International Council for the
Exploration of the Sea

C.M.1994/ENV:1

REPORT OF THE MARINE CHEMISTRY WORKING GROUP

Brest, 7–12 February 1994

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EXECUTIVE SUMMARY

Thirty-two scientists participated in the meeting of the Marine Chemistry Working Group (MCWG) at IFREMER, Brest, France, from 7–12 February 1994. A number of colleagues from North America were unable to attend the meeting due to financial constraints. This problem might be alleviated if the meeting of the MCWG were held after 1 April, which is the beginning of the Canadian fiscal year. The MCWG decided to strongly recommend that its 1995 meeting take place after this date in order to have a wider attendance from North America.

The meeting was conducted in sub-groups. Five plenary presentations were given, two by invited experts. The presentations gave rise to lively discussions which were often continued in the sub-groups. Plenary presentations at the meeting are given high regard.

Results of NUTS 5 (C.Res 1993/2:7:1a)

The intercomparison exercise has been completed, and a draft report has been discussed. Nitrate analyses showed good reproducibility (3%), comparable to earlier exercises including NUTS 4. Nitrite analyses showed a reproducibility of 5-10%. Phosphate analyses showed a reproducibility of 5-15%, similar to earlier exercises including NUTS 4. Ammonia analyses showed a reproducibility of more than 20%. This was disappointing and indicates a general need for the improvement of laboratory techniques and procedures for this determination. The study of individual errors indicates that substantial improvements can be expected since systematic errors represent the major contribution to the inaccuracy. It was observed that the labs with the poorest performance in the present round had not participated in earlier exercises and that the labs showing the poorest performance in the previous exercise have improved. There is evidence that rapid staff turnover has a deleterious effect on results. Through the exercise, labs showing good performance have been identified, as well as a number of labs who need to examine their techniques in order to improve their performance.

The MCWG concluded that laboratories should be strongly encouraged to participate in interlaboratory studies, as they evidently contribute to improved performance, and that proper training and motivation of staff is more important than buying state-of-the-art equipment.

The efforts of A. Aminot and D. Kirkwood and the resources made available by IFREMER and Lowestoft Fisheries Laboratory are acknowledged. It is recommended that ICES publish the report in the *ICES Cooperative Research Report* series.

Results of Step 4 of the Intercomparison Programme on the Analysis of CBs in Marine Media (C.Res. 1993/2:7:1b)

A draft report was presented by J. de Boer. The results of the analysis of the seal oil showed for the group as a whole that acceptable values were obtained only for the major CBs 138, 153 and 180. Several individual laboratories produced acceptable data for most CBs. The same conclusion was made for the analysis of CBs 118, 138 and 153 in the sediment sample. The quality of the data obtained for these CBs guaranteed that a study by the same group of laboratories on CB concentrations in a certain matrix would enable a detection of 50% changes in these levels. But the Sub-group emphasized that this should not discourage the laboratories from analysing other CBs; improvement in the quality of the analysis of other CBs is desirable because information on their concentrations is very much needed for a better interpretation of CB levels, and especially of the toxicological impact of CBs.

A very important conclusion of the report was the need to improve long-term precision; laboratories should establish a better control, e.g., by a regular analysis of reference materials. Also, laboratories should pay more attention to the calibration of their GCs.

In the context of coordinated monitoring programmes, the results of the exercise showed also that laboratories as a group are in general not capable of obtaining, for the moment, comparable results in lean fish muscle tissue. The sub-group, however, emphasized that some individual laboratories are able to determine CBs in lean fish muscle tissue.

The comments were unanimous in considering it a very comprehensive and good report. The MCWG proposed that the final report be published in the *ICES Cooperative Research Report* series. Some members raised their concern about the long time it normally takes within ICES to publish these reports; as an example, the report on the latest intercomparison exercise on PAHs and that of the second step of the CB intercomparison have not been published three years after this was recommended by the ICES Statutory Meeting. Given the progress that is currently usual in the analysis of organic contaminants, a delay in the publication might render the information less useful. J. de Boer and the RIVO and J. van der Meer of NIOZ are acknowledged for the work and resources put into this programme.

Results of lipid determinations in Step 4 of the Intercomparison Programme on CBs in Marine Media (C.Res. 1993/2:7:1c)

A literature survey will be prepared on methods in use for the determination of lipid classes. This survey is considered essential for the planning of any other activity. A workshop on lipids will be held prior to the next MCWG meeting. Until the problems in the determination of lipids are solved, the current practice of expressing data in a wet weight basis in geographical and trend monitoring programmes should be maintained. The lipid content of the tissues analysed can be given in addition when the analytical method used is clearly specified.

Guidelines on the analysis of CBs in sediments (C.Res. 1993/2:7:1d)

A draft report had been prepared by F. Smedes and J. de Boer. Some amendments will be made. A timetable has been set up to ensure that the document will be finalized at the end of this year. The document will be sent to ICES and the Oslo and Paris Commissions for inclusion in the monitoring guidelines for sediments.

Progress on evaluation of trace metal in estuarine water data held in ICES data bank (C.Res. 1993/2:7:1e)

Progress was limited owing to the absence of key people due to financial constraints. The MCWG intends to set up a study on estuarine processes affecting metal behaviour and fluxes, and on models which can be used to evaluate and predict these processes and fluxes. To this end, a workshop will be held prior to the next MCWG meeting. The study is important for the design of monitoring programmes, for the estimation of the riverine input of metals into the sea, and for the methodology to compare the degree of contamination of different estuaries.

Information on level of comparability achieved in recent interlaboratory studies (C.Res. 1993/2:7:1f)

At the meeting, only information on ICES interlaboratory studies was present. This information is summarized briefly in this report, more details can be found in the reports on NUTS 5 and the CB intercomparison programme which will be forwarded to ICES and are to be published in the *ICES Cooperative Research Report* series.

Relationship between trace metals and lipids in biological tissues (C.Res 1993/2:7:1g)

The sub-group discussed a draft paper based on data from the ICES data bank on trace metals and co-factors. It was clear that a strong correlation exists between fat content and dry matter fraction, and that in fish liver trace metal concentrations on a dry weight basis correlate negatively with the dry matter fraction. On a wet weight basis, the correlation was randomly positive or negative, on average zero. The study suggests that normalization on the dry matter fraction would lead to a better resolution than current practices employing lipid contents.

The amended paper will be sent to the Working Group on Statistical Aspects of Environmental Monitoring which meets in Halifax in April 1994.

Progress in the interlaboratory study on non-ortho CBs in fish oil (C.Res 1993/2:7:1h)

Twenty-two members of the MCWG and associated laboratories agreed to participate in this exercise. The participants were asked to undertake the determination of three non-ortho (CB 77, CB 126, CB 169), and two mono-ortho (CB 105, CB 156) chlorobiphenyls and a reference chlorobiphenyl (CB 153). A minimum of three and a maximum of six determinations were requested, with sufficient time in between to obtain an idea of long-term variability. Only 8 labs returned their results. This produced a rather limited set of data, but the results were quite satisfying and permitted some interpretations to be made. Based on these results, an additional separation step could be recommended. Distinct differences were also observed between the group using saponification and the group using sulphuric acid treatment. There was some discussion in the sub-group on this subject, but no decisive conclusions were possible. The sub-group recognized the need for further development and evaluation of the methods and the need for suitable reference materials. Work in this field is currently being undertaken by the Measurement and Testing Programme of the European Commission. ICES laboratories participating in this project are asked to present the results at the next MCWG meeting, subject to the agreement of the EC. The sub-group recommended that ICES subsequently undertake an intercomparison exercise to establish the necessary interlaboratory precision, before undertaking monitoring of non-ortho chlorobiphenyls. By that time, a non-compromised standard solution might be made available by the U.S. NIST to initiate the first step of the exercise.

Progress on investigations of similarities in patterns of CBs in marine species (C.Res 1993/2:7:1i)

The project investigating similarities in patterns of CBs in marine species is proceeding well and according to plan. A project report will be finalized during 1994 and can be presented at the 1995 MCWG meeting.

Progress in the investigation regarding differences in CB patterns between different species of marine mammals

Prior to the MCWG meeting in Brest, a workshop at Texel in the Netherlands was organized by J. Boon, Netherlands Institute for Sea Research, on CB patterns in sea mammals. Data on the concentrations of various CB congeners in the blubber of marine mammals and in their diet, obtained from data sets present at the participants' laboratories, were available. The ratio between each CB congener and the reference congener CB 153 was calculated. The results were compared in order to detect differences in the metabolic capacities of the animals. Together with data on terrestrial organisms (otters), in total data from more than 200 animals were used. Single congeners analysed by all laboratories that submitted data were selected as representatives of different metabolic groups. Plots of CB ratios for different marine and terrestrial mammals showed a very good correlation between data from the different laboratories. Metabolic activity of certain CBs, depending on the number of vicinal atoms present in a phenyl ring, their location at the phenyl ring and the number of ortho-chlorine atoms present could be clearly indicated. It was shown that ratios between potentially metabolizable CBs and CB 153 in marine mammals showed relatively wide margins, which means that a significant correlation between different CBs and CB 153, as observed in fish, is not present in marine mammals. Observations on the metabolic capacity of marine mammals can be useful for information on the condition of the animal as well as for the identification of genetic differences between animals of one species. J. Boon will present a full report of this study at the next MCWG meeting, after a second workshop has been held on this subject at which a further evaluation of the data will take place.

Review notes (C.Res. 1993/2:7:1k)

The MCWG assessed review notes on 3,3'-dichlorobenzidine, chlorinated alkanes, monocyclic aromatic hydrocarbons, natural marine toxins, toxaphene and modern pesticides. The papers on 3,3'-dichlorobenzidine, natural marine toxins and toxaphene will be sent to ACME after minor amendments.

The papers on chlorinated alkanes, monocyclic aromatic hydrocarbons and modern pesticides will be modified and discussed at the 1995 MCWG meeting.

The MCWG recommended that ICES contact the MTP of the EC to discuss the progress in developmental work on natural marine toxins, with a view to supporting their efforts within key laboratories.

It is planned to have new review notes on organotin, methyl-mercury and data management systems for chemicals transported over the sea at the next meeting.

Integrated study to examine processes of pollutant transfer and effects on biota (C. Res. 1993/2:7:8)

The MCWG underlined the importance of a study as outlined by A. Stebbing and had the opinion that it is very worthwhile to attempt to realize this project. It emphasized that a thorough planning is necessary, involving scientists with different disciplines from the design of the programme onwards. J. Boon agreed to act as representative of the MCWG in the initiating group, chaired by A. Stebbing, and will inform and possibly involve MCWG members as the programme develops.

ICES data bank on contaminants in sea water

J.R. Larsen requested the MCWG to evaluate the scientific value of this data bank and to advise whether the ICES Secretariat should continue to maintain the database. The MCWG recommended that ICES maintain the data base on contaminants in sea water. It recommended that ICES ask a small group of interested scientists to make an assessment of the current data.

The discussion on this topic raised the question as to whether an ICES Baseline Study on Contaminants should be organized in the near future. It was agreed to put this item on the agenda for the next meeting.

Additional quality assurance information to be included in the ICES data bank (JMG request)

The MCWG restated the need for an integrated QA programme associated with the monitoring programme. Specific items are:

1. Monitoring should not commence until RMs are available and a proficiency testing programme in place. Target values for these RMs could be set by a small number of expert laboratories. These RMs should be matrix matched.
2. Participating laboratories should supply information on CRMs used (also certified calibration solutions), including target and measured values, with all data. It is recommended to include all pertinent reference materials in the NOAA/IOC compendium along with matrix and analyte information in the ICES database. This is the most comprehensive and updated listing of RMs available.

3. Monitoring agencies should supply participating laboratories with blind samples and the laboratory should make data on the long-term precision available.
4. Laboratory data should include traceability of any internal reference material to a certified reference material or to a recent intercomparison exercise.
5. Information on and results of recent relevant intercomparison exercises (e.g. QUASIMEME, NOAA) should be listed in the database.
6. Quality assurance information should include data on analyses of normalizing parameters and on sampling and storage procedures.
7. Information should be present on the sample workup (digestion, extraction, etc.) and the detection method.
8. Copies of relevant quality control charts are not needed if all the other QA data are submitted.
9. ICES should not accept results expressed as technical mixtures or the sum of CB congeners.
10. Laboratories should maintain adequate storage and retrieval systems for QA and monitoring data.
11. Monitoring agencies should provide clear guidelines for the QA assessment of data.

Advice regarding organic contaminants that can be monitored on a routine basis in biota and/or sediments (JMG request)

In response to a request of the JMG, the MCWG considered organic contaminants which might be monitored in the future in biota and/or sediments. Taking environmental relevance and analytical capabilities into account, the assessment resulted in the following table.

Organic Contaminant	Recent I/C data available	QC material available	Laboratories capability
1. Chlorobiphenyls "ICES" 7 plus CBs 31, 105 and 156 (see note below)	Yes - sediment Yes - fatty tissue ? - lean tissue	CRMs (SRMs) and LRMs. Certified standards available	Most
2. Toxic CBs 77, 126 and 169	Yes - fatty tissue	Yes - in the near future	Some specialist laboratories
3. Organochlorine pesticides	Yes - fatty tissue Yes - sediment	CRMs (SRMs) available for some pesticides	Most
4. PAHs (ICES list of 10) (sediments and shellfish)	Yes - sediment	CRMs in sediment	Many
5. Dioxin/Furans	Yes (WHO)	Yes	Good for specialist laboratories
6. CHBs (toxaphene)	Validated methods required	RMs required	A few specialist laboratories
7. Organotin	Validated methods required	CRM - biota	A few specialist laboratories
8. Methyl mercury	Validated methods required		A few specialist laboratories
9. Polychlorinated naphthalenes	Validated methods required	CRMs needed	A few specialist laboratories
10. Chlorinated paraffins	Validated methods required	CRMs needed	A few specialist laboratories

The usefulness of biomarkers to detect many of these organics was recognized. The MCWG strongly supports the continued use and development of these techniques in future monitoring programmes.

Note:

Additional comments to the table by the coordinator of the ICES/IOC/OSPARCOM CB intercomparison exercises:

1) State-of-the-art of CB analysis

After final step 4 of the ICES/IOC/OSPARCOM CB intercomparison study the following can be concluded on the state-of-the-art of CB analysis of the 43 participating laboratories in this study:

a) Marine sediment

The group of laboratories is able to detect 50% differences between two samples for the CB congeners 188, 138 and 153. This refers to the analytical error and does not consider the natural variation.

A number of individual laboratories is able to detect smaller differences and is also able to detect 50% differences between two samples for the CBs 28, 31, 52, 101, 105, 156 and 180.

b) Sea oil

The group of laboratories is able to detect 50% differences between two samples for the CB congeners 138, 153 and 180. This refers to the analytical error and does not consider natural variation.

A number of individual laboratories is able to detect smaller differences and is also able to detect 50% differences between two samples for the CBs 52, 101, 105, 156 and 180. No laboratories are able to determine accurately the CBs 28 and 31. This is due to the high degree of metabolism for these CBs in seal.

c) Wet lean fish tissue

Although some individual laboratories seemed to be able to produce acceptable results for the analysis of the CBs 28, 31, 52, 101, 105, 118, 138, 153, 156 and 180 in wet lean fish tissue, the group of laboratories is not able to do so. The problems in the analysis of this type of matrix are related to the extraction. Solutions for this problem are likely to be found in the near future. For more fatty fish tissue the situation is expected to be better, but exact figures cannot be given because information on the extraction of wet fatty tissue is not available.

2) Degree of comparability in CB analysis
Standard deviations for the reproducibility obtained after the 4th step of the ICES/IOC/OSPARCOM CB intercomparison exercise:

a) Marine sediment

CBs 188, 138, 153	1.15 - 1.17*
CBs 28, 31, 52, 101, 105, 156, 180	1.21 - 1.33

b) Seal oil

CBs 138, 153, 180	1.12 - 1.16
CBs 52, 101, 105, 118, 156	1.20 - 1.65
CBs 28, 31	2.28 - 4.81

c) Wet fish tissue

CBs 101, 118, 138, 153, 180	1.57 - 1.68
CBs 28, 31, 52, 105, 156	1.93 - 3.84

*:1.17: standard deviation (SR), can roughly be read as 17%; an SR of 1.17 corresponds with a reproducibility (R) of 1.53 (roughly 53%).

1 OPENING OF THE MEETING

The Chairman, W. Cofino, opened the meeting at 10.00 hrs on 7 February 1994. Dr G. Pautot, Director of IFREMER Centre de Brest, welcomed the participants.

Working Group members introduced themselves and briefly described their main area of research interests and responsibilities in the field of marine chemistry. Apologies for absence were received from P. Yeats, T. Packard, B. Jansson, U. Harms, G. Weichart and L. Føyn. The MCWG noted with concern that members from North America were not able to attend the meeting owing to budget constraints. These problems might be less severe if the meeting were to be held after 1 April (the fiscal year in Canada ends in March). The MCWG concluded that it should attempt to have the meeting in April instead of February in order to have a greater chance that the North American colleagues could be present.

The list of participants is given in Annex 1 of this report.

2 ADOPTION OF THE AGENDA

The MCWG adopted the agenda distributed by the Chairman. The agenda is provided in Annex 2.

Plenary presentations were scheduled for 8 February (A. Aminot, J. de Boer and J. van der Meer) and 9 February (K. Delbeke, on invitation, A. Aminot and F. Galgani, on invitation).

The work was carried out in three sub-groups. The members and guests were grouped as follows:

Chemical Oceanography Sub-group:
S. Carlberg (**Chairman**)
A. Aminot, D. Kirkwood, M. Krysell, J. Olaffson and O. V. Olsen;

Trace Metals Sub-group:
P. Yeats/B. Pedersen (**Chairmen**)
G. Asmund, S. Berman, V. Beseda, W. Cofino, M. Leivuori, J. Olafsson, S. Westerlund

Organic Sub-group:
D. Wells (**Chairman**)
A. Abarnou, J. Biscaya, J. de Boer, J.P. Boon, S. Einarsson, M. Cleemann, K. Delbeke, H. Kankaanpää, J. Klungsøyr, J.R. Larsen, R.J. Law, E. Nixon, T. Nunes, R. Parris, P. Roose, J. van der Meer, J. Tronczynski, W. de Waal

3 REPORT OF THE 81ST STATUTORY MEETING

The Chairman informed the participants that all of the tasks requested for consideration by the MCWG at the 1993 Statutory Meeting were incorporated in the draft agenda.

4 REPORT OF RELATED ACTIVITIES

4.1 Joint Monitoring Group of OSPARCOM

S. Carlberg, Vice Chairman of JMG, chaired a meeting of the JMG Ad Hoc Working Group on Monitoring (AHWGM) in November 1993. At this meeting, two recommendations were accepted which are relevant for the MCWG:

- (AHWGM recommendation, 4.26.f)
  "that ICES be given the task of drawing up a list of those organic contaminants which can be monitored in biota and sediments on a routine basis, taking into account their environmental relevance and state of the art in analytical chemistry and quality assurance, and to define the necessary analytical performance characteristics;"
- (AHWGM recommendation, 4.26.g)
  "that ICES be requested to include additional quantitative quality assurance information in the ICES data base, covering for example, the composition of relevant reference materials, consensus values in intercomparison exercises, results submitted to intercomparison exercises and other appropriate data."

S. Carlberg noted that task 4.26.f represents a joint effort for MCWG and WGBEC, while 4.26.g is a task MCWG has to deal with. The JMG accepted these recommendations at its meeting in Dublin (24–28 January, 1994) and will request ICES for assistance. Formally, the MCWG should have this matter on its agenda in 1995. S. Carlberg emphasized the need for a rapid response and requested the MCWG to start to consider these items at the present meeting. The AHWGM recommendations were, therefore, included in the agenda.

4.2 Intergovernmental Oceanographic Commission (IOC)

Information concerning IOC activities was not available at the meeting, nor was an IOC representative present. The MCWG acknowledged the importance of good links with IOC. The MCWG requested its Chairman to seek contact with the IOC in order to restore communications.

4.3 ICES

4.3.1 ACME

The ACME decided that for each working group reporting to ACME, one ACME member will serve as the primary contact person and one or several members will serve as secondary contact person(s). The primary ACME contact person will provide assistance to the working group to understand the basis for the tasks that ACME requests of it, attend the meeting of the working group if possible, and obtain a copy of the draft report as soon as it is available to be able to begin preparing for the ACME meeting. The secondary contact person(s) will assist in these duties to the extent needed. The ACME intends with this approach to enhance its effectiveness. Individual members will be responsible for a detailed understanding of the work of a specific working group and its translation into draft sections of the ACME report. The ACME also hopes that this procedure will assist the working groups in better understanding the work requested of them by ACME.

S. Carlberg and J. Olafsson have been appointed, respectively, as the primary and secondary ACME contact persons.

4.3.2 Integrated Study of Pollutant Transfer and Effects on Biota

Dr Stebbing has been given the task of chairing a Steering Group on Integrated Study of Pollutant Transfer and Effects on Biota (C.Res.1993/2:7:8). This group is to

a) review existing data describing processes of pollutant transfer and effects on biota in the North Sea, based among others on the results of the Bremerhaven workshop;
b) consider relevant chemical and physical data (via ICES or informal contacts) which may affect contaminant distributions on a seasonal basis;
c) taking the above information into account, prepare a proposal for an integrated study to examine processes of pollutant transfer and effects on biota, for consideration by the WGBEC and WGMS at their next meetings.

The Steering Group should be composed of members of WGBEC, WGMS and MCWG which would work in the initial phases via correspondence. A discussion paper has been prepared by Dr Stebbing. The MCWG was requested to give its opinion on the present proposal and to provide advice. In addition, MCWG is requested to appoint a representative to the Steering Group. This item has been incorporated into the agenda of all sub-groups.

4.3.3 ICES database on contaminants in sea water

The ICES Environmental Data Scientist, J. R. Larsen, gave a short introduction to the sea water data presently held in the ICES Environmental Data Bank. The Data Bank holds data from 12 countries, collected in the period 1977-1992 and comprises approximately 20000 records. The question was raised as to whether the ICES Secretariat should continue to maintain this database and to receive new data. The group was requested to evaluate the scientific value of this type of data. This item was put on the agenda of all sub-groups.

4.4 The EC Measurements and Testing QUASIMEME Project

D. Wells presented the results of the first year of the QUASIMEME project. Interlaboratory studies dealing with metals in sediments, PCBs in fish oil and nutrients in sea water have been organized. The results were discussed at a Workshop in Portugal. At this workshop, seminars were also organized dealing with analytical methodology, sampling and quality management. A report containing the results of the interlaboratory studies will appear in March 1994. The proceedings of the Workshop will be published in May 1994. A special issue of Marine Pollution Bulletin will appear in September 1994.

At present, interlaboratory studies on trace metals in biological tissue, PCBs in sediments and PAHs are (or will be) organized. A start has been made with a proficiency testing programme on trace metals in sediments and PCBs in fish oil. The QUASIMEME project will expand its activities to sampling and sample preservation.

4.5 Quality Assurance in the Baltic Sea

J.R. Larsen gave a short update on the Quality Assurance projects in the Baltic Sea.

4.6 Other Activities

No issues were raised under this heading.

5 REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES

The Chairman informed the Group that no matters had been raised by members under this agenda item.

6 REQUESTS FROM ACME AND REGULATORY AGENCIES

The Chairman informed the Group that all requests had been incorporated into the agenda.

7 PLENARY PRESENTATIONS

Five presentations were given in plenary:

J. de Boer, J. van der Meer
The intercomparison programme on the analysis of CBs in marine media: where are we after four years of exercises?

A. Aminot, D. Kirkwood
The NUTS 5 interlaboratory study.

K. Delbeke (on invitation)
Associations between lipids and PCBs.

A. Aminot
Phosphorus speciation in particles and sediments in coastal and estuarine areas.

F. Galgani
Biological effects monitoring.

The presentations gave rise to lively discussions which were often continued in the sub-groups. The MCWG thanked all lecturers for their excellent presentations. The MCWG was particularly grateful to Dr Delbeke who specifically came to the meeting from Belgium to present her work and to take part in the discussions.

8 SUBGROUP ACTIVITIES AND DISCUSSIONS

8.1 Trace Metal Sub-group

8.1.1 Report on the progress in the evaluation of data held in the ICES data bank on trace metal concentrations in estuaries

P. Yeats has been working intersessionally on the available estuarine data. The primary sources of these data are the ICES data bank and data submitted by the Rijkswaterstaat, J-P. Chiffoleau, J.P. Mommaerts (MUMM, Belgium), P. Balls, S. Westerlund and by himself. These data cover many types of estuaries ranging from contaminated to rather pristine areas. A preliminary evaluation revealed that the characteristics of the estuaries, and consequently the relative importance of the processes by which the metals are released and transported from fresh water to the ocean, differ significantly. The sub-group had the impression that most studies deal with one or only a limited number of estuaries. In a number of cases, models have been constructed to evaluate and predict metal behaviour. It appears that such models have been validated to a limited extent for a single estuary. At present, no sufficient insight is available concerning the general validity or transferability of models. A good understanding of processes in estuaries and the performance and parametrization of models is highly important in order to plan improved estuarine monitoring programmes and to evaluate their results. It was concluded that the dataset has much potential with regard to obtaining a better understanding of estuarine processes and forms, in principle a good basis to test models. The item was also discussed with the Chemical Oceanography Sub-group, as the subject is also of interest to this group. It was decided that the members of the Chemical Oceanography Sub-group, as a first step, would try to find data sets, models and other relevant knowledge which give insight in nutrient behaviour and which would contribute to enhanced understanding of metal-nutrient relationships.

It was agreed that it should be attempted to establish a study along the lines described above. To this end, it is proposed to arrange a workshop on this subject including experts from different areas (e.g., P. Balls, J-P. Chiffoleau, W. Cofino, S. Westerlund, P. Yeats). The objectives of the workshop include the characterization of estuaries, the assessment of processes which are important in transporting metals to the ocean in the different types of estuaries, and the evaluation of different models to study estuarine processes and fluxes. The workshop could form the inception of a study which could be important for the design of monitoring programmes, for the estimation of riverine inputs to the open sea areas, and for the development of methodology for comparing the degree of contamination of different estuaries. The workshop should be arranged before the next MCWG meeting. W. de Waal agreed to look into the possibilities of making a Dutch model available to the group and arranging a plenary lecture by a Dutch expert on modelling metal behaviour and metal fluxes in estuaries. The outcome of the workshop will be presented at the 1995 MCWG meeting.

8.1.2 Study on the relationship between trace metal concentrations and lipid contents in biological tissues

The sub-group discussed a draft paper based on data from the ICES data bank on trace metals and co-factors. It was clear that a strong correlation exists between the fat content and the dry matter fraction, and that in fish liver trace metal concentrations on a dry weight basis correlate negatively with the dry matter fraction. On a wet weight basis, the correlation was randomly positive or negative, on average zero. The study suggests that in livers with high trace metal concentrations, normaliz-

ation on the dry matter fraction would lead to a better resolution than practices employing lipid contents.

The sub-group asked the authors to rewrite the draft paper, with the inclusion of the sub-group comments, and then convey it to the Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM) which meets in St. John's in April.

The sub-group requested the WGSAEM elaborate further on the model used in the draft report (a log/log model) and to see whether the model should be different for different metals and fish species. Before the statisticians start this work, J. Larsen, B. Pedersen and G. Asmund will do some further work with the data, including checking the data bank and identifying which data sets can be used for the study.

The importance of a reliable analytical method for lipids was stressed by the sub-group; it was felt that this problem is still unresolved. The sub-group further discussed the possibility that some of its members could measure the distribution of metals between the water phase and the lipid phases in fish liver, and investigate whether differences in the different fat fractions can explain some of the variability in the metal content of fish liver.

8.1.3 Information on the level of comparability among participating laboratories in the most recent intercomparison exercises

No information from recent interlaboratory studies was available at the meeting. The Trace Metal Sub-group suggested that the pertinent data be extracted from the QUASIMEME report for trace metals in sediments and the most recent annual NOAA report for trace metals in marine sediments and biota.

The data from both exercises have been treated in a different manner. S. Berman has agreed to attempt to rationalize the results so that the two exercises might be directly compared. The problem arising from total and partial decomposition methods should be noted and commented upon. The significance of the reported variances with regard to the resolution of spatial distribution studies also needs to be discussed.

8.1.4 Consider an integrated study to examine processes of pollutant transfer and effects on biota

The proposal for a project in the North Sea area, presented by Dr Stebbing, was discussed. The background for this agenda item was explained briefly, particularly the Bremerhaven studies by W. Cofino.

The sub-group agreed that the project in the North Sea area is very important, but very broad and needs experts in many fields, e.g., atmospheric deposition, biological and chemical processes, suspended particulate materials, modelling, etc. The discussion tended towards a multinational main project over a number of years which includes several sub-projects in specific fields. Such a project could be carried out as a cooperative research project, provided that the contribution of each participant fits within their present or foreseen research projects. Alternatively, funding from, e.g., the EC (the MAST project) might be possible. It was acknowledged that this is a long-term project needing a lot of work.

The sub-group noted similarities between this project and the Arctic Monitoring and Assessment Programme, including similar experts groups.

The sub-group did not immediately find any possible ongoing projects in their own fields which could join this project, but in some countries there might be other institutes to join it. The proposal will be presented in the other ICES working groups (the Sediment Working Group and the Biological Effects Working Group) for further handling.

No specific activities are planned under this agenda item for the forthcoming year.

8.1.5 Additional quality assurance information to be included in the ICES data bank

In response to AHWGM recommendation 4.26.g, with respect to Annex 9, the Trace Metals Sub-group suggested that :

1. Both the digestion and the detection method used should be noted.

2. Storage and sampling information should be included for all samples.

3. All pertinent reference materials in the NOAA/IOC compendium along with matrix and analyte information should be included in the database. This is the most comprehensive and updated listing of RMs available.

4. Information and results of recent relevant intercomparison exercises (e.g., QUASIMEME, NOAA) should be listed in the database.

5. Laboratory data should include traceability of any internal reference material to a certified reference material or to a recent intercomparison exercise.

6. Quality assurance information should include data on analyses of normalizing parameters.

7. Copies of relevant quality control charts are not needed if all the other QA data is submitted.

8.1.6 Review new contaminants, and determine where reviews or overviews would be warranted

S. Westerlund will ask a colleague to prepare a review on CH_3Hg (an updated review of new literature since the last ICES review on Hg). S. Westerlund emphasized that he could not guarantee that his colleague would actually take this task upon him.

S. Berman raised the question about speciation of metals, e.g., Cu, Ni, As, Cr in relation to different standards. The free metal ion is regarded as the most toxic. In the future, it will probably be necessary to determine the ionic species in water, effluents, etc. The speciation measurements will undoubtedly be of interest for marine studies. These ideas, although not new, are now being considered for actual regulations in the US. S. Berman and B. Pedersen will prepare a discussion paper for the next MCWG meeting about the need for establishing methods for speciated metals like Cu, Ni, As, Cr in sea water. In addition, S. Berman and B. Pedersen will attempt to invite an expert to present a plenary lecture on this topic at next year's MCWG meeting.

8.1.7 Evaluate the scientific reasons for ICES to continue to maintain a data base on contaminants in sea water

The sub-group stated that there will be a growing interest in estuarine and coastal sea water data. The interest will be for scientific as well as for monitoring purposes. The sub-group noted in particular that the Commissions have demonstrated a growing interest in estimating inputs of contaminants. Estuaries are important areas of trace metal activity. The concentration of the contaminant and the water flow in a river are insufficient to calculate the amount of contaminant actually reaching the sea. To estimate the load from rivers, the geochemical fate of metals in estuaries must be known. This implies that both the dissolved as well as the particulate phase should be analysed and the results maintained in a data base. Another aspect of monitoring is the growing interest in effects studies. For effects studies on, for instance, algae, information on concentrations of contaminants in sea water is indispensable.

It was emphasized that data quality had increased over the last ten years. Experience gained during international intercomparison exercises suggests that the quality of data sampled after 1985 has reached a level where these data could be considered as reliable. However, data collected before 1985 should still be maintained.

The feasibility of conducting an intercomparison exercise was discussed and it was noted that the necessary reference material exists and is available. This topic is dealt with under a separate agenda item.

Finally, the sub-group felt that the long series of observations on metals in sea water deserved to be assessed. It was pointed out that the last assessment was done in 1990, and covered data from the period 1985-1987. This assessment did not include estuaries due to unresolved problems with the metals/salinity relationships. A well-structured database with reliable information could be helpful in addressing this question.

8.1.8 Any other business

The need for a new intercalibration on trace metals in sea water was discussed. Obviously, many laboratories analyze sea water for trace metals, as judged by the increasing interest in sea water reference material. The measurements are not part of monitoring programmes. The last ICES intercomparison exercise on trace metals in sea water was performed around 1987. The sub-group recommended that ICES conduct a new interlaboratory study on metals in sea water paid by the participants. If ACME adopts this recommendation, S. Westerlund will send out a letter to potential participants in an intercomparison study with a question about their interest in an intercomparison, and a question about which elements could be of interest. S. Westerlund is the contact person.

The sub-group decided to request P. Yeats to act intersessionally as chairman.

8.2 Organic Sub-group

8.2.1 Report on the results of step 4 of the intercomparison programme on the analysis of CBs in marine media

The draft report on the results of Step 4 of the ICES/IOC/OSPARCOM Intercomparison Programme on the Analysis of CBs in Marine Media (J. de Boer and J. van der Meer, MCWG 94 8/2/1), presented by J. de Boer in Plenary Session, was reviewed by the Sub-group. The Chairman opened the discussion by recalling the presentation in plenary of the report, and pointing out the quantity and detail of the information obtained from this step of the exercise. The comments were unanimous in considering it a very comprehensive and good report. The Sub-group proposed that the final report be published in the *ICES Cooperative Research Report* Series. Some members raised their concern about the long time it normally takes within ICES to publish these reports; as an example, the report on the latest intercomparison on PAHs and that of the second step of the CB intercomparison have not been published three years after this was recommended by the ICES Statutory Meeting. Given the progress that is currently usual in

the analysis of organic contaminants, a delay in the publication might render the information less useful.

As in previous years, it was decided that editorial comments raised by members of the Sub-group should be sent to J. de Boer for inclusion in the final report before its submission for publication by the beginning of March 1994.

A very important conclusion of the report is the need to improve long-term precision; laboratories should establish a better control, e.g., by a regular analysis of reference materials. Also, laboratories should pay more attention to the calibration of their GCs.

The results of the analysis of the seal oil showed for the group as a whole that acceptable values were obtained only for the major CBs, 138, 153 and 180. Several individual laboratories produced acceptable data for most CBs. The same can be said about the analysis of CBs 118, 138 and 153 in the sediment sample. The quality of the data obtained for these CBs guaranteed that a study on CB concentrations by the same group of laboratories in the same matrices would enable a detection of 50% changes in these levels. But the Sub-group emphasized that this should not discourage the laboratories from analysing other CBs; improvement in the quality of the analysis of other CBs is desirable because information on their concentrations is very much needed for a better interpretation of CB levels, and especially of the toxicological impact of CBs.

In the context of coordinated monitoring programmes, the results of the exercise showed also that currently laboratories as a group are not capable of obtaining comparable results in lean fish muscle tissue. The subgroup, however, emphasized that some individual laboratories are able to determine CBs in lean fish muscle tissue.

The Sub-group thanked J. de Boer for the good, comprehensive report and for the work done. J. de Boer in his turn thanked the Sub-group members and the participants for their support given throughout this intercomparison exercise. J. de Boer said that a report on the overall assessment of the results of the exercise would be prepared, due to the great interest in the data and information generated. He had the intention of making this report for the next MCWG meeting.

It was also stressed that this exercise could be a very good example of the improvement of the analytical quality of determinations of other contaminants, especially complex mixtures.

8.2.2 Review of the results of lipid determinations in step 4 of the Intercomparison Programme on Analysis of CBs in Marine Media with a view to determining the need for conducting an intercomparison exercise on lipid determinations

This agenda item was treated with a broader view than only from the results of step 4 of the Intercomparison Programme on Analysis of CBs in Marine Media. This was largely a result of the highly relevant plenary lecture given by K. Delbeke just before the meeting of the subgroup. Her very thorough approach towards this subject clearly illustrated the pros and cons of different important methods in use for the extraction of lipids and for the extraction of hydrophobic organic compounds. An important additional problem is the restriction of the use of chlorinated solvents in some countries in the near future. The Sub-group decided that a thorough literature survey of methods in use for the determination of lipid classes is necessary before any intercalibration exercise on this subject is feasible. The following people were asked to supply information: A. Abarnou, W. de Waal, P. Roose, K. Delbeke, R. Parris, D. Wells and J. Boon. It was agreed that a workshop on lipids should be held prior to the next MCWG meeting. D. Wells and K. Delbeke will organize this workshop.

Until the problems in the determination of lipids are solved, the current practice of expressing data on a wet weight basis in geographical and temporal trend monitoring programmes should be maintained. The lipid content of the tissues analysed can be given in addition when the analytical method used is clearly specified.

8.2.3 Report on guidelines for the determination of chlorobiphenyls in sediments

A report had been prepared by F. Smedes and J. de Boer and was presented by the latter. The report contained quite substantial guidelines on how to analyse sediments for CBs. Several methods for extraction, clean-up, analysis and quality assurance were described. The report did not intend to give a rigid description of a method, but rather offered a number of possibilities for the determination of CBs together with critical remarks on less reliable methods. Several comments and contributions to the report were made. A plan for the finalization of the report was made with a timetable attached. J. Boon, J. Klungsøyr, R. Law, P. Roose, J. Tronczynski, and D. Wells will send contributions to J. de Boer before the end of May 1994. The Working Group on Marine Sediments in Relation to Pollution will be requested to provide comments, also. An updated version of the report will be prepared and sent to the people who have contributed to the report in September for peer review within six weeks. The finalized report

will be forwarded to the MCWG meeting in 1995 for information and sent to ICES and the Oslo and Paris Commissions for inclusion in their monitoring guidelines for marine sediments.

8.2.4 Provide for the contaminants currently monitored information on the level of comparability achieved among participating laboratories in the most recent relevant intercomparison exercise

Information on the level of comparability achieved among participating laboratories in recent intercalibration exercises can be found under agenda items 8.2.1, 8.2.12 and in the draft report on the results of the ICES/IOC/OSPARCOM Intercomparison Programme on the Determination of Chlorobiphenyl Congeners in Marine Media - Step 4.

8.2.5 Report on the progress in the intercomparison programme on non-ortho CBs in fish oil

At the 1993 MCWG meeting, it was agreed to undertake an informal pilot study on the determination of non-ortho and mono-ortho chlorobiphenyls in biota. Present members of the MCWG and any known associated laboratories were invited to participate in the exercise. Participating laboratories were asked to undertake the determination of three non-ortho (CB 77, CB 126, CB 169), and two mono-ortho (CB 105, CB 156) chlorobiphenyls and a reference chlorobiphenyl (CB 153). A minimum of three and a maximum of six determinations were requested, with sufficient time in between to obtain an idea of long-term variability. A total of 22 labs agreed to participate but only 8 labs returned their results. This produced a rather limited set of data, but the results were quite satisfying and permitted some interpretations to be made.

Based on the results, an additional separation step could be recommended. Distinct differences were also observed between the group using saponification and the group using sulphuric acid treatment. There was some discussion in the Sub-group on this subject, but no decisive conclusions were possible.

Regrettably, no information was available on the results obtained in the previous intercomparison exercise by L. Reutergårdh. The chairman of the MCWG was requested by the Sub-group to contact Prof. B. Jansson to request that the results be made available for the next MCWG meeting. The Sub-group recognized the need for further development and evaluation of the methods and the need for suitable reference materials. Work in this field is currently being undertaken by the Measurement and Testing Programme of the European Commission. ICES laboratories participating in this project are asked to present the results at the next MCWG meeting, subject to the agreement of the EC. The Sub-group recommended that ICES subsequently undertake an intercomparison exercise to establish the necessary interlaboratory precision, before undertaking monitoring of non-ortho chlorobiphenyls. By that time a non-compromised standard solution might be made available by the U.S. NIST to initiate the first step of the exercise.

8.2.6 Report on progress in the project investigating similarities in patterns of CBs in marine species

B. Jansson was unable to attend the MCWG meeting. He informed the group in writing that the project to investigate similarities in patterns of CBs in marine species is proceeding well and according to plan. A project report will be finalized during 1994 and can be presented at the 1995 MCWG meeting.

MCWG members are encouraged to forward information on this subject to B. Jansson.

8.2.7 Report on progress in the project investigating differences in CB patterns between different species of marine mammals

A workshop was organized by J. Boon, Netherlands Institute for Sea Research, on CB patterns in sea mammals at Texel in the Netherlands (2–4 February 1994), prior to the MCWG meeting in Brest. Preliminary results of this workshop were presented by J. Boon at the MCWG meeting. J. Klungsøyr, R. Law, D. Wells, and J. Boon participated in this workshop, together with P. Leonards of the Institute for Environmental Studies, Amsterdam, C. McKenzie of SOAFD, Aberdeen and C. Allchin of MAFF Burnham-on-Crouch. Data from J. Uthe Skaare (Veterinary Institute, Oslo) were also included in the data base.

Data on the concentrations of various CB congeners in the blubber of marine mammals and in their diet, obtained from data sets present at the participants' laboratories, were available. The ratio between each CB congener and the reference congener CB 153 was calculated. The results were compared in order to detect differences in the metabolic capacities of the animals (Boon, J.P., Oostlingh, I., van der Meer, J., and Hillebrand, M.T.J. 1994. A model for the bioaccumulation of chlorinated biphenyl congeners in marine mammals. Eur. J. Pharmacol. Section Environ. Toxicol. Pharmacol. (in press, expected March 1994). Together with data on terrestrial organisms (otters), in total data from more than 200 animals were used.

Single congeners analysed by all laboratories that submitted data were selected as representatives of different metabolic groups. Plots of CB ratios for different marine and terrestrial mammals showed a very good correlation

between data from the different laboratories. Metabolic activity of certain CBs, depending on the number of vicinal atoms present in a phenyl ring, their location at the phenyl ring, and the number of ortho-chlorine atoms present could be clearly indicated. It was shown that ratios between potentially metabolizable CBs and CB 153 in marine mammals showed relatively wide margins, which means that a significant correlation between different CBs and CB 153 as observed in fish (Boer, J. de, Stronck, C.J.U., Tracey, W.A., and van der Meer, J. 1993. Non-ortho and mono-ortho substituted chlorobiphenyls and chlorinated dibenzo-p-dioxins and dibenzofurans in marine and freshwater fish and shellfish from the Netherlands. Chemosphere 26:1823–1842.), is not present in marine mammals.

Observations on the metabolic capacity of marine mammals can be useful for information on the condition of the animal as well as for the identification of genetic differences between animals of one species. BCR CRM 349 (cod liver oil) was used for validation of the analyses but also served as an average pattern of the diet of marine mammals. A more extensive analysis of the food may further reduce some scattering in the data obtained. Members of the MCWG are encouraged to provide relevant data to J. Boon.

J. Boon will present a full report of this study at the next MCWG meeting, after a second workshop has been held on this subject, at which a further evaluation of the data will take place.

The Organic Sub-group thanked J. Boon for his presentation and for organizing the workshop. The participants in the workshop were encouraged to finalize their study and present the report at the next meeting.

8.2.8 Review Notes

8.2.8.1 3,3'-Dichlorobenzidine

This paper was presented by R. Law. The note summarized the available information on the production and use of 3,3'-dichlorobenzidine (primarily in the manufacture of pigments), its toxicity and occurrence in the environment, and the analytical methodology used in the studies to date. The discussion centred on the likely metabolism and potential for bioaccumulation of this compound, the latter representing the pathway to man. It was felt that the bioaccumulation factors reported in the literature were probably overestimates, as they were obtained from acute exposures to high concentrations; those resulting from chronic exposures in the environment would probably be lower. This, combined with the low levels of production (ca. 10,000 t/yr) and discharge, suggests that problems would be restricted to the vicinity of discharges and would not extend to the marine environment. The text will be modified to take account of these points, and the paper will be submitted to the ACME in 1994 for information.

8.2.8.2 Chlorinated alkanes in the marine environment

This paper was introduced by P. Roose. The note presents information on the chemical and physical properties of eleven chlorinated compounds, their sources, analysis, distribution in the marine environment, and toxicology. Many analyses of these compounds have been carried out in river water and potable water, and in the assessment of workplace exposure; data for the marine environment are sparse and this should be recorded. Additional data from the UK and France will be included. It should also be noted that, if released in bulk, these compounds will sink to the sea bed. R. Law will supply a paper reporting such an incident in Canada. The text on degradation of these compounds should be amplified. The data for concentrations in biota seem very high given the reported log K_{ow} values – are the data for 1975/1976 reliable? J. Klungsøyr reported that experiments conducted in Norway showed rapid uptake and depuration of these compounds, and he will supply further information. M. Krysell also agreed to provide additional information.

The units should be standardized, and a reference to a GESAMP document added to the list – in addition, the titles of articles should be given in the references. P. Roose will revise the document to incorporate all the additional information, and send it to R. Law and J. Klungsøyr who asked to see it.

The revised paper will be presented to MCWG 1995 for information. Thanks were expressed to P. Roose for preparing this useful document.

8.2.8.3 Monocyclic aromatic hydrocarbons

This note was introduced by P. Roose, and was structured in a similar way to the text on chlorinated alkanes. It was recommended that the title be changed to reflect the compounds described: "Benzene and its C1- and C2-alkyl derivatives". The tables will be simplified by alteration of the units and trimming the data to 2 or 3 significant figures. Some references in the text are missing from the reference list, and titles of papers should also be added. If any information is available on toxicity to marine biota, this should be added, and where levels in biota are quoted the proximity of sampling points to point sources should be indicated. Thanks are due to P. Roose for preparing this paper. It will be presented to MCWG 1995 after revision.

8.2.8.4 Natural marine toxins

This paper was presented by E. Nixon. All three classes of toxins are found in Atlantic waters. A number of countries conduct national monitoring programmes for PSP and/or DSP toxins. Despite the existence of chemical methods, monitoring is generally conducted using bioassays. Although the chemical methods (generally using HPLC) are useful for investigative purposes (identifying and quantifying individual toxins), they are generally not sufficiently robust or rapid to be used as a first-line control method during an outbreak. The EC maintains a group of reference laboratories with responsibility for the quality of monitoring programmes, and is also funding a programme of work at the University of Brussels aimed at the development of improved techniques. S. Berman drew attention to work conducted at NRCC-Halifax and will send material to E. Nixon. The French authorities have also recently been using antibody test kits as a screening method for DSP toxins.

The sub-group recommended that ICES contact the Measurement and Testing Programme of the EC to discuss the progress in developmental work, with a view to supporting their efforts within key laboratories. E. Nixon will add to the paper information on the difficulties with current methodology, and after modification the paper will be passed to ACME in 1994. E. Nixon was thanked for preparing the review note.

8.2.8.5 Toxaphene in the marine environment

This paper was presented by J. de Boer. It is based primarily on papers presented at a workshop in Canada in 1993, now published as a special issue of Chemosphere (Volume 27, No. 10). In comments by the sub-group, the need was stressed for development of a common nomenclature to avoid the present confusion. It was noted that five individual congeners are now commercially available, two of which are among the major peaks occurring in environmental samples. J. de Boer will be happy to receive further comments until the end of April. The paper will then be revised for publication in the open literature, with a copy to MCWG/ACME for information. D. Muir and J. de Boer were thanked for their preparation of this thorough and extensive review.

8.2.8.6 Notes on the presence of new (detected) pesticides in Dutch surface waters

This paper was presented by W. de Waal in the absence of the authors. The note presents useful information on a number of compounds, including organophosphorus pesticides, triazines, phenol and phenylurea herbicides, and chlorophenoxycarboxylic acids, but relies solely on experience from the Netherlands. The value of the document would be enhanced by the inclusion of information on the use and production of pesticides, data from other countries, and an assessment of their importance in the marine environment. This last point is of particular relevance as atrazine and simazine (for instance) are now regularly detected and quantified in estuarine and coastal waters around Europe, and other compounds are regularly detected in rivers and ground water. All MCWG members are requested to seek further information on these compounds within their national programmes, and to pass the information intersessionally to Robin Law. A group comprising R. Law, J. Tronczynski, W. de Waal and F. Smedes will prepare an expanded note for MCWG 1995. W. de Waal agreed to thank F. Smedes and J. Hermans for preparing this paper, and for stimulating this discussion within MCWG.

The sub-group asked the ACME to review the previous overview guidelines prepared by ACMP, and revise them for MCWG to use in future.

8.2.9 Discussion on atmospheric-benthic coupling (ABC proposal)

The sub-group considered the paper as a relevant intention to join complementary skills into a research project, if analytical quality is assured. The Organic Sub-group discussed the intended proposal briefly but thought that a detailed discussion should be held by the interested parties. It was suggested that the proposal not be submitted as a follow-up of the Bremerhaven Workshop but as an individual research proposal.

It was also stated that if MCWG involvement is sought, it should be requested as soon as possible, earlier than for the Bremerhaven Workshop. Nevertheless, several people were interested and will contact Dr Stebbing, the author of the proposal.

8.2.10 Draw up a list of those organic contaminants which can be monitored in biota and sediments on a routine basis, taking into account their environmental relevance and the state of the art in analytical chemistry and quality assurance; define the necessary analytical performance characteristics

Based on the environmental relevance of the chemicals and analytical capabilities of laboratories, the sub-group prepared the following table of organic contaminants that could be considered for monitoring in biota and sediments.

It is unlikely that all laboratories will develop the capability to reliably determine all required contaminants in biota and sediment, neither is it necessary. In the list in Table 1, all intended can be measured with reasonable reliability by some laboratories.

Compounds listed in 1–5 have CRMs and certified or well-characterized standards available. The matrices are not always an exact match, but the necessary QC materials are generally available.

Compounds 6–10 are important, but the general state-of-the-art of analysis and general QA/QC are not so widely developed. Development on these important contaminants should be encouraged.

In any monitoring programme, it should be remembered that it is the quality control of the **individual** laboratory against its own data that is important and not an overall assessment in an intercomparison programme.

A new manual on standard and reference materials for marine science is available: IOC/UNESCO Guide 25 Revised. Adrian Y. Cantillo, 1993.

Organic Contaminant	Recent I/C data available	QC material available	Laboratories capability
1. Chlorobiphenyls "ICES" 7 plus CBs 31, 105 and 156	Yes - sediment Yes - fatty tissue ? - lean tissue	CRMs (SRMs) and LRMs. Certified standards available	Most
2. Toxic CBs 77, 126 and 169	Yes - fatty tissue	Yes - in the near future	Some specialist laboratories
3. Organochlorine pesticides	Yes - fatty tissue Yes - sediment	CRMs (SRMs) available for some pesticides	Most
4. PAHs (ICES list of 10) (sediments and shellfish)	Yes - sediment	CRMs in sediment	Many
5. Dioxin/Furans	Yes (WHO)	Yes	Good for specialist laboratories
6. CHBs (toxaphene)	Validated methods required	RMs required	A few specialist laboratories
7. Organotin	Validated methods required	CRM - biota	A few specialist laboratories
8. Methyl mercury	Validated methods required		A few specialist laboratories
9. Polychlorinated naphthalenes	Validated methods required	CRMs needed	A few specialist laboratories
10. Chlorinated paraffins	Validated methods required	CRMs needed	A few specialist laboratories

The usefulness of biomarkers to detect many of these organics was recognized and the group strongly supports the continued use and development of these techniques in future monitoring programmes.

Note:

Additional comments to the table by the coordinator of the ICES/IOC/OSPARCOM CB intercomparison exercises:

1) State-of-the-art of CB analysis

After final step 4 of the ICES/IOC/OSPARCOM CB intercomparison study the following can be concluded on the state-of-the-art of CB analysis of the 43 participating laboratories in this study:

a) Marine sediment

The group of laboratories is able to detect 50% differences between two samples for the CB congeners 188, 138 and 153. This refers to the analytical error and does not consider the natural variation.

A number of individual laboratories is able to detect smaller differences and is also able to detect 50% differences between two samples for the CBs 28, 31, 52, 101, 105, 156 and 180.

b) Sea oil

The group of laboratories is able to detect 50% differences between two samples for the CB congeners 138, 153 and 180. This refers to the analytical error and does not consider natural variation.

A number of individual laboratories is able to detect smaller differences and is also able to detect 50% differences between two samples for the CBs 52, 101, 105, 156 and 180. No laboratories are able to determine accurately the CBs 28 and 31. This is due to the high degree of metabolism for these CBs in seal.

c) Wet lean fish tissue

Although some individual laboratories seemed to be able to produce acceptable results for the analysis of the CBs 28, 31, 52, 101, 105, 118, 138, 153, 156 and 180 in wet lean fish tissue, the group of laboratories is not able to do so. The problems in the analysis of this type of matrix are related to the extraction. Solutions for this problem are likely to be found in the near future. For more fatty fish tissue the situation is expected to be better, but exact figures cannot be given because information on the extraction of wet fatty tissue is not available.

2) Degree of comparability in CB analysis

Standard deviations for the reproducibility obtained after the 4th step of the ICES/IOC/OSPARCOM CB intercomparison exercise:

a) Marine sediment

CBs 188, 138, 153	1.15 - 1.17*
CBs 28, 31, 52, 101, 105, 156, 180	1.21 - 1.33

b) Seal oil

CBs 138, 153, 180	1.12 - 1.16
CBs 52, 101, 105, 118, 156	1.20 - 1.65
CBs 28, 31	2.28 - 4.81

c) Wet fish tissue

CBs 101, 118, 138, 153, 180	1.57 - 1.68
CBs 28, 31, 52, 105, 156	1.93 - 3.84

*:1.17: standard deviation (SR), can roughly be read as 17%; an SR of 1.17 corresponds with a reproducibility (R) of 1.53 (roughly 53%).

8.2.11 Consider which additional quality assurance information should be included in the ICES databank

J.R. Larsen informed the sub-group that problems arose during the last assessment of contaminant trends in biota by the OSPARCOM *Ad hoc* Working Group on Monitoring and many data sets were rejected due to the lack of QA information. It was stressed that these data were rejected because QA data were not available. Rejection was not a criticism of the data themselves.

The following problem areas were identified:

- QA measurements were not carried out during the entire period;
- For historic data, QA information was not submitted by the laboratories as it was not a part of the monitoring programmes at that time;
- QA data were not maintained by the laboratories;
- There is a lack of CRMs for particular analyte/-matrix combinations.

It was the opinion of the sub-group that this was an extensive waste of resources for the laboratory submitting the results and also for ICES and the assessors. The present situation could, in fact, be damaging to marine science.

The sub-group recommended that the monitoring agencies establish an integrated QA programme to meet the requirements of the monitoring programme and that:

- monitoring should not be started until RMs are available and a proficiency testing programme in place. Target values for these RMs could be set by a small number of expert laboratories. These RMs should be matrix matched;
- participating laboratories should supply information on CRMs used, including target and measured values, with all data;
- monitoring agencies should supply participating laboratories with blind samples and the laboratory should make available data on long-term precision;
- laboratories should maintain adequate storage and retrieval systems for QA and monitoring data;
- available certified calibration solutions should be used as part of the calibration procedure;
- ICES should not accept results expressed as technical mixtures or the sum of CB congeners;
- monitoring agencies should provide clear guidelines for the QA assessment of data.

8.2.12 Examine the feasibility of a PAH intercomparison programme

After the first stage of the ICES PAH intercomparison, a proposal for the second stage was circulated but very few people wanted to continue; the main reason for that was probably the relatively high fee they would have had to pay owing to the small number of participants.

A questionnaire was circulated later at the QUASIMEME workshop in February 1993. This showed that 21 laboratories were interested in a PAH intercomparison that the majority were already determining such compounds.

An invitation to participate in a QUASIMEME PAH intercomparison will be circulated at the end of February 1994, and the exercise will be performed from June to November 1994. The compounds to be analysed are as given in the list of MCWG ICES and the exercise will begin with the analysis of standard solutions in acetonitrile. The exercise will include some estimate of the laboratories' long-term precision: six replicates will be analysed with at least one week between each analysis.

The inclusion of this exercise in the QUASIMEME project is the only way to achieve the implementation of this study. The outcome of the exercise will be made available to MCWG.

8.2.13 Reviews on "new" contaminants

The extensive list of candidate compounds prepared at the 1993 MCWG meeting was reconsidered while discussing the need for reviews/overviews on "new" contaminants. A total of six review notes on compounds from this list had been prepared for this year's meeting and they were considered by the sub-group under agenda item 8.2.8.

In general, the sub-group considered that new ASMO monitoring strategies may influence the choice of the compounds and determinands intended for future documents.

The need for an update of the review/overview on organotin compounds prepared previously was proposed. W. de Waal volunteered to prepare an updated review note for the 1995 MCWG meeting. All participants were invited to provide information on organotin compounds intersessionally to W. de Waal.

Potential hazards of diverse chemicals transported at sea and discharged into the marine environment as the result of accidents were discussed. R. Law and J. Klungsøyr will prepare a note for the next meeting on existing systems of data management for such chemicals.

8.2.14 Any other business

The sub-group discussed the request from ICES to comment on the need to maintain the database on contaminants in water. The sub-group recommend that ICES ask a small group of interested scientists to make an assessment of the current data. ICES should ask institutes who submitted data to comment on the need to maintain the database.

The sub-group confirmed D. Wells as intersessional chairman for the coming year.

8.3 Chemical Oceanography Sub-group

8.3.1 Report on the results of the Fifth Intercomparison Exercise on the Analysis of Nutrients in Sea Water (NUTS 5)

The intercomparison exercise has now been completed and a draft report was presented by A. Aminot. The general contents of the report were discussed by the group. Some minor errors, that will be corrected in the final version, were pointed out. The sub-group stressed how helpful the combined experiences of the NUTS 5 and the QUASIMEME intercomparison exercises have been for pinpointing causes of discrepancies between laboratories. A useful bonus was the close links established between the organizing groups of the two exercises, and this made it easy to extract information from both data sets.

It was noted that the number of laboratories that submitted data for organic nitrogen and phosphorus concentrations was disappointingly low. This may have in part been attributable to the limited volume of the samples.

During his plenary presentation of the results of the exercise, A. Aminot drew the following conclusions:

- Nitrate analyses showed good reproducibility (3%), comparable to earlier exercises including NUTS 4;
- Nitrite analyses showed a reproducibility of 5–10%;
- Phosphate analyses showed a reproducibility of 5–15%, similar to earlier exercises including NUTS 4;
- Ammonia analyses showed a reproducibility of more than 20%. This was disappointing and indicates a general need for the improvement of laboratory techniques and procedures for this determination;
- The study of individual errors indicates that substantial improvements can be expected since systematic errors represent the major contribution to the inaccuracy.

The following conclusions were added by the sub-group:

- The labs with the poorest performance in the present round had not participated in earlier exercises.
- The labs showing the poorest performance in the previous exercise have improved.
- There is evidence that rapid staff turnover has a deleterious effect on results.
- Through the exercise, labs showing good performance have been identified, as well as a number of labs who need to examine their techniques in order to improve their performance.

Implications of the results from NUTS 5 for laboratories reporting data under, i.a., OSPARCOM programmes can be summarized as follows:

. Laboratories should be strongly encouraged to join intercalibration exercises since this evidently helps in identifying poor performance.
. Laboratories who have been identified as poor performers should try to identify their weaknesses and correct them.
. More important than buying state-of-the-art equipment is the proper training and motivation of staff.

The sub-group acknowledged the work of A. Aminot and D. Kirkwood in organizing the intercomparison exercise, and particularly the efforts of A. Aminot and his co-workers in preparing and distributing the samples. The sub-group also acknowledged the resources generously provided by IFREMER and the Fisheries Laboratory in Lowestoft.

The sub-group recommended that the report be published by ICES in the *ICES Cooperative Research Report* series.

8.3.2 Consider an integrated study to examine processes of pollutant transfer and effects on biota ("Atmospheric-benthic coupling; a proposal to follow up the ICES/IOC Bremerhaven Workshop" by T. Stebbing)

The specific objectives of the project proposal contain no direct references to chemical oceanography. However, expertise in chemical oceanography, for example in determination of nutrients, would be of use in identifying and characterizing fronts, discontinuities and areas of high biological activity.

In order to assess and explain the flux of organic carbon, nutrient measurements would be of great importance to the project.

8.3.3 Review of the paper "Does progress in nutrients measurement improve our retrospective trend analysis?" by Don Kirkwood

D. Kirkwood made a short presentation of the paper, pointing out that he presented something similar at a plenary session of the QUASIMEME III workshop in the Algarve in 1993.

It was pointed out that historical data were often geographically unsystematic and often obtained at inappropriate times of the year from a trend study point of view. Hence, in many cases, data cannot be used to tell whether nutrient concentrations are increasing or decreasing. S. Carlberg stressed that, ideally, nutrient fluxes rather than concentrations should be measured if the trend studies were intended to demonstrate cases of eutrophication, a view that was shared by the sub-group. It was decided that the question of historical trends should be addressed from two view points:

1) Trend studies. It is evident that historical data, because of the reasons mentioned above, very often cannot be considered as representative either in time or in space.

2) Data quality. Experience gained from intercomparison exercises has helped to focus on what information is critical in judging the quality of historical data. Once a laboratory has applied a suitable analytical method and had access to adequate equipment, the human factors become decisive for the result. A good proportion of historical data is probably reliable but over the most recent decades when the analytical techniques have become well-established, minor differences in the techniques are thought to have had much less effect on data quality than the expertise available in the application of these techniques. Highly skilled and well-motivated analysts are capable of producing high quality results with relatively unsophisticated equipment, while investment in the very best equipment is no guarantee of data quality if it is in the hands of an unskilled operator.

8.3.4 Review the paper on the WOCE Hydrographic Programme Observational manual

The Sub-group recalled that the origin of this task was a question from the previous ACMP as to whether the WOCE manual could be recommended for application in the whole ICES community. In this ongoing task, the sub-group this year reviewed a draft protocol for the determination of nutrients in sea water. J. Olafsson, who had reviewed the paper, gave the sub-group a detailed introduction into the contents together with his view on the different parts.

The paper does not claim to cover all aspects and all types of samples and instruments. The sub-group specifically wanted to point out the following limitations on its use in the WOCE programme:

- The paper mainly deals with a certain type of autoanalyser not available to every laboratory.

- The paper is written for work in a specific sea area, and needs to be adapted by anyone aiming to work in North Atlantic, surface waters, shelf waters or stratified waters.

In view of the limitations outlined above, the Sub-group concluded that the paper could be recommended as a guidebook but not as an all-inclusive manual. The subgroup acknowledged that the paper was very well written and that it can certainly be extremely useful and should be considered "required reading" for anyone attempting to measure nutrients with an autoanalyser.

8.3.5 Review the paper "The dissolved organic carbon controversy: an update", by J. Sharp

A. Aminot, who had prepared the review, started by giving the sub-group the background to the increased interest in measurements of dissolved organic carbon (DOC) in the past few years. The traditional method is based on persulphate oxidation of the organic matter.

The controversy started when Sugimura and Suzuki published a paper in 1988 in which they claimed that earlier measurements of DOC were in error due to weaknesses in the methods, and that the concentrations were in fact 3–5 times higher than those reported earlier. These findings started immense activity throughout the world to either confirm or dismiss these new data using the technique suggested by Sugimura and Suzuki (high temperature combustion, HTC, to oxidize the organic matter). However, it soon became evident that the new data could not be confirmed. Suzuki later retracted the findings, after careful inspection of the blank determination method originally used. There is no doubt that the original paper from 1988 has stimulated a very healthy discussion on the DOC methods, and that it has proven a most valuable contribution to the research field.

The main conclusions that can be drawn from a set of experiments on blanks in HTC carried out by A. Aminot and from the publication by J. Sharp (Oceanography 6 (1993):45–50) (MCWG 1994/8.3.5/1) are as follows:

- a careful blank correction is essential, irrespective of the method used;

- there is no significant difference between the persulphate oxidation method and HTC;

- the credibility of the persulphate oxidation technique has been restored.

8.3.6 Review paper on distribution patterns of nutrients for the explanation of regional phenomena

This agenda item could not be dealt with owing to the absence of the colleagues who had undertaken to prepare this paper.

8.3.7 Review the first draft paper on problems related to chemical analyses of constituents in anoxic waters

This agenda item could not be dealt with owing to the absence of the colleagues who had undertaken to prepare this paper.

8.3.8 Discuss the outcome of the tests on alternative standards for organic and total phosphorus determinations

A. Aminot presented a paper written by himself and R. Kérouel (MCWG 1994/8.3.8/1) "Organic and total phosphorus determination in sea water. Model compounds for checking the recovery".

The paper presents an investigation of the suitability of 10 different compounds for the above-mentioned purpose. After studying the results obtained by Aminot and Kérouel, the sub-group agreed on the following technical recommendations:

1. AEPA (2-aminoethylphosphoric acid) and PCC (phosphoryl choline chloride, calcium salt tetrahydrate) are suitable compounds for recovery tests given that they have proved hard to decompose in the oxidation stage of the total phosphorus determination.

2. It is important to use a seawater matrix for the recovery test as the salinity has been shown to influence the result.

3. The alkaline persulphate oxidation method is recommended in marine waters.

4. More efforts should be made to find suitable organophosphorus compounds containing C-P bonds for further recovery studies.

A. Aminot agreed to look intersessionally into suitable organophosphorus compounds containing C-P bonds and to report his findings at the forthcoming MCWG meeting.

8.3.9 ICES Data bank on contaminants in sea water

The sub-group is scientifically interested, but has no immediate need for this data bank.

8.3.10 Any other business

a) Preparations for NUTS I/C 6

According to the existing timescale, NUTS I/C 6 is scheduled for early 1997 or thereabouts.

A. Aminot and D. Kirkwood are presently prepared, in principle, to organize this exercise, but are not in a position to commit themselves for certain at this stage, and there are several points they wish the MCWG and potential participants to bear in mind:

- After NUTS I/C 4, their intention was to double the size of the exercise in time for NUTS I/C 5. This was achieved, partly as a result of their positive efforts to publicize the NUTS I/C.

- They are now convinced that the usefulness of such exercises has been fully demonstrated and are no longer prepared to devote time to publicity with a view to increasing the number of participants. The existing mailing list will be maintained and any additional laboratories wishing to participate will be accepted.

- Due to foreseeable financial constraints, it is possible that MAFF and IFREMER may be unable to devote resources to NUTS I/C 6 in the same measure as we have enjoyed in previous exercises. It follows that laboratories may have to become accustomed to the idea that their participation in NUTS I/C 6 may cost them money.

- Should it be necessary to charge for participation, neither MAFF nor IFREMER has the infrastructure necessary for the money-collecting process, and organizers would be looking towards the ICES Secretariat to perform this function.

- It is anticipated that the format of NUTS I/C 6 will not differ substantially from that of NUTS I/C 5, but efforts will be made to include silicate as a determinand, if at all possible.

b) Suggestions for plenary presentations in 1995:

Preliminary results of studies on CO^2 in North Atlantic waters (J. Olafsson)

Chemical analysis of anoxic waters (M. Krysell and/or K. Makela)

CO^2 production rates in the oceanic water column: Assessment by enzymatic analysis (T. Packard)

9 PLENARY DISCUSSIONS OF SUB-GROUP WORK

The outcome of plenary discussions on agenda items discussed in all sub-groups is presented below. The MCWG adopted all other actions and recommendations put forward by the sub-groups.

Integrated study of pollutant transfer and effects on biota

The MCWG underlined the importance of a study as outlined by A. Stebbing and was of the opinion that it is very worthwhile to attempt to realize this project. It emphasized that a thorough planning is necessary, involving scientists with different disciplines from the design of the programme onwards. J. Boon agreed to act as representative of the MCWG in the initiating group chaired by A. Stebbing and will inform and possibly involve MCWG members as the programme develops.

ICES database on contaminants in sea water

The MCWG recommended that ICES maintain the database on contaminants in sea water. It recommended that ICES ask a small group of interested scientists to make an assessment of the current data.

The discussion on this topic raised the question as to whether an ICES Baseline Study on Contaminants should be organized in the near future. It was agreed to put this item on the agenda for the next meeting.

Additional Quality Assurance information to be included in the ICES data bank

The MCWG reiterated the need for an integrated QA programme associated with the monitoring programme. Specific items are:

1. Monitoring should not be commenced until RMs are available and a proficiency testing programme is in place. Target values for these RMs could be set by a small number of expert laboratories. These RMs should be matrix matched.

2. Participating laboratories should supply information on CRMs used (also certified calibration solutions), including target and measured values, with all data. It is recommended to include all pertinent reference materials in the NOAA/IOC compendium, along with matrix and analyte information, in the ICES database. This is the most comprehensive and updated listing of RMs available.

3. Monitoring agencies should supply participating laboratories with blind samples and the laboratory should make data on the long-term precision available.

4. Laboratory data should include traceability of any internal reference material to a certified reference material or to a recent intercomparison exercise.

5. Information on and results of recent relevant intercomparison exercises (e.g., QUASIMEME, NOAA) should be listed in the database.

6. Quality assurance information should include data on analyses of normalizing parameters and on sampling and storage procedures.

7. Information should be present on the sample workup (digestion, extraction, etc.) and the detection method.

8. Copies of relevant quality control charts are not needed if all the other QA data are submitted.

9. ICES should not accept results expressed as technical mixtures or the sum of CB congeners.

10. Laboratories should maintain adequate storage and retrieval systems for QA and monitoring data.

11. Monitoring agencies should provide clear guidelines for the QA assessment of data.

10 ANY OTHER BUSINESS

D. Wells drew attention to the fact that W. Cofino had now finished four years as Chairman of the MCWG and reiterated his proposal of last year that W. Cofino should continue. D. Wells emphasized "that the MCWG was developing a new and valuable style of meeting, due to the changing work of the group. This was being achieved primarily as a result of the good leadership of the Chairman." The Working Group unanimously agreed with this proposal. W. Cofino accepted, but emphasized that he did not want to impinge on any rules nor would he prevent any other member from leading the group. W. Cofino would contact ICES to obtain advice and guidelines concerning the duration of a term as chairman.

11 RECOMMENDATIONS AND ACTION LIST

The action list and recommendations are given in Annexes 3 and 4, respectively.

12 DATE AND VENUE OF NEXT MEETING

The MCWG discussed the venue and time of the next meeting. The Icelandic participants offered to host the 1995 meeting at Reykjavik, Iceland. The MCWG acknowledged the invitation with appreciation. It was decided to plan the meeting for 3–7 April 1995.

13 CLOSURE OF THE MEETING

Staff members of IFREMER joined the closing session of the MCWG. On behalf of the Group, the Chairman thanked IFREMER, the secretariat and A. Abarnou and A. Aminot for the substantial efforts and excellent services they had provided.

The Chairman thanked the members for their contributions and hard work and closed the meeting at about 15.00 h on 12 February 1994.

ANNEX 1

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ANNEX 2

MARINE CHEMISTRY WORKING GROUP

Brest, France, 7-12 February 1994

AGENDA

1. Opening

2. Adoption of the agenda

3. Report of the 81st ICES Statutory Meeting

4. Reports on related activities
   - 4.1. Joint Monitoring Group of OSPARCOM
   - 4.2. International Oceanographic Commission
   - 4.3. ICES
   - 4.4. EC-BCR QA pilot project "QUASIMEME"
   - 4.5. Quality assurance in the Baltic Sea
   - 4.6. Other activities

5. Reports on projects and activities in member countries

6. Requests from ACME and regulatory agencies

7. Plenary presentations

   7.1. Invited lecture:
   Katrien Delbeke, Vrije Universiteit Brussel, Belgium:
   Associations between lipids and PCBs.

   7.2. J. de Boer:
   The intercomparison programme on the analysis of CBs in marine media: where are we after four years of exercises?

   7.3. A. Aminot, D. Kirkwood:
   The NUTS 5 interlaboratory study.

   7.4. A. Aminot:
   Phosphorus speciation in particles and sediments in coastal and estuarine areas.

   7.5. (A presentation on a topic related to effects of contaminants by a French expert)

8. Sub-group activities and discussions

   8.1. Trace Metal Sub-group

      8.1.1. (C.Res.1993/ 2:7:1e) Report on the progress in the evaluation of data held in the ICES data bank on trace metal concentrations in estuaries.

      8.1.2. (C.Res.1993/ 2:7:1g) Report on the results of the study on the relationship between trace metal concentrations and lipid contents in biological tissues.

      8.1.3. (C.Res.1993/ 2:7:1f) Provide for the contaminants currently monitored information on the level of comparability achieved among participating laboratories in the most recent relevant intercomparison exercise.

8.1.4. (C.Res.1993/ 2:7:8) Contemplate about an integrated study to examine processes of pollutant transfer and effects on biota.

8.1.5. (JMG) Consider which additional quality assurance information should be included in the ICES databank, e.g. the composition of relevant reference materials, consensus values in intercomparison exercises, results submitted to intercomparison exercises, and other appropriate data.

8.1.6. Review "new" contaminants and determine where reviews or overviews would be warranted.

8.1.7. Evaluate the scientific reasons for ICES to continue to maintain a data base on contaminants in sea water

8.1.8. Any other business raised by the sub-group.

8.2. Organic Sub-group

8.2.1. (C.Res.1993/ 2:7:1b) Report on the results of Step 4 of the Intercomparison Programme on the Analysis of CBs in Marine Media.

8.2.2. (C.Res.1993/ 2:7:1c) Review the results of lipid determinations in Step 4 of the Intercomparison Programme on Analysis of CBs in Marine Media with a view to determining the need for conducting an intercomparison exercise on lipid determinations.

8.2.3. (C.Res.1993/ 2:7:1d) Prepare guidelines on the analysis of CBs in sediments.

8.2.4. (C.Res.1993/ 2:7:1f) Provide for the contaminants currently monitored information on the level of comparability achieved among participating laboratories in the most recent relevant intercomparison exercise.

8.2.5. (C.Res.1993/ 2:7:1h) Report on the progress in the intercomparison programme on non-ortho CBs in fish oil.

8.2.6. (C.Res.1993/ 2:7:1i) Report on progress in the project investigating similarities in patterns of CBs in marine species.

8.2.7. (C.Res.1993/ 2:7:1j) Report on progress in the project investigating differences in CB patterns between different species of marine mammals.

8.2.8. (C.Res.1993/ 2:7:1k) Consider the review notes on

- 3,3'-dichlorobenzidine (MCWG 94 8/2/8/1);
- chlorinated alkanes (MCWG 94 8/2/8/2);
- monocyclic hydrocarbons (MCWG 94 8/2/8/3);
- natural toxins (MCWG 94 8/2/8/4);
- polychlorinated camphenes (MCWG 94 8/2/8/5);
- new order pesticides (MCWG 94 8/2/8/6)

with a view to prepare draft advice concerning these substances in the marine environment.

8.2.9. (C.Res.1993/ 2:7:8) Contemplate about an integrated study to examine processes of pollutant transfer and effects on biota.

8.2.10. (JMG) Draw up a list of those organic contaminants which can be monitored in biota on a routine basis, taking into account their environmental relevance and the state of the art in analytical chemistry and quality assurance. Define the necessary analytical performance characteristics.

8.2.11. (JMG) Consider which additional quality assurance information should be included in the ICES databank, e.g. the composition of relevant reference materials, consensus values in intercomparison exercises, results submitted to intercomparison exercises, and other appropriate data.

8.2.12. Examine the feasibility of a PAH intercomparison programme.

8.2.13. Review "new" contaminants and determine where reviews or overviews would be warranted.

8.2.14. Any other business raised by the sub-group.

8.3. Chemical Oceanography Sub-group

8.3.1. (C.Res.1993/ 2:7:1a) Report on the results of the Fifth Intercomparison Exercise on the Analysis of Nutrients in Sea Water and report on the implications of these results for laboratories reporting data under Oslo and Paris Commissions programmes.

8.3.2. (C.Res.1993/ 2:7:8) Contemplate about an integrated study to examine processes of pollutant transfer and effects on biota.

8.3.3. Review the paper 'Does progress in nutrients measurement improve our retrospective trend analysis? (MCWG 94 8/3/3).

8.3.4. Review the paper on the WOCE Hydrographic Programme Observational manual.

8.3.5. Review the paper on the determination and characterization of dissolved organic matter.

8.3.6. Review the paper on distribution patterns of nutrients for the explanation of regional phenomena, e.g., algal blooms.

8.3.7. Review the first draft paper on problems related to chemical analyses of constituents in anoxic waters.

8.3.8. Discuss the outcome of the tests on alternative standards for organic and total phosphorus determinations.

8.3.9. Any other business raised by the sub-group.

9. Plenary discussion of sub-group work

10. Any other business.

11. Recommendations and action list

12. Data and venue of next meeting

13. Closure of meeting

ANNEX 3

MARINE CHEMISTRY WORKING GROUP

Brest, France, 7-12 February 1994

ACTION LIST

W. Cofino	Contact IOC to restore communication.
	Organize workshop on estuarine behaviour of metals prior to next MCWG meeting.
W. de Waal	Attempt to make a model for metals in estuaries available and to arrange a plenary lecture on metal behaviour and fluxes in estuaries.
G. Asmund, J.R. Larsen, B. Pedersen	Amend paper on relationship between trace metal concentrations and lipid contents in biological tissue, convey it to WGSAEM.
J. Larsen, B. Pedersen, G. Asmund	Check ICES data bank on trace metals in biological tissue in relation to lipid contents, identify which data sets can be used for a detailed investigation.
S. Berman	Attempt to rationalize the outcome from the statistical evaluations of the NOAA and QUASIMEME interlaboratory studies so as to enable direct comparison of the results of these studies.
S. Westerlund	Ask colleague to prepare a review on CH_3Hg
S. Berman, B. Pedersen	Prepare a discussion paper on the need for establishing methods for speciated metals in sea water.
S. Berman, B. Pedersen	Attempt to invite expert for plenary lecture on metal speciation at MCWG meeting.
S. Westerlund	Send out questionnaire to investigate interest in interlaboratory study on trace metals in sea water, after acceptance of recommendation by ACME.
J. de Boer	Prepare an overall assessment of the results of the Intercomparison Programme on the Analysis of CBs in Marine Media.
P. Roose, K. Delbeke, S. Einarsson, J. Boon, R. Parris, D. Wells, A. Abarnou	Collect information on lipids in biological tissue and critically evaluate this literature in preparation for a possible report.
J. Tronczynski, R. Law, J. Boon, D. Wells, J. Klungsøyr, P. Roose	Send to J. de Boer information on the determination of CBs in sediments before end of May 94.
T. Nunes	Inform the Working Group on Marine Sediments in Relation to Pollution (meeting in Nantes, end of March 1994) on the progress of this topic.
J. Boon,J. Klungsøyr, R. Law, D. Wells	Present the results of the investigation of CB patterns in marine mammals.
D. Wells and K. Delbeke	Organize a workshop on lipids prior to the 1995 MCWG meeting.

F. Smedes, J. de Boer	Update and finalize the document "Guidelines for the determination of CBs in sediments" for September 1994. The document will be presented for information only, at the next MCWG meeting.
J. de Boer, W. Cofino, D. Wells	Provide information from the EU-M & T programme on methodology and reference materials for non-ortho CBs to the MCWG.
W. Cofino	Contact Prof. Jansson to request that the results of the first interlaboratory study on non-ortho CBs will be made available to the MCWG.
B. Jansson	Present a report on the Swedish project on similarities in patterns of CBs in marine species at the next MCWG meeting.
R. Law	Modify the text of paper on 3,3'-dichlorobenzidine and submit it to ACME for information.
R. Law	Provide information on an incident with bulk release of chlorinated alkanes into the marine environment in Canada to P. Roose.
J. Klungsøyr	Provide information on Norwegian experiments on chlorinated alkanes to P. Roose.
M. Krysell	Provide information on chlorinated alkanes to P. Roose.
P. Roose	Prepare revised paper on chlorinated alkanes for next MCWG meeting.
P. Roose	Prepare revised paper on monocyclic aromatic hydrocarbons for next MCWG meeting.
J. de Boer	Send a copy of the toxaphene paper to MCWG and ACME.
R. Law, J. Tronczynski, W. de Waal, F. Smedes	Prepare an expanded note on modern pesticides in marine waters.
D. Wells	Make information on the QUASIMEME interlaboratory study on PAHs available to the MCWG.
J. Boon	Represent MCWG in Steering Group on Integrated Study of Pollutant Transfer and Effects on Biota, contact ICES/MCWG members where necessary.
W. de Waal	Prepare an updated review note on organotin compounds.
All members	Provide information on organotins to W. de Waal.
R. Law, J. Klungsøyr	Prepare a note on existing systems for data management on chemicals transported over sea.
A. Aminot	Prepare a note on organophosphorus compounds containing C-P bonds which are suitable to check recoveries.
W. Cofino	Contact ICES about chairmanship of MCWG.

ANNEX 4

MARINE CHEMISTRY WORKING GROUP

Brest, France, 7-12 February 1994

RECOMMENDATIONS

1. The MCWG recommends that ACME

   a) review the overview guidelines, as prepared by ACMP, and revise them for future use by MCWG;

   b) review its publication procedures so as to accelerate the time scale of reporting.

2. The MCWG recommends that ICES maintain the database for contaminants in sea water.

3. The MCWG recommends that ICES contact the EC - Measurements and Testing Programme to discuss the progress of development work on analytical methods for determining natural marine toxins with the view to supporting their efforts within key laboratories.

4. The MCWG recommends that the report on results of the Fifth Intercomparison Exercise on the Analysis of Nutrients in Sea Water, prepared by A. Aminot and D. Kirkwood, be published in the *ICES Cooperative Research Report* series.

5. The MCWG recommends the final report of Step 4 of the Intercomparison Programme on the Analysis of Chlorobiphenyls in Marine Media, prepared by J. de Boer and J. van der Meer, be published in the *ICES Cooperative Research Report* series.

6. The MCWG recommends that ICES organize an intercomparison exercise on the analysis of non-ortho CBs in marine media prior to inclusion of such contaminants in monitoring programmes, after the results of a study in the context of the EC - Measurements and Testing Programme become available (end of 1995).

7. The MCWG recommends that ICES organize an intercomparison exercise on the analysis of trace metals in sea water, coordinated by S. Westerlund. This study is to be conducted on a subscription basis.

8. The MCWG recommends that a Workshop on Metals in Estuaries should be arranged prior to the next MCWG meeting, preliminarily under the chairmanship of Dr. Stig Westerlund (Sweden). The objectives of the workshop should include the characterization of estuaries, the assessment of processes which are important in transporting metals to the ocean in the different types of estuaries, and the evaluation of different models to study estuarine processes and fluxes.

9. The MCWG should accept the offer made by participants of the Icelandic Marine Research Institute to host the next meeting in Reykjavik, Iceland. The MCWG strongly recommends the meeting to be held after April 1 in order to maximize participation from North America. It is proposed to meet from April 3 -7, 1995 to carry out the following tasks:

   a) to assess the outcome of the ammonia questionnaire prepared in association with the Fifth Intercomparison Exercise on the Analysis of Nutrients in Sea Water;

   b) to discuss plans for the Sixth Intercomparison Exercise on the Analysis of Nutrients in Sea Water;

   c) to investigate the possibilities to organize an ICES baseline study on contaminants in the near future.

   d) to review the progress with respect to a project on estuarine behaviour of metals;

   e) to discuss the need for developing methods for the determination of speciated metals in sea water;

f) to review progress with respect to an interlaboratory study on analyses of trace metals in sea water and, if appropriate, devise a plan and timetable;

g) to review an overall assessment of the results of the Intercomparison Programme on the Analysis of CBs in Marine Media;

h) to review an assessment of methodology for the determination of lipids in biological tissue;

i) to assess the outcome of the investigation on CB-patterns in marine mammals;

j) to evaluate review notes on chlorinated alkanes, monocyclic aromatic hydrocarbons, modern pesticides in marine waters, organotin compounds and on data management systems for chemicals transported over sea;

k) to review a note on organophosphorus compounds containing C-P bounds which are suitable to check recoveries;

l) to review and report on the progress made in the determination of dissolved organic carbon;

m) to discuss plans for an intercomparison exercise on non-ortho CBs in marine media.