of a paper for MCWG 1989 on the atmospheric transport and deposition of CBs to the sea.

M. Ehrhardt

- to finalise the review on hydrocarbon analysis and prepare an executive summary for ACMP.

M.A.T. Kerkoff

- to arrange with colleagues the preparation of a paper on water quality modelling for the theme session at 1988 ICES Statutory Meeting.

L. Reutergårdh and D. Wells

- to prepare overviews on (a) planar molecules and (b) HCB and HCH in the marine environment.

All Sub-group members

- to supply relevant information for the above overviews.

Dr. Granmo

- to be approached to prepare a review of surface active agents in the aquatic environment.

Chemical Oceanography Sub-group

D. Kirkwood

- in collaboration with M Perttilä and A Aminot, to prepare samples of sea water for use in the I/C exercise for nutrients, organise details of this exercise and report results of these activities at MCWG 1989.

- in collaboration with W Schreurs, O Vagn Olsen and L Føyn, to exchange nutrient/hydrographic data in order to extend the trend analysis paper for nutrients.

Chairman

- to finalise 1988 MCWG report and submit a draft to sub-group chairmen and rapporteurs for comment and amendments.

- to submit copies of the above report to chairmen of WGEAMS and WGSATM in time for their respective meetings.

- to prepare an executive summary of the 1988 MCWG report and submit a copy to ACMP and to the Chairman of the Hydrography Committee. A copy of this report will be sent to all MCWG members.

- to prepare a report on matters arising at ACMP meeting in June 1988 and distribute it to all members of MCWG.

- to liaise with members on specific issues through the respective chairmen of sub-groups. For the 1988/89 period these will be:

  W. Cofino - Trace metals

  D. Wells - Organics

  S. Carlberg - Chemical oceanography

All members

- to consider the preparation of papers for the theme session on water quality modelling at 1988 ICES Statutory meeting.

- to keep the Chairman informed about all matters of relevance to MCWG either directly or through the respective sub-group chairman.

- Any member attending the third international symposium on reference materials at Bayreuth, May 1988, is urged to prepare a note on this meeting for presentation at the 1989 MCWG meeting.

## ANNEX 8

## RECOMMENDATIONS

### Recommendations to the Marine Environmental Quality Committee

Recommendation 1

The Marine Chemistry Working Group recommends that the report on the "Results of the Intercalibration Exercise on Analyses of Methyl Mercury in Biological Tissue", by Dr D. Cossa be published in the Cooperative Research Report Series.

Recommendation 2

The Marine Chemistry Working Group recommends that the "Report on an Intercomparison Study of the Determination of Polychlorinated Biphenyls (PCBs) Isomerids in Baltic Herring Oil" (6/OC/BT), by Dr L. Reutergårdh and Dr K. Litzén, be published in the Cooperative Research Report series.

Recommendation 3

The Marine Chemistry Working Group recommends that the papers "Techniques for the collection of SPM in sea water" by Dr P. Yeats and Dr L. Brügmann and "The Analysis of Organotin Compounds in Sea Water" by Dr A. Jensen be published in the Techniques in Marine Environmental Sciences series.

Recommendation 4

The Marine Chemistry Working Group recommends that all participants in intercomparison exercises organised and conducted by ICES Working Groups be sent a copy of the published report free of charge.

### Recommendations to the Advisory Committee on Marine Pollution

Recommendation 5

The Marine Chemistry Working Group recommends that

a) monitoring agencies be approached to consider the financing of the preparation and distribution of uncompromised reference materials to its laboratories as part of their commitment to quality assurance and good laboratory practice;

b) that monitoring agencies be approached to consider (1) the need for future intercomparison exercises and their types, and (2) the provision of the necessary finances for these exercises.

c) that monitoring agencies should ensure that their laboratories analyse representative materials on a regular basis, as part of their routine analyses, in order to provide an assessment of long-term variance for these analyses and to assist in the evaluation of trend monitoring data.

d) that when estimates are made of riverine or other fluxes to the marine environment, it is important to determine the reliability of such estimates and the confidence limits that can be placed on them for the following two reasons: (1) to show the range within which the best estimate lies, and (2) to determine those factors contributing most of the uncertainty in order to focus research to those areas and reduce the overall variability of the estimates.

## Recommendations to the Hydrography Committee

Recommendation 6

The Marine Chemistry Working Group recommends that an intercomparison exercise on determinations of nutrients in sea water be conducted according to the plans given in Annex 4, and coordinated by Dr D. Krikwood, with assistance by Dr M. Perttilä and Dr A. Aminot.

Recommendation 7

The Marine Chemistry Working Group recommends that measures should be implemented to stimulate and increase the reporting of oceanographic data to the ICES data bank, and protection of these date from inappropriate use, in order to encourage more ICES laboratories to contribute data to this data bank. In this context, it is proposed that:

a) Provision be made for the identification of the original institute, and possibly also the scientist associated with these data, rather than having the data be linked to country and research ship; and

b) Data should not be used, or distributed to, other bodies without the consent of the institute or individual responsible for the collection of the original data.

Recommendation 8

The Marine Chemistry Working Group recommends that further analysis of existing nutrient data for the North Sea and adjacent areas should be encouraged in relation to studies of temporal trends of nutrients.

Recommendation 9

The Marine Chemistry Working Group recommends that

a) the Working Group (Chairman: Dr G. Topping) meet for five days in February or early March 1989 at the Skidaway Institute of Oceanography, Savannah, Georgia, USA to carry out the following tasks:

   i) to review and report progress on the following intercomparison exercises:

      nutrients in sea water,
      CBs in marine samples,
      and selected hydrocarbons in marine samples;

   ii) to consider the results of the analyses of data from the Baseline Study of Trace Metals in Coastal and Shelf Sea Waters and prepare a final draft report;

   iii) to consider the review on hydrocarbon analysis in marine media and prepare an executive summary;

   iv) to review overviews on contaminants in the marine environment, particulary those on planar molecules and HCB and HCH;

   v) to continue the preparation of an overview on concentrations of nutrients and their temporal trends in the Oslo and Paris Commissions area.

b) a two-day meeting should be held (Convener: Dr W. Cofino) immediately prior to the next meeting of MCWG to complete the review of the baseline data for trace metals in coastal waters and to prepare a draft report on this exercise.