

Fol. 41 ENV

Advisory Committee on the Marine Environment

ICES CM 1996/Env:2
Ref.: E

**REPORT OF THE
MARINE CHEMISTRY WORKING GROUP**

Lisbon, Portugal
12–17 February 1996

This report is not to be quoted without prior consultation with the General Secretary. The document is a report of an expert group under the auspices of the International Council for the Exploration of the Sea and does not necessarily represent the views of the Council.

International Council for the Exploration of the Sea
Conseil International pour l'Exploration de la Mer

Palægade 2–4 DK-1261 Copenhagen K Denmark

TABLE OF CONTENTS

Section	Page
1	OPENING OF THE MEETING 1
2	ADOPTION OF THE AGENDA 1
3	REPORT OF THE 83RD ICES STATUTORY MEETING 2
4	REPORTS ON RELATED ACTIVITIES 2
4.1	OSPAR and HELCOM..... 2
4.2	Intergovernmental Oceanographic Commission (IOC) 2
4.3	ICES 2
4.4	EC-BCR QA Pilot Project..... 2
4.5	Other Activities..... 3
5	REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES 3
6	REQUESTS FROM ACME AND REGULATORY AGENCIES..... 3
7	PLENARY PRESENTATIONS 3
8	SUBGROUP ACTIVITIES AND DISCUSSIONS 3
8.1	Topics Put on Agenda by ACME 4
8.2	SIME 1996: Interlaboratory Study on PAH Metabolites..... 11
8.3	Workshop on Estuarine Processes Recommended by the INPUT Working Group to ASMO 12
8.4	Second Workshop on Background/Reference Concentrations 12
8.5	Other Issues: Trace Metal Subgroup 12
8.6	Other Issues: Organics Subgroup 13
8.7	Other Issues: Chemical Oceanography Subgroup..... 13
9	NOMINATION OF NEW CHAIRMAN..... 14
10	ANY OTHER BUSINESS..... 14
11	ACTION LIST AND RECOMMENDATIONS..... 14
12	DATE AND VENUE OF NEXT MEETING 14
13	CLOSURE OF THE MEETING 14
ANNEX 1:	LIST OF PARTICIPANTS 15
ANNEX 2:	AGENDA 18
ANNEX 3:	REFERENCES ON ORGANOTIN ANALYSIS 21
ANNEX 4:	LIPIDS AS A CO-FACTOR 22
ANNEX 5:	TRIS(4-CHLOROPHENYL)METHANOL AND TRIS(4-CHLOROPHENYL)METHANE IN THE MARINE ENVIRONMENT 26
ANNEX 6:	TABLE OF ORGANIC CONTAMINANTS THAT CAN BE MONITORED IN BIOTA AND SEDIMENTS ON A ROUTINE BASIS..... 33
ANNEX 7:	PROCEDURE FOR NOMINATION OF CHAIRMAN 34
ANNEX 8:	ACTION LIST 35
ANNEX 9:	RECOMMENDATIONS..... 37

1 OPENING OF THE MEETING

The Chairman, Dr W. Cofino, opened the meeting of the Marine Chemistry Working Group (MCWG) at 09.45 hrs on 12 February 1996. Cdr Medeiros Alves, Technical Director of the Instituto Hidrográfico, welcomed the participants.

The Portuguese Delegate to ICES, Dr Carlos Reis, then addressed the MCWG.

Working Group members introduced themselves and briefly described their main area of research interests and responsibilities in the field of marine chemistry.

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

2 ADOPTION OF THE AGENDA

The terms of reference for this meeting of the Marine Chemistry Working Group (C.Res.1995/2:14:2) are to:

- a) review and report on the plans for the Sixth Intercomparison Exercise on the Analysis of Nutrients in Sea Water (NUTS 6);
- b) develop monitoring guidelines for polycyclic aromatic hydrocarbons in sediments and biota, paying attention to appropriate detection limits, and the number of replicate samples required per sampling area in order to characterise the sampling area for sediments (with WGMS) and biota (with WGEAMS) (OSPAR 1.1);
- c) review and report on the progress in the Intercomparison Exercise on the Analysis of Trace Metals in Sea Water;
- d) review and report on the status of the EU-QUASIMEME project and its implications for the work of the MCWG;
- e) review the outcome of the QUASIMEME inter-laboratory study on planar CBs in marine media and advise on the development of guidelines for the sampling of marine biota (with WGEAMS) and their analysis for non-*ortho* and mono-*ortho* CBs (OSPAR 2.2);
- f) provide further information on analytical methods and choice of matrices for the measurement of the presence of organotin compounds in the marine environment (HELCOM 8);
- g) review and report on the outcome of the Workshop on Estuarine Behaviour of Metals;
- h) prepare draft advice on alternative methods for the determination of lipids in marine samples (OSPAR 2.1);

- i) review the results of co-ordinated investigations on lipids as co-factors and report on their implications for monitoring programmes;
- j) assess the review notes on modern pesticides, Irgarol 1051, tris(4-chlorophenyl)methane and tris(4-chlorophenyl)methanol, triphenyltin, butyltin and organo-mercury;
- k) update, where appropriate, the list of contaminants which can be monitored on a routine basis, including a discussion about actual analytical proficiency based on recent interlaboratory studies;
- l) review and report on progress on a joint study to compare and contrast the different results of using multivariate methods on a common data set on PCBs in fish-eating marine mammals;
- m) review and report on how published reports have utilised covariation between dissolved organic carbon (DOC) and other substances;
- n) provide a report on general principles (chemical and biological) governing the transfer of halogenated organic contaminants illustrated by a few examples, with the aim of facilitating a more detailed request by the Helsinki Commission;
- o) examine the feasibility of, and potential contributions to, an Environmental Status Report for the ICES area on an annual basis and report to ACME by the end of 1995.

The Chairman had incorporated these items into the agenda. The MCWG adopted this agenda, which is provided in Annex 2.

It was noted that only very few of the participants had received the report of the 1995 MCWG meeting. The Chairman agreed to discuss this matter with ICES.

A plenary presentation by J.F. Chiffolleau was scheduled for Wednesday, 14 February.

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

Chemical Oceanography Subgroup (Chairman: S. Carlberg)

A. Aminot, L. Føyn, D. Kirkwood, M. Krysell, K. Mäkelä, J. Olafsson and O. Vagn Olsen;

Trace Metals Subgroup (Chairman: B. Pedersen)

G. Asmund, G. Audunsson, S. Berman, V. Besada Montenegro, J.F. Chiffolleau, W. Cofino, M. Leermakers;

Organics Subgroup (Chairman: J. Klungsøyr)

A. Abarnou, J. Biscaya, J. de Boer, J.P. Boon, M. Cleemann, M. Haarich, B. Jansson, R.J. Law, M.

Lebeuf, E. Govern, T. Nunes, P. Roose, D. Wells, A. Van der Zande.

3 REPORT OF THE 83RD ICES STATUTORY MEETING

The Chairman informed the participants that all of the tasks requested for consideration by the MCWG at the 1995 ICES Annual Science Conference (83rd Statutory Meeting) were incorporated into the draft agenda.

4 REPORTS ON RELATED ACTIVITIES

4.1 OSPAR and HELCOM

Prior to the meeting, the ICES Environment Secretary, J. Pawlak, informed the Chairman about the following items arising from the 1996 meeting of the OSPAR Working Group on Concentrations, Trends and Effects of Substances in the Marine Environment (SIME 1996) which are to be put on the agenda of next year's MCWG meeting:

- It has been requested whether it is feasible to organize an interlaboratory study for PAH-metabolites. These compounds are considered to be important in connection with the monitoring of fish liver tumours.
- A request has been put forward to provide guidance on quality assurance of oxygen measurements – how should this be put into practice?
- Guidance is requested for the analysis of tributyltin in sediments.
- The INPUT working group has recommended that OSPAR organize a workshop on estuarine processes. Attention is to be paid to nutrients, trace metals and POPs. ICES has been requested to consider co-sponsoring this workshop. The MCWG is requested to give ICES its views regarding the importance of this workshop, to provide suggestions about the contents and to nominate experts who could attend the workshop on behalf of ICES.
- The Dutch delegation to SIME 1996 proposed to hold a second workshop on background/reference concentrations. ICES has been requested to consider co-sponsoring this workshop. The MCWG is requested to nominate volunteers to this workshop and to identify people who are willing to provide information and data that can be used in the preparation of this meeting.

4.2 Intergovernmental Oceanographic Commission (IOC)

S. Berman informed the group the IOC has commissioned NRC-Canada and NIST-USA to prepare two CRMs for trace metals in sediment. One-third of each material is reserved for developing countries. NRC and NIST will probably market the remaining portions.

4.3 ICES

No additional points were raised by ICES at the meeting

4.4 EC-BCR QA Pilot Project "QUASIMEME"

The three-year EC Pilot Project QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) will be complete at the end of March 1996 and will continue as a subscription-based Laboratory Testing Scheme. An extension to the range of the project has been proposed by the project group as an additional EC proposal for the Quality Assurance of Sample Handling within the fourth framework programme.

The first three years of the QUASIMEME project (1993–1996) has brought together some 90 marine laboratories throughout Europe with the specific intention of improving the quality of information, management and measurement of the mandatory chemical determinands in the marine monitoring programmes. There have been five rounds of the laboratory testing scheme between February 1993 and November 1995:

- Round 1 February 1993 to May 1993
Nutrients in sea water; CBs in fish oil and in standard solution; trace metals in sediment and in standard solution.
- Round 2 November 1993 to May 1994
Nutrients in sea water; CBs and OCPs in fish oil and sediment; trace metals in biota and sediment; trace metals in sediment extracts (learning exercise).
- Round 3 June 1994 to November 1994
Nutrients in sea water; CBs and OCPs in fish tissue, fish oil and sediment; trace metals in biota and sediment; PAHs in standard solution.
- Round 4 December 1994 to May 1995
Nutrients in sea water; CBs and OCPs in fish tissue and sediment; trace metals in biota and sediment; PAHs in standard solution and sediment extracts.
- Round 5 June 1994 to November 1995
Nutrients in sea water; CBs and OCPs in fish tissue, fish oil, sediment and standard solution; trace metals in biota and sediment; PAHs in standard solution and sediment extracts.

In many cases the materials in subsequent rounds of the exercise were repeat distributions and within each round there were generally two samples of similar matrix where the determinands were present at different

concentrations.

QUASIMEME has organized a series of workshops as part of the improvement and learning programme. The schedule of workshops and subjects are as follows:

- October 1993 Algarve, Portugal
Critical evaluation of the questionnaire and first intercomparison study
- October 1994 Dublin, Ireland
Evaluation of the methods for lipid measurement and the lipids I/C
- March 1995 Hamburg, Germany
Evaluation of methods for the measurement of trace metals in sediment and biota
- June 1995 Roskilde, Denmark
Evaluation of methods for the measurement of organochlorine residues in biota
- March 1996 Crieff, Scotland
Overview of the improvement in information, management and measurement of the QUASIMEME I

A preliminary exercise to determine the effect of sample handling and preparation of mussel tissue has been undertaken by a selected number of participants. The design of the experiment used a simple crossover approach whereby mussels were distributed both to participants and the reference laboratory and exchanged after preparation prior to the determination of the trace metals and organochlorine residues.

The effects of storing biota under different temperature regimes and tissue conditions have been studied. Changes in bulk composition of the matrices as well as the key contaminants have been monitored. These data will be reported to the QUASIMEME workshop in Crieff and published in a Marine Pollution Bulletin special issue.

The results of all of the exercises in the QUASIMEME Laboratory Testing Scheme and workshops have been published in separate special reports. These have been circulated to all participants and supportive key organizations (e.g., HELCOM, OSPAR, ICES). Papers from the first two years of the project have been published in Marine Pollution Bulletin, as will the proceedings of the final workshop in March 1996. Additional limited numbers of these reports are available from the QUASIMEME Project Office.

QUASIMEME has also commissioned the preparation of two videos. The first, QUASIMEME: The Quest for Quality, gave an overview of the aims and objectives of the project and its long-term direction. The second, on sample handling of biological material, is an example of a teaching video to supplement monitoring guidelines and laboratory information.

All of these reports, publications and videos have been sent to ICES, HELCOM and OSPAR.

Following the completion of the first phase of the QUASIMEME project, the effort will develop in two possible directions. The existing scheme of laboratory testing will no longer be based on the EU-funded studies, but will become a 'stand alone' International Laboratory Testing Scheme funded by the subscription of the participating laboratories. The nature and scope of the scheme will be widened to include all laboratories who contribute to national or international monitoring.

The QUASIMEME II Laboratory Testing Scheme has been developed and the first year's programme has been sent to all present QUASIMEME laboratories as well as other interested participants. ICES, HELCOM and OSPAR have been invited to propose a representative to join the Advisory Board of the Scheme.

The programme has been designed to support the QA requirements of the monitoring programmes of both OSPAR and HELCOM and will be open to all laboratories.

4.5 Other Activities

M. Krysell briefly commented upon his experiences as assessor for the Swedish Accreditation Body SWEDAC. He recommended that members of the MCWG take part in such activities if they have the chance to do so.

5 REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES

No reports were submitted under this heading.

6 REQUESTS FROM ACME AND REGULATORY AGENCIES

Requests from ACME were included in the agenda.

7 PLENARY PRESENTATIONS

J.J. Chiffolleau gave an interesting presentation on the behaviour of trace metals in estuaries. Handouts of his presentation were given to members who expressed their interest in them. The presentation clearly illustrated the need to understand trace metal behaviour in estuaries in order to be able to design a good monitoring programme and to make reasonable estimates of trace metal fluxes to the sea.

8 SUBGROUP ACTIVITIES AND DISCUSSIONS

For the sake of clarity, the outcome of the discussions on topics requested by ACME will be given first in this report

(Section 8.1). Then, the discussions about the three items arising from the SIME 1996 meeting (see Section 4.1) will be reported (Sections 8.2 to 8.4). Finally, any additional items discussed in the subgroups will be dealt with (Sections 8.5 to 8.7).

8.1 Topics Put on Agenda by ACME

a) Review and report on the plans for the Sixth Intercomparison Exercise on the Analysis of Nutrients in Sea Water (NUTS 6) (C.Res.1995/2:14:2a).

At the ICES Statutory Meeting in 1988, the Council recommended (C.Res. 1988/4:10) that a series of three intercomparison exercises for nutrients in sea water should be organized at approximately four-year intervals. NUTS I/C 6 represents the third of this series and, according to the time scale envisaged in recent years, the distribution of samples is due around the end of 1996.

However, with the requirements today laboratories have to demonstrate their proficiency or competence level more than every four years.

The ICES MCWG has benefited greatly from the expertise accumulated by IFREMER in the preparation of sample materials which underpinned the success of NUTS I/C 4 and NUTS I/C 5. It is widely recognized that the true economic cost of such materials is considerable and the MCWG fully appreciates that IFREMER is no longer able to support an exercise on the scale of NUTS I/C 6 on the highly generous terms enjoyed by the previous exercises.

The Chemical Oceanography Subgroup considers it inappropriate to attempt to organize a further exercise similar in principle and scale to NUTS I/C 5 *on a full cost-recovery basis* for a variety of reasons, examples being that it lacks the required infrastructure for handling the financial aspects, and also that it might be confusing for laboratories if a NUTS I/C 6 were to be offered in parallel with other similar initiatives such as the subscription scheme currently proposed to follow the EU-funded phase of QUASIMEME.

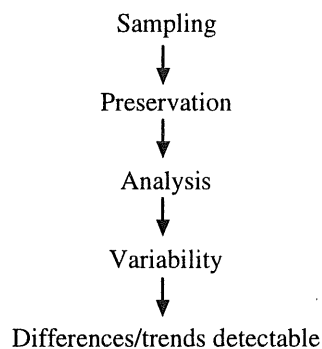
On the basis of information available pertaining to the proposed future structure and activities of the QUASIMEME scheme, the Subgroup is satisfied that it will fully meet the needs of marine laboratories in terms of proficiency testing exercises, etc. The frequency (twice yearly) and response times achieved by QUASIMEME in the three years to date is considered highly satisfactory.

The Subgroup therefore recommended that all prospective NUTS I/C 6 participants should be advised to join the QUASIMEME scheme and D. Kirkwood agreed to undertake a mailshot to this effect in the near future, as soon as it is known that the NUTS I/C 5 Report (Co-operative Research Report No. 213) has been fully distributed.

b) Develop monitoring guidelines for polycyclic aromatic hydrocarbons in sediments and biota,

paying attention to appropriate detection limits, and the number of replicate samples required per sampling area in order to characterise the sampling area for sediments (with WGMS) and biota (with WGEAMS) (OSPAR 1.1)

The Group considered that a tiered approach could be an appropriate means for responding to this query:



with reference to the performance of laboratories in intercomparison/proficiency programmes such as QUASIMEME.

It was also felt that, although the request was rather broad, there was little point in seeking a more focused query as it was unlikely to materialize. A review of the general aims of the new OSPAR Joint Assessment and Monitoring Programme (JAMP) also suggested that they were considering PAHs on a broad front and that their own aims were not as yet focused. It was agreed, therefore, that members of the group would work intersessionally to produce a series of guidelines and recommendations drawing on the wide and varied field experience within MCWG. Illustrations should include the use of mussels and sediment sampling within basin and shelf areas and estuaries, along gradients near oil platform transects, and in depositional/erosional areas.

The first component of this work will be to prepare an update of the paper on analytical methods published in 1991, and to compile limits of detection attainable for the measurement of PAHs in sediments.

It was also agreed that a draft paper would be prepared for MCWG 1997, during which the methodology and examples would be discussed and draft monitoring guidelines developed. Robin Law agreed to act as coordinator for this activity, and Ton Van der Zande, Jarle Klungsoyr, Patrick Roose and Jan Boon agreed to supply material for inclusion to R. Law by 15 August 1996. Jarle Klungsoyr also agreed to contact ICES for information concerning the ICES/HELCOM Baseline Study of Contaminants in Baltic Sea Sediments, as this was felt to be directly relevant. On the question of liaison with WGMS and WGEAMS, Teresa Nunes agreed to provide the link with WGMS, and Bo Jansson will be asked to inform WGEAMS of the work under way within MCWG and to pass comments to R. Law.

c) Review and report on the progress in the Intercomparison Exercise on the Analysis of Trace Metals in Sea Water

The intercomparison exercise on the analysis of trace metals in sea water proposed by the MCWG has been accepted by ICES. ICES has also granted some financial support to cover the cost of supplies, shipping and some travel.

Using a Danish vessel, two samples with respective salinities of about 25 and 10 will be collected in the Sound where Baltic Sea and Kattegat water meet. Canadian equipment will be provided by the National Research Council of Canada (NRCC). The collection will take place in August 1996 and the participants should receive their samples by the end of that month. In order to prepare a draft report for the MCWG at its next meeting in 1997, the deadline for the receipt of results will be three months later, around the end of November 1996.

A letter will be sent to prospective participants within the next few weeks with a response requested by the end of April. There is already a positive indication from about 40 laboratories and the exercise may be limited to about 70 participants.

The letter will also inquire whether the participants are interested in the inclusion of mercury as an analyte. If there is insufficient interest, this metal will not be included in order to preserve resources. Its inclusion greatly increases the amount of work to be done.

The elements studied will be As, Cd, Co, Cr, Fe, Mn, Ni, Pb and Zn. There are seawater CRMs available for all of these metals.

The NRCC laboratory will analyse the data and write a report in cooperation with the Marine Research Institute in Reykjavik, the Danish National Environmental Research Institute, the SOAEFD Marine Laboratory (Aberdeen) and IFREMER (Nantes). The SOAEFD Marine Laboratory has offered its facility to receive the results by electronic transmission. NRCC and the Marine Laboratory will work out the details.

d) Review and report on the status of the EU-QUASIMEME project and its implications for the work of the MCWG

The EU-funded QUASIMEME programme will end on 1 April 1996. Then the programme will evolve into a proficiency testing scheme on a subscription basis. This means that the laboratories can subscribe for different packages such as trace metals in biota or PAHs in sediments. For this subscription, they will receive samples for two interlaboratory studies per year for a specific analyte/matrix combination, and a report with the results of these studies. An advisory board will be installed, and OSPAR, HELCOM and ICES have been invited to join this board.

The advantage of the continuation of the QUASIMEME programme on a subscription basis is that now also laboratories from non-EU member states can join the programme. Another advantage is that there is a wider remit with regard to the number of determinands. The confidentiality of the data will be guaranteed. Laboratories are encouraged, however, to report their data to third parties (accreditation bodies, ICES, OSPAR, HELCOM) when and where appropriate. The initial list of analytes included in the programme consists of the mandatory determinands of the OSPAR JAMP, together with some of the voluntary determinands on the JAMP list. Additional determinands can be included when suggestions are received from either the participants or the monitoring bodies. A participation of ten laboratories per analyte/matrix combination is considered to be a minimum.

The MCWG considers QUASIMEME-II (the subscription-based programme) to be a valuable testing scheme and advises laboratories which are active in international marine monitoring programmes to participate in this programme. The MCWG does not consider it necessary to create a formal link with this project or with any other quality assurance group. The MCWG regards QUASIMEME-II to be a quality assurance service project. MCWG can use the results of QUASIMEME in its scientific work and in its advice regarding QA matters. The MCWG will continue to promote the importance of quality assurance for marine environmental measurements. In this context, participation in well-organized schemes such as those offered by NOAA, QUASIMEME or other organizers is highly encouraged and should, in principle, be mandatory.

The MCWG also concluded that now that the load of intercomparison exercises is covered by other groups, there is more time for scientific discussions and to focus on environmental problems. However, it will remain necessary for MCWG to build up knowledge on analytical methods of new contaminants. This may take place in the form of a mutual exchange of samples and methods between the members of MCWG or on a slightly broader scale in the form of organizing learning exercises on the determination of such compounds. It was emphasized that also for these small-scale interlaboratory studies some financial support may be needed. As soon as interlaboratory exercises reach the scale of a more routine proficiency testing, it is desirable that QUASIMEME, NOAA or another organization would take over the responsibility.

e) Review the outcome of the QUASIMEME interlaboratory study on planar CBs in marine media and advise on the development of guidelines for the sampling of marine biota (with WGEAMS) and their analysis for non-ortho and mono-ortho CBs (OSPAR 2.2)

D. Wells gave an overview of the participation in and the results of the QUASIMEME intercomparison exercise on planar CBs. The participants were invited to analyse both

a standard solution and a cod liver oil in duplicate. Of the 60 possible candidates, only 16 laboratories agreed to participate in the exercise. Of those, only 12 reported results for the standard solution and only 8 for the fish oil. The overall result in respect to the number of participants and the actual analytical quality was considered a disappointment. The variability of the data for the standard solution was in the range of 20–30 %, although the difficulties associated with this analysis are similar to those for the other CBs where a variability in the range 12 to 14 % is achieved. As far as the methods are concerned, all but two laboratories used an appropriate technique for the separation of planar CBs from the others, for example, graphite or Pyrene columns.

It was concluded that the methodology for the analysis of planar CBs is available and can be applied by most laboratories. A few laboratories produce good data, but in general the results are disappointing and below the quality required for monitoring programmes. It was further suggested that for monitoring purposes analysis of the regular CBs might be sufficient if the ratio of the planar CBs to the others is constant. The group concluded, however, that this is not acceptable in view of the toxicological significance of the planar CBs.

The MCWG recommended that planar CBs not be included in monitoring programmes aimed at the assessment of spatial distributions or temporal trends, but that their measurement be confined to research projects and to programmes in which the quality of fish products for human health are assessed.

f) Provide further information on analytical methods and choice of matrices for the measurement of the presence of organotin compounds in the marine environment (HELCOM 8)

Monitoring of organotin compounds is being considered by both OSPAR and HELCOM. The MCWG has been asked for advice regarding matrices and analytical methods.

Compounds to be measured

The compounds to be determined are tributyltin (TBT), triphenyltin (TPT) and their metabolites. The source for TBT is the antifouling treatment used on ships. TPT is also added to antifouling paints in smaller quantities (in the order of 10 % of TBT), and is additionally used in some countries as a pesticide, where locally elevated TPT concentrations may be encountered.

TBT is metabolized in organisms to DBT and MBT, the degree of metabolism depending upon the species. TBT is the most toxic of these three compounds. For biological tissues, however, measurement of TBT, DBT and MBT is needed in order to obtain an impression of the exposure. In sediments, TBT dominates. In water,

TBT, DBT, and MBT may occur in various ratios depending on the location and season.

The MCWG stated that a complete view of presence and exposure should be obtained and recommended therefore that TBT, DBT, and MBT all be measured.

Not much information on the biological effects of TPT is available. TPT is commonly found, and can occur in higher concentrations than those of TBT in some biological tissues. This is especially the case for locations remote from TBT hotspots such as harbours and marinas. This observation may result from a higher persistence of TPT compared to TBT. The MCWG recommended that TPT be included in marine monitoring programmes; DPT and MPT may be included as voluntary compounds. The analysis of these metabolites should be limited to areas where high levels of TPT are found.

Areas for monitoring

Obvious potential hotspots for TBT and its derivatives are harbours and marinas. In addition, enhanced concentrations may be found near shipping lanes. TPT is found both at these locations and in regions where it is used in agriculture. The MCWG recommended that monitoring of TBT, DBT, MBT, and TPT be considered around harbours, marinas and shipping lanes, and of TPT (and optionally its metabolites DPT and MPT) in regions where it is used in agriculture (e.g., the Rhine and Scheldt estuaries).

Compartments for monitoring

In general, sediments, bivalves and snails constitute good compartments for monitoring.

In harbours and marinas, TBT may occur in paint flakes in the sediments, implying that analysis of the unfractionated sediment is required if an estimate of the 'total' TBT content is sought. Shipping lanes may be located in sediment erosion or transport zones where predominantly coarse-grained, sandy sediments are found. The analysis of organotins in sandy sediments is extremely difficult owing to the low concentrations of organotins in those sediments. Measurements in a fractionated sediment (e.g., < 63 µm) are therefore recommended. This approach also implies that the concentrations of the organotins are normalized with respect to the sediment characteristics. Alternatively, measurements can be confined to sediment accumulation areas where fine-grained sediments can be found.

Bivalves and snails offer several advantages for monitoring temporal trends and spatial distributions: such organisms do not migrate very much and have a low capacity for biotransformation. In addition, very specific organotin-related biological effects have been observed for a number of species, enabling a coupling of chemical and biological effects monitoring. At many locations, however, suitable organisms are difficult to find. The

absence of sensitive organisms in areas where they have been present in the past may indicate toxic effects when elevated organotin concentrations are found in sediments.

Start and end of monitoring

The MCWG emphasized that the decision to start with monitoring should be based on concrete evidence of the need. Environmental managers should have a clear idea when a situation warrants the start of a monitoring programme and, equally important, at which point the objectives have been reached and the monitoring effort may be reduced or ended. This point of view has been stipulated in many ICES documents on monitoring strategy but seldom if ever seems to be put into practice. The MCWG also pointed out that the importance of monitoring organotins should be weighed against the monitoring of other compounds; when resources are limited, it might be appropriate to start monitoring organotins at the expense of monitoring another compound whose importance has declined (see also Section 8k).

The MCWG recommended that objectives as stated here be formulated and that a pre-study be conducted. The pre-study should include biological and chemical observations and an assessment of the magnitude of inputs. The observation of organotin-specific biological effects (e.g., shell thickening for bivalves or imposex for snails) provides a signal that monitoring could be worthwhile but should be substantiated with chemical measurements. The absence of biological effects in itself does not automatically imply that no problem is present as the sensitive species may already have been exterminated.

The MCWG emphasized that monitoring should only be commenced when analytical proficiency has been established. At present, few laboratories determine organotins at all. The interlaboratory studies which are available point to a low degree of comparability of data. The MCWG suggested therefore that the concept of having one or more expert laboratories conduct the monitoring programme be considered.

It was decided to investigate the number of laboratories involved in organotin analysis, the methods applied and the types of samples measured. Based on the outcome of this questionnaire, it may be considered to organize an interlaboratory study.

Analytical aspects

At the meeting, four laboratories with extensive experience in organotin analysis were present. It was concluded that several methods are available which give good results when properly applied, in particular with respect to TBT, DBT, MBT and TPT. The requirements for instrumentation and facilities do not pose great difficulties for most laboratories involved in marine monitoring. The measurements are difficult to get under

control, however.

A selection of papers describing the methodology was made and is included as Annex 3.

g) Review and report on the outcome of the Workshop on Estuarine Behaviour of Metals

The MCWG decided in 1995 in Reykjavik to organize a workshop in 1996 concerning the estuarine behaviour of trace metals. This workshop was planned to take place in February 1996, in Lisbon, just before the MCWG meeting, and J.F. Chiffolleau accepted to organize it and to contact the relevant persons during the intersessional period.

Unfortunately, the key persons contacted for this workshop could not participate for different reasons, mainly due to the absence of funding from their own institute. Consequently, the workshop could not take place, but instead a very informative lecture was given by J.F. Chiffolleau during the meeting covering the area of estuarine processes.

The opinion of the subgroup is that the estuarine behaviour of trace metals is still a subject of great interest. It was therefore suggested that the group takes an active part in the suggested workshop of the INPUT Working Group of OSPAR in 1996–1997, by participating in its organization or being invited to this workshop (see Section 8.3, below).

h) Prepare draft advice on alternative methods for the determination of lipids in marine samples (OSPAR 2.1)

No report was presented at the meeting due to a lack of information. However, methodological aspects were discussed under Section 8(i). It should be noted that both agenda items were formulated in a different way than agreed upon by the subgroup during last year's meeting.

i) Review the results of coordinated investigations on lipids as co-factors and report on their implications for monitoring programmes

Patrick Roose reported on the outcome of the intersessional work by a number of people (Alain Abarnou, Michael Haarich, Eugene Nixon, Patrick Roose) evaluating the use of lipids as a co-factor. The main conclusions were summarized in a paper presented at the meeting.

During the discussion of the paper, a number of conclusions were drawn, namely:

- Based on the information that is presently available, it becomes obvious that normalizing on the lipid content does not always reduce the variability of the data, due to the complexity of the processes that govern the uptake and elimination of contaminants.
- The use of lipid contents as a normalizing factor may

be a valid procedure, provided that the objectives of the study are properly set and that other relevant parameters are taken into consideration.

- Due to the lack of information in the literature, it is impossible to reach decisive conclusions on the usefulness of the lipid content as a co-factor.

It was concluded that:

- The lipid content is a valuable biological parameter and should be reported in the framework of monitoring programmes, despite the lack of decisive information on its usefulness as a normalizing factor.
- Further research is needed to establish the fundamental relationship between lipids and contaminants.

At the meeting it was noted that a project proposal on the relationship between lipids and contaminants has been submitted to the EU-S,M&T programme. Several MCWG members will be involved in this project. The results will be fed back to MCWG if the project receives funding (D. Wells).

The MCWG concluded that lipids should be determined as total lipids using basically the Bligh and Dyer method. The latter is considered to be the best presently available method for this purpose. The MCWG forwarded the paper presented at the meeting to ACME for information since it contains valuable information (see Annex 4).

j) Review the progress in the understanding of chemical associations of various metals and liver lipid types and indicate possible implications for monitoring programmes

New data on cod from Iceland were presented. The data covered analyses on trace metals, liver size, fat content, protein, ash and phosphorus. The gross parameters (ash, fat, protein, etc.) were all strongly interrelated. Log-log relations between some gross parameters (e.g., proteins) and metals showed good correlations indicating that in this data set the metal concentrations could be explained as resulting from biological variability.

The group agreed that the subject is still of interest and the opinion was strengthened that normalization is necessary for the interpretation of data on metals in biological tissues.

It was noted that a Danish-Norwegian-Icelandic study group will continue in 1996 to address these issues. Information from this study will be made available to the MCWG.

k) Assess the review notes on modern pesticides, Irgarol 1051, tris (4-chlorophenyl) methane and tris (4-chlorophenyl) methanol, triphenyltin, butyltin and organo-mercury

Modern pesticides

The review note on modern pesticides was not available. T. van der Zande would contact W. de Waal to look into

the status of this document.

Irgarol 1051

A paper had been prepared by R. Law (MCWG 1996/8.2.7/2). Its main use is in anti-fouling paints that do not contain TBT as an active biocide. Irgarol 1051 is one of the class of triazine herbicides which includes atrazine and simazine. The highest concentrations occur in marinas and ports, and low concentrations are seen in coastal areas; however, these findings are based on very limited data. More information is needed on the concentrations of Irgarol in affected waters before its environmental significance can be assessed, but it would be premature to add Irgarol to mandatory monitoring programmes. One major point on which no information is currently available is the scale of use; although this information is known to regulators, it is not openly available.

It was agreed that the paper should be revised, and any additional information that could be supplied by MCWG members should be incorporated. R. Law agreed to present a revised text to MCWG 1997. It was also felt that the introduction on TBT-derived problems should be shortened in the revision.

Tris (4-chlorophenyl) methanol and Tris (4-chlorophenyl) methane

A paper entitled 'Tris (4-chlorophenyl) methanol and Tris (4-chlorophenyl) methane in the marine environment – origin, distribution, toxicity and analysis' had been prepared by J. de Boer (MCWG 1996/8.2.7./3).

The sources and uses of these compounds are not well known. Possibilities include the production of dyes, additives in the technical formulations of DDT, and TCP as a metabolite of TCPMe. The toxicity of TCP and TCPMe is currently unknown. They are possible carcinogens, but the AMES test gave ambiguous results; mutagenic potency cannot however be excluded.

TCP can be detected by NCI-MS or GC/ECD whereas TCPMe should be measured with EI-MS or GC/ECD. Chromatographic clean-up with alumina yields problems, as compounds cannot be resolved; Florisil and GPC are better alternatives.

- B. Jansson asked whether the information is available from areas where DDT is still actively used. This is not the case.
- J. Boon asked whether the AMES test was carried out in the presence of a rat S9 fraction, which might bioactivate the compounds by the formation of active metabolites. This was confirmed.
- R. Law suggested that the section on analysis should precede the section on environmental occurrence. Also, the use of the abbreviation TCP for tris (4-chlorophenyl) methanol is confusing as it usually indicates trichlorophenols. He suggested using either TCPM or TCPMOH.

In view of the widespread occurrence of TCPM and

TCPMe, the MCWG concluded that these compounds should be the subject of study and considered for inclusion as voluntary determinands in monitoring programmes. The MCWG emphasised, however, that before monitoring is undertaken, more information is required (sources, usage and ecotoxicological aspects) and methodological arrangements (description of good methodologies, reference materials, comparability of data) need to be made.

The MCWG decided to undertake a collaborative study in order to obtain more information on the occurrence of these compounds. To this end, J. de Boer will provide methodological details and a standard solution to J. Klungsoyr, M. LeBeuf, M. Haarich, R. Law and A. Abarnou who will attempt to include the analysis of the compounds in samples which are to be measured in 1996. In addition, B. Jansson will provide data from sediment cores to the MCWG 1997 meeting.

The paper of J. de Boer is forwarded to ACME for information and included as Annex 5 to this report.

Butyltin compounds

A revision of a document considered last year was presented, based on the summary of Rijkswaterstaat report RIKZ-g5.007 by E.H.G. Evers and W.A.J. de Waal.

Information on legislation in some other countries has been included in this year's version of the document, according to a request from last year. At the meeting it was noted that in Ireland all organotins are banned for use on boats under 25 m in length.

The paper focuses strongly on the situation in the Netherlands and does not pay much attention to the work carried out, for instance, in France and the UK.

The MCWG passed this document on to the ACME for information and recommended that TBT be added to monitoring lists as a mandatory determinand (see also Section 8f).

Triphenyltin

An abstract was presented based on an existing report of the freshwater department of the Dutch Rijkswaterstaat (RIZA-RWS). The paper was interesting but limited in scope. It lacked a clear conclusion and recommendations as to what type of work is needed. J. Boon noted that TPT has also been found in whelks from the North Sea. Concentrations were highest in areas with high shipping activity, but these stations were also closest to the shore. Thus, it is unclear whether anti-fouling paints or agriculture was the source of TPT.

T. van de Zande will investigate whether people from Rijkswaterstaat are willing to extend the abstract. In that case, M. Lebeuf is willing to compile information on TPT from Canada. In addition, several members of the MCWG are willing to provide information on TPT in their countries.

The MCWG concluded that more research needs to be carried out before it can be decided whether phenyltins

should be added to monitoring lists.

- l) Update, where appropriate, the list of contaminants which can be monitored on a routine basis, including a discussion about actual analytical proficiency based on recent interlaboratory studies**

Metals

At the last MCWG meeting a comparison of the general performance of the NOAA and QUASIMEME interlaboratory studies on trace metals was presented (MCWG 1995/8.1.5). The performance regarding analyses of Cd, Hg, Zn, As, Cu, Pb, Cr and Ni in sediment and biota (and Al in sediment) was discussed. The conclusion was that it must be assumed that the competence of the selected laboratories on either side of the Atlantic is comparable and the elements are in principle possible to be monitored on a routine basis. The Group was informed that the NOAA Interlaboratory Study included more than the elements mentioned. The group thought it would be valuable to obtain information about the performance on these elements in the NOAA study. It was therefore decided that the performance in recent NOAA and QUASIMEME Interlaboratory Studies should be summarized. Shier Berman volunteered to do this for the next MCWG meeting.

The Group also discussed the importance of speciation in relation to metal monitoring. For example, currently total As in biota is generally monitored but the analysis of the inorganic fraction would be more relevant. It was noted that very little information is available on the actual analytical proficiency for metal speciation such as organic As and Sn in marine matrices.

The Group underlined that this would be an important task for any interlaboratory study in the future in order to make it possible to incorporate these types of compounds on a routine basis in a monitoring programme.

Organic compounds

The table of contaminants established last year has been updated with more information on CRMs and the latest results of interlaboratory studies. The updated table is given in Annex 6.

The QUASIMEME office will provide ICES with the report of the QUASIMEME programme, paying specific attention to what can be obtained in terms of between-laboratory precision. This will be provided after the QUASIMEME Crieff Workshop in March 1996.

- m) Review and report on progress on a joint study to compare and contrast the different results of using multivariate methods on a common data set on PCBs in fish-eating marine mammals**

This collaborative activity was the subject of a thorough presentation at MCWG 1995, and the subsequent year has seen a process of refinement.

J. Boon presented some new findings regarding concentration-dependent metabolism. As the process was understood last year, the observed metabolism of certain CB congeners could occur for two main reasons: starvation of the animals, or induction of MFO enzyme systems with increasing concentration. These possibilities have been investigated by the use of condition factors: blubber thickness and lipid content for common (harbour) seals and porpoises, and length/weight relationships in the otter. For the harbour seal there was some (negative) correlation with condition factors and so starvation could play a role, but for the other two species there was no relationship and so enzyme induction must be the major cause. A draft paper will shortly be submitted to Environmental Science and Technology. This project has provided a good example of collaboration within MCWG, both yielding additional information on processes using data gathered within national programmes, and building upon the extensive programme of intercomparison exercises conducted within ICES. J. Boon and his co-authors were thanked by the members of MCWG for undertaking this project and carrying it to a successful conclusion.

Following the completion of the first phase of this study, an expanded data set will be compiled during 1996. Preliminary results from the application of a range of multivariate methods will be discussed at a workshop (tentatively set to precede MCWG 1997, in Texel) and a progress report will be made to the subgroup at next year's meeting. The aim is to complete this work by 1998.

n) Review and report on how published reports have utilized covariation between dissolved organic carbon (DOC) and other substances

The Chemical Oceanography Subgroup was presented with a review paper by Mikael Krysell entitled, 'TOC, DOC and POC in chemical oceanography'. The subgroup members expressed their appreciation of the thorough work carried out by the author.

The topics of the paper were discussed mainly from two points of view: the value of measurements of organic compounds in chemical oceanographic research and, secondly, their usefulness in marine monitoring programmes. In discussion, members reported about monitoring programmes in coastal waters where POC measurements are conducted and related to oxygen concentrations.

Organic carbon is measured in the oceans mainly because it plays a very important role in the global carbon cycle, with implications regarding, for example, global warming through elevated atmospheric carbon dioxide levels. The usefulness of TOC and DOC for oceanographic purposes is very limited, and indeed very few successful attempts to use these parameters as tracers for ocean mixing processes have been reported. It is indeed even hard to find papers describing any kind of correlation between organic carbon and other chemical or biological

parameters. The main reasons are the problems of measuring TOC/DOC accurately in sea water and, more importantly, that they are insufficiently characterized parameters with strongly varying composition and behaviour between different sea areas.

Important aspects of TOC/DOC, apart from the global carbon cycle, are their role in association with metals and organic contaminants within the oceans and their potential role as sources of carbon and nitrogen in primary production.

The MCWG cannot see any reason to recommend generally that DOC/TOC should be included in monitoring programmes. Data on organic carbon can be useful if monitoring programmes are targeted to answer specific questions or as a co-variate for a well-defined purpose.

The MCWG considered it worthwhile that the paper be expanded to include estuaries. M. Krysell agreed to take this task upon himself and to seek contact with J. Tronczynski for (possible) additional input.

o) Provide a report on general principles (chemical and biological) governing the transfer of halogenated organic contaminants illustrated by a few examples, with the aim of facilitating a more detailed request by the Helsinki Commission

J. Boon gave a short presentation on the general principles that govern the bioaccumulation of neutral organic contaminants by marine organisms. A. Abarnou pointed out his recent paper on the topic, 'La bioaccumulation : l'exemple des PCB', in which some of the various chemical and biological aspects of the transfer of halogenated organic compounds through the food chains have been described. This paper is summarized in the following paragraph.

Bioaccumulation of contaminants reflects the ability of aquatic organisms to concentrate and store chemicals from water (bioconcentration) and from food (biomagnification). The bioaccumulation depends on the physico-chemical properties of the compounds and biological factors. A high octanol-water ratio (K_{ow}) and a high persistence are required for the compound to be bioaccumulated. From the K_{ow} of the substance it becomes possible to determine its bioaccumulation potential. Biological factors such as respiration, feeding, growth, and reproduction affect the extent of bioaccumulation. The PCB bioaccumulation model presented in the paper takes into consideration the characteristics of the chemicals and the various biological processes in order to calculate the contamination levels in the organisms and the relative importance of the different contamination sources.

Considering the complexity of food-chain transfer and bioaccumulation of contaminants, the subgroup agreed that the preparation of a review note focusing on specific halogenated organic contaminants (i.e., HCB, PCBs,

PCDD/Fs, DDT and metabolites) and illustrated by several examples is the best way to satisfy the HELCOM request. A. Abarnou, with the collaboration of J. Boon, M. Lebeuf, V. Loizeau and T. van der Zande, accepted to prepare the review note for next year's meeting.

p) Examine the feasibility of, and potential contributions to, an Environmental Status Report for the ICES area on an annual basis and report to ACME by the end of 1995

Some examples of annual reports were mentioned and discussed in order to obtain a feeling for what was requested or what was possible:

- 'The environmental conditions in the sea areas around Sweden', representing the approach by an institute to present its results of relevance to the national monitoring programme;
- 'Havsutsikt' ('Outlook over the sea'), representing a national Swedish effort to briefly summarize the results of the national monitoring programme on an annual basis and in a form to make it easily accessible to the general public;
- 'The environmental state of the Baltic Sea', which represents the efforts of the Environment Committee of the Helsinki Commission to present an annual update of some selected topics concerning the Baltic marine environment.

The discussion is summarized in the following paragraphs.

A well-prepared (annual) report on the environmental status could be useful and at the same time it could be a good way of advertizing the competence of ICES in this field. Before embarking on such a project, the target group of the report should be clearly defined. The target could be the scientific world, but their needs are already covered through the open literature. The public and politicians constitute another target group. A number of members felt, however, that the public and the politicians generally are more interested in their own national waters and that, therefore, their needs are in most countries already covered through national reports. It was proposed that the report would focus on particular subjects that could be selected from the work carried out by the ICES Working Groups. Such a report does not need to be produced on an annual basis. In addition or as an alternative, there could be a task for ICES to collect information about 'grey reports', e.g., lists of national publications from different countries about the marine environment or information where such lists are available. Internet might be an interesting medium on which to make this information available.

A timely publication of such an annual environmental status report, while it still has the value of providing novel information, would be very resource demanding and would put a lot of strain on the capacity of the ICES Secretariat. Since the reporting of data from Member

Countries of ICES is too slow as compared to the needs of the production of the report, this would have to be based, e.g., on national contributions of information which then is to be integrated into an ICES-wide report. Several of the ICES Subject/Area Committees have negative experience from making reports from national contributions since these are very often not delivered on time or not delivered at all.

The MCWG did not come to a firm conclusion but tended to reject the idea of assembling data on an annual basis into an environmental status report. Instead, it has a preference for an attractive series of reports published with a lower frequency on particular topics which are interesting to policymakers and scientists and which reflect the work carried out by different ICES working groups. The MCWG sees an important, structuring role for the ACME. The ACME should define topic areas for inclusion in the report, give tasks to working groups and integrate the information submitted.

The MCWG would be willing to provide relevant new information on subjects chosen by the group every few years.

The idea of an annual report could warrant a theme session at an ICES Annual Science Conference where the subject could then be further developed.

8.2 SIME 1996: Interlaboratory Study on PAH Metabolites

MCWG had also been asked by ICES to consider the possibility of mounting an intercomparison exercise concerning the determination of PAH metabolites, usually determined in bile. In discussion, it was felt that these determinations are currently undertaken as a research activity rather than as a routine monitoring component. PAH metabolites (generally hydroxy-compounds) are determined in fish bile in order to evaluate exposure to PAHs, as these compounds are rapidly metabolized and generally do not accumulate in tissues (Law and Biscaya, 1994). The turnover of PAHs in fish can be very rapid (up to 99 % in 24 hr) (Varanassi *et al.*, 1989) and so the metabolite concentrations reflect only the immediately preceding period (one to a few days) and do not act as an integrator over longer periods (weeks or months). Induction of the cytochrome P450 enzyme systems takes 2-5 days, and so fish must remain exposed for this period to attain an equilibrium. Daily variations in bile production in individual fish also present a limitation to the application of this technique in a monitoring context, as no normalizing factor has been established to date.

Point sources can exert effects in limited areas (e.g., oil platforms typically have an area of contamination up to 2-3 km downstream) and mobile fish may also move in and out of such areas over relatively short periods.

The methodology for determination of PAH metabolites is not as yet fully developed and validated for monitoring

purposes, and both standard and reference materials are currently unavailable. In addition, very few laboratories are making these measurements at the present time, and an intercomparison exercise was felt to be premature at this stage.

Law, R., and Biscaya, J.L. 1994. Polycyclic aromatic hydrocarbons (PAH) — problems and progress in sampling, analysis and interpretation. *Marine Pollution Bulletin*, 29: 235–241.

Varanasi, U., Stein, J.E., and Nishimoto, M. 1989. Biotransformation and disposition of polycyclic aromatic hydrocarbons (PAH) in fish. *In Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*. Ed. by U. Varanasi. CRC Press, Boca Raton, Florida.

8.3 Workshop on Estuarine Processes Recommended by the INPUT Working Group to ASMO

The MCWG supported the idea to organize the workshop. Information about its objectives and design is limited, however. The MCWG pointed therefore to the activities and research of different groups and projects (e.g., the JONUS and EROS programmes), the expertise of which should be used in such a workshop.

J.F. Chiffolleau and M. Leermakers are interested in participating in this workshop and can suggest a number of key persons who could be invited. The Group recommended that ICES fund the participation of the working group members in order to make it possible for them to attend the meeting.

8.4 Second Workshop on Background/Reference Concentrations

The MCWG supported the idea of a Second Workshop on Background/Reference Concentrations proposed by the Dutch Delegation to SIME, and agreed on the relevance of organizing a workshop on background/reference concentrations of contaminants. It was felt that there is sufficient new information to justify this.

The MCWG expressed strong doubts about the possibility of establishing background concentrations of nutrients. The MCWG also felt that to establish reference concentrations, meaning concentrations representative of the situation prior to the proposals for reduction of nutrient loads, would be difficult.

The Group pointed out the importance of having the definitions of background and reference concentrations well established by the workshop. In order to improve the outcome, the Group suggested that the existing report be revised before the workshop, taking all ICES comments from 1995 into account and that all participants at the workshop receive the revised version of the report (and the comments) in advance.

J. Klungsøyr (sediment cores from Shagevale), M. Lebeuf (sediment cores St. Lawrence estuarine area), P. Roose (naturally occurring organochlorine compounds), and R. Law (PAHs) will send new information to the organizers of the workshop. The same persons were in principle interested in participation in such a workshop with respect to the organic compounds. L. Føyn was nominated by the Chemical Oceanography Subgroup for participation in the workshop.

8.5 Other Issues: Trace Metal Subgroup

Quality of the data in the ICES data bank

The subgroup suggested that it should be possible to include in the data files they send to ICES the following:

- If the laboratories used more than one CRM, the data for all of them should be included.
- The procedure used to calculate the detection limit should be reported.
- All results of the laboratory in QUASIMEME exercises should be reported, preferably by giving their code to ICES.

Mercury speciation

A report on mercury speciation in sea water was presented by M. Leermakers. This report was based on the conclusions of a NATO-ARW entitled: 'Global and regional mercury cycles: sources, fluxes and mass balances', held in Novosibirsk, July 1995. The subgroup thought the paper to be very complete and informative.

However, in view of the publication of a large part of this document within the NATO-ARW proceedings, the subgroup asked that a summary should be made of this report and possible recommendations for monitoring programmes should be included.

In this regard it was pointed out that monitoring studies are limited to the assessment of total mercury concentrations whereas speciation data (in particular methylmercury concentrations) are of particular importance in biological effects studies. The formation of methylmercury in coastal and estuarine waters and sediments (including dredged sediment) may have a significant influence on the methylmercury uptake by fish. It is thus recommended that methylmercury be analysed within monitoring programmes in problem areas. In addition, estimation of riverine inputs to the sea should take the complex nature of the estuarine behaviour of mercury into account.

The subgroup also thought that an updated paper on organomercury compounds in biota would be very valuable. M. Leermakers volunteered to prepare this.

New Chairman for the Trace Metal Subgroup

The subgroup appointed Gert Asmund as the Trace Metal

Subgroup Chairman for next year's meeting and the intersessional period.

8.6 Other Issues: Organics Subgroup

New contaminants

J. de Boer will prepare an overview on polychlorinated diphenyl ethers (PCDEs).

M. Haarich will invite G. Rimkus (Lebensmittel- und Veterinäruntersuchungsamt Schleswig-Holstein, Neumünster, Germany) to prepare an overview on nitro-musk compounds and, in addition to that, to give a plenary presentation on this subject.

Topics for next year's meeting

P. Roose will present results of research on the presence of chlorinated solvents and benzene, toluene and xylene (BTEX) in fish.

M. Lebeuf will give a presentation on the occurrence of chlorinated dioxins and furans in sediments, including some core studies.

A. Abarnou will present results of a study on bioaccumulation and biomagnification of PCBs in the food chain.

M. Cleemann will attempt to arrange a presentation on the Arctic Monitoring and Assessment Programme (AMAP).

B. Jansson will prepare a short discussion paper on the formation of bioaccumulating and toxic HCB metabolites and the levels of these compounds in marine organisms.

J. de Boer will prepare a short discussion paper on toxaphene, including aspects of analysis and tolerance levels.

Chairmanship of the Subgroup

The subgroup Chairman, J. Klungsøyr, was appointed as chairman for the next intersessional period by acclamation.

8.7 Other Issues: Chemical Oceanography Subgroup

Units for nutrients and oxygen

The question of the use of proper units for nutrients and oxygen was raised. After some discussion of examples of the confusion that still exists even in referee journals, Alain Aminot accepted the task of presenting a small paper on this topic for the next MCWG meeting.

Ammonia questionnaire

Following the recommendations of the group in 1995, the report on the evaluation of the ammonia questionnaire was sent to the participants who had responded, and a version has been prepared for publication in the open literature. This latter version was revised in order to remove less important details but the analytical section was augmented. From the literature on the determination of ammonia, reagent concentrations were discussed in order to identify the ranges of optimum conditions for the reaction. The main points can be summarized as follows:

- 1) As sea water (35 PSS) contains about 0.8 mmol l⁻¹ bromide, the addition of chlorine produces a mixture of bromine and bromine derivatives which may react with each other and lead to a loss of ammonia. It may therefore be prudent to ensure an excess of chlorine (concentration > 0.8 mmol l⁻¹) to aid the formation of monochloramine.
- 2) A pH between 10.5 and 11 ensures adequate stability for monochloramine and avoids erratic blanks (instability for pH < 10.5).
- 3) The indo-phenol blue (IPB) reaction is said to be made self-buffering by an excess of phenol over alkalinity (Mantoura and Woodward, 1983), but the phenol/chlorine ratio should not be so high that it prevents IPB formation.
- 4) To prevent precipitation of magnesium at the high pH of the reaction, sufficient buffering capacity is required. A slight stoichiometric excess (120 %) is recommended, i.e., 65 mmol l⁻¹ in the reaction medium.
- 5) No improvement can be expected from UV irradiating a nitroprusside catalyzed reaction.
- 6) Among other details, protection of the entire process from light should be the rule during colour development.

Future work programme

The following items were discussed and proposed for contribution to the next meeting:

- Don Kirkwood will present a review of total nitrogen methods.
- Ole Vagn Olsen will prepare a discussion paper on the reliability of old nutrient data.
- Mikael Krysell will present a discussion paper on particulate organic carbon (POC) in anoxic waters.
- Mikael Krysell will present and possibly demonstrate the methods used at SMHI for quality assurance of data to be loaded in the database.

- Alain Aminot will put together a presentation of methods for oxygen determination and their quality assurance.
- All members are asked to contribute with descriptions of the quality control procedures used by their labs on nutrient analysis.

Election of Subgroup Chairman

Stig Carlberg was re-elected with acclamation as chairman for the intersessional period.

9 NOMINATION OF NEW CHAIRMAN

The present MCWG Chairman has completed the maximum period of chairmanship (two terms of three years each). A procedure for the nomination of a new Chairman was introduced and agreed upon (see Annex 7). Four MCWG members were nominated as candidates: J. Boon, S. Carlberg, R. Law and B. Pedersen. The candidates briefly commented upon their candidacy. Prior to the election, the Chairman recalled the important contributions each candidate had made to the MCWG and thanked them for their willingness to be a candidate. B. Pedersen was then elected by the MCWG to be put forward to ACME as new Chairman.

10 ANY OTHER BUSINESS

The MCWG was pleased to receive, by courier, two copies of the 'near-final draft' of ICES Cooperative Research Report No. 213, the final report on NUTS I/C 5. Its authors, A. Aminot and D. Kirkwood, note that in the two years since they presented this report to the MCWG in Brest (February 1994), their very best efforts in Scottish-English have been translated into American-English. The authors are prepared to believe that this was the accidental product of some out-of-control software package. They find it hard to believe that this is

deliberate ICES policy, but if it is, they would appreciate some guidelines on this subject.

11 ACTION LIST AND RECOMMENDATIONS

The action list and recommendations are given in Annexes 8 and 9, respectively.

12 DATE AND VENUE OF NEXT MEETING

The MCWG discussed the venue and time of the next meeting. The Rijksstation voor Zeevisserij in Ostend, Belgium, offered to host the 1997 meeting of the MCWG. The MCWG acknowledged the invitation with appreciation. It was decided to plan the meeting for 3-8 March 1997.

13 CLOSURE OF THE MEETING

Staff members of the Instituto Hidrografico joined the closing session of the Working Group. On behalf of the MCWG, the Chairman, W. Cofino, thanked them for their warm hospitality, the immaculate organization, and for the efforts and services they provided.

In addition, he thanked the Subgroup Chairmen for their efforts and support, and all members for their hard work. Finally, he thanked all members of the MCWG for the very good cooperation and support he has received during his chairmanship. B. Pedersen thanked W. Cofino on behalf of the group for his activities as Chairman of MCWG.

The Chairman then closed the meeting at about 15.00 hrs.

ANNEX 1

LIST OF PARTICIPANTS

Name	Address	Telephone	Facsimile	E-mail
Wim Cofino (Chairman)	Institute for Environmental Studies Vrije Universiteit De Boellelaan 1115 NL-1081 HV Amsterdam The Netherlands	+31 20 44 49 535	+31 20 44 49 553	wcofino@ivm.vu.nl
Alain Abarnou	IFREMER, Centre de Brest B.P. 70 29280 Plouzané France	+33 98.22.43.57	+ 33 98.22.45.48	aabarnou@ifremer.fr
Alain Aminot	IFREMER, Centre de Brest B.P. 70 29280 Plouzané France	+33 98 22 43 61	+33 98 22 45 48	
Gert Asmund	Nat. Environmental Research Inst. Arctic Env. Tagensvej 135 2200 Copenhagen N Denmark	+45 35 82 14 15	+45 35 82 14 20	gfomgeri@inet. uni-c.dk
Gudjon A. Audunsson	Icelandic Fisheries Laboratories P.O. Box 1390 Skulagata 4 121 Reykjavik Iceland	+35 4562 0240	+35 4562 0740	gudjon@rfisk.is
Shier Berman	Institute for National Measurement Standards National Research Council Ottawa, K1A 0R6 Canada	+1 613 .993. 3520	+1 613 993 2451	shier@iecems.lan. nrc.ca
Victoria Besada Montenegro	Inst Español de Oceanografía Centro Oceanografico de Vigo Apartado 1552 36280 Vigo Spain	+34 86 492111	+34 86 492351	insovigo@cesga.es
Jacob de Boer	DLO - Netherlands Institute for Fishery Investigations P.O. Box 68 1970 AB IJmuiden The Netherlands	+31 2555 64736	+31 2555 64644	j.deboer@rivo.dlo.nl
José Biscaya	Ministério da Defesa Marinha Instituto Hidrografico Rua das Trinas, 49 1296 Lisboa Codex Portugal	+351 1 3955119	+351 1 3960515	ihqph@telepac.pt
Jan P. Boon	NIOZ P.O. Box 59 1790 AB Den Burg Texel, The Netherlands	+31 222 369466 +31 222 369300	+31 222 319674	boon@nioz.nl

ANNEX 1 (continued)

Name	Address	Telephone	Facsimile	E-mail
Stig Carlberg	SMHI Oceanographical Laboratory Byggnad 31 Nya Varvet S-42671 Västra Frölunda Sweden	+46 3169 6511	+46 3169 0418	scarlberg@smhi.se
Jean-François Chiffolleau	IFREMER/Centre de Nantes B.P. 1105 Rue de l'Île d'Yeu 44311 Nantes Cedex 03 France	+33 4037 4000	+33 4037 4075	jfchiffo@ifremer.fr
Marianne Cleemann	Nat. Environ. Research Institute P.O. Box 358 4000 Roskilde Denmark	+45 4630 1200	+45 4630 1114	mkmc@wpgate.dmu.min.dk
Lars Føyn	Institute of Marine Research P.O. Box 1870 Nordnes 5024 Bergen Norway	+47 5523 8500 +47 5523 8501 (direct)	+47 5523 8584	lars@imr.no
Michael Haarich	Inst. f. Fischerei Ökologie Labor Sülldorf Wüstland 2 D-22589 Hamburg Germany	+49 40 31908650	+49 40 31908603	
Bo Jansson	Inst of Appl Env Res Stockholm University S-106 91 Stockholm Sweden	+46-8674 7220	+46-828 7829	bo.jansson@mailbox.swipnet.se
Don Kirkwood	MAFF Fisheries Research Lab Lowestoft Suffolk NR33 0HT U.K.	+44 1502 524425	+44 1502 513865	d.s.kirkwood@dfr.maff.gov.uk
Jarle Klungsøyr	Institute of Marine Research P.O. Box 1870 Nordnes 5024 Bergen Norway	+47 5523 8500	+47 5523 8584	jarle.klungsoyr@imr.no
Mikael Krysell	SMHI Oceanographic Laboratory Byggnad 31 Nya Varvet S-426 71 Västra Frölunda Sweden	+46 3169 6542	+46 3169 0418	mkrysell@smhi.se
Robin Law	MAFF Fisheries Laboratory Burnham on Crouch Essex CM0 8HA U.K.	+44 1621 782658	+44 1621 784989	r.j.law@dfr.maff.gov.uk
Michel Lebeuf	Maurice Lamontagne Institute Department of Fisheries and Oceans P.O. Box 1000 Mont-Joli Québec G5H 3Z4 Canada	+1 418 775 0690	+1 418 775 0542	m_lebeuf@qc.dfo.ca

ANNEX 1 (continued)

Name	Address	Telephone	Facsimile	E-mail
Martine Leermakers	Vrije Universiteit Brussels Dept. of Analytical Chemistry Pleinlaan 2, 1050 Brussels Belgium	+32 2 6293263	+ 32 2 6293274	analchem@vnet3.vub.ac .be
Kalervo Mäkelä	Finnish Institute of Marine Research (FIMR) P.O. Box 33 00931 Helsinki Finland	+358 0613941	+358 061394494	k.makela@fimr.fi
Teresa Nunes	Inst Español de Oceanografía Centro Oceanografico de Vigo Apartado 1552 36280 Vigo Spain	+34 86 49 21 11	+34 86 49 23 51	:insovigo@cesga.es
Jon Olafsson	Marine Research Institute Skulagata, 4 P.O. Box 1390 121 Reykjavik Iceland	+354 552 0240	+354 562 3790	jon@hafro.is
Ole Vagn Olsen	Danish Institute for Fisheries Research Charlottenlund Slot 2920 Charlottenlund Denmark	+45 33 96 34 08	+45 33 96 34 34	vo@dfu.min.dk
Britta Pedersen	National Environmental Research Institute P.O. Box 358 DK 4000 Roskilde Denmark	+45 46301209	+45 46301114	hmbpe@dmu.dk
Patrick Roose	Rijksstation voor Zeevisserij Ankerstraat, 1 8400 Oostende Belgium	+32 59 320805	+32 59 330629	
David Wells	SOAEFD, Marine Laboratory P.O. Box 101, Victoria Road Aberdeen AB9 8DB U.K.	+44 1224 876544 +44 1224 295368 (direct)	+44 1224 295511	wellsd@marlab.ac.uk
Carlos Vale	IPIMAR Av. Brasilia 1400 Lisboa Portugal	+351 1 3010814	+351 1 301 5948	
Antony E. van der Zande	RIKZ P. O. Box 207 9750 AE Haren The Netherlands	+31 50 53 31 301	+31 50 53 40 772	vdzande@rws.rikz.minv enw.nl

ANNEX 2

AGENDA

- 1 Opening of the meeting
- 2 Adoption of the agenda
- 3 Report of the 83rd ICES Statutory Meeting
- 4 Reports on related activities
 - 4.1 OSPARCOM and HELCOM

Official requests have been included in the agenda. For HELCOM advice is requested regarding organotins (agenda item 8.1.3/8.2.4) and the transfer of halogenated organic compounds in food chains (agenda item 8.2.10). For OSPARCOM, advice on guidelines is requested for sampling and analysis of organic chemicals in marine media (agenda items 8.2.1 and 8.2.3).
 - 4.2 Intergovernmental Oceanographic Commission
 - 4.3 ICES

ICES has given the MCWG two tasks to be carried out jointly with WGEAMS and WGMS (monitoring guidelines for PAHs in biota and sediments) respectively, with WGEAMS (review outcome of QUASIMEME interlaboratory study on planar CBs and preparation of guidelines for sampling and analysis of marine biota for these compounds). In addition, the MCWG is requested to consider which contributions it can make to an annual Environmental Status Report for the ICES area. This item is on the agenda of all subgroups.
 - 4.4 EU-BCR QA pilot project "QUASIMEME"

Dr Wells has been requested to provide an update.
 - 4.5 Other activities

Members who wish to make a presentation under this item should prepare a note for the MCWG report.
- 5 Reports on projects and activities in member countries

Members who wish to make a presentation under this item should prepare a note for the MCWG report.
- 6 Requests from ACME and regulating agencies

Requests which have arisen prior to this agenda being produced have been included.
- 7 Plenary presentations
 - 7.1 J.F. Chiffolleau Trace metal behaviour in estuaries: the Seine and the Gironde estuaries (France) as two examples.
- 8 Subgroup activities and discussions
 - 8.1 Trace Metal Subgroup
 - 8.1.1 (C.Res.1995/2:14:2 c) Review and report on the progress in the Intercomparison exercise on the Analysis of Trace Metals in Sea Water. *[In Reykjavik it was agreed that B. Pedersen, J. Olafsson, J.F. Chiffolleau and S. Berman would co-ordinate this exercise.]*
 - 8.1.2 (C.Res.1995/2:14:2 d) Review and report on the status of the EU-QUASIMEME project and its implications for the work of the MCWG.
 - 8.1.3 (C.Res.1995/2:14:2 f) Provide further information on analytical methods and choice of matrices for the measurement of the presence of organotin compounds in the marine environment (HELCOM 8).

ANNEX 2 (continued)

- 8.1.4 (C.Res.1995/2:14:2 g) Review and report on the outcome of the Workshop on Estuarine Behaviour of Metals. *[This workshop has not taken place due to problems getting the participants together despite several attempts of J. Chiffolleau. The subgroup needs to decide whether it is viable to pursue this matter further.]*
- 8.1.5 (C.Res.1995/2:14:2 i) Review the results of coordinated investigations on lipids as co-factors and report on their implications for monitoring programmes.
- 8.1.6 (C.Res.1995/2:14:2 j) Review the progress in the understanding of chemical associations of various metals and liver lipid types and indicate possible implications for monitoring programmes. *[In Reykjavik it was noted that a Danish/Norwegian/Icelandic study group would address these associations. An update on the progress will be given.]*
- 8.1.7 (C.Res.1995/2:14:2 l) Update, where appropriate, the list of contaminants which can be monitored on a routine basis, including a discussion about actual analytical proficiency based on recent interlaboratory studies.
- 8.1.8 (C.Res.1995/2:14:2 p) Examine the feasibility of, and potential contributions to, an Environmental Status Report for the ICES area on an annual basis.
- 8.1.9 Any other business raised by the subgroup. *[Among others, the Metals Subgroup needs to appoint a chairperson to deal with matters which may arise intersessionally and who can chair the subgroup next year.]*
- 8.2 Organic Subgroup
- 8.2.1 (C.Res.1995/2:14:2 b) Develop monitoring guidelines for polycyclic aromatic hydrocarbons in sediments and biota, paying attention to appropriate detection limits, and the number of replicate samples required per sampling area in order to characterise the sampling area for sediments (with WGMS) and biota (with WGEAMS) (OSPAR 1.1). *[Please appoint a coordinator who will liaise with WGEAMS and WGMS intersessionally.]*
- 8.2.2 (C.Res.1995/2:14:2 d) Review and report on the status of the EU-QUASIMEME project and its implications for the work of the MCWG.
- 8.2.3 (C.Res.1995/2:14:2 e) Review the outcome of the QUASIMEME interlaboratory study on planar CBs in marine media and advise on the development of guidelines for the sampling of marine biota (with WGEAMS) and their analysis for non-ortho and mono-ortho CBs (OSPAR 2.2).
- 8.2.4 (C.Res.1995/2:14:2 f) Provide further information on analytical methods and choice of matrices for the measurement of the presence of organotin compounds in the marine environment (HELCOM 8).
- 8.2.5 (C.Res.1995/2:14:2 h) Prepare draft advice on alternative methods for the determination of lipids in marine samples (OSPAR 2.1). *[W. de Waal agreed in Reykjavik to act as co-ordinator of a group of laboratories working on lipid research and to report on the progress of this work at the present meeting.]*
- 8.2.6 (C.Res.1995/2:14:2 i) Review the results of co-ordinated investigations on lipids as co-factors and report on their implications for monitoring programmes. *[P. Roose agreed in Reykjavik to act as co-ordinator of a group of laboratories working on lipid research and to report on the progress of this work at the present meeting.]*
- 8.2.7 (C.Res.1995/2:14:2 k) Assess the review notes on modern pesticides, Igarol 1051, tris(4-chlorophenyl) methane and tris(4-chlorophenyl) methanol, triphenyltin, butyltin and organomercury. *[W. de Waal, R. Law, J. de Boer and G. Ducastel agreed to prepare these notes or to make arrangements therefore.]*

ANNEX 2 (continued)

- 8.2.8 (C.Res.1995/2:14:2 l) Update, where appropriate, the list of contaminants which can be monitored on a routine basis, including a discussion about actual analytical proficiency based on recent interlaboratory studies. *[This list has been compiled at the 1995 MCWG meeting and can be found in the report thereof.]*
- 8.2.9 (C.Res.1995/2:14:2 m) Review and report on progress on a joint study to compare and contrast the different results of using multivariate methods on a common data set on PCBs in fish-eating marine mammals. *[This work would be carried out by J. Boon, D. Wells, J. Klungsøyr, P. Leonards, R. Law and E. Storr-Hansen.]*
- 8.2.10 (C.Res.1995/2:14:2 o) Provide a report on general principles (chemical and biological) governing the transfer of halogenated organic contaminants illustrated by a few examples, with the aim of facilitating a more detailed request by HELCOM. *[A first attempt to deal with this request has been made in Reykjavik.]*
- 8.2.11 (C.Res.1995/2:14:2 p) Examine the feasibility of, and potential contributions to, an Environmental Status Report for the ICES area on an annual basis.
- 8.2.12 Any other business raised by the subgroup. *[Among others, the subgroup needs to appoint a chairperson who deals intersessionally with matters which may arise and who may chair the subgroup next year.]*
- 8.3 Chemical Oceanography
- 8.3.1 (C.Res.1995/2:14:2 a) Review and report on the plans for the Sixth Intercomparison Exercise on the Analysis of Nutrients in Sea Water (NUTS 6). *[This item may encompass the report which A. Aminot would prepare regarding the stability of silica samples.]*
- 8.3.2 (C.Res.1995/2:14:2 d) Review and report on the status of the EU-QUASIMEME project and its implications for the work of the MCWG.
- 8.3.3 (C.Res.1995/2:14:2 n) Review and report on how published reports have utilised covariation between dissolved organic carbon (DOC) and other substances.
- 8.3.4 (C.Res.1995/2:14:2 p) Examine the feasibility of, and potential contributions to, an Environmental Status Report for the ICES area on an annual basis.
- 8.3.5 Any other business raised by the subgroup. *[Among others, the subgroup needs to appoint a chairperson to deal with matters which may arise intersessionally and who may chair the subgroup next year.]*
- 9 Plenary discussion of subgroup work
- 10 Nomination of new chairperson for the Marine Chemistry Working Group
The present chairman has completed the maximum period of chairmanship (two terms of three years each). The MCWG will elect a person who will be nominated as chairperson to ACME. Please note that ACME is not bound to accept the nomination, as discussed in the 1995 MCWG report.
- 11 Any other business
- 12 Recommendations and action list
- 13 Data and venue of next meeting
- 14 Closure of meeting

ANNEX 3

REFERENCES ON ORGANOTIN ANALYSIS

- Waldock MJ, Waite ME, Miller D, Smith DJ & Law RJ (1989). the determination of total tin and organotin compounds in environmental samples. Aquatic Environment Protection: Analytical Methods, MAFF Directorate of Fisheries Research, Lowestoft (4), 25 pp.
- Stäb, J.A., Brinkman, U.A.Th and Cofino W.P., (1994). Validation of the analysis of organotin compounds using alkylation and gas chromatography. *J. Appl. organometallic Chem.* 8, 577-585.
- Stäb, J.A., W.P. Cofino, B. van Hattum and U.A.Th. Brinkman (1993). Comparison of GC/MSD and GC/AED for the determination of organotin compounds in the environment. *Fresenius J. Anal. Chem.* 347, 247-255.
- Stäb, J.A., B. van Hattum, P. de Voogt and U.A.Th. Brinkman (1992). Preparation of pentylated organotin standards for use in trace analysis with gas chromatography. *Microchim. Acta* 109, 101-106.
- Stäb, J.A., M Frenay, I.L. Freriks, U.A.Th. Brinkman, and W.P. Cofino (1995). Survey of nine organotin compounds in the Netherlands using the zebra mussel (*Dreissena polymorpha*) as biomonitor. *Environ. Toxicol Chem.* 14, 2023-2032.

Refs. HBr extraction method:

- Meinema, H.A., T. Burger-Wiersma, G. Versluis-de Haan, and E.Ch. Gevers (1978). Determination of trace amounts of butyltin compounds in aqueous systems by gas chromatography/mass spectrometry. *Environ. Sci. Technol.* 12, 288-293.
- Gomez-Ariza, J.L., R. Beltrán, E. Morales, I. Giraldez, and M. Ruiz-Benitez (1995) Acid extraction treatment of sediment samples for organotin speciation; occurrence of butyltin and phenyltin compounds on the Cadiz coast, south-west Spain. *Appl. Organometallic Chem.* 9, 51-64.

Comparison of hexane/tropolone extraction vs. direct derivatization with tetraethylborate, followed by extraction:

- Jantzen, E. and Wilken R.-D. (1991). Organotin compounds in harbour sediments-analysis and critical examination. *Vom wasser*, 76, 1-11. (in German with English summary).

Extraction and derivatization with tetraethyl borate:

- Wilken, R.-D., J. Kuballa, and E. Jantzen (1994) Organotins: their analysis and assessment in the Elbe river system, northern Germany. *Fresenius J. Anal Chem.* 350, 77-84.
- Lalère, B., J. Szpunar, H. Budzinski, P. Garrigues, and O.F.X. Donard. Speciation analysis for organotin compounds in sediments by capillary gas chromatography with flame photometric detection after microwave assisted leaching. *Analyst*, submitted.
- Donard, O.F.X., B. Lalère, F. Martin, and R. Lobinski (1995). Microwave assisted leaching of organotin compounds from sediments for speciation analysis. *Anal. Chem.* 67, 4250-4254.

Hydride/methylation

- Plzák, Z., M. Polanská, and M. Suchánek (1995). Identification and determination of butyltin compounds in water by ion trap gas chromatography-mass spectrometry after conversion to methyl or hydride derivatives. *J. Chromatography A*, 699, 241-252.

ANNEX 4

LIPIDS AS A CO-FACTOR

INTRODUCTION

The use of the lipid content of biological tissue to normalize the concentration of lipophilic organic compounds measured in marine environmental samples is a widespread and common practice. The rationale behind this approach presupposes a close correlation between the lipids and the organic contaminants which should allow a reduction in the variability of the data. This approach may also enhance the comparability of data originating from (a) the same species from different geographical regions, (b) different species from the same region, (c) the same species from the same region, and (d) different species from different regions. In addition to normalizing data for spatial distribution monitoring, this method may also be used to reduce the variability of temporal trends.

There are, however, some serious implications when this approach is used. Firstly, it is essential that a clear correlation exists between the determinand and the normalizing factor (lipid content). Secondly, the variance of the measurement of the normalizing factor must be the same as or lower than the variance of the determinand measurement. The general term 'lipids' refers to a complex mixture of molecules with a broad range of chemical properties. It is therefore equally important to describe what is meant by the term 'lipid' for these measurements, especially when data are to be compared in national or international monitoring programmes.

This Annex evaluates the objectives and use of lipids as a cofactor in marine environmental monitoring, and the current knowledge related to lipids in this application.

USE OF AND NEED FOR A NORMALIZING FACTOR

In principle, normalization should reduce the variability and enhance the comparability of data by eliminating the influence of cofactor covariations (i.e., grain size fraction in sediments or lipid levels in biota). Thus, normalization is useful when comparing different sample types, such as silty and sandy sediments, different species of fish, or different sediment fractions or tissue types. Apart from that, the methods used for the determination of the normalizing factor such as lipids must ensure that the techniques used result in reliable measurements and always yield the same quality within predetermined limits of accuracy, precision, and repeatability. The quality of the data on the cofactor should be significantly better than that required for the determinand and the dynamic range should cover all likely natural variations in the measured parameters.

In marine environmental monitoring, a number of situations would benefit from data normalization:

- 1) comparison of contaminant levels between different tissues/organisms of single individuals, e.g., when the distribution of contaminants in tissues is evaluated to study transfer mechanisms, transformation processes, metabolization, persistence, toxicity and toxicological effects;
- 2) comparison of contaminant levels in a particular tissue/organism of different/many individuals of a certain species from a specific area, e.g., assessment of existing levels, target or non-target screening, comparison of relative concentrations;
- 3) comparison of contaminant levels in the same species for different years, e.g., for the assessment of temporal trends;
- 4) comparison of contaminant levels in the same species for different areas, e.g., for the assessment of spatial distribution both on a small (e.g., regional) and large (e.g., convention area) scale;
- 5) comparison of contaminant levels in different species for the same area, e.g., when investigating the transfer of contaminants between species of the same trophic chain;
- 6) comparison of contaminant levels in different species for different areas, e.g., when monitoring spatial distribution and a certain species cannot be found at all locations;
- 7) comparison of contaminant levels in different species for different areas and different years.

The following sections will discuss the conditions under which lipids are suitable as a cofactor.

LIPIDS AS A COFACTOR

Introduction

Lipophilic contaminants in biota are generally normalized to the extractable or total tissue lipid content, which is operationally defined. For this simple approach, the relationship between the contaminant concentration and the lipid content is assumed to be linear (Hebert and Keenleyside, 1995). In principle, this implies that either an increase or a decrease in lipid levels is reflected by an increase or decrease in contaminant levels, with a constant ratio. This assumption can only be valid if the following conditions are met:

- the mechanisms that govern the accumulation, storage, and elimination of contaminants are

comparable for all species and individuals and independent of food, digestion, and physiology;

- the chemical and physical properties and the composition of the lipids or certain lipid fractions do not differ or do not influence the uptake, accumulation, metabolism, or elimination of the contaminants.

Both conditions can only be met if the uptake and elimination of contaminants are governed solely by physico-chemical processes, such as equilibrium partitioning, as was suggested previously by several authors (Scura and Theilacker, 1977; Schneider, 1982; Duinker and Boon, 1985). The validity of this approach is discussed below.

Relationship between lipid content and contaminant concentration

A positive correlation between the contaminant concentration and the lipid content has been reported by a number of authors (Schaefer *et al.*, 1976; Goerke *et al.*, 1979; Schneider, 1982; Delbeke *et al.*, 1995; Cooreman *et al.*, 1996; Roose *et al.*, in press). This would certainly justify the use of lipids as a normalizing factor, but is it enough? Kelly and Campbell (1994) questioned the use of lipids as a normalizing factor due to the lack of a clear relationship between the cofactor and the contaminants. They found both positive and negative correlations between lipid content and contaminant levels. This could, however, be due to differences in sampling time (seasonal variations). Bignert *et al.* (1993) made similar observations, but could not clearly relate the variations to the sampling time (seasonal variation). This indicates, at least, that fat content alone is probably not enough to normalize the contaminant data, certainly not for higher organisms such as fish. Furthermore, if the uptake and elimination of contaminants are only the result of equilibrium processes, the concentrations on a lipid basis should be independent of the age (size) of the fish. Again, both situations are reported in the literature. De Boer (1988) reported an increase in the concentrations of CBs in cod liver with age (size) of the fish. Roose *et al.* (in press) reported both the absence of a relationship between PCB concentrations in cod muscle and an increase in PCB concentrations in cod liver with age (size) of the fish. Not only does sampling time (season) play an influential role in the relationship between contaminant concentration and lipid content, but tissue type and age of the animal also appear to be important.

Other authors argue that an improvement in normalizing on a lipid basis is made when only selected lipid classes are used. Schneider (1982) and Petersen *et al.* (1995) concluded that the total neutral lipids (sum of free fatty acids, triglycerols, cholesterol and cholesterol esters) are the best available basis for the normalization of highly lipophilic contaminant data. Similar conclusions were made by Delbeke *et al.* (1995) for contaminant data in different species from the same sampling location. The

question can therefore be raised as to whether contaminant data should be expressed in relation to a selected class of lipids. Although the authors demonstrated a reduction of the variance between species and within species, it remains to be determined whether this step is sufficient when normalizing data on a neutral lipid basis. Karl and Lehmann (in prep.) demonstrated an increase in lipid content (total lipid content) of mackerel with age of the fish in waters around the British Isles. In other fishing grounds, levels appeared more or less constant with the length of the fish. This only further suggests that lipid content alone is insufficient.

Contaminant concentrations in organisms are the result of a combination of uptake (through water and food) and elimination (excretion, metabolism) mechanisms and not only the result of relatively simple thermodynamic processes. It is therefore unlikely that the lipid content alone, even if selected lipid classes are used, will sufficiently cover the natural variations in concentrations.

Analysis

The quality of lipid determinations should be significantly better than the quality of the contaminant data. At present, a number of techniques are used to determine the total lipid content in biological material. The method described by Bligh and Dyer (1959) using chloroform, methanol, and water would appear to be the most efficient, convenient, and reliable technique for the extraction of total lipids (Booij and van den Berg, in press; de Boer and van der Meer, in prep.; ICES, 1993), while minimizing the extraction of non-lipid impurities such as proteins (de Koning *et al.*, 1985). Non-lipid impurities can significantly enhance the variability of contaminant data. This was demonstrated by Delbeke *et al.* (1995), who discovered the presence of a significant amount of non-lipid co-extracts during a 'total lipid extraction' based on the method of Folch *et al.* (1957). Moreover, at present there does not appear to be a reliable alternative to the Bligh and Dyer method available (Ackman and Klungsøyr, 1994).

An additional dimension to the complexity of the problem is added when it is necessary to determine lipid classes. Traditionally this has been done using either thin layer chromatography (TLC) or adsorption chromatography. A more recent adaptation of TLC is the Iatroscan technique which has also proved to be a reliable tool for both the qualitative and quantitative determination of selected lipid classes. Finally, high performance liquid chromatography systems (HPLC) coupled to a suitable detector such as a mass spectrometer (MS) or an Evaporative Mass Detector (EMD) can also be used (Myher and Kuksis, 1995).

Although an improvement in the quality of lipid determinations is certainly necessary (Bailey and Wells, 1994), at present the question should focus more on the rationale behind the determinations.

ALTERNATIVE NORMALIZATION METHODS

At present, no reliable alternatives have been reported that can replace lipids as a cofactor in marine environmental monitoring. It has been suggested that water content may be a useful normalizing factor for organic contaminants. It is evident that there is a functional relationship between lipid content and water content, which has been used intensively for many years to estimate fat content by fish processing industries. However, the relationship between water content and concentration of organic contaminants could be regarded as an indirect relationship. Chemical and physical properties of organic contaminants and lipids are similar, thus indicating a possible association, whereas this is not the case for water content and organic contaminants.

CONCLUSIONS

Although the use of lipids as a normalizing factor has proved to be a valid tool in marine environmental science, there are some limitations to this practice that need to be understood. Based on the above discussion, it is evident that solely and simply dividing contaminant concentrations by the lipid fraction will not eliminate natural variations. Correlations between lipid content and contaminant concentrations have been established, but the relationship is not always the same and needs, in any case, to be further studied. Moreover, the use of lipids as the sole normalizing factor is only valid if the uptake of organic contaminants is solely the result of equilibrium partitioning between the organism's lipids and the surrounding environment. Although this assumption might be appropriate for relatively simple organisms such as mussels, it will certainly not be the case for more complex organisms such as fish. The contributions of food and metabolism in complex organisms cannot be neglected. Using selected lipid classes could further enhance the comparability of the data but, again, this requires further investigation. The Bligh and Dyer method (1959) is, at present, the best available technique for the determination of total lipids. The total lipid content can be used in marine environmental studies, provided that additional selection criteria, such as sampling time, age, and sex, are used.

References

- Ackman, R., and Klungsøyr, J. 1994. Current problems with lipid measurement. Proceedings of the QUASIMEME Lipid Workshop, Dublin, 13–16 October 1994.
- Bailey, S.K., and Wells, D.E. 1994. The measurement of lipids as a co-factor for organic contaminants in biota. Proceedings of the QUASIMEME Lipid Workshop, Dublin, 13–16 October 1994.
- Bignert, A., Göthberg, A., Jensen, S., Litz, N., Odsjö, M., Olsson, M., and Reutergårdh, L. 1993. The need for adequate biological sampling in ecotoxicological investigations: a retrospective study of twenty years pollution monitoring. *Science of the Total Environment*, 128: 121–139.
- Bligh, E.G., and Dyer, W.J. 1959. A rapid method of total lipid extraction and purification for organic compounds. *Canadian Journal of Biochemistry and Physiology*, 37: 911–917.
- Booij, K., and van den Berg, C. In press. Comparison of techniques for the extraction of lipids and PCBs from benthic invertebrates. *Bulletin of Environmental and Contaminant Toxicology*, 53.
- Cooreman, K., Roose, P., and Vyncke, W. 1996. EROD monitoring in dab from the Belgian Continental Shelf: seasonal variation and relation to organochlorines. *In Proceedings of the Symposium on the 1993 North Sea Quality Status Report*.
- de Boer, J. 1988. Chlorobiphenyls in bound and non-bound lipids of fishes: Comparison of different extraction methods, *Chemosphere*, 17(9): 1803–1810.
- de Boer, J., and van der Meer, J. In prep. Report on the results of the ICES/IOC/OSPARCOM intercomparison exercise on the determination of chlorobiphenyl congeners in marine media—step 4. ICES Cooperative Research Report.
- de Koning, A.J., Evans, A.A., Heyenrych, C., Purcell, C.J., and Wessels, P.H. 1985. A critical investigation of a number of different methods of lipid determination in fish meal, with particular emphasis on corrections required in these determinations. *Journal of Sci Food Agriculture*, 36: 177–185.
- Delbeke, K., Teklemariam, T., de la Cruz, E., and Sorgeloos, P. 1995. Reducing variability in pollution data: the use of lipid classes for normalisation of pollution data in marine biota. *International Journal of Environmental and Analytical Chemistry*, 58: 147–162.
- Duinker, J.C., and Boon, J.P. 1985. PCB congeners in the marine environment—A review. *In Organic Micropollutants in Aquatic Environment. Proceedings of the 4th European Symposium*, edited by the Commission of the European Communities, Vienna, Commission of the European Communities, pp. 187–205.
- Folch, J., Lees, M., and Sloane Stanley, G.H. 1957. A simple method for the isolation and purification of total lipids from animal tissues. *Journal of Biological Chemistry*, 226: 497–509.
- Goerke, H., Eder, G., Weber, K., and Ernst, W. 1979. Patterns of organochlorine residues in animals of

- different trophic levels from the Weser Estuary. *Marine Pollution Bulletin*, 10: 127–133.
- Hebert, C.E., and Keenleyside, K.A. 1995. To normalize or not to normalize? Fat is the question. *Environmental Toxicology and Chemistry*, 14: 801–807.
- ICES, 1993. Report of the ICES Marine Chemistry Working Group. ICES CM 1993/Env:1, p.13.
- Karl, H., and Lehmann, I. In prep. Spatial distribution and length-concentration relationship of organochlorine residues in the edible part of mackerel (*Scomber scombrus*).
- Kelly, A.G., and Campbell, L.A. 1994. Organochlorine contaminants in liver of cod (*Gadus morhua*) and muscle of herring (*Clupea harengus*) from Scottish waters. *Marine Pollution Bulletin*, 28: 103–108.
- Myher, J.J., and Kuksis, A. 1995. General strategies in chromatographic analysis of lipids. *Journal of Chromatography*, B671: 3–33.
- Petersen, G., St. John, M., Rimek, A., and Schneider, R. 1995. Comparison of chlorobiphenyl congener and pesticide concentrations in cod tissues in relation to their lipid class composition. ICES CM 1995/E:14. 8 pp.
- Roose, P., Cooreman, K., and Vyncke, W. In prep. PCBs in cod (*Gadus morhua*), flounder (*Platichthys flesus*), blue mussel (*Mytilus edulis*) and brown shrimp (*Crangon crangon*) from the Belgian continental shelf in the period 1983–1993: relation to biological parameters and trend analysis. *ICES Journal of Marine Science*.
- Schaefer, R.G., Ernst, W., Goerke, H., and Eder, G. 1976. Residues of chlorinated hydrocarbons in North Sea animals in relation to biological parameters. *Berichte der Deutschen Wissenschaftlichen Kommission für Meeresforschung*, 24: 225–233.
- Schneider, R. 1982. Polychlorinated biphenyls in cod tissues from the Western Baltic. Significance of equilibrium partitioning and lipid composition in the bioaccumulation of lipophilic pollutants in gill-breathing animals. *Meeresforschung*, 29: 69–79.
- Scura, E., and Theilacker, G. 1977. Transport of the chlorinated hydrocarbon PCB in a laboratory marine food chain. *Marine Biology*, 40: 317–325.

Acknowledgement

This review has been prepared by P. Roose, Fisheries Research Station, Ostend, Belgium, M. Haarich, Federal Fisheries Research Centre, Hamburg, Germany, E. Nixon, Fisheries Research Centre, Abbotstown, Ireland, and A. Abernou, IFREMER, Centre de Brest, France.

ANNEX 5

TRIS(4-CHLOROPHENYL)METHANOL AND TRIS(4-CHLOROPHENYL)METHANE IN THE MARINE ENVIRONMENT: ORIGIN, ANALYSIS, DISTRIBUTION, AND TOXICITY

J. de Boer
Netherlands Institute for Fisheries Research
Ijmuiden, The Netherlands

Abstract

Tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane (TCPMe) are globally widespread contaminants. They have been found in fish, birds, and marine mammals from various parts of the world. TCPM concentrations in marine mammals from the North Sea are around 1–2 mg/kg on a lipid weight basis. TCPM and TCPMe are highly bioaccumulative and a 10- to 100-fold biomagnification from fish to marine mammals is suggested. There is a lack of knowledge on production figures, origin, and application of these compounds. There is also very little information about their toxicity. There are indications of a possible carcinogenic character. Toxicological research on these two compounds is recommended as a first step. Depending on the results of such research, TCPM and TCPMe may be seriously considered for inclusion as voluntary determinands in international monitoring programmes.

Origin, production, and use

Tris(4-chlorophenyl)methanol and tris(4-chlorophenyl)methane have been detected as micro-contaminants in the marine environment since 1989 (1). Several abbreviations are used for these compounds, such as 4,4',4''-TCP, TCP, TCPM and TCPM-OH for tris(4-chlorophenyl)methanol and 4,4',4''-TCPMe, TCPMe, and 4,4',4''-TCPM for tris(4-chlorophenyl)methane. In this paper the abbreviations TCPM and TCPMe will be used. TCPM and TCPMe (Figure 1) are structurally related to DDT and dicofol (1,1,1-trichloro-2,2-bis(4-chlorophenyl)methanol (Figure 2).

There is little information available on the sources of TCPM and TCPMe. From citations in the patent literature, the use of these compounds in synthetic (optically active) high polymers and lightfast dyes for acrylic fibers was suggested as sources for the environmental presence of TCPM and TCPMe (Jarman *et al.*, 1992; Michaels and Lewis, 1985; 1986). TCPM may be a metabolite of TCPMe or tris(4-chlorophenyl)methylchloride (TCPC), both of which are used in the production of dyes. However, some of the patent literature is rather new and it is questionable whether that use would completely account for the apparent long-time presence of TCPM and TCPMe in the environment.

Figure 1. Structural formulas for (a) TCPM and (b) TCPMe.

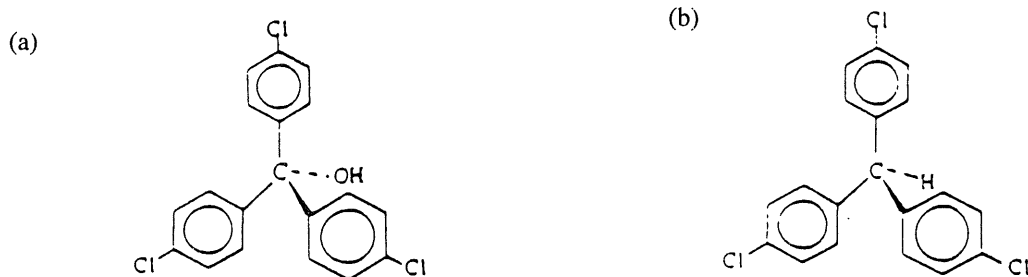
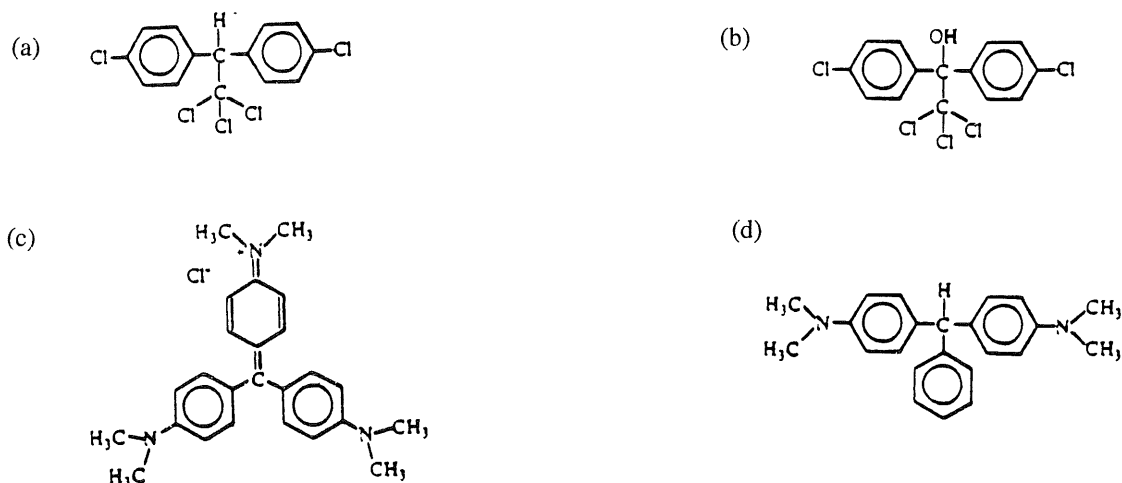


Figure 2. Structural formulas for (a) p,p' DDT, (b) Dicofol, (c) Basic violet 3, and (d) malachite green.



Another source of TCPM and TCPMe may be the pesticide DDT. Buser (1995) showed that under conditions such as those used in the technical synthesis of DDT, 4,4',4''-TCPMe and two additional isomers 2,2',4''- and 2,4',4''-TCPMe were formed in small amounts. In two technical DDT mixtures Buser (1995) determined the same isomers in total amounts of 150–180 mg/kg, of which about one-third was 4,4',4''-TCPMe. These impurities in commercial DDT mixtures may have contributed to environmental levels of TCPM and TCPMe, but probably do not completely explain these levels. It is likely that the presence of TCPM and TCPMe in the marine environment originates from various sources. As with DDT, formulations of dicofol may contain impurities of TCPM (Jarman *et al.*, 1992). Other citations from an American Chemical Society Chemical Abstracts Search (CAS) mention TCPM as a starting product for the manufacture of anthelmintic drugs (Jarman *et al.*, 1992) and anti-ecdysone activity of TCPM, similar to the agrochemical Triarimol (Jarman *et al.*, 1992). Obviously, there is an urgent need for more information on the production and use of TCPM and TCPMe.

Analytical methods

Extraction of TCPM and TCPMe from biological materials or sediments is generally carried out by Soxhlet extraction with dichloromethane (Walker *et al.*, 1989; Rahman *et al.*, 1993) or mixtures of dichloromethane with n-hexane (Jarman *et al.*, 1992) or n-pentane (de Boer *et al.*, 1996). Zook *et al.* (1992) used a cold column extraction with dichloromethane/n-hexane (50:50, v/v).

Florisil columns are used for the separation of lipids and the target compounds (Walker *et al.*, 1989, Jarman *et al.*, 1992, Rahman *et al.*, 1993). Zook *et al.* (1992) used a dialysis technique with a polyethylene film for the removal of lipids, followed by gel permeation chromatography (GPC) using S-X3 Bio beads with dichloromethane/n-hexane (50:50, v/v), carbon column chromatography and florisil columns. De Boer *et al.* (1996) have tried to avoid the use of florisil because of the extensive pre-treatment and its relative instability. They used GPB, Bio beads S-X3 with dichloromethane/n-hexane (50:50, v/v) for the separation of lipids and TCPM and TCPMe. The GPC elution was carried out twice and was followed by a silica gel column fractionation to separate TCPM and TCPMe from PCBs. The recovery of a TCPM spike in a seal blubber extract in this method was 90 %. The same authors reported that TCPM was unstable during a sulphuric acid treatment and that TCPM could not be separated from lipids by alumina column chromatography (de Boer *et al.*, 1996).

Gas chromatography is the method of choice for the determination of TCPM and TCPMe. Non-polar or medium-polar columns, such as DB5 (Walker *et al.*, 1989; Jarman *et al.*, 1992), DB17 (Jarman *et al.*, 1992; de Boer, 1995), CP Sil 8 (de Boer *et al.*, 1996) and CP Sil 12 (de Boer *et al.*, 1996) can be used. TCPM and TCPMe elute relatively late in the chromatograms, normally just before octachloronaphthalene, with GC oven temperatures around 270–300 °C. Splitless injection can be used (de Boer *et al.*, 1996).

Three different detection methods have been used to date: GC/ECD (Walker *et al.*, 1989; Jarman *et al.*, 1992; Zook *et al.*, 1992), GC/EI (electron impact)-MS (Walker *et al.*, 1989; Jarman *et al.*, 1992; Buser, 1995; Rahman *et al.*, 1993; de Boer *et al.*, 1996; Zook *et al.*, 1992), and GC/NCI (negative chemical ionisation)-MS (de Boer *et al.*, 1996; Zook *et al.*, 1992). The ions used for identification and quantification in GC/MS are 111, 139, 141, 251, 362, 364 (TCPM, EI-MS), 362, 346, 348 (TCPM, NCI-MS), 311, 313, 346, 348 (TCPMe, EI-MS) and 346, 348 (TCPMe, NCI-MS). Much more fragmentation is observed in the EI spectra compared to the NCI spectra (Figure 3). As is to be expected, the most prominent peaks in the NCI spectra are due to the molecular ions.

De Boer *et al.* (1996) have compared the sensitivity of the three detection techniques for TCPM and TCPMe (Table 1). Generally, compounds with less than four chlorine atoms are rather difficult to determine in environmental samples by means of GC/NCI-MS because of the extremely low sensitivity (de Boer, 1995). However, for TCPM the electronegativity of the oxygen apparently helps to increase sensitivity, thereby resulting in good analyte detectability for this compound. Clearly, GC/NCI-MS is not the method of choice for TCPMe because of low sensitivity (Table 1). This confirms the role of the oxygen atom observed with TCPM. Both GC/EI-MS and GC/ECD are suitable alternatives, but MS-based detection is preferred because of its higher selectivity. GC/EI-MS, in principle, can also be used for the determination of TCPM with m/z 139 used for quantification. However, quantification on such a low mass is easily disturbed by interferences of mass fragments of other compounds. This was clearly demonstrated by comparing EI and NCI results for TCPM in a variety of samples (de Boer *et al.*, 1996). Depending on the sample, results up to 10-fold too high were obtained by GC/EI-MS. Such problems are normally not encountered in the GC/EI-MS determination of TCPMe for which the relatively high m/z value of 311 is used. The different sensitivity of TCPM and TCPMe for the two MS techniques necessitates replicate injections of the extract containing TCPM and TCPMe. Even though it is time-consuming, it results in a sensitive and selective analysis of both compounds.

Table 1. Detection limits of TCPM and TCPMe (de Boer *et al.*, 1996).

Method	GC/ECD		GC/EI/MS		GC/NCI-MS	
	CP Sil 8		CP Sil 8/12a		CP Sil 8/12a	
	TCPM	TCPMe	TCPM	TCPMe	TCPM	TCPMe
Detection limit (pg)	10	10	30	10	3	100
Detection limit $\mu\text{g}/\text{kg}$	0.1	0.1	0.2	0.07	0.02	0.7

The use of ECD detection only causes a small loss in sensitivity (Table 1), but a considerable loss in selectivity. ECD, therefore, can be used for screening TCPM and TCPMe, but confirmation by GC/NCI-MS or GC/EI-MS, respectively, will often be essential.

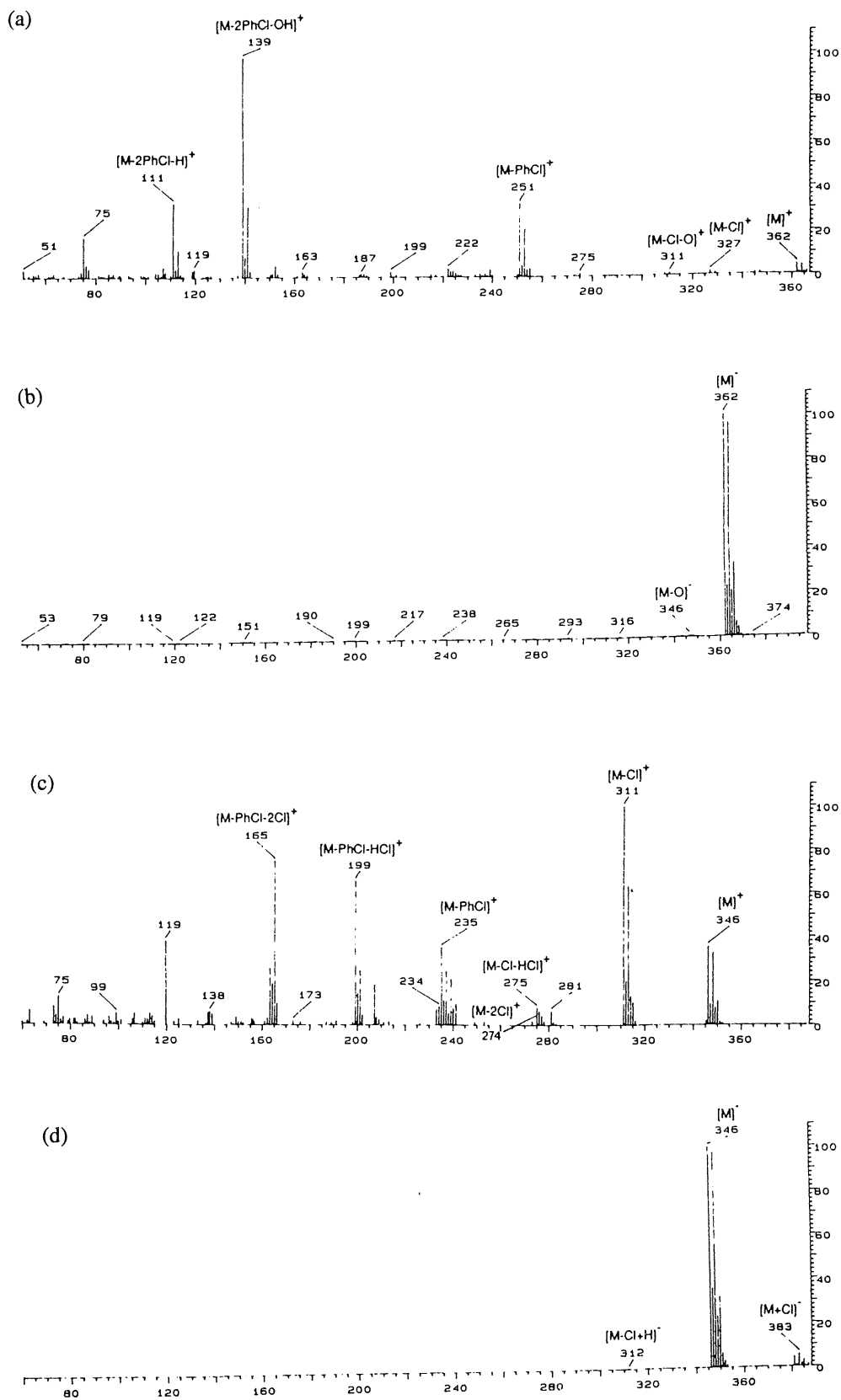
Distribution in the marine environment

TCPM and TCPMe are present in fish, birds, and marine mammal samples on a global scale. Walker *et al.* (1989) reported the presence of TCPM in scale from Puget Sound (northwest USA) after synthesis of TCPM as an analytical standard. Jarman *et al.* (1992) reported the presence of TCPM and TCPMe in various birds and marine mammals from the Arctic, Antarctica, Australia, and the USA. The presence of TCPM in a variety of environmental tissues from different areas in Canada was semi-quantitatively determined by Norstrom and Simon (1989). The presence of TCPM and TCPMe in adipose tissue and livers of seals from the Baltic Sea was reported by Zook *et al.* (1992). De Boer *et al.* (1996) reported the presence of TCPM and TCPMe in several marine mammals, cod liver, and mussels from the North Sea and the Dutch Wadden Sea. TCPMe was synthesized by these authors and its presence in North Sea and Wadden Sea samples was confirmed. They also reported the presence of TCPM and TCPMe in eel from the Rhine delta and several other Dutch rivers and in sediment from the Rhine delta. Rahman *et al.* (1993) reported the presence of TCPM in cod liver oil and mackerel oil originating from the southern North Sea. The same authors also reported the presence of TCPM and TCPMe in Italian human milk at levels of 2.5 and 1.6 $\mu\text{g}/\text{kg}$, respectively. An overview of the levels of TCPM and TCPMe reported in marine environmental samples is given in Table 2.

A considerable data set is available for TCPM, but the quantity of TCPMe data is limited because TCPMe was only recently synthesized as an analytical standard (de Boer *et al.*, 1996). The results vary from <1 to 6,800 $\mu\text{g}/\text{kg}$ on a lipid weight basis in some fish samples and polar bear liver, respectively, which shows that TCPM and TCPMe are highly bioaccumulative. A considerable bioconcentration of TCPM and TCPMe is also expected on the basis of the octanol-water partition coefficients calculated by the C log P method (Hansch and Leo, 1979). Log K_{ow} is 6.0 for TCPM and 6.5 for TCPMe.

Most data originated from marine mammal samples. Only in the North Sea have fish (cod liver and mackerel), shellfish (mussels), and marine mammal samples have been analysed. TCPM concentrations in these samples suggest a strong biomagnification of TCPM from fish to seals, porpoise, and dolphins in the order of magnitude of 10- to 100-fold. The total number of samples analysed from the different areas is relatively small. It is, therefore, difficult to make any conclusions about the natural variation of TCPM concentrations in marine mammals. However, data of other halogenated microcontaminants in marine mammals, such as PCBs, show that the natural variation can be relatively large (Duinker *et al.*, 1989). The range of TCPM concentrations found in the marine mammals therefore indicates that significant differences in biomagnification between the different species are unlikely.

Figure 3. Mass spectra of TCPM in (a) the EI and (b) the NCI mode, and of TCPMe in (c) the EI and (d) the NCI mode (de Boer *et al.*, 1996).



TCPM concentrations in cod liver are comparable to those reported for HCB and p,p'-DDT in the same matrix (de Boer, 1995). Rahman *et al.* (1993) reported that TCPM and TCPMe concentrations in Italian human milk were two to three orders of magnitude lower than the detected levels of other organochlorine compounds such as DDT. This could suggest a metabolism of TCPM and TCPMe in the human body. However, the calculation method used in that study may have resulted in less accurate TCPM and TCPMe data because analytical standards were not available and the calculation was based on the assumption of equimolar responses of TCPM, TCPMe, and CB 169 in GC/EI-MS.

TCPM was found in two samples originating from 1952 (Table 2). These data show that TCPM has been present in the environment for at least 45 years. More recent data on TCPM in organisms from the St. Lawrence River show that current levels are about ten-fold higher than in 1952.

TCPM is reported in samples from areas around the world. One reason for this ubiquitous occurrence may be the presence of the 4-chlorophenyl rings in the compound, which are found in other persistent contaminants, such as p,p'-DDT and its metabolites (p,p'-DDD and p,p'-DDE). This structure is also found in bis(4-chlorophenyl)sulfone which was recently reported as a new persistent contaminant (Olsson and Bergman, 1995). The 4-chlorophenyl structure appears to be highly resistant to transformation in the environment. TCPM concentrations on a lipid weight basis decrease from 180–360 µg/kg in eel from the Rhine delta, to 40 µg/kg in cod liver from the southern North Sea, to 6 µg/kg in cod liver from the northern North Sea (Table 2). Only in fish samples from the Mediterranean were TCPM and TCPMe detected at levels below 1 µg/kg lipid weight. This suggests a relationship between high TCPM concentrations and densely populated, industrialized areas. High TCPM concentrations in samples from the Baltic Sea and Lake Ontario and low TCPM concentrations in samples from Antarctica support this hypothesis.

Contamination of biota and sediment in the Rhine estuary with, for example, PCBs and organochlorine pesticides has remained essentially constant for the last three years (de Boer, 1995). Although this may be different with regard to TCPM and TCPMe, a comparison of sediment samples from 1992 with eel samples from 1994 from the same area may give at least an indication of the distribution of TCPM and TCPMe in biota and sediments. When comparing the concentrations in fish expressed on a lipid weight basis with those in sediment expressed on an organic carbon basis, the fish/sediment ratios are in the range 1.1–14 for TCPM, and 2.8–13 for TCPMe. These ratios roughly correspond with those determined for PCBs in the same area (ratio 1–5) (de Boer, 1995). They are much higher than the ratio range of 0.2–1 for polychlorinated terphenyls (PCTs) in the same area (Wester *et al.*, 1996). These data suggest that the adsorption characteristics of TCPM and TCPMe to sediments are comparable to those of PCBs.

Toxicity

There are almost no data available on the toxicity of TCPM and TCPMe. Michaels and Lewis (1985) have reported a toxicity study on five azo and triphenylmethane dyes. In that study Basic Violet 3, with a structure in which the basic structure of TCPM can be recognized (Figure 2), shows the highest toxicity, i.e., a survival rate of $20.7 \pm 6.6\%$ at a dye concentration of 5.0 mg/L of microbiota in a plating medium incorporated with dye. The structures of TCPM and TCPMe also closely resemble that of malachite green (Figure 2), a well known carcinogenic dye, which easily forms radicals. The presence of a compound resembling such a carcinogenic substance in fish could have serious consequences.

Hoogenboom (1996) carried out an Ames test with TCPM and TCPMe. In order to determine a positive result in this test, two criteria are used. The number of revertants should be dose-related and the positive response should be reproducible. In the study of Hoogenboom, no dose-related increase in the number of revertants was observed with either TCPM or TCPMe. However, an increased number of revertants was observed at the highest dose of 5 mg TCPM and 5 mg TCPMe. It was difficult to evaluate the toxicity of the compounds based on the presence of microcolonies due to precipitation of both compounds at this dose-level. The authors concluded that the positive results require confirmation in an independent trial and, until then, no definite conclusion can be drawn with respect to the mutagenic potential of TCPM and TCPMe. It is clear that more knowledge on the toxicity and particularly on the carcinogenic potential of TCPM and TCPMe should become available.

Conclusions

There is little information on sources, production figures, and application of TCPM and TCPMe. Their use in synthetic high polymers and dyes for acrylic fibers and their presence in technical DDT are some suggestions for their environmental presence. TCPM and TCPMe are, however, globally distributed in the marine environment. The concentrations of TCPM and TCPMe in North Sea fish, although based on a small number of samples, are comparable to those of HCB and DDT. Based on this observation and on the calculated log K_{ow} values of 6.0–6.5, TCPM and TCPMe appear to be highly bioaccumulative. High TCPM and TCPMe levels in marine mammals from all over the world indicate a strong biomagnification, in the order of magnitude of 10–100 from fish to marine mammals. Their

Table 2. Concentrations of TCPM and TCPMe in various samples from the marine environment.

Sample	Location	Year	TCPM µg/kg ^a	TCPMe µg/kg ^a	References
Harbour seal blubber	Puget Sound, USA	1972–1982	23–750		Walker <i>et al.</i> , 1989
Northern fur seal blubber	St. Lawrence River, Canada	1981	5–29		Jarman <i>et al.</i> , 1992
Harp seal fat	St. Lawrence River, Canada	1952	2		Jarman <i>et al.</i> , 1992 Norstrom and Simon, 1988
Ringed seal liver	Baltic Sea	1980–1987	3,000		Zook <i>et al.</i> , 1992
Ringed seal adipose tissue	Baltic Sea	1980–1987	900		Zook <i>et al.</i> , 1992
Comm seal blubber	Dutch Wadden Sea	1990–1992	750–2,000		de Boer <i>et al.</i> , 1996
Antarctic fur seal milk	South Georgia Island, Antarctica	1984–1985	< 2–2.7		Jarman <i>et al.</i> , 1992
Australian sea lion milk	Kangaroo Island, Australia	1987	< 7		Jarman <i>et al.</i> , 1992
California sea lion milk	California (central coast), USA	1988	19		Jarman <i>et al.</i> , 1992
Belgua whale fat	St. Lawrence River, Canada	1984–1986	1–41		Jarman <i>et al.</i> , 1992 Norstrom and Simon, 1988
Beluga whale fat	St. Lawrence River, Canada	1952	4		Jarman <i>et al.</i> , 1992 Norstrom and Simon, 1988
Whitebeaked dolphin blubber	Newfoundland, Canada	1982	184		Norstrom and Simon, 1988
Whitebeaked dolphin blubber	Dutch Wadden Sea	1992	570		de Boer <i>et al.</i> , 1996
Whitebeaked dolphin blubber	Southern North Sea	1990	1,400		de Boer <i>et al.</i> , 1996
Common dolphin blubber	Dutch Wadden Sea	1992	220		de Boer <i>et al.</i> , 1996
Harbour porpoise blubber	Southern North Sea	1990	1,000		de Boer <i>et al.</i> , 1996
Polar bear fat	Arctic, Canada	1984	35		Jarman <i>et al.</i> , 1992 Norstrom and Simon, 1988
Polar bear liver	Arctic, Canada	1983	4,000–6,800		Jarman <i>et al.</i> , 1992 Norstrom and Simon, 1988
Herring gull egg	Lake Ontario, Canada	1971–1985	94–3,300		Jarman <i>et al.</i> , 1992 Norstrom and Simon, 1988
Peregrine falcon egg	Crofton (central coast), BC, Canada	1989	250–5,300		Jarman <i>et al.</i> , 1992
Great blue heron egg	Crofton (central coast), BC, Canada	1986	36		Jarman <i>et al.</i> , 1992
Cod liver	Northern North Sea	1992	6	2	de Boer <i>et al.</i> , 1996
Cod liver	Southern North Sea	1993	40		de Boer <i>et al.</i> , 1996
Cod liver oil	Southern North Sea	1987	51	3	Rahman <i>et al.</i> , 1993
Mackerel oil	Southern North Sea	1987	35	0.6	Rahman <i>et al.</i> , 1993
Mussels	Dutch Wadden Sea	1994	13	< 6	de Boer <i>et al.</i> , 1996
Tuna, perch, angler, mullet	Mediterranean Sea	1992	< 1	< 1	Rahman <i>et al.</i> , 1993
Yellow eel	Rhine delta, The Netherlands	1994	180–360	37	de Boer <i>et al.</i> , 1996
Sediment ^b	Rhine delta, The Netherlands	1992	26–160	4–13	de Boer <i>et al.</i> , 1996

^a µg/kg lipid weight

^b concentration in sediment in µg/kg total organic carbon

persistence seems to be caused by the presence of the 4-chlorophenyl ring structures. Adsorption of TCPM and TCPMe to sediments is comparable to that of PCBs.

TCPM and TCPMe concentrations in biota and sediments can be determined by GC/ECD, GC/EI-MS, and GC/NCI-MS after Soxhlet extraction and separation from lipids by GPC, florisil, and/or silica gel columns. GC/EI-MS is preferred for detection of TCPMe and GC/NCI-MS is preferred for detection of TCPM.

There is a lack of toxicological knowledge of these compounds. Based on structural comparisons and on information from a first Ames test, there are indications of a carcinogenic character of TCPM and TCPMe, but obviously confirmation of this suggestion is required.

Further toxicological research on TCPM and TCPMe is needed to obtain a better estimation of the possible risks to human health and marine ecosystems posed by the presence of TCPM and TCPMe in the marine environment. Depending on the results of such research and given the current concentrations of TCPM and TCPMe in the marine environment, there may be good reasons to include TCPM and TCPMe as voluntary determinands in international monitoring programmes.

References

- Boer, J. de. 1995. Analysis and biomonitoring of complex mixtures of persistent halogenated micro-contaminants. Ph.D. Thesis, Free University, Amsterdam, The Netherlands.
- Boer, J. de, Wester, P.G., Evers, E.H.G., and Brinkman, U.A.Th. 1996. Determination of tris(4-chlorophenyl)methanol and tris(4-chlorophenyl)methane in fish, marine mammals and sediment. *Environ. Pollut.*
- Buser, H.R. 1995. DDT, a potential source of environmental tris (4-chlorophenyl)methanol. *Environ. Sci. Technol.*, 29: 2133–2139.
- Duinker, J.C., Hillebrand, M.T., Zeinstra, T., and Boon, J.P. 1989. Individual chlorobiphenyls and pesticides in tissues of some cetacean species from the North Sea and the Atlantic Ocean: tissue distribution and biotransformation. *Aquatic Mammals*, 15: 95–124.
- Hansch, C., and Leo, A.J. 1979. Substituent constants for correlation analysis in chemistry and biology. J. Wiley, New York, USA.
- Hoogenboom, L.A.P. 1996. Salmonella/microsome test with tris(4-chlorophenyl)methanol and tris(4-chlorophenyl)methane. Draft report LHO.RIK.95.04, RIKILT-DLO, Wageningen, The Netherlands.
- Jarman, W.M., Simon, M., Norstrom, R.J., Bruns, S.A., Bacon, C.A., Simaret, B.R.T., and Riseborough, R.W. 1992. Global distribution of tris(4-chlorophenyl)methanol in high trophic level birds and mammals. *Environ. Sci. Technol.*, 26: 1770–1774.
- Michaels, G.B., and Lewis, D.L. 1985. Sorption and toxicity of azo and triphenylmethane dyes to aquatic microbial populations. *Environ. Toxicol. Chem.*, 4: 45–50.
- Michaels, G.B., and Lewis, D.L. 1986. Microbial transformation rates of azo and triphenylmethane dyes. *Environ. Toxicol. Chem.*, 5: 161–166.
- Norstrom, R., and Simon, M. 1988. Presence of tris(chlorophenyl)methanol in Canadian environmental tissue samples. Report-CRD-88-7, Canadian Wildlife Service, Chemistry Research Division, Hull, Quebec, Canada.
- Olsson, A., and Bergman, Å. 1995. A new persistent contaminant detected in Baltic wildlife: bis(4-chlorophenyl)sulfone. *Ambio*, 24: 119–123.
- Rahman, M.S., Montanarella, L., Johansson, B., and Larsen, B. 1993. Trace levels of tris(4-chlorophenyl)methanol and -methane in human milk. *Chemosphere*, 27: 1487–1497.
- Walker, W., Riseborough, R.W., Jarman, W.M., Lappe, B.W., Lappe, J.A., Tefft, J.A., and de Long, R.L. 1989. Identification of tris (chlorophenyl)methanol in blubber of harbour seals from Puget Sound. *Chemosphere*, 18: 1799–1804.
- Wester, P.G., de Boer, J., and Brinkman, U.A.Th. 1996. Determination of polychlorinated terphenyls in aquatic biota and sediment with gas chromatography/mass spectrometry using negative chemical ionisation. *Environ. Sci. Technol.*, 30: 473–480.
- Zook, D.R., Buser, H.R., Bergquist, P.A., Rappe, C. 1992. Detection of tris(4-chlorophenyl)methanol in ringed seal (*Phoca hispida*) from the Baltic Sea. *Ambio*, 21: 557–560.

ANNEX 6

Table 1. Organic contaminants that can be monitored in biota and sediments on a routine basis.

Organic contaminant	Recent I/C data available ¹⁾	QC material available	Laboratory's capability ⁸
1. Chlorobiphenyls, CBs 101, 118, 138, 153, 180	Yes (sediment, lean and fatty fish tissue, mussel, seal oil) ²⁾	CRMs (SRMs) and certified standards Biota: BCR CRM 349, 350, IAEA: MA-B-3-OC, 351, NIST 1588, NRC CARP-1 Sediments: BCR CRM 536, IAEA 357, NIST 1939, NRC HS-1, HS-2	Sediment: CBs 118, 138, 153, S _R 3) 15%, R 50% Seal oil: CBs 138, 153, 180, S _R 15%, R 50% Fish oil: CBs 101, 118, 138, 153, 180, S _R 15%, R 50% Lean fish, mussel: CBs 118, 138, 153, 180, S _R 50-70%, R 200%-330%
2. Non-ortho CBs 77, 126, 169	Yes (fish oil) ⁴⁾	No	Some specialist laboratories; s _R 20-50%, R 65-200% (fish oil)
3. Organochlorine pesticides HCHs, DDT, DDD, DDE, HCB, dieldrin, <i>trans</i> -nonachlor	Yes (sediment, mussel, lean and fatty fish tissue, fish oil) ⁵⁾	CRMs and certified standards	Fish oil: s _R 15-30%, R 50-100% Sediment: s _R 35-100%, R 130-800% Mussel, lean and fatty fish: S _R 25-100%, R 85-800%
4. PAHs	Yes (raw sediment extract)	CRMs and certified standards Biota: NISR 1974 Sediments: IAEA 357, NIST 1941, NRC HS-3, HS-4, HS-5, HS-6, SES-1, CRM 535	Raw sediment extract: S _R 20-35%, R 65-130%
5. Chlorinated dioxins and furans	No ⁹⁾	CRMs and certified standards (NRC, CARP1)	Some specialist laboratories
6. CHBs (toxaphene)	Yes ⁶⁾	No	Some specialist laboratories; s _R ca. 50%, R 200% (fish oil)
7. Organotin (TBT, TPT)	No	CRM (TBT), NRC sediment PACS-1, fish (Japan, NISH)	Some specialist laboratories
8. Methyl mercury	No ⁷⁾	NRC: DORM-2, DOLT-2, LUTS-1, TORT-2	Some specialist laboratories

1) This column refers to work carried out with regard to marine environmental analyses.

2) Refs: ICES Cooperative Research Reports on ICES/IOC/OSPARCOM CB intercomparison exercise; QUASIMEME reports on CB intercomparison exercises (1993-1995).

3) s_R standard error; R; reproducibility4) Refs: Voogt, P. de *et al.* 1994. Anal. Chem., 66: 1012-1016; Wells, D.E. Report on ICES intercomparison exercise on non-ortho CBs, MCWG 1994; Quasimeme report round 5, 1996, Aberdeen, U.K.

5) Ref: QUASIMEME reports on CB and OCP intercomparison exercises (1994-1995).

6) Ref: Andrews, P.A. 1995. Chemosphere 31: 4393-4402; a second study is under way.

7) Recently information from an intercomparison exercise in sediment came available in the EU (S,M&T). A CRM (sediment) is in preparation.

8) Where the between laboratory coefficient of variation (SR) exceeds 50% it is reasonable to conclude that there is insufficient agreement for the group of laboratories, as a whole, to undertake these measurements. A selection of more experienced laboratories would be recommended.

9) Information on non-marine matrices is available from WHO studies.

ANNEX 7

PROCEDURE FOR NOMINATION OF CHAIRMAN

(Copy Of Paper Which Has Been Handed Out)



**International Council for the Exploration of the Sea
Marine Chemistry Working Group**

Nomination for Chairman MCWG 1997–1999

The following persons have been suggested as candidates and have accepted the candidacy:

Jan Boon
Stig Carlberg
Robin Law
Britta Pedersen

The proposed nomination procedure is as follows:

Only formal delegates to the MCWG can vote. The list provided by ICES used to send the invitations for this meeting is used to identify these delegates. According to this definition, the following attendees of this meeting are delegates to the MCWG:

Alain Abarnou	Michael Haarich
Alain Aminot	Bo Jansson
Gert Asmund	Don Kirkwood
Gudjon Audunsson	Jarle Klungsøy
Shier Berman	Mikael Krysell
Victoria Beseda Montenegro	Robin Law
Jacob de Boer	Kalervo Mäkelä
José Biscaya	Teresa Nunes
Jan Boon	Jon Olafsson
Stig Carlberg	Ole Vagn Olsen
Jean-Francois Chiffolleau	Britta Pedersen
Marianne Cleemann	Patrick Roose
Wim Cofino	Dave Wells
Lars Føyn	

Please notify me if you are not on this list but do not agree with this.

Prior to the nomination procedure, members can nominate a candidate in addition to the four candidates mentioned above.

The candidates will be given the opportunity to comment briefly upon their candidacy. The candidate to be nominated needs a majority of the votes. In a first round, MCWG delegates will be given the opportunity to vote for one of the candidates. If in this first round no candidate obtains a majority of the votes, a second round will be held. In the second round, the MCWG delegates can vote for one of the two candidates which received the most votes in the first round.

I thank the candidates that they have accepted the candidacy on behalf of the group!

Wim Cofino, Tuesday 13 February 1996

ANNEX 8

ACTION LIST

W. Cofino	Notify ICES Headquarters that only a very few members of the MCWG have received the report of the 1995 meeting.
D. Kirkwood	Send a letter to prospective NUTS 6 participants to advise them to participate in the new QUASIMEME Laboratory Testing Scheme.
J.Boon, P. Roose, J. Klunsgøyr, T. van der Zande	Provide R. Law with information about methodology on PAH analyses and examples of monitoring to be used for draft monitoring guidelines.
J. Klunsgøyr	Contact ICES for information about PAH monitoring from the HELCOM Baltic Sea Monitoring Study.
T. Nunes	Maintain the link with MCWG and WGMS regarding the development of guidelines for PAH analysis.
B. Jansson	Inform WGEAMS about the work underway in MCWG on PAHs and inform R. Law.
R.Law	Coordinate the preparation of a draft document on monitoring PAHs, to be submitted to the MCWG in 1997.
B. Pedersen	Invite laboratories to participate in interlaboratory studies for trace metals in sea water.
B. Pedersen, G. Asmund, S. Berman	Organize the interlaboratory study on trace metals in sea water.
S. Berman	Evaluate the interlaboratory study on trace metals in sea water.
D. Wells, W. Cofino	Send out a questionnaire on organotin analysis, and consider the possibilities to organize an interlaboratory study on this topic.
D. Wells	Provide information on lipids arising from QUASH to MCWG (if relevant).
G. Asmund	Make information from the Danish/Norwegian/Icelandic study on associations between metals and lipids available to the MCWG.
J. de Boer	Send methodological details about TCPM and TCPMe and a standard solution to J. Klunsgøyr, M. LeBoeuf, M. Haarich, R. Law and A. Abarnou; make concise report on findings from the analyses.
J. Klunsgøyr, M. LeBoeuf, M. Harrich, R. Law, and A. Abarnou	Analyse TCPM and TCPMe in marine samples, report data to J. de Boer.
B. Jansson	Provide data on TCPM and TCPMe to MCWG in 1997.
D. Wells	Provide ICES with the report of the QUASIMEME programme, paying attention specifically to what can be obtained in terms of between-laboratory precision, soon after the QUASIMEME Crieff Workshop in March 1996.
D. Wells	Prepare report on Texel meeting on multivariate methods for MCWG 1997.
M. Krysell	Update the paper on DOC/TOC to include estuaries, seek contact with J. Tronszynski for (possible) additional input.

ANNEX 8 (continued)

A. Abarnou, J. Boon, M. Lebeuf, V. Loizeau, T. van der Zande	Prepare a review note on the food-chain transfer and bioaccumulation of contaminants, focusing on halogenated organic compounds and illustrated with examples.
S. Berman	Summarize the performance of recent NOAA and QUASIMEME interlaboratory studies.
J. Klungsøyr, M. Lebeuf, P. Roose, R. Law	Send new information relevant for the establishment of background/reference concentrations to the organizers of the OSPAR SIME workshop on this topic.
G. Asmund	Act intersessionally as chairman of the Trace Metal Subgroup.
P. Roose	Present results of research on the presence of chlorinated solvents and benzene, toluene and xylene in fish.
M. Lebeuf	Give a presentation at MCWG 1997 on the occurrence of chlorinated dioxins and furans in sediments.
A. Abarnou	Present results of a study on the biomagnification and bioaccumulation of PCBs in the food chain.
M. Cleemann	Arrange a presentation on the results from the Arctic Monitoring and Assessment Programme (AMAP).
B. Jansson	Prepare a short discussion paper on the formation of bioaccumulating and toxic HCB metabolites and the levels of these compounds in marine organisms.
J. de Boer	Prepare a short discussion paper on toxaphene including aspects of analysis and tolerance levels.
J. Klungsøyr	Act intersessionally as chairman of the Organic Subgroup.
A. Aminot	Prepare a concise paper on units for nutrients and oxygen.
D. Kirkwood	Prepare a review of total nitrogen methods.
O. Vagn Olsen	Prepare a discussion paper on the reliability of old nutrient data.
M. Krysell	Prepare a discussion paper on particulate organic carbon (POC) in anoxic waters.
M. Krysell	Prepare a presentation on, and possibly demonstrate, the methods used at SMHI for quality assurance of data to be loaded in the database.
A. Aminot	Prepare a paper on methods for oxygen determination and their quality assurance.
All members	Contribute with descriptions of the quality control procedures used by their laboratories in nutrient analysis.
S. Carlberg	Act intersessionally as chairman of the Subgroup on Chemical Oceanography.
J. Klungsøyr, B. Jansson, de Zande, T. Nunes, M. Cleemann, P. Roose, M. LeBeuf, A. Abarnou, M. Haarich, E. McGovern.	Seek information on current use and production volumes of Irgarol 1051 in their countries and send data to R. Law.

RECOMMENDATIONS

Recommendation 1

The MCWG recommends that NUTS 6 not be organized and that all prospective NUTS 6 I/C participants should be advised to join the new QUASIMEME Laboratory Testing Scheme.

Recommendation 2

The MCWG recommends that ICES not offer to arrange interlaboratory studies aiming to fulfill the needs of regular proficiency testing but rather uses the resources for interlaboratory studies to support research and development.

Recommendation 3

The MCWG does not recommend that an interlaboratory study for PAH metabolites be conducted in view of the small number of laboratories measuring these compounds, the lack of well-validated methods, and the absence of reference materials.

Recommendation 4

The MCWG recommends that planar CBs not be included in monitoring programmes aimed at the assessment of spatial distributions or temporal trends, but that their measurement be confined to research projects and to programmes in which the quality of fish products for human health are assessed.

Recommendation 5

The MCWG recommends that ICES support the OSPAR Workshop on Background/Reference Concentrations.

Recommendation 6

The MCWG recommends that J.F. Chiffolleau and M. Leermakers represent ICES at and contribute to the workshop organized by the INPUT Working Group of OSPAR in 1996 or 1997.

Recommendation 7

The MCWG recommends that B. Pedersen be appointed as its new Chairman.

Recommendation 8

The MCWG (B. Pedersen, Chairman) should accept the offer made by the Rijksstation voor Zeevisserij in Ostend, to host the next meeting in Belgium. This meeting should be held from 3–8 March 1997 to carry out the following tasks:

- a) review the first draft guidelines for monitoring PAHs;
- b) review the outcome of the interlaboratory study on trace metals in sea water;
- c) assess the need and possibilities to organize an interlaboratory study in the field of organotin analysis;
- d) review the progress of studies looking into the associations between metals and lipids in biological tissues and report on the implications for marine monitoring;
- e) review progress in the collaborative study on TCPM and TCPMe;
- f) review and report on progress on a joint study to compare and contrast the different results of using multivariate methods on a common data set on PCBs in fish-eating marine mammals;
- g) review the performance for metals of laboratories in recent NOAA and QUASIMEME interlaboratory studies and derive indicators for performance which can be used in the design of monitoring programmes as a representative estimate for between-laboratory variability;
- h) review the outcome of the workshop on estuarine processes organized by the INPUT Working Group of OSPAR and discuss its implications for the MCWG;
- i) review the overview papers on chlorinated solvents and BTX in fish, chlorinated dioxins and furans in sediments, the formation of HCB metabolites, toxaphene, Irgarol 1051 and phenyltins;
- j) update where appropriate the list of contaminants which can be monitored on a routine basis, including a discussion about actual analytical proficiency based on recent interlaboratory studies;
- k) review the paper on bioaccumulation and biomagnification of PCBs in the food chain, with the aim of facilitating a more detailed request on the transfer of halogenated compounds in food chains by the Helsinki Commission;
- l) review papers on units for nutrients and oxygen, total nitrogen methods, the reliability of old nutrient data, and POC in anoxic waters;
- m) review the paper on quality assurance of data to be loaded in a database and prepare general guidelines for this activity;
- n) review the paper on methods for oxygen determination and their quality assurance and provide guidance for OSPAR;
- o) review descriptions of members' protocols for quality control procedures used in their laboratories on nutrient analysis;
- p) review the updated paper on DOC/TOC in sea water including estuaries.

