**Marine Habitat Committee** **ICES CM 2000/E:01**
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**REPORT OF THE**

# MARINE CHEMISTRY WORKING GROUP

**ICES, Copenhagen**
**28 February–3 March 2000**



International Council for the Exploration of the Sea

Conseil International pour l'Exploration de la Mer

Palægade 2–4 DK–1261 Copenhagen K Denmark

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## 1 OPENING OF THE MEETING

The Chair, Dr B. Pedersen, opened the meeting of the Marine Chemistry Working Group (MCWG) at 10.00 hrs on 28 February 2000. The General Secretary of ICES, Mr David Griffith, welcomed MCWG to the ICES Secretariat. MCWG participants introduced themselves and briefly described their main area(s) of research. The list of participants is given in Annex 1. The Chair passed on greetings from absent members and friends of the group.

## 2 ADOPTION OF THE AGENDA

The terms of reference for this meeting of the Marine Chemistry Working Group are copied below.

ICES C.Res.1999/2:E:01

The **Marine Chemistry Working Group** [MCWG] (Chair: Dr B. Pedersen, Denmark) will meet at ICES Headquarters from 28 February to 3 March 2000 to:

A. Chemical Oceanography Subgroup

a) review progress on the application of high temperature techniques for the determination of total nitrogen in sea water;

b) review information on experience in the use of automated *in situ* chemical oceanographic systems for the observation of chemical variables;

c) review a comparison of spectrophotometric and volumetric alternatives for quantification in the Winkler method for the determination of dissolved oxygen in sea water and report on the outcome;

d) review the use of chemical data in numerical modelling and the possible implications for future work in modelling and in field sampling programmes, including the preparation of a workshop or joint session with the WGSSO in 2001.

B. Organics Subgroup

a) review the updated list of relevant certified reference materials for organic compounds for use in marine monitoring;

b) critically evaluate the lists of priority contaminants prepared in relevant regional and international organizations;

c) review new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane (TCPMe) in fish and in marine mammals from eastern Canada, including the results of the TCPM and TCPMe interlaboratory study, second phase;

d) review information on volatile organic contaminants in biota;

e) review new information on the analysis of PAH metabolites in bile and critically review the robustness of the methods;

f) review new information on the use of membrane systems for sampling;

g) review new information on the monitoring and analysis of toxaphene.

C. Trace Metals Subgroup

a) critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations;

b) review, in conjunction with WGSSO, information on estuarine transport of trace metals and report on the outcome of the techniques available and the comparability of their results;

c) review new information on the use of membrane systems for sampling;

d) review new information on the use of contaminant concentrations in biological media as environmental indicators to detect trends, including supplementary work to the Icelandic cod study on the relationship between trace element concentrations in cod liver and various cofactors.

D. Plenum

a) review and endorse the updated list of contaminants which can be monitored on a routine basis;

b) review information on QA systems used in laboratories involved in marine monitoring and report the outcome;

c) provide assistance for a proposed HELCOM workshop on background/reference values for concentrations of nutrients and chemical contaminants in the Baltic Sea area [HELCOM 2000/4];

d) discuss matters referred to from the three subgroups, as necessary.

The Chair had incorporated all of these items into the agenda. The annotated agenda that was distributed in advance of the meeting is provided in Annex 2.

The agenda was adopted after the addition of the following four new items, suggested at the meeting:

1) commenting on the new guidelines for HELCOM (to be introduced by the former Chair of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea, Mikael Krysell);

2) a presentation of the latest results of the QUASH sediment work package (presented by F. Smedes);

3) a presentation of the events following an oil spill accident in France (presented by J. Tronczynski);

4) a review of the merged chlorophyll report, prepared by the MCWG (A. Aminot) and the Working Group on Phytoplankton Ecology (WGPE) to be published in the ICES TIMES series.

The work outlined in the extended agenda was carried out in three subgroups or in plenary. The members and guest participants were grouped as follows:

**Chemical Oceanography Subgroup (COSG):** S. Carlberg (Chair), A. Aminot, L. Føyn, M. Krysell, K. Nagel, J. Ólafsson, O. Vagn Olsen, E.L. Poutanen, E. Sahlsten;

**Trace Metals Subgroup (TMSG):** G. Asmund (Chair), B. Pedersen, P. Woitke, V. Besada, S. Ólafsdottir, K. Parmentier, C. Pohl;

**Organics Subgroup (OSG):** J. de Boer (Chair), J. Klungsøyr, E. Andrulewicz, A.J. Biscaya, M. Cleemann, E.H.G. Evers, M. Haarich, B. Jansson, M. Lebeuf, E. McGovern, T. Nunes, P. Roose, A. Talvari, J. Tronczynski, R. Law, M. Raemaekers.

## 3 REPORT OF THE 87TH ICES STATUTORY MEETING

The Chair informed the meeting that all the tasks requested for consideration by MCWG at the 1999 ICES Annual Science Conference (87 th Statutory Meeting) had been incorporated into the agenda. Under this agenda point, the ICES Environment Adviser, Janet Pawlak, informed MCWG about relevant news from and/or concerning ICES. This includes the coming 100-year anniversary of ICES, discussions concerning plans to improve the knowledge of the work of ICES for a wider audience, and plans to arrange a Dialogue Meeting in Bonn concerning environmental issues in autumn 2000. J. Pawlak also reported on ongoing discussions between the Helsinki and OSPAR Commissions and ICES concerning data handling by ICES, including database holdings. Concern had been expressed that it is very important that data handling is as efficient as possible and a workshop has therefore been planned to be held at ICES in November 2000 at which practical problems related to this topic will be considered.

## 4 REPORTS ON RELATED ACTIVITIES

### 4.1 OSPAR and HELCOM

There was no official request from OSPAR. The Chair had incorporated the official requests from HELCOM in the agenda.

### 4.2 Intergovernmental Oceanographic Commission (IOC)

During the MCWG meeting in 1998, different initiatives to improve contact between ICES MCWG and the IOC were discussed, as there was a general feeling that the two organizations have several areas of interest in common. It was decided that all MCWG members should try to seek information about IOC and report back at the next MCWG meeting. Not much information was presented at the 1999 meeting. It was however decided that the MCWG should continue to work on improving the contact with the IOC. Jacob de Boer had had some contact with Dr Tony Knap at the Bermuda Biological Station, a contact that possibly could be explored further. Harry Dooley, the ICES Oceanographer, also informed the meeting through the Chair that there is an ongoing contact between ICES and IOC. This is described in more detail in Annex 3.

### 4.3 QUASIMEME

Dr D. Wells had informed the Chair that he would not be able to attend the meeting due to other obligations at his own institute, which had been decided at the last minute. Nevertheless, MCWG was informed about QUASIMEME work through the minutes from the last QUASIMEME Advisory Board meeting. Jacob de Boer reported on the biological tissue samples that were recently prepared or are under preparation for QUASIMEME. The request for other types of samples than those that had been used so far and other topics of relevance for QUASIMEME were also discussed in the subgroups. The outcome of these discussions is dealt with in the reports from the different subgroups.

### 4.4 Any Other Activities

Nothing was reported under this agenda item.

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

Under this agenda item, MCWG was informed about an ongoing EU project concerning PAH metabolites involving the Netherlands (IVM) and Norway. For further information about the project, see Agenda Item 8.1.3.5. It was suggested in one of the subgroups that it should be more or less mandatory for the participants to prepare a very short presentation for this agenda point, as exchange of information concerning relevant projects in ICES Member Countries is seen as a very important aspect of the work of MCWG. However, no decision was taken on this matter, but it was suggested that it could be discussed further at the next MCWG meeting.

## 6 REQUESTS FROM ACME AND REGULATORY COMMISSIONS

All requests from ACME were included in the agenda. See also Agenda Item 4.1.

## 7 PLENARY TOPICS

### 7.1 Ecological Modelling

Karl Iver Dahl-Madsen from EMC at DHI Water and Environment in Denmark was invited to give a presentation on ecological modelling. The presentation was meant to serve as a starting point for discussion in MCWG and planning of a possible joint session or workshop with WGSSO in 2001.

In the presentation, the traditional way of monitoring (cruise-based monitoring) was questioned as it is considered to be very expensive and to give only a few and not representative data, since they were usually not even nearly synoptical. Also the delay, in some cases months or even years, in making the measured data available was strongly criticized. Among other things, models can be useful tools for explaining the behaviour of the environment, for carrying out environmental impact assessments in complex situations, and for structuring data collection.

A three-dimensional model of the Danish Sea, which contains water levels, currents, salinity, temperature and nutrient transport, was presented as an example. Chlorophyll simulation for January to October 1999 as well as changes in concentrations of inorganic nitrogen for February to October 1999 were also demonstrated. Odense Fjord, which is considered to be the best monitored estuary in Denmark and has all kinds of problems, was given as another example of possibilities provided by modelling.

In the presentation, it was recommended that measurements in intensive monitoring programmes should be made in several relevant periods depending on the frequency response of the system. As an example of an optimal situation in Danish waters, one could have 5–6 buoys supported by small ships to make frequent visits to take calibration samples near the buoys and to supplement sampling for parameters such as total P and total N which, at present, cannot be measured automatically. Furthermore, the measurement programme should be supported by synchronized measurements by using automated equipment as much as possible, remote sensing and ships-of-opportunity. These data, together with good model(s), would provide the best possible results and interpretation of the behaviour of the ecosystem.

### 7.2 The Marine Programme of the European Environmental Agency

Dr Anita Künitzer, Project Officer for the Marine Environment at the European Environment Agency (EEA), provided an overview of the relevant EEA activities and programmes.

### 7.3 Human Health Aspects of Seafood Contamination with Methylmercury and Persistent Organochlorine Compounds

Philippe Grandjean from the University of Southern Denmark and Boston University was invited to give a presentation on the coupling between contaminants in seafood and human health. Below is a short abstract of the presentation that was given at the meeting.

"Neurotoxicity due to both methylmercury and PCBs is well documented from unfortunate poisoning incidents. However, the dose-effect relationships have been poorly documented, and the degree of confounding and interaction between mercury and PCBs has not been considered in past epidemiological studies. We first generated a cohort of 1022 consecutive singleton births during 1987–1988 in the Faroe Islands, where increased methylmercury exposure is mainly due to consumption of pilot whale meat. We measured total mercury concentrations in cord blood and maternal hair collected at parturition.

Because prenatal neurotoxic effects would be permanent, assessment of neurobehavioral functions was postponed to the age of seven years, where the children could undergo detailed testing. A total of 917 of the cohort children underwent thorough examinations. Significant exposure-related dysfunctions were seen in most neuropsychological tests and were most pronounced in the domains of language, attention, and memory. Some mercury-associated effects were also seen in delayed latencies for evoked potentials and in blood pressure regulation. The associations remained significant after adjustment for covariates and also after exclusion of children with high maternal hair-mercury concentrations or high cord PCB concentrations. Overall, the cord-blood mercury concentration appeared to be the best risk indicator, and PCB seemed less important. A second cohort of 182 singleton term births was generated in 1994 with more detailed documentation of organochlorine exposures. However, effects attributable to PCBs have not been identified so far at annual examinations up to age 54 months. In conclusion, subtle adverse effects on brain function associated with prenatal methyl-mercury exposure appear to be widespread, with early dysfunction being detectable at exposure levels currently considered safe. Effects of PCB exposure are less apparent, but may be masked by the overriding methylmercury neurotoxicity."

### 7.4 Final Results of the European MATT Project

Jacob de Boer introduced this project on toxaphene, which was also prepared by E. McGovern and J. Klungsøyr. The study was financed by EU-FAIR, and was a 2½-year project with participants from Ireland, Germany, the Netherlands, and Norway. It consisted of: a literature review; a clean-up study to develop and check different methods for clean-up of samples; a gas chromatography study to find the optimal injection technique and resolution; a mass spectrometry study to check the benefits and limitations of this technique compared to GC-ECD; an interlaboratory study involving four analytical laboratories; a baseline study to map levels of toxaphene in fish from European waters; and, finally, a toxicology study. Six compounds were initially analysed (Parlar Nos. 26, 50, 62, 40, 41, 44) but only results for Nos. 26, 50, and 62 will be considered in the final report due to analytical difficulties in obtaining accurate results for Nos. 40, 41, and 44. Multidimensional GC (MDGC) also showed that peak 26 consists of more than one congener. A method developed by Gerhard Rimkus using gel permeation chromatography with an HPLC clean-up was mentioned

specifically as it effectively separates toxaphene congeners from potentially interfering CBs. Replicate analyses of herring oil CRM showed standard deviations of approximately 30 % between the four laboratories.

Results from the baseline study were presented. Samples of different species (e.g., plaice, mackerel, herring, halibut, hake, cod, and farmed salmon) were collected from the Baltic Sea, the North Sea, the Irish Sea, the North Atlantic Ocean, and the Norwegian, Iceland, and Barents Seas. Levels for the sum of Parlar 26, 50, and 62 varied between 0.2–73 ng $g^{-1}$ wet weight in muscle and most values were at the lower end of this range. It was concluded that relatively low levels occurred in fish from European sea areas. By comparison, the German tolerance level is 100 ng $g^{-1}$ ww for sum 26, 50, and 62 in fish fillet. *In vitro* and *in vivo* studies on carcinogenicity in rats revealed that the cod liver extract prepared during the study was more potent than both the technical formulation and the UV-irradiated mixture, but less potent than TCDD, which was tested for comparative purposes. Further work will be conducted to develop some conclusions on risk levels from the consumption of fish for the final project report.

## 8 SUBGROUP ACTIVITIES AND DISCUSSIONS

For the sake of clarity, the outcome of the discussions on topics requested from the 87th Statutory Meeting will be presented in Section 8.1. Then, additional items discussed in the subgroups will be dealt with in Sections 8.2 to 8.4, below.

### 8.1 Topics Requested from the 87th Statutory Meeting

These topics were discussed in plenum and/or in all subgroup activities (see also Agenda Item 9).

#### 8.1.1 a) review and endorse the updated list of contaminants which can be monitored on a routine basis

MCWG reviewed the tables with summary data for nutrients, trace metals, and organics, as well as plotted data from a 3.5-year period in 1996–1999. Generally, two more rounds had been conducted for most parameters since the last review of the list.

However, COSG noted that two more rounds of interlaboratory studies for nutrients had been conducted on sea water and three more rounds had been conducted involving low salinity (estuarine) waters.

MCWG agreed that there was not much difference from year to year and that it would be enough to make an assessment of the laboratory performance every three years, i.e., the next assessment should be done in 2002. If new compounds of concern arise and need to be incorporated in monitoring programmes, the list should, of course, be updated accordingly.

Different suggestions for how to assess and present the information were also discussed.

It was proposed that for the coming assessment, the tabled data should be divided into relevant groups of laboratories. COSG suggested that the tabled data should represent only laboratories in ICES Member Countries.

MCWG considered it useful for support of the QA evaluation on monitoring data that summary reports of the performance of laboratories performing analyses for specific monitoring programmes, e.g., HELCOM, OSPAR, and MEDPOL, should be made available to the respective organization so that

- data assessment groups can easily include information on the comparability and reliability of routine monitoring data in their assessment; and
- lists of mandatory parameters in a certain monitoring programme can be evaluated based on information about which parameters can be monitored on a routine basis.

Furthermore, it was suggested that the table should show the cumulative results for the entire period since 1996, as in the existing table, and—in addition to that—the corresponding data for only the three-year period since the last assessment, in order to demonstrate the last year's development.

MCWG also noted that the summary table presented to the meeting had been calculated based on a different criterion compared to the previous years. The so-called group success indicator used to be calculated on the basis that at least 75 % of the laboratories should have a Z-score $< 2$, whereas the new table was based on that at least 80 % of the laboratories should have Z-scores $< 2$. In order to decide on which criterion would be best suited to demonstrate

improvement in laboratory performance, the summary tables discussed by MCWG in 1998, 1999, and 2000 should be recalculated using both the 75 % and the 80 % criteria.

Furthermore, MCWG commented that it would be most useful if the results were presented together with data on

- the homogeneity of the test samples, and
- the stability of the test samples,

since this would make it easier to assess the significance of/cause for the extreme values produced by some laboratories in every exercise.

The long-term performance of laboratories in proficiency testing schemes can, e.g., be evaluated using the re-scaled sum of Z-scores (RSZ) provided by QUASIMEME for particular matrix/parameter combinations. According to the figures provided by QUASIMEME, several laboratories achieved RSZ-values outside the usual limits ($-2 < RSZ < 2$) for a variety of metal/matrix combinations indicating an unsatisfactory long-term performance. This was also the case for other parameters. The significance of the re-scaled sum of Z-scores (RSZ) when assessing the long-term performance of a laboratory was briefly discussed by the members of the group both in plenary at the meeting and also after the meeting via the MCWG mailbox. Different opinions about the usability of RSZ were expressed and several suggestions for improvement were made, such as:

- the re-scaled sum of Z-scores (RSZ) should be calculated and presented only for laboratories in ICES Member Countries and only for those who participated during a minimum of three calendar years (see also text below);
- all figures should include information on the number of rounds which were used to calculate the RSZ;
- regarding trace metals in sediments, RSZ-values out of range may be caused by the problem that the QUASIMEME database contains trace metal results produced by either a total or a partial digestion of sediments; therefore, there is a strong need for harmonization of analytical procedures used for the determination of trace metals in sediments or at least for a separation of the QUASIMEME data according to the digestion procedure;
- it should be emphasized that the information can only be regarded as qualitative, as the number of runs in combination with the suggested formula could penalize or alternatively favour some participants.

Members of MCWG were encouraged to make direct contact with Dave Wells as the inventor of the RSZ concept, who unfortunately was not present at the meeting, for discussing further technical details concerning RSZ.

TMSG had, in previous years, taken a somewhat different approach than the other two subgroups when assessing the contaminants that can be monitored on a routine basis. They had calculated the lowest concentration of a parameter for sediment and biota that can be monitored in a particular matrix on a routine basis by a group, based on the percentage of satisfactory results in a round and these results were presented in tabular form. These tables have now been reviewed and updated. Seawater data were also included. Satisfactory results for a group performance was defined as if the majority (here > 60 %) of laboratories received Z-scores between $-2 < Z < 2$ for an individual parameter/matrix combination. A decreasing number of successful laboratories with decreasing analyte concentration were seen. This is in accordance with the non-linear relationship between decreasing analyte concentration and an increasing value of variation coefficients in intercomparison exercises known as the HORWITZ-function (Albert, R., and Horwitz, W. 1997. Analytical Chemistry, 69: 789–790). A table with the lowest concentrations of trace metals in sea water, sediments, and biota was compiled (see below) for which more than 60 % of the participating laboratories achieved a good performance. TMSG suggested that care should be taken when assessing data from a monitoring programme with concentrations lower than those given in the table, as routine monitoring of contaminants, if using the whole population of participating laboratories, only can be carried out down to these concentrations. This highlights the importance of providing a performance summary specific for a particular monitoring programme, as the information given in the table below is based on the whole population of participating laboratories.

**Table 8.1.1.1.** Lowest concentrations of trace elements in sea water, sediments, and biota which can be monitored on a routine basis by the majority of laboratories (according to the percentage of satisfactory results in the QUASIMEME LPS, 1996–1999; for sea water, 1998–1999 only).

| Metal | Sea water $\mu g\ l^{-1}$ | Sediments $mg\ kg^{-1}$ dw | Biota $mg\ kg^{-1}$ ww |
|---|---|---|---|
| Zn | 7 | 75 | ≤ 4.6 |
| Cd | ≤ 0.09 | ≤ 0.011 | Fish tissue 0.005 |
| Pb | 0.5 | 40 | Problems for the majority of the labs |
| Cu | ≤ 0.9 | 17 | ≤ 0.26 |
| Cr | 2 | 28 | ≤ 0.14 |
| Ni | ≤ 14 | 23 | For cod liver and muscle: 0.1 |
| As | ≤ 1.2 | 6 | ≤ 1.3 |
| Hg | 0.007 | 0.12 | ≤ 0.028 |
| Se | | | 0.4 |
| Al | | Value not available* | |
| Mn | | ≤ 750 | |
| Fe | | ≤ 2.8% | |
| Li | | ≤ 35 | |
| Sc | | ≤ 7.6 | |

'≤' means that only a less than concentration can be given and not a minimum concentration for which more than 60 % of the laboratories achieved satisfactory results ($-2 < Z < 2$). A minimum concentration could not be given from the results of the QUASIMEME LPS, as the concentrations of the samples used were not low enough.

*Method dependent. Some laboratories do not use hydrofluoric acid for complete dissolution of the sample. There is generally no detection limit problem for aluminium.

It was agreed that the Chairs of the subgroups, with Dave Wells, should prepare a note intersessionally for the next MCWG meeting on how a presentation of performance can best be standardized taking the advice from the different groups into account. It was suggested that Dave Wells be the lead person (to be confirmed) in this work.

### 8.1.2 b) review information on QA systems used in laboratories involved in marine monitoring and report the outcome

Jarle Klungsøyr outlined how the QA assessments were performed for the MON reports of 1993 and 1998. A small group of experts received and assessed QA data extracted from the ICES database. In 1998 the assessment included results from intercomparison exercises, CRMs, and information about the performance of each laboratory. One severe difficulty was the lack of pre-defined criteria for acceptance of data as well as missing QA information. Gert Asmund suggested that a quick assessment of the laboratory data could be based on diagrams representing the performance of the single laboratory from the relevant period (see, e.g., Science of the Total Environment, 245 (2000): 203–219). Peter Woitke distributed a note (see Annex 4) reviewing examples of QA criteria used by different European organizations. The subgroup felt that MCWG should provide input to ICES on the way in which a data filter could be organized and operated and also with regard to which QA data should be reported to the database.

A small subgroup of MCWG members will prepare a note on this issue for discussion at next year's meeting taking the information provided in Annex 4 into account. It was also suggested that someone with practical experience in this field be invited to give a presentation at the next MCWG meeting as an introduction to a broader discussion in the group.

(Subgroup Members: Peter Woitke, Jarle Klungsøyr, Britta Pedersen, Marianne Cleemann, Patrick Roose (to be confirmed), plus a member from ICES who is familiar with the ICES database.)

### 8.1.3 c) provide assistance for a proposed HELCOM workshop on background/reference values for concentrations of nutrients and chemical contaminants in the Baltic Sea area [HELCOM 2000/4]

Eugene Andrulewicz gave a short background on the origin of this request. The idea originates from a HELCOM Environment Committee (EC) meeting held with the aim of improving the assessment work and the harmonization with OSPAR activities. The values could also serve as reference values for criteria in matters relating to activities such as dumping of dredged materials, and help to describe what can be considered as a healthy environment to the broader public. E. Andrulewicz described a number of approaches that are currently suggested, such as the use of historical data for nutrients, and data from deep sediment cores to establish historic concentrations in sediments. MCWG was asked to provide assistance and recommendations on this subject and especially on what methods should be used to define background concentrations and to give guidance on how these values should be derived.

MCWG then referred to earlier comments that were made with respect to the report of the first OSPAR Workshop on Background Reference Concentrations, dealing with similar problems in the OSPAR area, at the 1995 MCWG meeting in Reykjavik, and felt that these comments are still relevant. In 1997, COSG thoroughly reviewed the report from the Second OSPAR/ICES Workshop on Background/Reference Values and found that their comments were also still relevant. It was noted that the Second OSPAR/ICES Workshop on Background/Reference Values took another, somewhat more pragmatic/practical approach to the problem.

Concerning the proposed HELCOM workshop for the Baltic Sea area, MCWG pointed to the following:

- it is important to clearly define the terms “background concentration” and “reference concentration”, respectively;
- it is important that the report from the workshop describes precisely how the different values are derived;
- item number 4 in the “Draft Terms of Reference for the Workshop” could be misleading if concentration values derived from the OSPAR Workshop are to be considered for the Baltic Sea area, as those concentrations are not relevant for the Baltic Sea; however, the methodology from the OSPAR workshops should be considered for the proposed HELCOM workshop;
- concerning nutrients, COSG already concluded in 1997, inter alia, “Physical processes, such as upwelling in coastal areas, can displace large water volumes and cause rapid changes in the nutrient concentrations by bringing in, e.g., Atlantic water; consequently, the natural range of nutrient concentrations in a certain area can be quite large and include high concentrations. Contamination by nutrients from anthropogenic sources will not necessarily make significant changes to the concentration range for the nutrients. Consequently, the use of so-called “background concentrations” would be misleading since they will not reveal any changes caused by anthropogenic sources.” This statement should also be applicable for the Baltic Sea.

Bo Jansson remarked that the OSPAR background/reference values were hardly used during the preparation of the QSR 2000 report, and that “effect levels” were used instead. TMSG also advised that when looking at metals in sediment cores, the composition of the sediment samples must be taken into account. This was partly the case for the OSPAR work, where the background/reference values were separated by region. MCWG agreed to make all relevant information, such as the SIME report on environmental assessment criteria, available to HELCOM, and to provide further assistance when needed.

In addition, TMSG made some specific comments regarding trace metals. These are presented below.

Real background values defined as prehistoric concentrations for trace metals in sea water are probably something that can never be obtained. Based on some results of one of the members of the group (Christa Pohl) presented at the meeting, TMSG suggested that as a practical reference value for the Baltic area for trace metals in sea water, the present-day winter concentrations found in the Baltic relatively far from pollution sources can be used. However, it is important to remember that sea-water concentrations are always dependent on season, area, depth, salinity, and the presence or absence of oxygen.

Based on the work of Christa Pohl and using the method suggested above for setting practical reference values for the concentrations of trace metals in Baltic sea water, the following values were derived (all results in ng $kg^{-1}$):

Cd 10–20
Pb 10–30
Cu 300–500 in the western Baltic
500–700 in the central Baltic
Hg 1–8
Zn 600–1200

It was noted that the concentrations were rather close to those generally found in the open Atlantic.

TMSG found that there was insufficient information available at the meeting for any conclusion regarding actual reference concentrations of trace metals in biota and sediments to be reached.

TMSG agreed that the subject is both important and also highly relevant for MCWG. It was therefore suggested that the item should be discussed further next year. Lars Føyn, Victoria Besada, Michael Haarich, and Christa Pohl (to be confirmed) volunteered to prepare a note for such a discussion.

## 8.2 Chemical Oceanography Subgroup (COSG)

### 8.2.1 a) review progress on the application of high temperature techniques for the determination of total nitrogen in sea water

Nitrogen is one of those elements with a high turnover rate in aquatic systems and which is, along with phosphorus, one of the factors controlling the efficiency of biological processes. Besides inorganic forms (nitrate, nitrite, ammonia) nitrogen can be fixed in large amounts in particulate and dissolved organic materials. Due to the significance of nitrogen in the biogeochemical cycle, the determination of the amount of nitrogen bound in organic materials may be of great importance to balance the nitrogen budget in aquatic systems.

A generally accepted method for the determination of total dissolved nitgrogen (TDN) in natural sea-water samples is the wet digestion suggested by Koroleff, which has been used with some modifications by many laboratories in recent years. Compared to the determination of, e.g., nutrient salts, intercalibration exercises for TDN are less satisfactory. Although the individual steps of this method are quite simple, performing the method is rather time consuming and several factors may contribute to the different results obtained by different laboratories.

In recent years, efforts have been made to introduce other methods for the determination of TDN in marine samples which are less time consuming and can be performed automatically. Besides high temperature catalytic oxidation (HTCO) methods, UV digestion using AutoAnalyzer Systems have been tested by several laboratories. Although comparable results have been obtained for some sets of samples collected in defined areas, it has not yet been proven that either method can be generally applied to all marine samples. The efficiency of these methods can be strongly influenced by factors such as salinity, amount of inorganic nitrogen compounds, or the amount of organic material present in the sample. At present, it is difficult to make a general statement on which method may give accurate results for all types of water.

International comparisons between the different methods for the determination of TDN are currently being performed and programmes have started to analyse the chemical mechanisms of the methods in detail; results are expected in one or two years.

COSG decided to continue monitoring progress on this topic and report results in the next year or two. Claus Nagel volunteered to take the lead.

### 8.2.2 b) review information on experience in the use of automated *in situ* chemical oceanographic systems for the observation of chemical variables

This item has been on the agenda for a couple of years as an initiative of COSG and with the aim of assisting members either for selection in the purchase of commercial systems on the open market or for the development of systems in their own institutes.

In the absence of a new review report that had been promised for the meeting, COSG members briefly described their experiences and discussed other available information on the subject. The conclusion was that although there are several promising systems commercially available or under development, they were not aware of an automated *in situ* system

for chemical observations that could complement monitoring programmes by operating for extended periods of time in non-sheltered waters.

COSG agreed to return to this item in the future when sufficient new information is available.

### 8.2.3 c) review a comparison of spectrophotometric and volumetric alternatives for quantification in the Winkler method for the determination of dissolved oxygen in sea water and report on the outcome

Ole Vagn Olsen presented a report on a comparison of two variants of the Winkler method for determination of dissolved oxygen in sea water, namely, the classical Winkler titration and a variant where the absorbance of the yellow colour of the triiodine complex, formed after dissolving the precipitate in sulfuric acid, is measured in a spectrophotometer at 456 nm.

The aim of the comparison was to see if the slightly simpler and faster photometric variant could be used for routine calibration of *in situ* oxygen sensors.

A calibration of the spectrophotometric variant was prepared by analysing solutions of the reagent in sulfuric acid oxygenated with 0, 5, 10, and 15 ml of a potassium iodate solution. The calibration graph was linear. Both methods are highly reproducible but gave different results due to a systematic error in the photometric variant. Since the classical Winkler titration is generally accepted as producing correct results, the logical way to bring the two variants into agreement is to calibrate the spectrophometric variant with the classical titrimetric variant.

### 8.2.4 d) review the use of chemical data in numerical modelling and the possible implications for future work in modelling and in field sampling programmes, including the preparation of a workshop or joint session with the WGSSO in 2001

The basis for discussions under this item was the plenary presentation on mathematical modelling of aquatic ecosystems by Karl Iver Dahl-Madsen.

At the MCWG meeting in 1999, it was concluded that no unique, simple approach for monitoring nutrient fluxes from estuarine environments seems possible and that it seems unrealistic to build a general strategy for monitoring nutrient inputs to coastal waters. Ecological modelling is seen as a possibility to optimize the existing heavy monitoring programmes.

In the presentation, the usefulness of the present monitoring strategy as well as traditional cruise-based monitoring was questioned. In the discussion, it was pointed out that models are useful for short-term forecasting and for making scenarios. The more traditional monitoring has proven to be useful for detecting, e.g., long-term changes in the environment. It was also noted that since monitoring cruises have a long tradition it might be sometimes difficult for chemists to see what kind of possibilities modelling can offer and how and what kind of data could be used for modelling work. Marine chemists are not used to seeing this kind of immediate application of their data. Modelling was considered to have a potential role, e.g., in early warning systems for plankton blooms and bathing water quality.

The modeller's request for a large volume of less accurate data was discussed at length. COSG concluded that it is still important to produce quality-assured data but the purpose of the data determines the quality level. In any case, the data user has the responsibility of selecting data which fulfill his/her quality requirements. This requires that the quality of the data is known. To fulfill the wish of modellers to have large volumes of data very quickly, $O_2$, $CO_2$, fluorescence, and pH were identified as possible parameters where continuous measurements could be started. The importance of having correct boundary values in the models was stressed since, in some cases, only a small difference in the value used might cause a major difference in the final model result. Attention should always focus on the interpretation of the model results and misuse of the results.

To facilitate the preparations and planning of a possible joint meeting/workshop with WGSSO, COSG concluded that it is important to:

- continue communications between modellers and chemists;
- clearly define the problems for which models are needed and data needs in relation to time and space;
- start discussions on restructuring monitoring programmes and existing resources used for monitoring and modelling;

- continue discussions on future cooperation on modelling, not only among physical modellers, but also including chemical and biological modellers who are devoted to process modelling.

It was recommended that a joint session with the Working Group on Shelf Seas Oceanography (WGSSO) be arranged in 2001 either as an extended MCWG or WGSSO meeting, attended by interested members, or by hosting a back-to-back meeting of the two working groups with a one-day overlap.

### 8.3 Organics Subgroup (OSG)

#### 8.3.1 a) review the updated list of relevant certified reference materials for organic compounds for use in marine monitoring

The tables of certified reference materials (CRMs) originally prepared for the 1998 MCWG meeting were updated and presented to MCWG 2000 (see Annex 5). The tables are primarily based on marine matrices and only include CRMs derived from the freshwater environment where alternatives are not available or the material is of particular interest.

The following comments/caveats apply to the tables:

- Values preceded by an asterisk (*) are non-certified. All other values are certified.
- These tables are for information. Although every effort has been made to ensure that the tables are accurate, users of CRMs should consult vendors for full and accurate information.
- Certified calibration materials and standards are not included.
- These tables do not purport to be complete and all CRMs listed may not be commercially available.
- Methylmercury is not considered an organic contaminant for the purposes of this list.

The following websites provide information and details on CRMs:

- USA NIST http://ois.nist.gov/srmcatalog
- NRC Canada http://www.ems.nrc.ca
  http://www.imb.nrc.ca/crmp_e.html
- UK Laboratory of the Government Chemist http://www.lgc.co.uk/
- Institute of Reference Materials / EC Joint Research Centre http://www.irmm.jrc.be/rm/catalogue.html

There are some reference (non-certified) values for NIST materials that are not yet included in the tables; these will be included in future updates.

It was noted during discussions that SRM 1945 (whale blubber) may no longer be available, and there was no other marine mammal-based CRM known to the group. The difficulties previously experienced by European scientists in acquiring SRM 1945 due to CITES (Convention of International Trade in Endangered Species) restrictions were also stressed.

The availability of other potentially useful CRMs and the development of new CRMS was discussed. In particular, the European project “CERMUS” has delivered a CRM certified for CBs in mussels which will become available during 2000. The European “CHRONO” project is expected to provide two new fish CRMs, a herring CRM certified for chlorobiphenyls (CBs) and a chub CRM certified for non-*ortho* CBs. This information will also be included in future updates.

The lack of suitable CRMs for laboratories engaged in OSPAR/HELCOM monitoring was noted. Concentration ranges in currently available CRMs are generally inappropriate and there do not appear to be any open sea marine sediment CRMs currently available.

It was agreed that the tables provide very useful information and should be updated on a regular basis. Evin McGovern agreed to do this for MCWG 2001 for organic compunds. It was agreed that a similar list for compounds other than organics would be very useful. Peter Woitke and Elisabeth Sahlsten agreed to prepare tables for trace elements and nutrients, respectively.

### 8.3.2 b) critically evaluate the lists of priority contaminants prepared in relevant regional and international organizations (with TMSG)

Bo Jansson gave a short overview of the work going on to identify contaminants of special concern within the EU and OSPAR.

The European Commission has made a proposal to the European Parliament containing a list of compounds to be included in the proposed Water Framework Directive (WFD). The WFD covers groundwater, surface water, fresh water and coastal water within 1 nautical mile (approximately 1.8 km) of the coast. The selection of compounds is based on a procedure called Combined Monitoring-based and Modelling-based Priority Setting (COMMPS). A Nordic and a Danish database have been used for modelling concentrations of candidate compounds in the environment. Compounds are not ranked within the single lists, and no proposals for analysis in matrices other than water are included within the proposed WFD. The proposal is likely to be accepted by the European Parliament in its present form.

OSPAR also has a working group called DYNAMEC which is trying to identify hazardous substances as defined in the Esbjerg Declaration. DYNAMEC is currently discussing a preliminary list of about 400 compounds in order to prepare a list on substances of special concern, which could perhaps comprise 50–60 compounds. The selection will be based on monitoring data indicating environmental concentrations, effect data, and the inherent properties of the compounds. The list should include the compounds on the WFD list, and be completed by the summer of 2000.

It became clear that there would be no opportunity for MCWG to comment on the WFD list later on. The OSPAR list, however, will form the basis for further discussions of the matrices in which the monitoring should be conducted and the methods to be used, and MCWG is likely to be asked to advise on these aspects and associated quality control issues through ACME. During the meeting a small subgroup of MCWG members prepared comments on the WFD list which is attached as Annex 6.

It was agreed to follow up on this topic and report back next year if there is any new information available.

### 8.3.3 c) review new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl) methane (TCPMe) in fish and in marine mammals from eastern Canada, including the results of the TCPM and TCPMe interlaboratory study, second phase

Michel Lebeuf presented new results regarding *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in marine mammals. The sources of these compounds are still not known, but one theory suggests that TCPM is a contaminant in technical DDT products, and that TCPM is converted to TCPMe in the environment.

TCPM and TCPMe were measured in blubber samples of seals and whales from the St. Lawrence Estuary and the Gulf of St. Lawrence in Canada using ion-trap mass spectrometry (MS/MS) detection. Detectable concentrations of both TCPM and TCPMe were observed in all of the samples analysed. Concentrations of these compounds varied with species ranging from 1.7 to 153 and from 1.3 to 50.6 ng $g^{-1}$ lipid weight for TCPM and TCPMe, respectively. TCPM was present at concentrations from 1.3 to 10 times higher than TCPMe. The highest levels of both TCPM and TCPMe were observed in adult male beluga whales (*Delphinapterus leucas*) from the St. Lawrence Estuary, while adult female beluga whales from the same area showed levels similar to those in the seals examined. Among the four seal species investigated, TCPM and TCPMe levels were the highest in grey (*Halichoerus grypus*) and hooded seals (*Cystophora cristata*), and lowest in harp seals (*Phoca groenlandica*). Intermediate levels were found in harbour seals (*Phoca vitulina*). Based on limited data, concentrations of TCPM and TCPMe in marine mammal blubber from North America seem to be similar to those observed in samples from Russia and Asia, but about 10 times lower than those seen in samples from Europe.

Ratios of both 4,4′-DDE/Σ-DDT and TCPM/Σ-TCP were very similar between animals from the same species. Strong correlations between Σ-TCP and Σ-DDT were also observed for each species of mammals, most likely indicating that both Σ-TCP and Σ-DDT are bioaccumulated in marine mammals. In discussion, M. Lebeuf indicated that similar correlations were also seen with ΣCB concentrations.

Michel Lebeuf also presented his own and others' data for TCPM and TCPMe in fish samples from Canada and Europe (Annex 7). Both compounds are found in almost all Canadian fish samples and the levels of TCPM are again generally higher than those of TCPMe. This has not been the case in studies in the Baltic and along the Dutch/Belgian coasts, where higher concentrations of TCPMe compared to TCPM have been found. Differences in the ratio between the compounds may depend on the proximity of various sources, trophic level and/or interferences in analytical methods.

A comparison of Σ-TCP and Σ-DDT in fish samples showed no correlation between those parameters, which does not support the theory that DDT formulations are a major source of TCPM/TCPMe compounds.

It was agreed that Jacob de Boer will coordinate an interlaboratory study on TCPM and TCPMe in two fish samples and a standard solution, as agreed at MCWG 1999. Michel Lebeuf, Patrick Roose, and Michael Haarich will participate in this study. Marc Raemaekers and Jarle Klungsøyr will also try to participate, but this is not certain at the moment. One or two laboratories from outside MCWG, experienced in this analysis, will also be invited to participate. In addition, Jacob de Boer, Michel Lebeuf, Patrick Roose, and Michael Haarich will each analyse 5 flatfish samples for TCPM and TCPMe, and Robin Law will endeavour to supply extracts from 5 flounder samples and 5 porpoise samples derived from UK studies for analysis in Canada, in order to study potential differences in concentrations between the western and eastern sides of the North Atlantic Ocean. Michel Lebeuf will present the results of this study at MCWG 2001.

### 8.3.4 d) review information on volatile organic contaminants in biota

Two papers were presented on studies of volatile organic contaminants in biota. The first paper entitled "Volatile organic compounds in various marine organisms from the southern North Sea" was presented by Patrick Roose (Annex 8). The second paper, entitled "Solvents in water and fish from Lake Mälaren in Sweden", was presented by Bo Jansson (Annex 9).

The first presentation reported concentration levels of 12 priority volatile organic compounds (VOCs) in two species of vertebrates and four species of invertebrates from sampling stations in the southern North Sea. The analyses were performed using a purge and trap system coupled to GC-MS. In general, concentration levels of VOCs found were of the same order of magnitude as those previously reported in the literature. The concentrations of the chlorinated hydrocarbons (CHCs), with the exception of chloroform, tended to be lower than those of the monocyclic aromatic hydrocarbons (MAHs). The experimental data were statistically evaluated using both cluster and principal component analysis (PCA). From the results of cluster analysis and PCA, no specific groups could be distinguished on the basis of geographical, temporal or biological parameters. However, based on the cluster analysis and the PCA, the VOCs could be divided into three groups, $C_2$-substituted benzenes, CHCs and benzene plus toluene. This division could be related to different types of sources. Finally, it was shown that organisms can be used to monitor the presence of VOCs in the marine environment, and the observed concentration levels were compared with proposed safety levels.

The second presentation reported concentration levels of 13 of the 16 volatile organic compounds investigated in water and fish from Lake Mälaren in Sweden. The analyses were performed using solid phase micro-extraction (SPME). That technique was considered to be useful for the determination of these solvents in both water and biological samples. However, internal standards have to be extremely pure and background contamination is difficult to avoid in the laboratory, and may emanate from ambient air. For each compound, the fish-water partition coefficient ($K_{fw}$) was determined. Concentrations of volatile organic compounds determined in water were found to compare well with those inferred from the concentrations in fish. Xylenes were present at the highest concentrations, followed by chloroform and toluene. It was concluded that the overall levels of solvents in both water and biota from Lake Mälaren were low.

The comments of the subgroup related mainly to the difficulties of avoiding contamination in these analyses, and the way in which analytical detection limits were calculated given the often high background levels.

It was recommended that the information presented be included in the MCWG report as Annexes 8 and 9.

### 8.3.5 e) review new information on the analysis of PAH metabolites in bile and critically review the robustness of the methods

The Chair of OSG contacted David Wells concerning this topic. It relates to a European project that is currently under way, which aims to develop a fish oil reference material certified for PAH metabolites. During the course of the project an intercomparison exercise has already been held, and development of the reference material has begun. This has involved the preparation of contaminated fish oil, and tests to study and prevent the oxidation of PAH metabolites in these matrices. Standard solutions have also been prepared and are being tested for stability. As the results of this project are still emerging, it is too early to make a presentation at this year's meeting. David Wells has agreed to do so at MCWG 2001, by which time the results of a second intercomparison exercise should also be available.

### 8.3.6 f) review new information on the use of membrane systems for sampling (with TMSG)

After the presentation by Erik Evers on the current status of the use of membrane systems for sampling (OSG and TMSG), the status for sampling trace elements in sea water was briefly discussed. At present, ion-exchange based

membranes are being studied for the use of seawater analyses, but is was concluded that the state of the art is not so well evolved that they can be used on a broader scale for sea water monitoring of trace elements. It was mentioned that some positive results exist from an earlier investigation made in Canada. One of the unsolved problems is that parts of the trace metals are bound in complexes that are not absorbed to the ion exchangers. Furthermore, calibration of the system is difficult.

Erik Evers gave a presentation on a collaborative research project in the Netherlands in which they have investigated the utility of semi-permeable membrane devices (SPMD) for sampling in the marine environment.

The SPMD tested consists of low-density polyethylene (LDPE) lay-flat tubing filled with a lipid medium (generally triolein). The SPMD devices have been used for sampling a wide range of non-polar to moderately polar organic contaminants in both water and air by passive diffusion. With proper calibration (to take account of differences in water flow and ambient temperature during deployment) these devices allow the determination of concentrations of highly hydrophobic compounds (HOC) which are present at ultra-trace levels, truly dissolved and bioavailable in the water phase. In the marine environment, data for dissolved organic contaminants are relatively sparse, and these determinations are generally not included within marine monitoring programmes. This is because the determination of concentrations of HOC by conventional techniques, such as liquid-liquid extraction and solid phase extraction, is difficult, and often requires the collection of large-volume samples. Passive sampling using SPMDs offers a number of advantages over conventional techniques, and also can supplement "mussel watch" type studies where these animals are not available.

It was agreed to follow up this topic and report back next year if there is any new information available, e.g., from a recent interlaboratory study performed within the frame of an EU project. The project had, however, faced some problems due to the patenting system, which may delay an efficient introduction of the use of SPMDs.

#### 8.3.7 g) review new information on the monitoring and analysis of toxaphene

Jacob de Boer presented the results from the toxaphene intercomparison exercise. Samples of toxaphene in standard solutions were distributed along with three biological extracts (capelin oil, cod liver oil, and seal blubber), and a total of 16 laboratories reported data. The results are presented in Annex 10. Between-laboratory coefficients of variation varied between 19 % and 57 % for individual congeners, and 62 % and 82 % for the determination of total toxaphene. The higher variance associated with the total toxaphene measurement may have been at least partly due to the fact that no single formulation standard was distributed to the participants, and it was suggested that the report should include additional information about the methods used by the different laboratories.

### 8.3.8 Trace Metals Subgroup (TMSG)

#### 8.3.8.1 a) critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations

With OSG, see Section 8.1.3.2.

#### 8.3.8.2 b) review, in conjunction with WGSSO, information on estuarine transport of trace metals and report on the outcome of the techniques available and the comparability of their results

This item was not treated, as the experts in this field did not attend the meeting.

#### 8.3.8.3 c) review new information on the use of membrane systems for sampling

With OSG, see Section 8.1.3.6.

#### 8.3.8.4 d) review new information on the use of contaminant concentrations in biological media as environmental indicators to detect trends, including supplementary work to the Icelandic cod study on the relationship between trace element concentrations in cod liver and various cofactors

TMSG reviewed the article on the effect of nutritional status of Icelandic cod on macroconstituents and trace elements in cod liver by Guðjon Auðunsson (G. Auðunsson, 1999. The effect of nutritional status of Icelandic cod (*Gadus morhua*) on macroconstituents and trace elements in the liver. Rit Fiskideildar, 16: 111–129), which was recently published. The subject was initiated in TMSG and had been on the agenda for the last three years. It was therefore very

satisfactory that the work has resulted in a publication and the author was congratulated for his efforts. There has, however, been little progress in further work to investigate if the relations found for Icelandic cod have a more general applicability, using cod liver data from the ICES database. TMSG agreed that Gert Asmund as the TMSG Chair should ask Jørgen Nørrevang Jensen (ICES Environmental Data Scientist) to take the lead in this task and Guðjon Atli Auðunsson and Gert Asmund volunteered to assist him.

### 8.4 Other Issues: Chemical Oceanography Subgroup

#### 8.4.1 Chlorophyll *a* methodology

A few years ago the Marine Chemistry Working Group (MCWG) and the Working Group on Phytoplankton Ecology (WGPE) started cooperative efforts intending to define Quality Assurance aspects for the determination of chlorophyll *a* and to recommend a procedure for its ***routine*** determination, ***as a biomass marker,*** in marine waters. Alain Aminot and Francisco Rey, from the two WGs, respectively, were given the task to finalize the corresponding papers. At its meeting in 1999, ACME agreed to annex the two papers (after removal of the overlapping parts) to its report. However, after the 1999 ACME meeting, ICES reconsidered and decided to merge the two papers and publish them as an issue of the ICES TIMES series. A. Aminot and F. Rey were contacted again for this task in late 1999. The procedure is derived from the recommendations of the SCOR Working Group 78 of UNESCO published in the Monograph on Oceanographic Methodology No. 10 (Jeffrey *et al.*, 1997). It is an updated version of classical procedures based on a 90 % acetone extraction and three possible measurement methods, two spectrophotometric (Jeffrey and Humphrey, 1975; Lorenzen, 1967) and one fluorometric (Holm-Hansen *et al.*, 1965).

The document was discussed by the ICES/OSPAR Steering Group on Quality Assurance of Biological Measurements Related to Eutrophication Effects (SGQAE) in February 2000. The main comment from SGQAE was that "the described method is no longer the most commonly used in many countries" and SGQAE suggested an additional expert review. As no further information on "a most commonly used method" was given and since UNESCO recommends the described method, MCWG did not agree to postpone its publication. Nevertheless, it was agreed that it would not be called "a standard method".

SGQAE also suggested increasing (for practical reasons) the allowable delay between sampling and filtration from 1 hour to 24 hours. MCWG disagreed with such a long delay and recalled that the HELCOM COMBINE Manual recommends performing the filtration ***immediately*** after sampling.

Two other points were discussed in the Chemical Oceanography Subgroup of MCWG about: 1) the specific extinction coefficient (SEC) used in the Lorenzen equation, and 2) the use of ethanol as an alternative solvent.

***SEC in the Lorenzen equation***

The method of Lorenzen (1967) uses the SEC value of 91.1 taken from the literature (which gives the factor of 11.0 = 1000/91.1 in his equations). Jeffrey and Humphrey (1975) re-established SEC values and found 87.67 l $g^{-1}$ $cm^{-1}$ for chlorophyll *a*. This difference has been pointed out in the UNESCO monograph (Jeffrey *et al.*, 1997; Appendix F) where it is mentioned that the chlorophyll *a* concentration obtained from Lorenzen's equations is about 4 % lower than those from the equations of Jeffrey and Humphrey.

In the ICES procedure, the fluorometric method is calibrated with chlorophyll standards controlled by spectrophotometry using also the SEC established by J&H. In order to maintain consistency in the document, F. Rey (on behalf of WGPE) and A. Aminot suggested that the same SEC should be used for the three spectroscopic measurements, i.e., the Jeffrey and Humphrey value of 87.7, which is more reliable and widely used. MCWG agreed on this amendment and, consequently, 11.4 will replace the factor 11.0 in the Lorenzen equation.

***The extraction solvent: ethanol versus acetone***

The ICES procedure recommends extracting chlorophyll using 90 % acetone, in accordance with the UNESCO monograph which considers that absorption coefficients of chlorophyll and pheopigments *a* are more precisely known in 90 % acetone. However, the procedure described in the HELCOM COMBINE Manual is based on ethanol extraction and many laboratories from North European countries use this solvent on the recommendation of previous workers in this area in the 1980s (Marker *et al.*, 1980; Nusch, 1980; Arvola, 1981). In addition, the International Standard method (ISO 10260) is also based on an ethanol extraction.

A. Aminot prepared a document that compares the essential characteristics of the two solvents with regard to the routine determination of chlorophyll *a* from natural phytoplankton populations. The main conclusions are described below.

- Solvents should preferably contain 5–10 % water. Ninety percent (90 %) acetone is almost a standard since accurate SEC values have been determined with it. For ethanol, 90 % to 96 % grades seem equally acceptable since the water proportion does not significantly affect optical characteristics of the extracts.
- Chlorophyll a shows a good stability in ethanol, both before and after acidification (acetone is also acceptable for that criterion).
- Ethanol is more efficient than acetone for extraction of chlorophyll a from some green and blue-green algae. Such algal species may dominate in freshwater and low-salinity areas (e.g., Baltic Sea).
- Acetone gives high extraction recoveries from mixed populations and field marine samples (in particular if diatoms dominate) when adequate procedures are used (such as grinding or sufficient extraction time).

MCWG notes that:

- acetone remains an acceptable solvent for most natural populations, particularly in the more marine areas, and for this reason it is still recommended by UNESCO for routine work;
- the frequency and proportion of difficult-to-extract algae in the Baltic Sea may justify the use of ethanol, which is more efficient than acetone, in order to overcome a potential risk of underestimation of the biomass by chlorophyll a measurements;
- however, specific extinction coefficients in ethanol are more or less controversial and there is a need that a SEC value be more accurately determined or be accepted by consensus within the community of the concerned marine scientists.
- In addition, MCWG points out that:
- for any spectrophotometric measurement technique, acidification procedures should always be used in those situations where proportions of pheopigments can be significant; this reduces risks of overestimation of chlorophyll (information on concentration of pheopigment is not useful in itself);
- attention should be paid to the fact that changing the extraction solvent may modify the ratio pheopigments/chlorophyll *a*.

Finally, it is suggested that the text of the section "Alternative methods" in the document for the TIMES series be amended to take the above considerations on ethanol into account, for application to Baltic conditions. The amendments will be submitted by MCWG to F. Rey for consideration and approval, and then to the ICES Secretariat as an amendment to the manuscript submitted for the TIMES series in 1999.

### 8.4.2 Oxygen Tables

In 1986, UNESCO recommended that the equations of Benson and Krause (1984) should now be used for the calculation of oxygen solubility, and the solubility tables updated accordingly. However, revised tables still have not been published. MCWG points out that the values in the UNESCO International Oceanographic Tables previously published are low by 0.1 % since they are based on ideal gas molar volumes instead of actual $O_2$ molar volumes.

MCWG discussed whether it would be useful for ICES to publish revised solubility tables. With the present widespread use of personal computers, tables are not as necessary as they were in the past; however, it is important that users can check the equations they have entered in their computers and the only way to accomplish this is to offer them a limited number of solubility data covering the usual range of natural conditions. For example, "tables" could give solubility values every 1–2 °C in temperature and every 1–2 (PSS78) in salinity.

A paper detailing the recommended equations was prepared by A. Aminot and is annexed to the present report as Annex 11.

After a suggestion by the ICES Oceanographer, Harry Dooley, MCWG agreed that the recommended formulas and some limited tables should be made available on the ICES website, accompanied by the appropriate background materials (e.g., references, conversion coefficients to be used, etc.).

### 8.4.3 Work Programme

COSG agreed on the following items for intersessional work and for consideration at the meeting in 2001:

- Review and report oxygen determinations in sea water by the Winkler titration and membrane electrodes (Patrick Roose).
- Review a report from a multiship experiment of sampling and determination of chemical variables in sea water (Patrick Roose).
- Review and report on progress in the modelling of marine biogeochemical processes. (Jon Ólafsson).
- Review and report on progress in the studies of estuarine behaviour of nutrients.
- Review and report on the present knowledge about total nitrogen, total phosphorus, and total organic carbon in sea water, their speciation, and arguments for their use in monitoring programmes.
- Joint activity with WGSSO to discuss and report on the requirements on chemical data, particularly nutrients and oxygen, for use in numerical modelling as well as the use of models in optimization of monitoring programmes (Alain Aminot to provide some examples from monitoring).

### 8.4.4 Appointment of COSGChair

COSG unanimously appointed Mr Stig Carlberg (Sweden) to serve as Chair for the intersessional period and for the meeting in 2001.

## 8.5 Other Issues: Organics Subgroup (OSG)

### 8.5.1 Oil spill from "*MV Erika*"

Jacek Tronczynski gave the subgroup an update on the current status of the recent massive oil spill on the Atlantic coast of France. Currently an estimated 10 000 to 15 000 tonnes of heavy fuel oil have been spilled into the sea and subsequently beached. A similar quantity of oil remains in the half of the vessel on the seabed at 100 m depth and efforts are under way to recover that portion of the cargo. As stated by the shippers, the cargo consisted of No. 2 fuel oil (No. 6 fuel oil in the US), a heavy fuel oil containing 25 % aliphatics and 50 % aromatics. The ship broke into two pieces approximately 50 miles offshore on 12 December 1999 and oil began to come ashore on 24 December; now affecting around 400 miles of coastline, including areas of major production of mussels and oysters for human consumption. The monitoring programme includes 70 sampling sites and mussels are taken for analysis twice per month at present; this will be decreased to once per month in the future. The routine monitoring includes the determination of the 16 priority parent PAHs established by the US EPA, supplemented by more extensive analysis using GC/MS for a wider range of compounds on an occasional basis. ΣPAH concentrations rose rapidly once the oil came ashore, e.g., chrysene concentrations increased by a factor of 200 times. The maximum concentration observed to date is 5000 $\mu g\ kg^{-1}$ dry weight for ΣPAH in mussels. Bile samples have also been taken from fish for the determination of PAH metabolites as an indication of exposure in offshore areas. This monitoring programme will continue for one year in the first instance. The spill is indeed an ecological disaster for seabirds and wildfowl, with 300 000 dead birds estimated to date.

OSG expressed its great concern about oil spills and their effects on the marine environment especially contaminants such as certain PAHs, and urged the establishment and/or strengthening of preventative measures intended to reduce their occurrence. This applied both to major spills such as that from the Erika, and to the increasing number of small spills, many involving fuel oil, that are now occurring worldwide. A session concerning oil spills, their effects and associated protocols for incident response will be developed for MCWG 2001.

### 8.5.2 QUASH Interlaboratory Study (with TMSG)

Foppe Smedes reported on the results of the QUASH Interlaboratory Study on sieving and normalization of geographically different sediments (Round 5). The main objective of this study was to compare and validate different normalization procedures that are used in marine monitoring programmes within the OSPAR, HELCOM, and MEDPOL convention areas.

In order to make comparisons of contaminant levels among different geographical areas and to minimize the effect of varying hydrological and weather conditions on the sample constitution, it is necessary to correct contaminant contents

for differences in sample composition. The cofactors (normalizers) that have been studied were (1) organic carbon content, (2) aluminium, and (3) lithium. Clay and organic carbon contents can be regarded as primary normalizers which are directly responsible for the sorption capacity of sediments.

It appeared that laboratories frequently did not produce reliable results for all three cofactors, which is an unsound basis for proper evaluation of the data with respect to normalization. For the coarse grain samples, OC and Al had high between-laboratory variability. For the fine grain sample, the agreement was much better, except for OC, which showed similar variability in both sediment types, which can be attributed to the use of differing analytical methodologies, such as loss-on-ignition and wet digestion, but also to incomplete removal of the inorganic carbon fraction. The between-laboratory variability for cofactors and contaminants in the reference samples did not meet the target values set by QUASIMEME. On average, the CV values were two times higher than the QUASIMEME target. It was concluded that the design of the exercise would allow proper testing of procedures but was hampered by poor analytical performance. The variability in cofactors and contaminants in the fine-grained reference samples was however much better in comparison with the coarse grained reference sample. Partial digestion methods for the analysis of metals in sediments provided, as expected, lower levels of metals in the coarse reference sediment. However, in the fine fraction no significant difference was observed between partial and total digestion techniques. From the results obtained after sieving a reference sample, it became apparent that the sieving process introduced no additional error (< 7 %) compared to the between-laboratory variability of the sieving yield (12 %) and the QUASIMEME analytical target (12.5 %).

In order to study the normalization procedures from a range of geographical areas, laboratories collected a sample from their own area and sieved it to yield the following fractions: > 63 µm, < 63 µm, 20–63 µm, and < 20 µm. Together with the untreated sample, a set of 5 samples was obtained with a wide grain-size variation, though in principle equally polluted as they are in equilibrium in the environment. Application of a normalization procedure to these fractions should therefore not yield different results. This represents the ultimate test for the use of cofactors in data normalization.

When considering sieving as a normalization technique, it should be borne in mind that the content of the cofactors in sieved sediments from different geographical origins still varies significantly, by up to factors of 3, 2, and 2 for OC, Al, and Li, respectively. Thus, a further correction for grain size differences seems to be needed, also after sieving. The difference in cofactor contents between the fractions of < 20 µm and < 63 µm in the obtained data set were small with respect to the geographic variability. This will automatically reduce the differences observed between the < 20 µm and < 63 µm fractions.

The cofactors were evaluated in three different ways:

1) by investigating correlations;

2) by seeking a decrease of the CVs observed in the data set;

3) by seeking a decrease in the averaged Z-values in comparison with the mean values.

For metals, the exercise revealed that excellent correlations with intercepts close to zero were observed for those laboratories using partial digestion methods. Due to the contribution of metals and cofactors in the mineral structure of the sediments, the data for laboratories using total digestion methods yielded large non-zero intercepts in correlation plots. Consequently, the effectiveness of normalization was much enhanced in this study by the use of partial digestion techniques.

CBs were related very well to OC content, whilst for PAHs there was some decrease in variability when related to OC content, but some further evaluation is necessary in this case as PAHs behaved differently in the 20–63 µm fraction. This may be an additional indication that the < 20 µm sediment fraction is most appropriate for monitoring purposes rather than the larger fractions, however, the nature of the PAHs bound in this intermediate fraction needs to be established, and their bioavailability and potential for biological effects needs to be evaluated more fully before such a decision can be justified.

The most important conclusion of the exercise was that use of the “untrue” values for Li and Al (and other metals) obtained by partial digestion methods in this study appeared to yield excellent correlations between cofactors and metals and, consequently, are to be recommended in future monitoring studies.

Some questions were raised in the discussions after the presentation. Attention was drawn to the importance of the size range of soot particles in relation to PAHs, and the implications of the results for the future of the sediment guidelines

(analysis of sieved fractions, digestion for metals, etc.) were also discussed. It was noted that the certification of metal concentrations in most sediment CRMs was based on total digestion, although some CRMs from BCR were available where a partial digestion method had been used when setting the concentrations. It was also mentioned that biological effects data are generally obtained using total sediments only, and not a sieved fraction.

Based on the work presented and the discussions that ensued, MCWG strongly recommends that:

- the analysis of OC content be standardized.

MCWG considered it inappropriate to make any firm recommendations on the subject of sieving or digestion methods based on the result of the exercise as this issue would be dealt with by the Working Group on Marine Sediments in Relation to Pollution (WGMS) at their meeting, the week following the MCWG meeting.

OSG thanked Foppe Smedes for presenting his work to MCWG.

### 8.5.3 Dioxins

The issue of dioxins in fish was discussed in view of the recent Belgian dioxin crisis. In the Belgian incident, contamination was caused by used oil containing polychlorinated biphenyls. The oil also contained a high level of polychlorinated dibenzofurans.

Data from the Netherlands from 1992 were presented that suggested that the major contribution to the toxic equivalent (TEQ) values observed in fish was due to non-*ortho* and mono-*ortho* CBs. In general, this was a factor of 2–4 times higher than the PCDD/PCDF component of the TEQ values.

The World Health Organization's approved dietary intake (ADI) guidelines for dioxin are 1–4 pg $kg^{-1}$ body weight $day^{-1}$. Based on this value there may be serious implications for future consumption of fishery products. Also, legislation introduced in Belgium subsequent to the dioxin crisis introduced a limit for the sum of 7 CBs, of 200 ng $g^{-1}$ lipid for animal products with less than 2 % lipid content. Although this does not include fish, if a similar limit is introduced in Europe that is valid for fish, even fishery products from relatively pristine areas may exceed it.

Some information on current and recent projects relating to dioxins was also presented. In particular, the "SCOOP" project is investigating dioxin intake in the European population through the diet.

In some European countries few data are available on the concentrations of dioxins in fish, presumably due—at least in part—to the difficulty and expense of these analyses.

It was agreed that Jacob de Boer would present a summary of recent data on dioxins, furans, and dioxin-like PCBs in fish at the 2001 MCWG meeting.

### 8.5.4 Organotin compounds in the marine environment

Erik Evers reported on the status of the review note on the "Distribution and effects of tributyltin—an update to mid-1999" which was originally presented to MCWG in 1999. The note, prepared by Robin Law and Erik Evers, has been published in the 1999 ACME Report as Annex 3, and has also been given as information to the OSPAR SIME Working Group (SIME 00/3/19, to be taken into account when considering a proposal for a one-off survey of organotin compounds (SIME 00/3/8) and the Draft OSPAR Background Document on organic tin (SIME 99/5/3)).

The review has since been updated for external publication [Marine Environmental Research, under revision] and now includes articles published as late as the end of 1999, focusing on the changes in environmental occurrences and effects observed following the ban on the use of TBT on small boats, i.e., with a major focus on the continuing use of TBT-based antifoulants on vessels > 25 m in length.

Monitoring

There was information from the recent SIME meeting (Stockholm, 21–25 February 2000) that trend monitoring of the levels and effects of TBT under the Coordinated Environmental Monitoring Programme (CEMP) was recommended as mandatory for all Contracting Parties from the year 2003 onwards. The possibility of conducting a one-off survey could no longer be supported (Draft Summary Record SIME 00/13/1, item 3.22).

Quality Assurance

There are certified reference materials available for TBT prepared under the EU/BCR SM&T programme, at least one sediment (BCR 462, a re-certified material with lower concentrations than when originally issued) and a mussel sample (BCR 477, proving to be an excellent reference material). A freshwater sediment material (BCR 646) is in the final stages of certification. Two proficiency testing exercises have been conducted within QUASIMEME, with reasonable results being obtained in the first study. Within the second study some problems occurred due to the extended work load requested of the laboratories, combined with a protocol instructing the laboratories to use specified and unfamiliar methods.

Further Information

Questions regarding the problems caused by organotins in the Netherlands have been recently raised in the Dutch parliament, both because of the results of a Dutch study on sediment concentrations in the Dutch delta area, including saltwater lakes, and following a blocking action undertaken by an NGO preventing the transport of dredged materials from harbours in the Netherlands to the open sea. One consequence will probably be to support the proposal to phase out the use of TBT-based antifouling paints on large vessels by the year 2003, and the removal of such coatings from all ships and constructions by 2008 at the IMO meeting in 2000.

Recently, Greenpeace in Germany published some results of TBT measurements in sportswear, and a few weeks later in flatfish. This has intensified activities within the responsible health authorities, but has generated little discussion by the general public. One reason for the decreasing interest in such information might be the assumption that the risks of hazardous substances are exaggerated by Greenpeace, both quantitatively (e.g., chemical content in the Brent Spar constructions) and qualitatively (toxic effects on human health by sportswear).

Discussion topics

A discussion in the Organics Subgroup focused mainly on the following topics:

- the lack of information on concentrations in biota;
- the need for a proper risk assessment regarding human consumers;
- a toxicological evaluation of organotin compounds (a report on a study on toxicological and oestrogenic effects is available from the Institute of Environmental Studies, Free University of Amsterdam);
- the reliability of TBT analysis with respect to both extraction and detection techniques.

At the last minute, MCWG was asked by ICES to consider the possibility of preparing guidelines for the analysis of TBT and other organic tin compounds in biota. OSG thought that it was not the right time to do this as more relevant information that will soon be available will significantly contribute to the development of such guidelines.

### 8.5.5 Polybrominated diphenylethers (PBDEs)

Jacob de Boer gave an update on current work concerning these compounds as a number of laboratories are now making determinations of PBDEs in marine samples. A current BSEF-funded study involving RIVO, NIOZ, and CEFAS includes an intercomparison study, and this is currently under way. Samples have been sent to 25 laboratories worldwide, with a deadline for receipt of data by 1 April 2000. The determination of 3 congeners (BDE47, BDE99, and BDE209) is mandatory, and data for other congeners may be supplied on a voluntary basis. Currently, world production is shifting to a formulation primarily containing decabromodiphenylether (BDE209) because of concerns about bioaccumulation and potential effects of formulations comprising mainly less-brominated congeners (penta- to octa-bromodiphenylethers). From a recent study in the Netherlands, high concentrations of BDE209 were observed in SPM from two locations in the Western Scheldt Estuary, one close to a production site in Termeuzen (NL) and one close to the harbour of Antwerp (B). Within the BSEF-funded study, analysis of PBDEs has now been optimized, but it proved necessary to use two different columns for complete analysis of all congeners, due to problems with the thermal degradation of BDE209 both in heated injection systems and on the GC column during analysis. BDE209 is now analysed using a short capillary column (approximately 12 m), whilst all other congeners are determined following separation using a 50 m column, so as to maximize chromatographic resolution. Using shorter columns with a lower resolving power, for instance, BDE153 can co-elute with tetrabromobisphenol-A. Detection is conducted using negative-ion chemical ionisation mass spectrometry (NICIMS) with detection of bromine at 79 and 81 Da.

Bo Jansson indicated that a three-year project is under way at his institute to study photolysis of BDE209, as one of the outstanding questions concerns the extent of debromination of this compound in the environment to yield lower-brominated and more bioavailable congeners. In soil, reduction of BDE209 to congeners as small as hexa-bromo BDEs has been reported, as was also observed in laboratory experiments of photodegradation. Commercially produced formulations of decabromodiphenylether contain approximately 97 % BDE209, with the major impurities being octa- and nona-BDEs.

A number of conferences and workshops to be held in 2000 will concentrate on, or include sessions related to, PBDEs. Under the BSEF-funded study mentioned above, a small workshop will be held in the Netherlands in June 2000. Under the Toxic Substances Initiative, a further workshop concerning PBDEs will also be held in June 2000 in Canada. Finally, papers and posters have been solicited for a session on PBDEs to be held at the SETAC Third World Congress to be held in Brighton, UK in May 2000, and for a session on PBDEs to be held at Dioxin 2000 in Monterey, California, in August. Jacob de Boer also agreed to provide a further update of work in progress at MCWG 2001.

### 8.5.6 New contaminant overviews

A number of studies have recently been undertaken at the CEFAS Burnham-on-Crouch Laboratory concerning the use of booster biocides in copper-based antifouling paints developed as replacements for TBT-based formulations following the ban on small boats. Robin Law offered to prepare a short review note on this topic, covering the use, environmental occurrence, and likely effects of booster biocides, in conjunction with his colleague Kevin Thomas who conducted this work. Jacek Tronczynski also offered to add further relevant information from his own laboratory, and these three co-authors will prepare a review note intersessionally. All MCWG members are requested to pass any relevant information from their own countries and programmes to Robin Law by 1 July 2000.

Bo Jansson suggested that a review of the current information available concerning chlorinated and/or brominated PAH may be timely, as a number of these compounds have recently been detected in biota from the Baltic Sea. All MCWG members are requested to pass any relevant information from their own countries and programmes to Bo Jansson by 1 July 2000, and he will prepare a short review note for MCWG 2001.

### 8.5.7 QUASIMEME Review

No dramatic developments have been seen in the performance of laboratories participating in the QUASIMEME Laboratory Performance Studies (LPS). The LPS reviews are updated each year, which is sufficient. David Wells asked the MCWG to discuss what figures and tables would be relevant in further LPS reviews.

Although the graphs in the review do not give an idea about the evolution of the performance of a single laboratory, they do give a good impression of the overall performance of the group of participating laboratories. Individual feedback is given to laboratories following each round of performance tests; it is difficult to show the performance results for all laboratories in a single graph, if it is possible at all.

### 8.5.8 HELCOM Annexes on Quality Assurance

Mikael Krysell, a member of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), introduced a number of papers and annexes from the 2000 meeting for review and comments by OSG. The latter relates to the HELCOM Manual on QA guidelines. OSG commented that the information in the papers appeared to be somewhat scattered and therefore a little difficult to evaluate. It was suggested that it would have been more convenient to see the QA Manual as a whole. However, the latter is only available (though freely accessible) from the HELCOM website, though the issue of a printed version is currently under consideration. OSG commented somewhat on the confusion that may arise due to the use of both the terms QA (Quality Assurance) and QC (Quality Control), but it was explained that both terms are clearly defined in the manual. Another comment related to the fact that variability was discussed both in relation to sampling and sampling strategies, and the analytical methods. This was considered to be confusing, and it was suggested that the discussion relating to sampling strategies would be better placed elsewhere. Comments were also made on the fact that a number of QA measures are mentioned (e.g., checking for recovery) without further guidance on how to use the information, for instance, whether to correct data for the determined recovery or not. The aim, however, was to make people aware of these measures, and the further details can be found within the technical manual of HELCOM. Finally, some comments were made on the units and conversions table. The concentrations of organic contaminants and metals in the water column are expressed as ng $dm^{-3}$, but it is not specified whether this relates to the dissolved or particulate phase. Halogenated organic contaminants in biota are expressed as ng $kg^{-1}$ on a lipid basis, but it was suggested that in that case µg $kg^{-1}$ would be more appropriate. Moreover, reporting the data on a fresh weight basis with additional information on the lipid content was considered to

be more appropriate for this purpose. OSG also inquired whether this is an ongoing project; this was confirmed and further new annexes can be expected for comment at MCWG 2001.

### 8.5.9 Presentations for MCWG 2001

Michel Lebeuf is currently involved in a three-year project concerned with toxaphene in eastern Canada. The project is barely under way, but initial results of the study will be available by next year. Michel agreed to prepare a presentation for MCWG 2001 on the status and findings of the work at that time.

### 8.5.10 Quality Peak Identification System (QPID)

Erik Evers described this project, which aims to carry out broad screening of organic contaminants in the marine and estuarine environments and the identification of those compounds which present biological hazards. The rationale for the project is that presently a large number of organic contaminants in the marine environment have not been identified and so are not considered in monitoring programmes. Also, the relationship between chemical contamination and the results obtained from bioassays (e.g., toxicity tests, determination of exposure and effects biomarkers) is difficult to establish. Furthermore, most screening data that are currently available are not systematically stored in accessible databases and are therefore not available for future and retrospective evaluation of monitoring data.

A modification of the current approach has been proposed with the aim of creating comprehensive databases for organic contaminants. Extracts of samples from different marine compartments can be analysed by GC-EI-MS in full scan mode, and these data can be processed by specialist software (AMDIS: Automated Mass Spectral Deconvolution and Identification System). This software, coupled to NIST98 MS-library and calculated retention indices for each chromatographic peak, permits the identification of compounds including those occuring as minor peaks in GC-MS chromatograms, as well as the automatic deconvolution of partially resolved peaks and thus extraction of identifiable spectra. Chemical data for 700 compounds are currently stored in the database programme, together with ecotoxicological data from bioassays. Both the chemical and toxicological information will be used to help identify the most relevant hazardous compounds.

The project is under further development at RIKZ and also seeks eventual expansion and cooperative research with laboratories in other ICES Member Countries. This includes, for instance, further developments in data management protocols, methods for clean-up and fractionation of sediment extracts, data for polar pesticides in sea water, work in different geographical areas, more diverse toxicological endpoints, input from QSAR models, and the extension of chemical data to those derived using LC-MS/MS.

### 8.5.11 Appointment of OSG Chair

OSG unanimously appointed Jacob de Boer to serve as Chair for the intersessional period and for the meeting in 2001.

## 8.6 Other Issues: Trace Metals Subgroup (TMSG)

### 8.6.1 Appointment of Chair

TMSG unanimously appointed Gert Asmund to serve as Chair for the intersessional period and for the meeting in 2001.

### 8.6.2 Review and comment preliminary guidelines concerning quality assurance in the Baltic Sea Marine Monitoring Programme (COMBINE) drafted by SGQAC

Mikael Krysell, the outgoing Chair of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), introduced some papers from the 2000 meeting for review and comments by TMSG. TMSG discussed the subject and decided that the Chair of TMSG should ensure that specific comments made on certain areas were turned over to Mikael Krysell directly. TMSG made some remarks concerning units: e.g., using % for expressing oxygen saturation; whether kg is preferable to $dm^3$, since the volume is dependent on pressure, temperature, and salinity, and the mass is faster, more accurate and easier to determine. The Chair of COSG drew attention to the 1998 report of the MCWG meeting in Stockholm in which this subject was thoroughly discussed. It was mentioned that in scientific reporting, the unit mole (mmole, μmole, nmole) is used more and more often instead of g (mg, μg, ng), e.g., metals in solution are more often reported in nmole $kg^{-1}$. However, heavy metals in suspended particulate matter should still be expressed in mg $kg^{-1}$ like sediment concentrations.

TMSG suggested that the total suspended matter load (SPM) should be taken up into the list (unit mg $dm^{-3}$).

### 8.6.3 Questions and recommendations to QUASIMEME from TMSG

David Wells had asked MCWG to discuss any suggestions for improvements of QUASIMEME as well as other topics of interest for the programme. After a short discussion on the subject, TMSG had the following suggestions/questions/comments to QUASIMEME:

- Is it possible to know which concentration ranges will be prepared in the next exercise?
- It should be possible to take part in and only pay for one exercise with one round/year if a laboratory so wishes.
- There is a need for sea water samples with natural levels of trace elements or near-natural levels.
- There is also a need for more variation in the biological sample matrices.
- The samples should be sent according to the timetable, because the laboratories have to plan their analytical work and to integrate the QUASIMEME samples in their "routine laboratory work".
- The Baltic Sea Research Institute in Warnemünde (through Christa Pohl) would like to invite the staff of QUASIMEME to take part in an expedition (e.g., Oktober 2000) to take natural samples in the Baltic from three different water bodies (low salinity (7–9), higher salinity (12–14), and anoxic water) using the equipment of QUASIMEME.

## 9 PLENARY DISCUSSION OF SUBGROUP WORK

Topics of more general interest for all three subgroups were discussed during the meeting and all agenda items were discussed in plenary on the last day of the meeting.

## 10 ANY OTHER BUSINESS

Jørgen Nørrevang Jensen, who is now responsible for the contaminant/biological effects databases at ICES, gave a short presentation on the ICES databases, including plans for the future, which mainly involve the biological data.

In the discussions after the presentation, MCWG recommended that the different databases held at ICES should be merged, meaning that it should be easy to combine data from all of them. There was also a wish that the software to submit data should be more user-friendly.

A new Chair for MCWG should be appointed for the coming three years and this item was therefore scheduled under this agenda point. MCWG nominated Robin Law to serve as Chair for the coming three-year period.

## 11 RECOMMENDATIONS AND ACTION LIST

The Action List and Recommendations are given in Annexes 12 and 13, respectively.

## 12 DATE AND VENUE OF THE NEXT MEETING

MCWG discussed the venue and dates of the next meeting. The Canadian member kindly offered to host the 2001 meeting of MCWG at the Insitut Maurice-Lamontagne in Mont-Joli, Quebec, Canada. MCWG acknowledged the invitation with appreciation. It was decided to plan the meeting for 26 February–2 March (week 9) in 2001.

## 13 CLOSURE OF THE MEETING

Staff members of ICES joined the closing session of MCWG. On behalf of MCWG, the Chair, B. Pedersen, thanked them for the superb organization, and for the support and services they provided.

In addition, she thanked the Subgroup Chairs for their efforts and support, and all the participants for their hard work.

On behalf of the entire MCWG, the Chair of OSG, J. de Boer, thanked the retiring Chair for her excellent work as Chair of MCWG for the last 4 years.

The Chair then closed the meeting at 14.00 hrs on 3 March 2000.

## ANNEX 1: LIST OF PARTICIPANTS

| Name | Subgroup | Address | Telephone | Telefax | E-mail |
|---|---|---|---|---|---|
| Alain Aminot | COSG | IFREMER<br>Centre de Brest<br>B.P. 70<br>29280 Plouzané<br>France | +33.298224361 | +33.298224548 | aaminot@ifremer.fr |
| Eugene Andrulewicz | OSG | Sea Fisheries Institute<br>Department of Fisheries Oceanography and Marine Ecology<br>ul. Kollataja 1<br>PL 81-332 Gdynia<br>Poland | +48.58201728 | +48.58202831 | eugene@mir.gdynia.pl |
| Gert Asmund (TMSG Chair) | TMSG | National Environmental Research Institute<br>Department of the Arctic Environment<br>Tagensvej 135<br>2200 Copenhagen N<br>Denmark | +45.35821415 | +45.35821420 | gas@dmu.dk |
| Victoria Besada | TMSG | Instituto Español de Oceanografia<br>Centro Oceanografico de Vigo<br>Apartado 1552<br>Cabo Estay-Canido<br>E-36280 Vigo<br>Spain | +34986 492111 | +34986 492351 | victoria.besada@vi.ieo.es |
| José Biscaya | OSG | Instituto Hidrografico<br>Rua das Trinas, 49<br>1293-049 Lisboa<br>Portugal | +351.213914103<br>+351 213914000 | +351.13960515<br>+351 213914199 | quimica@hidrografico.pt<br>bisaya@mail.telepac.pt |
| Stig Carlberg (COSG Chair) | COSG | SMHI<br>Oceanographical laboratory<br>Byggnad 31, Nya Varvet<br>SE-42671 Västra Frölunda<br>Sweden | +46.31751 8976 | +46.31751 8980 | stig.carlberg@smhi.se |
| Marianne Cleemann | OSG | Danish Veterinary and Food Administration<br>IFEF<br>Mørkhøj Bygade 19<br>2860 Sørborg<br>Denmark | +453395 6000 | | mcl@fdir.dk |
| Jacob de Boer (OSG Chair) | OSG | Netherlands Institute for Fisheries Research<br>P.O. Box 68<br>Haringkade 1<br>1970 AB IJmuiden<br>The Netherlands | +31.255564736 | +31.255564644 | j.deboer@rivo.wag-ur.nl |
| Erik H.G. Evers | OSG | National Institute for Coastal and Marine Management/RIKZ<br>Dept. of Analytical Chemistry<br>P.O. Box 20907<br>NL-2500 EX The Hague<br>The Netherlands | +31.703114312 | +31.703114600 | h.g.evers@rikz.rws.minvenw.nl |
| Michael Haarich | OSG | Bundesforschungsanstalt für Fischerei<br>Institut fur Fischereiökologie<br>Wüstland 2<br>D-22589 Hamburg<br>Germany | +49.4031908650 | +49.4031908603 | haarich.ifo@bfa-fisch.de |

| Name | Subgroup | Address | Telephone | Telefax | E-mail |
|---|---|---|---|---|---|
| Bo Jansson | OSG | Institute of Applied Environmental Research<br>Stockholm University<br>S-106 91 Stockholm<br>Sweden | +46.86747220 | +46.87581360 | bo.jansson@itm.su.se |
| Jarle Klungsøyr | OSG | Institute of Marine Research<br>P.O. Box 1870<br>Nordnes<br>5817 Bergen<br>Norway | +47.55238500 | +47.55238584 | jarle.klungsoyr@imr.no |
| Mikael Krysell | COSG | Danish Water Quality Institute<br>Agern Allé 11<br>DK-2970 Hørsholm<br>Denmark | | | mkr@dhi.dk |
| Robin Law | OSG | CEFAS<br>Burnham Laboratory<br>Remembrance Ave<br>Burnham on Crouch<br>Essex CMO8HA<br>UK | + 44 1621 787200 | +44 1621 784989 | r.j.law@cefas.co.uk |
| Michel Lebeuf | OSG | Insitut Maurice-Lamontagne<br>C.P. 1000<br>850 Route de la mer<br>G5H 3Z4 Mont-Joli<br>Quebec<br>Canada | +1.4187750690 | +1.4187750542 | lebeufm@dfo-mpo.gc.ca |
| Evin McGovern | OSG | Marine Institute<br>Marine Environment and Health Services Division<br>Abbotstown<br>Castleknock<br>Dublin 15<br>Ireland | +353.1.8210111 | +353.1.8205078 | evin.mcgovern@marine.ie |
| Klaus Nagel | COSG | Baltic Sea Research Institute<br>Seestrasse 15<br>D-18119 Warnemünde<br>Germany | +49.3815197331 | +49.3815197302 | klaus.nagel@io-warnemuende.de |
| Teresa Nunes | OSG | Instituto Español de Oceanografia<br>Centro Oceanografico de Vigo<br>Apartado 1552<br>Cabo Estay-Canido<br>E-36280 Vigo<br>Spain | +34.986492111 | +34.986492351 | teresa.nunes@vi.ieo.es |
| Sølveig Ólafsddottir | TMSG | Marine Research Institute<br>P.O. Box 1390<br>Skúlagata 4<br>121 Reykjavik<br>Iceland | +354 5520240 | +354 5623790 | solveig@hafro.is |
| Jon Ólafsson | COSG | Marine Research Institute<br>P.O. Box 1390<br>Skulagata 4,<br>IS-121 Reykjavik<br>Iceland | +354.5520240 | +354.5623790 | jon@hafro.is |
| Ole Vagn Olsen | COSG | Danish Institute for Fisheries Research<br>Kavalergarden 6<br>2920 Charlottenlund<br>Denmark | +45 33963408 | +4533963434 | vo@dfu.min.dk |

| Name | Subgroup | Address | Telephone | Telefax | E-mail |
|---|---|---|---|---|---|
| Koen Parmentier | TMSG | Free University of Brussels<br>Pleinlaan 2<br>1050 Brussels<br>Belgium | +32 26293266 | +32 26293266 | kparment@rub.ac.be |
| Britta Pedersen (MCWG Chair) | TMSG | National Environmental Research Institute<br>P.O. Box 358<br>Frederiksborgvej 399<br>DK 4000 Roskilde<br>Denmark | +45.46301209 | +45.46301114 | bpe@dmu.dk |
| Christa Pohl | TMSG | Baltic Sea Research Institute<br>Seestrasse 15<br>18119 Warnemünde<br>Germany | +49 3815197331 | +49 3815197302 | christa.pohl@io-warnemunde.de |
| Eeva-Liisa Poutanen | COSG | Finnish Institute of Marine Research<br>P.O. Box 33<br>00981 Helsinki<br>Finland | +385 9613941 | +385 961394434 | poutanen@fimr.fi |
| Marc Raemaekers | OSG | Sea Fisheries Department<br>Ministry of Agriculture<br>Ankerstraat 1<br>8400 Oostende<br>Belgium | +32 59342268 | +32 59330629 | mraemaek@mail.dma.be |
| Patrick Roose | OSG | Management Unit Mathematical Model of the North Sea<br>3e en 23e Linieregimentsplein<br>8400 Oostende<br>Belgium | +3253700131 | +3259704935 | p.roose@mumm.ac.be |
| Elisabeth Sahlsten | COSG | Swedish Meteorological and Hydrological Institute<br>Oceanographic Services Unit<br>Nya Varvet 31<br>42671 V. Frölunda<br>Sweden | +46 317518990 | +46 317518980 | elisabeth.sahlsten@smhi.se |
| Anne Talvari | OSG | Estonian Environmental Research Centre<br>Marja 4D<br>Tallinn<br>Estonia | +6112919 | +0039 372 6112 901 | talvari@klab.envir.ee |
| Jacek Tronczynski | OSG | IFREMER<br>Centre de Nantes<br>DEL/PC<br>B.P. 21105<br>Rue de l'Ile d'Yeu<br>44311 Nantes<br>France | +33240374136 | +33240374075 | jtronczy@ifremer.fr |
| Peter Woitke | TMSG | Federal Environmental Agency<br>FG II 3.6<br>P.O. Box 33 00 22<br>D-14191 Berlin<br>Germany | +49.3089032566 | +49.3089032285 | peter.woitke@uba.de |

## ANNEX 2: AGENDA

**1 OPENING OF THE MEETING**

**2 ADOPTION OF THE AGENDA**

**3 REPORT OF THE 87TH ICES STATUTORY MEETING**

**4 REPORTS ON RELATED ACTIVITIES**

**4.1 OSPAR AND HELCOM**
Any official requests from OSPAR or HELCOM which have arisen prior to this agenda being produced have been included

**4.2 Intergovernmental Oceanographic Commission (IOC)**
At the MCWG meeting in 1998 it was decided that all members of the MCWG should try to seek information about IOC and report back at the next MCWG.

**4.3 Laboratory Performance Study "QUASIMEME II"**
Dr Wells has been requested to provide an update.

**4.4 Other Activities**
Members who wish to make a presentation under this item should prepare a note for the MCWG

**5 REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES**
All members who wish to make a presentation on this item should prepare a note for the MCWG

**6 REQUESTS FROM ACME AND REGULATORY AGENCIES**
Requests from ACME which have arisen prior to this agenda being produced, have been included

**7 PLENARY PRESENTATIONS**

**7.1 Karl Iver Dahl-Madsen**
Ecological Modelling

**7.2 Anita Künitzer**
The marine programme of the Environmental Agency

**7.3 Phillippe Grandjean**
Human health aspects of seafood contamination with methylmercury and persistent organochlorine compounds

**7.4 J. de Boer, E. McGovern, and J. Klungsøyr**
Presentation of the final results of the European MATT project

**8 SUBGROUP ACTIVITIES AND DISCUSSIONS**
**Justifications for working in subgroups:**
*The Marine Chemistry Working Group is a large working group organised primarily in three parallel subgroups, the Chemical Oceanography Subgroup, the Organics Subgroup, and the Trace Metals Subgroup. The work in all three subgroups is supported by plenary discussions. Plenary discussions add value to the work in the subgroups.*

**8.1 Plenum and/or in all subgroup activities (see also agenda point 9)**

8.1.1 a) review and endorse the updated list of contaminants which can be monitored on a routine basis; (*The list of contaminants that can be monitored by different laboratories with good comparability is useful to Member Countries and regulatory commissions; it is updated each year on the basis of intercomparison exercises carried out during the previous year.)*

8.1.2 b) review information on QA systems used in laboratories involved in marine monitoring and report the outcome; *(QA systems are topics of major concern in laboratories monitoring*

*marine environmental parameters; MCWG keeps a regular review of new systems of QA relevant to its topics of concern.)*

8.1.3 c) provide assistance for a proposed HELCOM workshop on background/reference values for concentrations of nutrients and chemical contaminants in the Baltic Sea area *(This item is a request from HELCOM; [HELCOM 2000/4].)*

**8.2 Trace Metal Subgroup**

8.2.1 a) critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations; *(Given the tens of thousands of chemicals produced and used in industrial and other applications, it is important to develop a means to determine which chemicals may be potentially serious contaminants of the marine environment.)*

8.2.2 b) review, in conjunction with WGSSO, information on estuarine transport of trace metals and report on the outcome of the techniques available and the comparability of their results; (*This is part of the MCWG work to review the distribution and transport of contaminants in the estuarine environment.)*

8.2.3 c) review new information on the use of membrane systems for sampling; *(These systems are being reviewed for application to monitoring contaminants in the marine environment.)*

8.2.4 d) review new information on the use of contaminant concentrations in biological media as environmental indicators to detect trends, including supplementary work to the Icelandic cod study on the relationship between trace element concentrations in cod liver and various co-factors *(It is important to determine good indicators of contamination in the marine environment that can be monitored regularly with minimal analytical and environmental variances. The extended Icelandic cod liver study continues work from previous years to determine the influence of fat content in the liver of cod on concentrations of trace metals in this tissue.)*

8.2.5 Any other business raised by the subgroup (*Among others, the Trace Metal Subgroup needs to appoint a Chair to deal with matters which may arise intersessionally and who can chair the subgroup next year.)*

**8.3 Organics Subgroup**

8.3.1 a) review the updated list of relevant certified reference materials for organic compounds for use in marine monitoring;
(*MCWG maintains a current listing of CRMs for organic compounds available for use in marine monitoring; this list needs to be updated annually.)*

8.3.2 b) critically evaluate the lists of priority contaminants prepared in relevant regional and international organizations;
*(Given the tens of thousands of chemicals produced and used in industrial and other applications, it is important to develop a means to determine which chemicals may be potentially serious contaminants of the marine environment.)*

8.3.3 c) review new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane (TCPMe) in fish and in marine mammals from eastern Canada, including the results of the TCPM and TCPMe interlaboratory study, second phase*;*
*(This project was initiated several years ago among MCWG members on the basis of concerns regarding these contaminants in the marine environment.)*

8.3.4 d) review information on volatile organic contaminants in biota;
*(This is to evaluate information on the distribution and potential effects of these contaminants in the marine environment.)*

8.3.5 e) review new information on the analysis of PAH metabolites in bile and critically review the robustness of the methods;
*(This activity has been requested by WGBEC, which requires an evaluation of current methods for measuring PAH metabolites in bile and a recommendation of the best method for use in*

*biological effects monitoring. Dr Wells will inform MCWG about progress in the European project on the certification of PAH metabolites in bile as background information.)*

8.3.6 f) review new information on the use of membrane systems for sampling;
*(These systems are being reviewed for application to monitoring contaminants in the marine environment.)*

8.3.7 g) review new information on the monitoring and analysis of toxaphene;
*(Owing to continuing concerns about the distribution and effects of toxaphene in the marine environment, it is relevant to consider the results of recent research on this topic.)*

8.3.8 Any other business raised by the subgroup *(Among others, the Organics Subgroup needs to appoint a Chair to deal with matters which may arise intersessionally and who can chair the subgroup next year.)*

### 8.4 Chemical Oceanography Subgroup

8.4.1 a) review progress on the application of high temperature techniques for the determination of total nitrogen in sea water;
*(There has been much discussion about the most appropriate means of monitoring total nitrogen in sea water; this provides the opportunity for MCWG to consider the application of high temperature techniques.)*

8.4.2 b) review information on experience in the use of automated *in situ* chemical oceanographic systems for the observation of chemical variables;
*(This study is part of the work on chemical oceanographic conditions and methods coordinated by MCWG.)*

8.4.3 c) review a comparison of spectrophotometric and volumetric alternatives for quantification in the Winkler method for the determination of dissolved oxygen in sea water and report on the outcome;
(*This is part of the work of MCWG in reviewing and evaluating methods for measuring chemical properties in marine and estuarine environments.)*

8.4.4 d) review the use of chemical data in numerical modelling and the possible implications for future work in modelling and in field sampling programmes, including the preparation of a workshop or joint session with the WGSSO in 2001;
*(Recent developments and status of physical models for coastal circulation will be reviewed so as to understand the inherent accuracy, resolution, assumptions and parameterisations, etc., in relation to biological parameterisations. This is necessary to appropriately couple physics and population dynamics to provide meaningful calculations of population development.)*

8.4.5 Any other business raised by the subgroup (*Among others, the Chemical Oceanography Subgroup needs to appoint a Chair to deal with matters which may arise intersessionally and who can chair the subgroup next year.)*

## 9 PLENARY DISCUSSION OF SUBGROUP WORK

## 10 ANY OTHER BUSINESS

Among others, the group needs to suggest a new Chair for the next three years.

## 11 RECOMMENDATIONS AND ACTION LIST

## 12 DATE AND VENUE OF THE NEXT MEETING

## 13 CLOSURE OF THE MEETING

## ANNEX 3: 20th IOC ASSEMBLY OBSERVER'S REPORT

The ICES Oceanographer represented ICES during part of the 20th Session of the IOC Assembly that was held in Paris from 29 June to 9 July 1999. He attended from 30 June to 2 July, covering three Agenda Items, viz.,

- Agenda Item 3 on Ocean Sciences, which included Oceans and Climate, Oceans and Global Change, WRCP (World Climate Research Programme), OOPC and GODAE, Ocean CO2. ICAM and other Coastal Zone Programmes, Marine Pollution Research and Monitoring, and Ocean Science and Living Marine Resources (OSLR).
- Agenda Item 4 on Ocean Services which included Data and Marine Information Management, Mapping, and IDNDR-Related Activities such as Storm Surges and El Niño.
- Agenda Item 5 on Operational Observing Systems including the Global Ocean Observing System (GOOS), Global Climate Observing System (GCOS), Integrated Global Ocean Services System/Ship of Opportunity (IGOSS/SOOP), Global Sea Level Observing System (GLOSS), Data Buoy Cooperation Panel (DBCP), and J-COMM (Joint Technical Commission for Oceanography and Marine Meteorology (J-COMM).

**Agenda Item 3**

Dr Gould, Director of the WOCE and CLIVAR International Project Offices (IPOs), reviewed progress in WCRP activities. He drew attention in particular to CLIVAR (Climate Variability Project) which is bigger than any international programme ever attempted. It attracted more than 60 countries to the CLIVAR Conference held in December 1998 in UNESCO. He considers that such a large effort requires an expanded infrastructure, the cost of which is insignificant compared to the total cost of CLIVAR. The IOC contribution to the WCRP is heavily relied on to maintain the current infrastructure, and Dr Gould urged the Member States to increase their contributions so that CLIVAR can be run efficiently. He noted that regional extensions of the CLIVAR International Project Office (IPO) are planned with regional offices.

It was noted that the OOPC is organising jointly with the Upper Ocean Panel of CLIVAR, OCEANOBS 99, a major international Conference on Ocean Observations for Climate for 18–22 October this year in St. Raphael, France. It will be hosted by CNES, the French space agency. Attention was also drawn to a new project called Argo. Argo hopes to establish a global array of 3000 autonomous profiling floats with a three-dimensional spacing. These floats can be programmed on deployment to dive to a preset depth of say 1000 or 2000 metres where they drift with the current for 10 to 15 days and then rise to the surface. During their ascent they will record temperature and salinity. Upon reaching the surface they will transmit their stored data by satellite and continue this cycle unattended for several years. This new technology makes the oceanographer's and modeller's dreams of a global, real-time reporting network on the state of the ocean an economic practicality.

A proposal to terminate the present IOC-JGOFS Ocean $CO_2$ Advisory Panel and develop with SCOR/JGOFS a new Panel with a new membership consistent with the new terms of reference that reflect the OOPC and GOOS needs for ocean $CO_2$ expertise was endorsed. It should be recalled that this activity is one in which ICES used to be directly involved under the flag of the IOC/SCOR/IAPSO JPOTS.

The Assembly was informed of a number of ICAM (Integrated Coastal Area Management) related activities carried out by IOC during the intersessional period, viz:

- The IOC/LOICZ/START Workshop on Climate Change and Coastal Processes in West Africa in November 1998 in Benin;
- The Coastal Ocean Advanced Science and Technology Studies (COASTS) Programme Expert Consultation (20–21 January 1999, Paris) which worked on the preparation of an overview and synthesis of the interdisciplinary global coastal ocean science (physical-biological-chemical-geological) and the organization of an international workshop for the year 2000;
- The launching of a Website on ICAM together with NOAA, The World Bank and the Center for the Study of Marine Policy (Delaware);
- The publication of a reference textbook entitled "Integrated Coastal and Ocean Management, Concept and Practices", published in 1998;
- The IOC/KMI International Workshop on ICAM, (Seoul, Korea, April 1998) focusing on policy coordination mechanisms, and the integration of science in ICAM;
- The IOC/COI/EU Atlas on the sensibility of the shallow water areas of Seychelles, and its follow up.

The Chair of GIPME, Dr Michael Bewers, introduced the item dealing with marine pollution. He pointed out that detailed restructuring of the GIPME Programme, which requires the concurrence of the three co-sponsoring agencies, IOC, IMO and UNEP, was planned for a GESAG (GIPME Expert Scientific Advisory Group) meeting in April 1999. However, this meeting has been delayed. The detailed restructuring of GIPME which has been planned for some time, will now be undertaken in draft form during mid-1999 in preparation for a GESAG meeting that will be convened once reorganisation at UNEP has been completed.

The Assembly reaffirmed its strong support for the general IOC activities on OSLR (Ocean Science on Living Resources). It recommended that the OSLR programme develop closer linkages with FAO.

IOC and SCOR have jointly appointed Dr Gentien, IFREMER (France), as Chair of GEOHAB (Global Ecology and Oceanography of Harmful Algal Blooms). GEOHAB is a plan for coordinated scientific research and cooperation to develop international capabilities for assessment, prediction and mitigation of harmful algae. It is a science programme within a general framework provided by the IOC HAB Programme and builds on the results of both the SCOR/IOC Working Group on the Physiological Ecology of HAB and the ICES/IOC Working Group on Harmful Algal Bloom Dynamics (WGHABD). The scientific goal of GEOHAB is to determine ecological and oceanographic mechanisms underlying the population dynamics of harmful algae, by the integration of biological and ecological studies with chemical and physical oceanography, supported by improved observation systems. Improved global observation systems will be required to resolve the influences of environmental factors (anthropogenic and climate-related) on distributions and trends in HAB occurrence.

**Agenda Item 4**

Mr Ben Searle, Chair of the IOC Committee on IODE (International Oceanographic Data and Information Exchange), described progress in the work of his Committee. This included mention of the development of the Global Directory of Marine (and Freshwater) Professionals (GLODIR), and of standards for marine libraries and information centres. The IOC is also continuing its participation as a UN Partner in the Aquatic Sciences and Fisheries Abstracts (ASFA) and sponsors ASFA CD-ROM subscriptions to a number of African Member States. The MEDI (Marine Environmental Data and Information) Pilot Project, a cooperative venture between the IODE data and information communities, has resulted in the development of a specific and user-friendly software for the creation of meta-data records in a standard format, ensuring compatibility or convertibility with the emerging ISO standard for meta-data and other major national standards.

**Agenda Item 5**

The latest progress in the development of the Global Ocean Observing System (GOOS) was described by the Chair of I-GOOS, Dr Angus McEwan. The broad range of GOOS activities is provided at http://ioc.unesco.org/goos. GOOS is being incorporated into the Integrated Global Observing Strategy (IGOS). IGOS links the efforts of the UN sponsors of the *in situ* global observing systems and the existing national space agencies through the Committee on Earth Observation Satellites (CEOS). It is intended to (a) improve understanding for governments of global observing plans, by providing an overarching view, (b) provide a framework for decisions on the continuity of observations of key variables, and c) assist in ensuring cooperation between the research and operational domains. It is hoped that the arrival of global coordination of observations marks the development of a new paradigm for the use and application of science in which "ownership" of data and information can be subordinated to the collective benefit of society. It was therefore agreed that IOC should participate in the IGOS Partners Forum.

A GOOS Initial Observing System (GOOS-IOS) has now been defined from a number of existing observing systems, as a means of demonstrating that GOOS is starting from a finite base. I-GOOS, in recognising its value, noted that a mechanism was needed for accepting systems as additions to the IOS and in due course for formal approval of the GOOS so defined.

With the pace at which new regional groupings and activities in the name of GOOS are being proposed, some caution has been expressed at the guiding definitions for such groupings. It was emphasised that regional alliances and national ocean observing coordination bodies have a valuable role to play in ensuring satisfactory linkages with and between such initiatives. In this context I-GOOS drafted a Resolution concerning the IOC co-sponsorship of a GOOS working group of ICES.

The progress achieved by GOOS is clear. GOOS has now moved from a concept to an implementable reality, especially as far as open ocean observations in support of weather and climate forecasting are concerned. GOOS is now seen throughout the intergovernmental system as the prime vehicle for coordinated ocean observations. Although GOOS will take decades to develop, the first building blocks are now in place.

The creation of J-COMM is being seen as a much needed implementation infrastructure for GOOS, and which represents a major step forward in the global integration of operational global observations. J-COMM's terms of reference are to: (i) further develop the observing networks; (ii) implement data management systems; (iii) deliver products and services; (iv) provide capacity building to Member States; and (v) assist in the documentation and management of the data in international systems. J-COMM will be a partnership, with 50 % of its members from meteorology and 50 % from oceanography. Reporting to it will be specialist advisory panels, probably including in the first instance panels on (i) the ocean surface (SST) and marine meteorology; (ii) the upper ocean (temperature, salinity, carbon dioxide); and (iii) sea-level (GLOSS). J-COMM will be advised by GOOS bodies (GSC and I-GOOS), by GCOS and by the World Weather Watch (WWW) of the WMO and IODE of IOC. In turn it will report to the sponsors: IOC and WMO. The IODE will not be within J-COMM but will be strongly linked to it. In future there is the potential for specific technical subgroups similar to J-COMM to be formed to deal with different areas of GOOS data collection and management (e.g., pollution, living resources).

## ANNEX 4: EXAMPLES OF QA CRITERIA USED BY DIFFERENT EUROPEAN ORGANIZATIONS

Monitoring the marine environment and assessment of the marine environmental status require the collection of data by a very large number of laboratories, particularly on an international level. In order to be able to compare data with some confidence, an implementation of a variety of QA procedures in monitoring laboratories as well as in data collection centers must be regarded as indispensable. An established QA system consists of:

- validation of the data collecting methods, that means the experimental proof and documentation that these methods are fit for their intended purpose, and
- use of and participation in internal and external routine quality control measures.

There is general agreement that a QA system for analytical laboratories should be based on the European standard EN 45001 or the ISO guide 25, respectively. Both documents will be substituted by the international standard ISO 17025 in 2000. Consequently, procedures for accreditation of laboratories will be changed in the forthcoming years.

Despite the fact that QA is regarded as absolutely necessary in marine monitoring, the evaluation of the data quality is more or less a matter of discussion. When it comes to the assessment of the marine environmental status based on monitoring data, rules about how QA information should be used to provide data assessors with reliable data are far from being generally accepted. There are at least several questions to be answered:

- How far should certified reference materials (CRMs) or internal laboratory control samples match the sample matrix and contaminant levels in the routine monitoring samples?
- How can information provided by control charts for accuracy, precision or blanks be used to give an estimation of the uncertainty of the analytical procedure, and
- How can this uncertainty be incorporated in, e.g., the determination of temporal trends or spatial distributions of contaminants in the marine environment?
- What is the significance of detection or determination limits of analytical procedures owing to different methods used by data reporting laboratories to calculate these parameters?
- What is the best approach to take into account the performance of laboratories in intercomparison exercises and proficiency testing schemes in evaluating the quality of reported monitoring data?

MCWG should discuss approaches to incorporate QA information in the assessment of monitoring data. Some principles have already been described and might be applied and adjusted respectively to the objectives of individual marine monitoring programmes. Examples of what criteria have been applied to results of proficiency testing schemes are given below:

*Analytical Quality Control Scheme of Nordrhein-Westfalen (Germany, 1992)*

70 % of the laboratory means within control limits set by the regulatory agency and within-laboratory standard deviation within specified control limits.

*Analytical Quality Control Scheme of Baden-Württemberg - Water (Germany, 1994)*

Percentage of acceptable means of an individual laboratory must be higher than or equal to the squared percentage of accepted values of all laboratories for all investigated matrix/parameter combinations (i.e., 80 % acceptable values of all laboratories means 64 % acceptable values of one laboratory).

*UK National Marine Analytical Quality Control Scheme (Mar. Pollut. Bull. 36, 1994, 30–31)*

Participation in at least 60 % of all matrix/parameter/round combinations is necessary.

80 % of the laboratory means must be within limit values of a maximum tolerable bias as set by the organizer of the proficiency test (depending on the concentration, as an absolute or a relative error).

*NOAA requirements for environmental monitoring (Environ. Tox. Chem. 16, 1997, 1345–1350)*

Analysis of certified reference materials or standard solutions; allowable bias: ± 25 % (trace metals) or ± 30 % (organic contaminants) of the certified value.

*UK Acid Waters Monitoring Network (Sci. Tot. Environ. 216, 1998, 113–119)*

Value of a maximum tolerable bias is set by the organizer of the proficiency test (depending on the concentration, as an absolute or a relative error).

70 % of the laboratory means within these limits is satisfactory.

90 % of the laboratory means within these limits is very good.

*Analytical Quality Control Guideline for Water Analysis (LAWA, Guideline A-3, Germany, 1989)*

70 % of the laboratory means within control limits set by the regulatory agency; within-laboratory standard deviation within specified control limits.

A recent publication by Dobson *et al*. (J. Environ. Monit., 1999, 1**:** 91–95) gives an example on how QA data are used in the *UK National Marine Analytical Quality Control Scheme* for an assessment of monitoring data. The advantage of this approach is that the whole QA system of a laboratory, including the use of validated methods and information on internal quality measures, is incorporated in the assessment of a laboratory's performance.

## ANNEX 5: REFERENCE MATERIALS FOR ORGANIC CONTAMINANTS IN MARINE BIOTA AND MARINE SEDIMENTS

The following comments apply to these tables:

- the compiled tables are for information. Although every effort has been made to ensure that these tables are accurate, users of CRMs should consult vendors for full and accurate information;
- certified calibration materials and standards are not included;
- these tables do not purport to be complete and all the CRMs listed may not be commercially available;
- methylmercury is not considered an organic contaminant for the purposes of this list.

List of suppliers:

- NIST: USA, National Institute of Standards and Technology;
- IAEA: UN, International Atomic Energy Agency;
- BCR: EC, Bureau of Community Reference, now EC Institute for Reference Materials and Measurements (IRMM);
- NRC: Canada, National Research Council, Institute for National Measurement Standards (INMS);
- NWRI: Canada, National Water Research Institute, Environment;
- CIL: USA, Cambridge Isotope Laboratories;
- NIES: Japan, National Institute for Environmental Standards, Environment Agency .

**Table A5.1a.** Reference materials for organic contaminants in marine biota. Values preceded by an asterisk (*) are non-certified; all other values are certified.

| ***Code*** | **SRM-1974a** | **SRM-2974** | **140/OC** |
|---|---|---|---|
| ***Organization*** | **SRM-NIST** | **SRM-NIST** | **IAEA** |
| ***Country of origin*** | USA | USA | |
| ***Matrix*** | Mussel tissue | Mussel tissue | *Fucus* (sea plant homogenate) |
| ***UNITS*** | µg $kg^{-1}$ | µg $kg^{-1}$ | µg $kg^{-1}$ |
| ***AS*** | Dry weight | Dry weight | |
| [±] ***expressed as*** | ± 95% CI | ± 95% CI | |
| UNITS OF ISSUE | 3 × 15 g | 8 g | 30 g |
| ***FORM*** | | Freeze-dried | |
| **Hydrocarbons** | | | |
| **Resolved aliphatics** | | | *13 mg/kg |
| **Unresolved aliphatics** | | | *26 mg/kg |
| **Pristane** | | | 50 |
| **Phytane** | | | 56 |
| **Sum alkanes (C14-C34)** | | | 11 mg/kg |
| **Total aromatics** | | | *5.8 mg/kg |
| **Unresolved aromatics** | | | *0.35 mg/kg |
| **Anthracene** | 6.1 ± 1.7 | 6.1 ± 1.7 | 14 |
| **Benz[*a*]anthracene** | 32.5 ± 4.7 | 32.5 ± 4.8 | 25 |
| **Benzo[*b*]fluoranthene** | 46.4 ± 3.7 | 46.4 ± 4.0 | *37 |
| **Benzo[*k*]fluoranthene** | 20.18 ± 0.84 | 20.2 ± 1.0 | 19 |
| **Benzo[*a*]pyrene** | 15.63 ± 0.65 | 15.63 ± 0.80 | 20 |
| **Benzo[*e*]pyrene** | 84.0 ± 1.9 | 84.0 ± 3.2 | 26 |
| **Benzo[*ghi*]perylene** | 22.0 ± 2.2 | 22.0 ± 2.3 | 20 |
| **Chrysene** | 44.2 ± 2.3 | 44.2 ± 2.7 | 40 |
| **Dibenz[*a,h*]anthracene** | | | *4.5 |
| **Dibenz[*a,c*]anthracene** | | | |
| **Dibenz[*a,j*]anthracene** | | | |
| **Fluoranthene** | 163.7 ± 9.1 | 163.7 ± 10.3 | 88 |
| **Fluorene** | | | *6.5 |
| **Indeno[1,2,3-*cd*]pyrene** | 14.2 ± 2.8 | 14.2 ± 2.8 | 33 |
| **1-Methylphenanthrene** | | | 11 |
| **2-Methylphenanthrene** | | | 19 |
| **Naphthalene** | 23.5 ± 4.4 | | 17 |
| **Perylene** | 7.68 ± 0.27 | 7.68 ± 0.35 | |
| **Phenanthrene** | 22.2 ± 2.4 | 22.2 ± 2.5 | 76 |
| **Pyrene** | 151.6 ± 6.6 | 151.6 ± 8.0 | 67 |
| **Triphenylene** | 50.7 ± 5.9 | 50.7 ± 6.1 | |
| **Total aliphatics** | | | *27 mg/kg |
| ***n*-C17** | | | 890 |
| ***n*-C18** | | | 99 |
| **UVF Chrysene** | | | *3.5 mg/kg |
| **UVF ROPME oil** | | | *29 mg/kg |

**Table A5.1b.** Reference materials for organic contaminants in marine biota. Values preceded by an asterisk (*) are non-certified; all other values are certified.

| *Code* | **SRM-1974a** | **SRM-1588a** | **SRM-1945** | **SRM-2974** | **MA-A-3/OC** | **MA-A-1/OC** | **140/OC** | **CRM 598** |
|---|---|---|---|---|---|---|---|---|
| ***Organization*** | **SRM-NIST** | **SRM-NIST** | **SRM-NIST** | **SRM-NIST** | **IAEA** | **IAEA** | **IAEA** | **BCR** |
| ***Country of origin*** | USA | USA | USA | USA | | | | EC |
| ***Matrix*** | Mussel tissue | Cod liver oil | Whale blubber | Mussel tissue | Shrimp homogenate | Copepoda | *Fucus* (sea plant homogenate) | Cod liver oil |
| ***UNITS*** | μg $kg^{-1}$ | μg $kg^{-1}$ | μg $kg^{-1}$ | μg $kg^{-1}$ | ng $g^{-1}$ | ng $g^{-1}$ | μg $kg^{-1}$ | μg $kg^{-1}$ |
| ***AS*** | Dry weight | | Wet weight | Dry weight | Dry weight | Dry weight | | |
| [±] ***expressed as*** | ± 95% CI | ± 95% CI | ± 95% CI | ± 95% CI | | | | |
| UNITS OF ISSUE | 3 × 15 g | 5 × 1.2ml/ ampoule | Set 2, 15 g / ampoule | 8 g | 35 g | 30 g | 30 g | 5 g |
| ***FORM*** | | | | Freeze-dried | Freeze-dried | Freeze-dried | | |
| **PESTICIDES** | | | | | | | | |
| **Hexachlorobenzene** | | 157.8 ± 5.0 | 32.9 ± 1.7 | | 0.32 ( 0.2–0.44) | | *1.3 | 55.7 ± 2.0 |
| **α-HCH** | | 85.3 ± 3.4 | 16.2 ± 3.4 | | 15 | 10 (1.6–18.4) | *1.4 | 42 ± 3 |
| **β-HCH** | | | *8.0 ± 1.4 | | | | 4.6 | 16 ± 3 |
| **γ-HCH** | | 24.9 ± 1.7 | 3.30 ± 0.81 | | 3.2 | 8.2 | *11 | 23 ± 4 |
| **Aldrin** | | | | | 0.7 ( 0.2–1.2) | 14 ( 0–33) | *0.76 | |
| ***trans*-Chlordane** | 16.6 ± 1.7 | | | 16.6 ± 1.8 | | | | 6.9 ± 1.6 |
| ***cis*-Chlordane** | 17.2 ± 2.8 | 167.0 ± 5.0 | 46.9 ± 2.8 | 17.2 ± 2.9 | | | *1.4 | 24.4 ± 1.8 |
| **Heptachlor** | | | | | 2.4 | | *3 | |
| **Heptachlor epoxide** | | 31.6 ± 1.5 | 10.8 ± 1.3 | | | | *0.79 | |
| ***trans*-Nonachlor** | 18.0 ± 3.6 | 214.6 ± 7.9 | 231 ± 11 | 18 ± 3.6 | | | | 39 ± 4 |
| **Dieldrin** | 6.2 ± 1.3 | 155.9 ± 4.5 | *37.5 ± 3.9 | | | | 1.7 | 59 ± 4 |
| ***cis*-Nonachlor** | 6.84 ± 0.90 | 94.8 ± 2.8 | 48.7 ± 7.6 | 6.84 ± 0.92 | | | | |
| **Oxychlordane** | | | 19.8 ± 1.9 | | | | | 11.0 ± 1.8 |
| **2,4′-DDE** | *5.26 ± 0.27 | 22.0 ± 1.0 | 12.28 ± 0.87 | | | | | |
| **4,4′-DDE** | 51.2 ± 5.5 | 651 ± 11 | 445 ± 37 | 51.2 ± 5.7 | 4.7 (1.3–8.1) | 6.1 ( 1.5–17.1) | 1.2 | 610 |
| **2,4′-DDD** | *13.7 ± 2.8 | 36.3 ± 1.4 | 18.1 ± 2.8 | | | | | 30 |
| **4,4′-DDD** | 43.0 ± 6.3 | 254 ± 11 | 133 ± 10 | 43 ± 6.4 | 0.81( 0.05–1.57) | | 0.7 | 400 |
| **2,4′-DDT** | *8.5 ± 1.9 | 156.0 ± 4.4 | 106 ± 14 | | | | | |
| **4,4′-DDT** | 3.91 ± 0.59 | 524 ± 12 | 245 ± 15 | 3.91 ± 0.60 | 3.2 ( 0–6.7) | 8.3 (3.4–13.2) | 2.2 | 179 |
| **Mirex** | | | 28.9 ± 2.8 | | | | | |
| **Endrin** | | | | | | | *0.71 | |
| **α-Endosulfan** | | | | | | | *0.9 | |
| **Total PCBs** | | | | | | | | |
| **TOTAL** | | | | | | | | |
| **Aroclor 1242** | | | | | | 120 ( 67–173) | | |
| **Aroclor 1254** | | | | | 33 ( 0–67) | 140 (70–210) | *25 | |
| **Aroclor 1260** | | | | | | | *12 | |

**Table A5.1c.** Reference materials for organic contaminants in marine biota. Values preceded by an asterisk (*) are non-certified; all other values are certified.

| *Code* | SRM-1974a | SRM 1588a | SRM-1945 | SRM-2974 | 140/OC | CARP - 1 | CRM 349 | CRM 350 | EDF-2525 | EDF-2526 |
|---|---|---|---|---|---|---|---|---|---|---|
| ***Organization*** | **SRM-NIST** | **SRM-NIST** | **SRM-NIST** | **SRM-NIST** | **IAEA** | **NRC** | **BCR** | **BCR** | **CIL** | **CIL** |
| ***Country of origin*** | USA | USA | USA | USA | | Canada | EC | EC | USA | USA |
| ***Matrix*** | Mussel tissue | Cod liver oil | Whale blubber | Mussel tissue | *Fucus* (sea plant homogenate) | Common carp | Cod liver oil | Mackerel oil | Fish | Fortified fish |
| ***UNITS*** | μg $kg^{-1}$ | μg $kg^{-1}$ | μg $kg^{-1}$ | μg $kg^{-1}$ | μg $kg^{-1}$ | ng $kg^{-1}$ | μg $kg^{-1}$ | μg $kg^{-1}$ | ng $kg^{-1}$ | ng $kg^{-1}$ |
| ***AS*** | Dry weight | | Wet weight | Dry weight | | Wet weight | Wet weight | Wet weight | Wet weight | Wet weight |
| [±] ***expressed as*** | ± 95% CI | ± 95% CI | ± 95% CI | | | ± 95% CI | ± 95% CI | ± 95% CI | | |
| UNITS OF ISSUE | 3 × 15 g | 5 × 1.2 ml / ampoule | Set 2, 15 g / ampoule | 8 g | 30 g | 6 × 9 g | 2 g ampoules | 2 g ampoules | Set 1, 10 g / ampoule | Set 1, 10 g / ampoule |
| ***FORM*** | | | | Freeze-dried | | Slurry | | | Slurry | Slurry |
| **PCBs** | | | | | | μg $kg^{-1}$ | | | | |
| **PCB 18** | *33 ± 11 | | 4.48 ± 0.88 | | | | | | | |
| **PCB 28** | *79 ± 15 | 28.32 ± 0.55 | *14.1 ± 1.4 | | 1.7 | | 68 ± 7 | 22.5 ± 4.0 | | |
| **PCB 31** | *76 ± 21 | 8.33 ± 0.28 | *3.12 ± 0.69 | | | | | | | |
| **PCB 32** | | | | | 1.8 | | | | | |
| **PCB 44** | 72.2 ± 7.4 | 35.1 ± 1.4 | 12.2 ± 1.4 | 72.7 ± 7.7 | | | *75 | *44 | | |
| **PCB 49** | 88.8 ± 5.0 | 29.9 ± 0.84 | 20.8 ± 2.8 | 88.8 ± 5.7 | 1.6 | | | | | |
| **PCB 52** | 115 ± 11 | 83.3 ± 2.3 | 43.6 ± 2.5 | 115 ± 12 | 3.8 | 124 ± 32 | 149 ± 20 | 62 ± 9 | | |
| **PCB 66** | 101.4 ± 4.4 | 54.7 ± 1.5 | 23.6 ± 1.6 | 101.4 ± 5.4 | | | | | | |
| **PCB 77** | | | | | | | | | 2376 ± 672 | 523 ± 45 |
| **PCB 87** | 54 14* | 56.3 ± 1.1 | 16.7 ± 1.4 | | | | | | | |
| **PCB 95** | 83 ± 17 | 36.5 ± 1.1 | 33.8 ± 1.7 | 83 ± 17 | | | | | | |
| **PCB 99** | 70.9 ± 4.0 | | 45.4 ± 5.4 | 70.9 ± 4.5 | | | | | | |
| **PCB 101** | 128.3 ± 9.7 | 126.5 ± 4.3 | | 128 ± 10 | 2.4 | | 370 ±17 | 165 ± 9 | | |
| **PCB 101/90** | | | 65.2 ± 5.6 | | | 124 ± 37 | | | | |
| **PCB 105** | 53.0 ± 3.4 | 60.2 ± 2.3 | 30.1 ± 2.3 | 53 ± 3.8 | 0.49 | 54 ± 24 | | | | 144 ± 63 |
| **PCB 110** | 127.3 ± 8.6 | 76.0 ± 2.0 | 23.3 ± 4.0 | 127.3 ± 9.4 | | | | | | |
| **PCB 118** | 130.8 ± 3.6 | 176.3 ± 3.8 | 74.6 ± 5.1 | 130.8 ± 5.3 | 1 | 132 ± 60 | 456 ± 31 | 143 ± 20 | | 321 ± 70 |
| **PCB 126** | | | | | | | | | 834 ± 277 | 521 ± 70 |
| **PCB 128** | 22.0 ± 3.4 | 47.0 ± 2.4 | 23.7 ± 1.7 | 22 ± 3.5 | | | *104 | *41 | | |
| **PCB 138** | | | | | 1.7 | | | | | |
| **PCB 138/163** | | | | | | | *765 | *274 | | |
| **PCB 138/163/164** | 133.5 ± 9.5 | 263.5 ± 9.1 | 131.5 ± 7.4 | 134 ± 10 | | 102 ± 23 | | | | |
| **PCB 149** | 87.6 ± 2.3 | 105.7 ± 3.6 | 106.6 ± 8.4 | 87.6 ± 3.5 | 1.2 | | | | | |
| **PCB 151** | 25.6 ± 3.5 | 54.8 ± 2.1 | 28.7 ± 5.2 | 25.6 ± 3.6 | | | | | | |
| **PCB 153** | 145.2 ± 7.6 | 273.8 ± 7.7 | 213 ± 13 | 145.2 ± 8.8 | 1.7 | 83 ± 39 | 938 ± 40 | 317 ± 20 | | |
| **PCB 156** | 7.43 ± 0.99 | 27.3 ± 1.8 | 10.3 ± 1.1 | 7.4 ± 1.0 | 0.17 | | | | | |
| **PCB 169** | | | | | | | | | 181 ± 264 | 515 ± 44 |
| **PCB 170** | 5.5 ± 1.1 | 46.5 ± 1.1 | | 5.5 ± 1.1 | *0.21 | | | | | |
| **PCB 170/190** | | | 40.6 ± 2.6 | | | 22 ± 8 | | | | |
| **PCB 180** | 17.1 ± 3.8 | 105.0 ± 5.2 | 106.7 ± 5.3 | 17.1 ± 3.8 | 0.43 | 46 ± 14 | 280 ± 22 | 73 ± 13 | | |
| **PCB 183** | 16.0 ± 2.4 | 31.21 ± 0.62 | 36.6 ± 4.1 | 16.0 ± 2.4 | | | | | | |
| **PCB 187** | | | 105.1 ± 9.1 | | | | | | | |
| **PCB 187/182** | | | | | | 36 ± 16 | | | | |
| **PCB 187/159/182** | 34.0 ± 2.3 | 35.23 ± 0.83 | | 34.0 ± 2.5 | | | | | | |
| **PCB 194** | | 15.37 ± 0.61 | 39.6 ± 2.5 | | | | *38 | | | |
| **PCB 195** | | | 17.7 ± 4.3 | | | | | | | |
| **PCB 201** | | 12.18 ± 0.46 | 16.96 ± 0.89 | | | | | | | |
| **PCB 206** | | | 31.1 ± 2.7 | | | | | | | |
| **PCB 209** | | | 10.6 ± 1.1 | | | | | | | |

**Table A5.1d.** Reference materials for organic contaminants in marine biota. Values preceded by an asterisk (*) are non-certified; all other values are certified.

| ***Code*** | **SRM-1588a** | **MA-A-3/OC** | | **140/OC** | **CARP-1** | **CRM 477** | **NIES11** | **EDF-2525** | **EDF-2526** |
|---|---|---|---|---|---|---|---|---|---|
| *Organization* | **SRM-NIST** | **IAEA** | **IAEA** | **IAEA** | **NRC** | **BCR** | **NIES** | **CIL** | **CIL** |
| *Country of origin* | USA | | | | Canada | EC | Japan | USA | USA |
| ***Matrix*** | Cod liver oil | Shrimp homogenate | Copepoda | *Fucus* (sea plant homogenate) | Common carp | Mussel tissue | Fish tissue | Fish | Fortified fish |
| ***UNITS*** | µg $kg^{-1}$ | ng $g^{-1}$ | ng $g^{-1}$ | µg $kg^{-1}$ | ng $kg^{-1}$ | mg $kg^{-1}$ | µg $g^{-1}$ | ng $kg^{-1}$ | ng $kg^{-1}$ |
| ***AS*** | | Dry weight | Dry weight | | Wet weight | Wet weight | | Wet weight | Wet weight |
| [±] ***expressed as*** | ± 95% CI | | | | ± 95% CI | ½-width of 95% CI of mean | | | |
| **UNITS OF ISSUE** | 5 × 1.2ml/ ampoule | 35 g | 30 g | 30 g | 6 × 9 g | 14 g | 20 g | Set 1, 10 g / ampoule | Set 1, 10 g / ampoule |
| ***FORM*** | | Freeze-dried | Freeze-dried | | Slurry | | | Slurry | Slurry |
| **Dioxins and furans** | | | | | | | | | |
| **2,3,7,8 - TCDF** | | | | | 11.9 ± 2.7 | | | 22 ± 1.6 | 17 ± 1.5 |
| **1,2,3,7,8 - PCDF** | | | | | 5.0 ± 2.0 | | | 4.9 ± 0.56 | 40 ± 3.7 |
| **2,3,4,7,8 - PCDF** | | | | | | | | 14 ± 1.3 | 38 ± 3.5 |
| **1,2,3,4,7,8 - HxCDF** | | | | | | | | 8.2 ± 3.7 | 80 ± 8.4 |
| **1,2,3,6,7,8 - HxCDF** | | | | | | | | 2.7 ± 1.2 | 63 ± 5.5 |
| **1,2,3,7,8,9 - HxCDF** | | | | | | | | 0.76 ± 0.35 | 58 ± 7.0 |
| **2,3,4,6,7,8 - HxCDF** | | | | | | | | 2.3 ± 1.9 | 60 ± 5.5 |
| **1,2,3,4,6,7,8 - HpCDF** | | | | | | | | 4.4 ± 6.0 | 83 ± 9.2 |
| **1,2,3,4,7,8,9 - HpCDF** | | | | | | | | 0.63 ± 0.23 | 73 ± 7.7 |
| **OCDF** | *1.00 | | | | | | | 2.6 ± 1.3 | 190 ± 22 |
| **1,2,7 - TCDD** | *0.32 | | | | | | | | |
| **1,2,3,4 - TeCDD** | *0.38 | | | | | | | | |
| **2,3,7,8 - TCDD** | *0.21 | | | | 6.6 ± 0.6 | | | 17 ± 1.4 | 19 ± 1.4 |
| **1,2,3,7,8 - PCDD** | | | | | 4.4 ± 1.1 | | | 4.0 ± 0.57 | 40 ± 3.0 |
| **1,2,3,4,7,8 - HxCDD** | | | | | 1.9 ± 0.7 | | | 0.77 ± 0.27 | 60 ± 4.8 |
| **1,2,3,6,7,8 - HxCDD** | *0.39 | | | | 5.6 ± 1.3 | | | 3.0 ± 1.2 | 56 ± 4.8 |
| **1,2,3,7,8,9 - HxCDD** | *0.22 | | | | 0.7 ± 0.4 | | | 0.79 ± 0.26 | 60 ± 4.4 |
| **1,2,3,4,6,7,8 - HpCDD** | | | | | 6.5 ± 1.8 | | | 1.4 ± 0.53 | 76 ± 5.9 |
| **OCDD** | *1.01 | | | | 6.3 ± 1.9 | | | 7.2 ± 3.7 | 192 ± 14 |
| **Alpha-tocopherol** | *134.2 ± 2.5 | | | | | | | | |
| | | | | | | | | | ng $kg^{-1}$ |
| **Triphenyltin (as chloride)** | | | | | | | *6.3 | | |
| **Tributyltin (TBT)** | | | | | | 2.2 ± 0.19 | 1.3 ± 0.1 | | |
| **Dibutyltin (DBT)** | | | | | | 1.54 ± 0.12 | | | |
| **Monobutyltin (MBT)** | | | | | | 1.50 ± 0.28 | | | |

**Table A5.2a.** Reference materials for organic contaminants in marine sediments. Values preceded by an asterisk (*) are non-certified; all other values are certified.

| ***Code*** | **SES-1** | **HS-3B** | **HS-4B** | **HS-5** | **HS-6** | **SRM 1944** | **EC-1** | **EC-4** | **EC-8** | **CRM -535** |
|---|---|---|---|---|---|---|---|---|---|---|
| *Organization* | **NRC-CNRC** | **NRC-CNRC** | **NRC-CNRC** | **NRC-CNRC** | **NRC-CNRC** | **SRM-NIST** | **NWRI** | **NWRI** | **NWRI** | **BCR** |
| ***Country of origin*** | Canada | Canada | Canada | Canada | Canada | USA | Canada | Canada | Canada | EU |
| *Matrix* | Estuarine sediment | Harbour sediment | Harbour sediment | Harbour sediment | Harbour sediment | New York New Jersey Waterway sediment | Harbour sediment | Harbour sediment | Lake sediment | Freshwater harbour sediment |
| *UNITS* | mg $kg^{-1}$ | mg $kg^{-1}$ | mg $kg^{-1}$ | mg $kg^{-1}$ | mg $kg^{-1}$ | mg $kg^{-1}$ | µg $g^{-1}$ | µg $g^{-1}$ | µg $g^{-1}$ | mg $kg^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight |
| [±] ***expressed as*** | | 90%CI | 90%CI | 90%CI | 90%CI | | | | | ½-width of 95% CI of mean |
| ***UNITS OF ISSUE*** | 200 g | 100 g | 100 g | 200 g | 200 g | 50 g | 100 g | 100 g | 100 g | 40 g |
| ***FORM*** | Freeze-dried | | | Freeze-dried | Freeze-dried | | | | | |
| **PAHs** | | | | | | | | | | |
| **Acenaphthene** | *7.21 | 1.25 | 0.09 | 0.23 ± 0.10 | 0.23 ± 0.07 | *0.57± 0.03 | | *0.032 | *0.013 | |
| **Acenaphthylene** | | 0.6 | 0.3 | <0.15 | 0.19 ± 0.05 | | | *0.048 | *0.028 | |
| **Anthracene** | *1.63 | 2.76 | 0.46 | 0.38 ± 0.15 | 1.1 ± 0.4 | 1.77 ± 0.33 | 1.2 | *0.124 | *0.041 | |
| **Benzo[*a*]anthracene** | *1.31 | 7.91 | 1.46 | 2.9 ± 1.2 | 1.8 ± 0.3 | 4.72 ± 0.11 | 8.7 | *0.712 | *0.168 | 1.54 ± 0.10 |
| **Benzo[*b*]chrysene** | | | | | | 0.63 ± 0.10 | | | | |
| **Benzo[*a*]fluoranthene** | | | | | | 0.78 ± 0.12 | | | | |
| **Benzo[*b*]fluoranthene** | | | | 2.0 ± 0.15 | 2.8 ± 0.6 | 3.87 ± 0.42 | 7.8 | *0.753 | *0.208 | 2.29 ± 0.15 |
| **Benzo[*k*]fluoranthene** | | | | 1.0 ± 0.4 | 1.43 ± 0.15 | 2.30 ± 0.20 | 4.4 | *0.560 | *0.294 | 1.09 ± 0.15 |
| **Benzo[*b,k*]fluoranthene (combined value)** | | 12.8 | 3.32 | | | | | | | |
| **Benzo[*j*]fluoranthene** | | | | | | 2.09 ± 0.44 | | | | |
| **Benzo[*a*]pyrene** | *1.21 | 5.8 | 1.55 | 1.7 ± 0.8 | 2.2 ± 0.4 | 4.30 ± 0.13 | 5.3 | *0.675 | *0.207 | 1.16 ± 0.10 |
| **Benzo[*e*]pyrene** | | | | | | 3.28 ± 0.11 | 5.3 | *0.747 | *0.531 | 1.86 ± 0.13 |
| **Benzo[*ghi*]perylene** | *1.21 | 3.88 | 1.23 | 1.3 ± 0.3 | 1.78 ± 0.72 | 2.84 ± 0.10 | 4.9 | *0.576 | *0.176 | |
| **Biphenyl** | | 0.41 | 0.04 | | | *0.32 ± 0.07 | | | | |
| **Chrysene/Triphenylene** | | | | | | | *9.2 | *1.073 | *0.378 | |
| **Chrysene** | *1.32 | 8.77 | 1.76 | 2.8 ± 0.9 | 2.0 ± 0.3 | 4.86 ± 0.10 | | | | |
| **Coronene** | | 0.83 | 0.31 | | | | | | | |
| **Dibenz[*a,h*]anthracene** | *1.30 | 0.89 | 0.34 | 0.2 ± 0.1 | 0.49 ± 0.16 | 0.424 ± 0.069 | *1.3 | *0.241 | *0.316 | |
| **Dibenz[*a,c*]anthracene** | | | | | | 0.335 ± 0.013 | | | | |
| **Dibenz[*a,j*]anthracene** | | | | | | 0.50 ± 0.044 | | | | |
| **Dibenz*[a,i]*pyrene** | | 0.59 | 0.16 | | | | | | | |
| **Dibenzofuran** | | 2.2 | 0.14 | | | | | | | |
| **Dibenzothiophene** | | 1.19 | 0.11 | | | *0.62 ± 0.01 | | | | |
| **Fluoranthene** | *1.58 | 25.33 | 3.33 | 8.4 ± 2.6 | 3.54 ± 0.65 | 8.92 ± 0.32 | 23.2 | *1.087 | *0.462 | |
| **Fluorene** | *1.42 | 2.38 | 0.16 | 0.4 ± 0.1 | 0.47 ± 0.12 | *0.85 ± 0.03 | | *0.088 | *0.019 | |
| **Indeno[1,2,3-*cd*]pyrene** | *1.28 | | | 1.3 ± 0.7 | 1.95 ± 0.58 | 2.78 ± 0.10 | 5.7 | *0.564 | *0.034 | 1.56 ± 0.14 |
| **1-Methylphenanthrene** | | | | | | *1.7 ± 0.1 | | | | |
| **Naphthalene** | *3.62 | 2.14 | 0.22 | 0.25 ± 0.07 | 4.1 ± 1.1 | 1.65 ± 0.31 | | *0.058 | *0.01 | |
| **Perylene** | | | | | | 1.17 ± 0.24 | *1.1 | *0.28 | *0.202 | |
| **Phenanthrene** | *1.37 | 18.8 | 1.91 | 5.2 ± 1.0 | 3.0 ± 0.6 | 5.27 ± 0.22 | 15.8 | *0.732 | *0.234 | |
| **Pyrene** | *4.09 | 18 | 2.55 | 5.8 ± 1.8 | 3.0 ± 0.6 | 9.70 ± 0.42 | 16.7 | *1.085 | *0.327 | 2.52 ± 0.18 |
| **Picene** | | | | | | 0.518 ± 0.093 | | | | |
| **Triphenylene** | | | | | | 1.04 ± 0.27 | | | | |
| **Benzo[*c*]phenathrene** | | | | | | 0.76 ± 0.10 | | | | |
| **Pentaphene** | | | | | | 0.288 ± 0.026 | | | | |
| **1-Methylnaphthalene** | | 0.73 | 0.16 | | | *0.52 ± 0.08 | | | | |

**Table A5.2b.** Reference materials for organic contaminants in marine sediments. Values preceded by an asterisk (*) are non-certified; all other values are certified.

| ***Code*** | **CS-1** | **HS-1** | **HS-2** | **SRM 1944** | **EC-1** | **EC-4** | **EC-8** | **CRM - 536** |
|---|---|---|---|---|---|---|---|---|
| *Organization* | **NRC-CNRC** | **NRC-CNRC** | **NRC-CNRC** | **SRM-NIST** | **NWRI** | **NWRI** | **NWRI** | **BCR** |
| ***Country of origin*** | Canada | Canada | Canada | USA | Canada | Canada | Canada | EU |
| *Matrix* | Harbour sediment | Harbour sediment | Harbour sediment | New York New Jersey Waterway sediment | Harbour sediment | Harbour sediment | Lake sediment | Freshwater harbour sediment |
| *UNITS* | μg $kg^{-1}$ | μg $kg^{-1}$ | μg $kg^{-1}$ | mg $kg^{-1}$ | μg $g^{-1}$ | μg $g^{-1}$ | μg $g^{-1}$ | μg $kg^{-1}$ |
| ***AS*** | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight | Dry weight |
| [±] ***expressed as*** | ± SD | ± SD | ± SD | | | | | ½-width of 95% CI of mean |
| ***UNITS OF ISSUE*** | 200 g | 200 g | 200 g | 50 g | 100 g | 100 g | 100 g | 40 g |
| ***FORM*** | Freeze-dried | Freeze-dried | Freeze-dried | | | | | |
| **Pesticides** | | | | μg $kg^{-1}$ | ng $g^{-1}$ | ng $g^{-1}$ | ng $g^{-1}$ | |
| **Hexachlorobenzene** | | | | 6.03 ± 0.35 | *5.4 | *2.2 | *97.50 | |
| ***cis*-Chlordane** | | | | 16.51 ± 0.83 | | | | |
| ***trans*-Nonachlor** | | | | 8.20 ± 0.51 | | | | |
| **4,4′-DDT** | | | | 119 ± 11 | | | | |
| **PCBs** | | | | μg $kg^{-1}$ | ng $g^{-1}$ | ng $g^{-1}$ | ng $g^{-1}$ | |
| **PCB 8** | | | | 22.3 ± 2.3 | | | | |
| **PCB 18** | | | | 51.0 ± 2.6 | *47.4 ± 16.1 | *3.7 ± 1.6 | *2.1 | |
| **PCB 28** | | | | 80.0 ± 2.7 | *48.7 ± 17.0 | *6.8 ± 1.8 | *5.2 | 44 ± 5 |
| **PCB 31** | | | | 78.7 ± 1.6[1] | | | | |
| **PCB 44** | | | | 60.2 ± 2.0 | *64.7 ± 31.4 | *7.5 ± 2.9 | *10.4 | |
| **PCB 49** | | | | 53.0 ± 1.7 | | | | |
| **PCB 52** | | | | 79.4 ± 2.0 | *99.4 ± 43.2 | *12.5 ± 5.7 | *14.2 | 38 ± 4 |
| **PCB 66** | | | | 71.9 ± 4.3 | | | | |
| **PCB 77** | | | | | *4.1 | | | |
| **PCB 87** | | | | 29.9 ± 4.3 | *44.9 ± 14.5 | *8.3 ± 1.5 | *6.9 | |
| **PCB 95** | | | | 65.0 ± 8.9 | | | | |
| **PCB 99** | | | | 37.5 ± 2.4 | | | | |
| **PCB 101/90** | | | | 73.4 ± 2.5 | | | | |
| **PCB 101** | | 1.62 ± 0.21 | 5.42 ± 0.34 | | *109.4 ± 74.4 | *22.4 ± 9.5 | *18.2 | 44 ± 4 |
| **PCB 105** | | | | 24.5 ± 1.1 | *34.2 ± 13.5 | *8.1 ± 3.2 | *5.9 | 3.5 ± 0.6 |
| **PCB 110** | | | | 63.5 ± 4.7 | *120.1 ± 67.3 | *29.1 ± 11.5 | *18.8 | |
| **PCB 118** | | | | 58.0 ± 4.3 | *79.8 ± 37.1 | *17.8 ± 7.7 | *12.5 | 28 ± 3 |
| **PCB 126** | | | | | *0.7 | | | |
| **PCB 128** | | | | 8.47 ± 0.28 | *14.5 ± 6.4 | *4.6 ± 2.2 | *2.7 | 5.4 ± 1.2 |
| **PCB 137** | | | | | *3.8 ± 1.0 | *1.7 ± 0.7 | | |
| **PCB 138** | | 1.98 ± 0.28 | 6.92 ± 0.52 | | *72.0 ± 26.3 | *28.7 ± 9.7 | *14.8 | 27 ± 4 |
| **PCB 138/163/164** | | | | 62.1 ± 3.0 | | | | |
| **PCB 141** | | | | | *19.4 ± 4.0 | *8.3 ± 2.0 | | |
| **PCB 149** | | | | 49.7 ± 1.2 | | | | 49 ± 4 |
| **PCB 151** | | 0.48 ± 0.08 | 1.37 ± 0.07 | 16.93 ± 0.36 | *16.6 ± 4.9 | *9.4 ± 3.7 | *2.5 | |
| **PCB 153** | | 2.27 ± 0.28 | 6.15 ± 0.67 | 74.0 ± 2.9 | *68.2 ± 22.1 | *27.3 ± 7.5 | *11.4 | 50 ± 4 |
| **PCB 156** | | | | 6.52 ± 0.66 | | | | 3.0 ± 0.4 |
| **PCB 163** | | | | | | | | 17 ± 3 |
| **PCB 169** | | | | | *<0.016 | | | |
| **PCB 170** | | 0.27 ± 0.05 | 1.07 ± 0.15 | | *16.8 ± 7.6 | *11.8 ± 2.5 | *4.3 | 13.4 ± 1.4 |
| **PCB 170/190** | | | | 22.6 ± 1.4 | | | | |
| **PCB 180** | | 1.17 ± 0.15 | 3.70 ± 0.33 | 44.3 ± 1.2 | *44.9 ± 23.2 | *26.1 ± 11.0 | *7 | 22 ± 2 |
| **PCB 183** | | | | 12.19 ± 0.57 | *15.2 ± 7.6 | *8.4 ± 4.1 | *1.8 | |
| **PCB 187/159/182** | | | | 25.1 ± 1.0 | | | | |
| **PCB 194** | | 0.23 ± 0.04 | 0.61 ± 0.07 | 11.2 ± 1.4 | *13.1 ± 5.6 | *6.9 ± 3.1 | *2.3 | |
| **PCB 195** | | | | 3.75 ± 0.39 | | | | |
| **PCB 196** | | 0.45 ± 0.04 | 1.13 ± 0.12 | | | | | |
| **PCB 201** | | 0.57 ± 0.07 | 1.39 ± 0.09 | | *7.3 ± 5.0 | *8.1 ± 2.0 | *0.5 | |
| **PCB 206** | | | | 9.21 ± 0.51 | *7.0 ± 3.0 | *3.2 ± 1.6 | *3.7 | |
| **PCB 209** | | 0.33 ± 0.1 | 0.90 ± 0.14 | 6.81 ± 0.33 | *1.4 ± 0.8 | *1.6 ± 2.0 | *9.3 | |
| **Total PCBs** | 1.15 ± 0.60 | 21.8 ± 1.1 | 111.8 ± 2.5 | | 2.00 | *0.577 | *0.621 | |

**Table A5.2c.** Reference materials for organic contaminants in marine sediments. Values preceded by an asterisk (*) are non-certified; all other values are certified.

| *Code* | SRM 1944 | EC-1 | EC-4 | EC-8 | DX-1 | DX-2 | CRM-462 | EDF-2513 |
|---|---|---|---|---|---|---|---|---|
| ***Organization*** | **SRM-NIST** | **NWRI** | **NWRI** | **NWRI** | **NWRI** | **NWRI** | **BCR** | **CIL** |
| ***Country of origin*** | USA | Canada | Canada | Canada | Canada | Canada | EU | USA |
| *Matrix* | New York New Jersey Waterway sediment | Harbour sediment | Harbour sediment | Lake sediment | Great Lakes blend | Lake Ontario sediments | Coastal sediment | Fortified soil |
| ***UNITS*** | mg $kg^{-1}$ | µg $g^{-1}$ | µg $g^{-1}$ | µg $g^{-1}$ | pg $g^{-1}$ | pg $g^{-1}$ | µg $kg^{-1}$ | ng $g^{-1}$ |
| ***AS*** | Dry weight | | | | | | | Dry weight |
| [±] ***expressed as*** | | | | | | | Expanded uncertainty[1] | |
| ***UNITS OF ISSUE*** | 50g | 100g | 100g | 100g | 50g | 50g | 25g | 10g |
| ***FORM*** | | | | | | | | Reference 1 |
| **Other chlorinated compounds** | µg $kg^{-1}$ | ng $g^{-1}$ | ng $g^{-1}$ | ng $g^{-1}$ | | | | |
| **1,4-dichlorobenzene** | | *30.9 | | *57.65 | | | | |
| **1,3-dichlorobenzene** | | *5.9 | *6.8 | *42.69 | | | | |
| **1,2-dichlorobenzene** | | *4.9 | *6.8 | *5.21 | | | | |
| **1,3,5-trichlorobenzene** | | *2.7 | *4.4 | *46.24 | | | | |
| **1,2,4-trichlorobenzene** | | *3.4 | *6.7 | *67.01 | | | | |
| **1,2,3-trichlorobenzene** | | *2.3 | *1.9 | *2.74 | | | | |
| **1,2,4,5-tetrachlorobenzene** | | *3.4 | *2.4 | *56.67 | | | | |
| **1,2,3,4-tetrachlorobenzene** | | *1.5 | *1.6 | *17.39 | | | | |
| **1,2,3,5-tetrachlorobenzene** | | *0.76 | *0.34 | *5.53 | | | | |
| **Pentachlorobenzene** | | *1.7 | *1.9 | *30.16 | | | | |
| **Hexachlorobenzene** | | *5.4 | *2.2 | *97.50 | | | | |
| **Hexachlorobutadiene** | | *0.66 | *0.55 | *21.33 | | | | |
| **Octachlorostyrene** | | *6.0 | *1.04 | *22.18 | | | | |
| **Antifouling** | | | | | | | | |
| **Tributyltin (TBT)** | | | | | | | 54 ± 15 | |
| **Dibutyltin (DBT)** | | | | | | | 68 ± 12 | |
| **Dioxins and furans** | µg $kg^{-1}$ | ng $g^{-1}$ | ng $g^{-1}$ | ng $g^{-1}$ | pg $g^{-1}$ | pg $g^{-1}$ | µg $kg^{-1}$ | ng $g^{-1}$ |
| **2,3,7,8 - TCDF** | *0.039 ± 0.015 | | | | *89 ± 44 | *134 ± 61 | | 0.45 ± 0.03 |
| **1,2,3,7,8 - PCDF** | *0.045 ±0.007 | | | | 39 ± 14 | 46 ± 10 | | 0.87 ± 0.04 |
| **2,3,4,7,8 - PCDF** | *0.045 ± 0.004 | | | | 62 ± 32 | 88 ± 28 | | 0.86 ± 0.06 |
| **1,2,3,4,7,8 - HxCDF** | *0.22 ± 0.03 | | | | 714 ± 276 | 825 ± 348 | | 0.88 ± 0.05 |
| **1,2,3,6,7,8 - HxCDF** | *0.09 ± 0.01 | | | | 116 ± 37 | 153 ± 61 | | 0.95 ± 0.09 |
| **1,2,3,7,8,9 - HxCDF** | *0.019 ± 0.018 | | | | *28 ± 42 | *36 ± 45 | | 0.82 ± 0.06 |
| **2,3,4,6,7,8 - HxCDF** | *0.054 ± 0.006 | | | | *57 ± 36 | *70 ± 47 | | 0.91 ± 0.06 |
| **1,2,3,4,6,7,8 - HpCDF** | *1.0 ± 0.1 | | | | 2397 ± 796 | 3064 ± 745 | | 1.27 ± 0.11 |
| **1,2,3,4,7,8,9 - HpCDF** | *0.040 ± 0.006 | | | | 137 ± 62 | 152 ± 84 | | 1.12 ± 0.12 |
| **OCDF** | *1.0 ± 0.1 | | | | 7122 ± 2406 | 7830 ± 3087 | | 2.25 ± 0.15 |
| **2,3,7,8 - TCDD** | *0.133 ± 0.009 | | | | 263 ± 53 | 262 ± 51 | | 0.46 ± 0.03 |
| **1,2,3,7,8 - PCDD** | *0.019 ± 0.002 | | | | 22 ± 8 | 28 ± 14 | | 0.96 ± 0.06 |
| **1,2,3,4,7,8 - HxCDD** | *0.026 ± 0.003 | | | | 23 ± 7 | 25 ± 8 | | 0.90 ± 0.06 |
| **1,2,3,6,7,8 - HxCDD** | *0.056 ± 0.006 | | | | 77 ± 27 | 85 ± 33 | | 0.87 ± 0.05 |
| **1,2,3,7,8,9 - HxCDD** | *0.053 ± 0.007 | | | | 53 ± 24 | 58 ± 19 | | 0.90 ± 0.06 |
| **1,2,3,4,6,7,8 - HpCDD** | *0.80 ±0.07 | | | | 634 ± 182 | 757 ± 320 | | 1.39 ± 0.10 |
| **OCDD** | *5.8 ± 0.7 | | | | 3932 ± 933 | 4402 ± 1257 | | 3.51 ± 0.22 |
| **Total toxic equivalent (TEQ)** | *0.25 ± 0.01 | | | | | | | |

[1]Expanded uncertainty $U = k.u_c$ calculated according to ISO/BIPM guide with coverage factor k = 2.

## ANNEX 6: COMMPS COMPOUNDS OF POSSIBLE CONCERN FOR THE MARINE ENVIRONMENT

The Marine Chemistry Working Group (MCWG) discussed the chemicals proposed as chemical parameters in the proposed Water Framework Directive. The directive is meant to cover coastal waters up to one nautical mile from the coast. MCWG tried to predict how relevant these parameters would be to describe contamination in off-shore areas and made the following comments to the proposed compounds:

| **Compound(s)** | **Relevance for the marine environment** |
|---|---|
| PAHs | High |
| Naphthalene | High (include in PAH group) |
| Anthracene | High (include in PAH group) |
| Pentachlorophenol | Probably low (survey) |
| Chlorpyrifos | Probably low (not found in estuaries) |
| Hexachlorobenzene | High |
| Trichlorobenzenes | Probably low |
| Chlorfenvinphos | Unknown (found in estuaries, antifouling agent, survey) |
| Diuron | Unknown (found in estuaries, antifouling agent, survey) |
| Trifluralin | Probably low (not found in coastal waters) |
| Trichloromethane | Low (low levels in coastal waters) |
| Dichloromethane | Low (low levels in coastal waters) |
| 1,2-Dichloroethane | Low (low levels in coastal waters) |
| Isoproturon | Unknown (limited database, survey) |
| Endosulfan | Low (limited use) |
| Alachlor | Unknown (low levels found in coastal waters, survey) |
| Hexachlorobutadiene | Low (not found in coastal waters) |
| Hexachlorocyclohexane | High |
| Atrazine | High |
| Simazine | High |
| Benzene | Low |
| $C_{10–13}$Chloroalkanes | Unknown (limited database, difficult to analyse, survey) |
| Di(2-ethylhexyl)phthalate | High |
| Octylphenols | High |
| Nonylphenols | High |
| Tributyltin compounds | High (including triphenyltin compounds) |
| Pentachlorobenzene | Probably low (survey) |
| Brominated diphenyl ethers | High |
| Nickel | Low |
| Lead | High |
| Cadmium | High |
| Mercury | High (speciation necessary) |

The COMMPS list is based on water and sediment levels (measured and predicted) and does not take bioaccumulation into account. The compounds to be studied in the marine environment also have to include some of the classical pollutants. Compounds used as substitutes for the organotins as antifouling agents, such as irgarol and copper (speciation!), may also be considered. At least the following substances thus have to be considered when chemical parameters for the marine environment are decided:

| **Compound(s)** | **Relevance for the marine environment** |
|---|---|
| PCBs | High |
| DDTs | High |
| Polychlorinated dioxins/furans | High |
| Toxaphene | High |
| Irgarol | High (antifouling agent) |
| Copper | Probably high (antfouling agent) |

The distribution between dissolved phase and adsorption to suspended particles also has to be taken into account when the monitoring of the different compounds is planned.

# ANNEX 7: CONCENTRATIONS OF *TRIS* (4-CHLOROPHENYL) METHANOL AND *TRIS* (4-CHLOROPHENYL) METHANE IN FISH

**Michel Lebeuf[a], Jacob de Boer[b], Michael Haarich[c], Patrick Roose[d]**

[a] Maurice Lamontagne Institute, Mont-Joli, Québec, Canada
[b] DLO-Netherlands Institute for Fisheries Research, IJmuiden, The Netherlands
[c] Institute of Fishery Ecology, Hamburg, Germany
[d] Royal Belgian Institute for Natural Sciences, Oostende, Belgium

## Abstract

*Tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) were determined in fish samples from Europe and Eastern Canada. TCPM and TCPMe were found in most of the samples analysed. Levels of TCPM were generally higher than those of TCPMe, resulting in average TCPM/Me ratios > 1. Differences in TCPM/Me ratios could be due to differences in the proximity of the various sources, in the trophic levels of the fish and to the presence of interferences in analytical methods. We suggest that an interlaboratory validation study be conducted to improve our ability to compare results from different laboratories and geographic regions.

## Introduction

*Tris*(4-chlorophenyl)methanol(TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) are among the newest persistent organic pollutants (POPs) reported in environmental samples. TCPM was first found in marine mammals in the late 1980s (Walker *et al*., 1989). Soon after, the presence of TCPM was reported, along with the qualitative presence of its presumed precursor, TCPMe, in both marine mammals and birds (Zook *et al*., 1992; Jarman *et al*., 1992). These two compounds were then quantified in sediments, fish, marine mammals and human milk (Rahman *et al*., 1993, de Boer *et al*., 1996; de Boer, 1997). Recent studies have confirmed that these compounds are ubiquitous in the marine environment and that they are bioaccumulated, since organisms at the top of the aquatic food chain, such as birds and mammals, have the highest reported levels (de Boer *et al*., 1996; Muir *et al*., 1996a, 1996b; Lebeuf *et al*., 1998; Falandysz *et al*., 1999; Minh *et al*., 1999; Watanabe *et al*., 1999; Lebeuf *et al*., 2000).

Few data are available on the toxicity of these compounds. In rats, Poon *et al*. (1997) reported that short-term exposure to TCPM led to the induction of liver enzymes and resulted in higher spleen weights and elevated white blood cell and lymphocyte counts. Recently, Foster *et al*. (1999) demonstrated that TCPM modifies reproductive physiology in the male rat. There is clearly a need for more information on the toxicity of these compounds.

The principal source of TCPM and TCPMe to the marine environment is unknown. These compounds may originate from a variety of sources including the production of synthetic high polymers and of light-fast dyes for acrylic fibres, and the manufacture of anthelminthic drugs (Jarman *et al*. 1992). Other potential sources include agrochemicals such as formulations of Dicofol and technical DDT, both of which contain structurally related compounds (Jarman *et al*., 1992). Walker *et al*. (1989) did not detect TCPM in technical formulations of DDT at a level above 0.1 %. More recently, Buser (1995) showed that, under conditions used in the synthesis of technical DDT, 10 TCPMe isomers were formed in small amounts. However, the link between Σ-TCP (TCPM and TCPMe) and technical DDT in environmental samples has not been clearly established.

During the last few years, several members of the MCWG expressed an interest in studying these compounds. Following the initiative of the DLO-Netherlands Institute for Fisheries to distribute TCPM and TCPMe standards, several laboratories volunteered to set up an analytical method for these compounds and to collect data in various environmental samples. The present paper summarises the results obtained in fish samples specifically, and provides an overview of data reported in the scientific literature. The main objective of this paper is to compare the levels and ratios of TCPM/Me in various fish species from different areas in Europe and Canada. In addition, the relationship between Σ-TCP and Σ-DDT levels is assessed to verify the hypothesis that technical DDT is the main source of TCPMe in the marine environment.

## Methods

Most laboratories applied very similar methods of extraction, clean-up and fractionation, yet different techniques were used to quantify the compounds. Although all laboratories used capillary columns (HRGC) to isolate the compounds of interest, the selectivity of the different detection methods varied. For instance, the Canadian laboratory used LRMS/MS;

the studies conducted by Rahman *et al*. (1993), Falandysz *et al*. (1999), and by the Netherlands laboratory were done with LRMS, while the German and Belgian laboratories used ECD.

**Results**

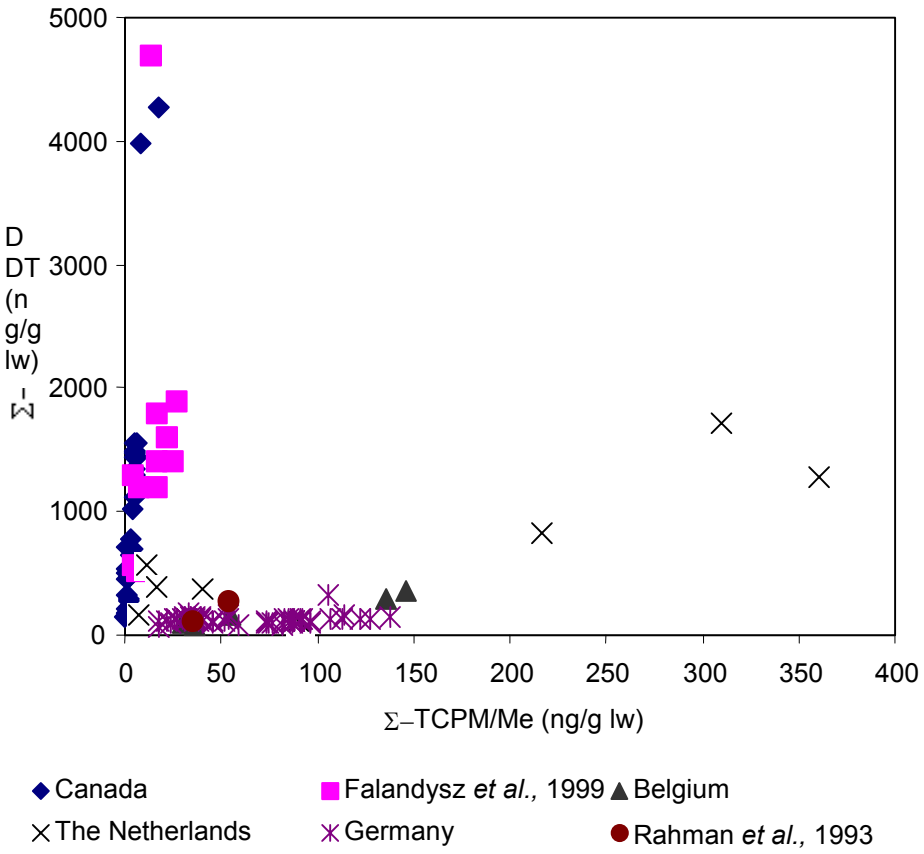
TCPM and TCPMe were detected in most of the fish samples (Table A7.1). Samples of yellow eel from the Netherlands, and of dab from the Belgium coast, contained the highest concentrations of TCPM and of TCPMe, respectively. In comparison to samples from Europe, levels of both TCPM and TCPMe in Canadian fish samples were relatively low. In particular, concentrations of these compounds in lake trout from Lake Ontario were also low. In general, TCPM levels in most of the fish species examined were higher than those of TCPMe. However, this is not the case for some fish samples from the Belgian coast and the Baltic south coast. These samples show an opposite tendency, with higher concentrations of TCPMe compared to TCPM.

**Discussion**

The data on TCPM and TCPMe in fish samples do not allow us to draw a clear conclusion regarding the relative degree of contamination of the examined areas. There are too many variables involved, which complicate the comparison of TCPM and TCPMe levels between these areas. In addition to the different analytical methods used by the laboratories involved, the analyses were conducted on several different tissues, from several different species of fish. The dissimilar TCPM/Me ratios could also be related to differences in the proximity of sources and to differences in the trophic levels and habitats of the fish species sampled. Nevertheless, one can appreciate that these compounds are universally distributed in the marine environment.

To determine if technical DDT is the main source of TCPMe in the marine environment, the levels of Σ-DDT (DDT and its metabolites) are plotted against the tissue concentrations of Σ-TCPM/Me (Figure A7.1). There is clearly no significant correlation between Σ-DDT and Σ-TCPM/Me in fish tissues, which does not support the hypothesis that technical DDT is the main source of environmental TCPM and TCPMe. It is noteworthy that, in Canadian fish samples, the Σ-DDT: Σ-TCPM/Me ratio is approximately 10 times higher than that in most of the European fish samples. In contrast, the levels of TCPM and TCPMe in some European fish, as reported by Falandysz *et al*. (1999), are more similar to those in Canadian fish samples and the Σ-DDT: Σ-TCPM/Me ratios in these samples also resemble Canadian values.

**Figure A7.1.** The relationship between Σ-DDT and Σ-TCPM/TCPMe in fish.




## Conclusion

There is a need for additional studies to assess the levels of TCPM and TCPMe in fish samples. However, the fish species selected must be comparable in terms of their trophic level and habitat and the analyses should be conducted on a standard tissue or tissues. An interlaboratory calibration study is needed if we are to improve our ability to compare analytical results from different geographic areas. There is also a need for more information on the toxicity of TCPM and TCPMe.

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# ANNEX 8: VOLATILE ORGANIC COMPOUNDS IN VARIOUS MARINE ORGANISMS FROM THE SOUTHERN NORTH SEA

Patrick Roose[1] and Udo A. Th. Brinkman[2]

[1]Ministry of Small Enterprises, Traders and Agriculture, Sea Fisheries Department (CLO Ghent), Ankerstraat 1, 8400 Oostende, Belgium[§]
[2] Free University, Department of Analytical Chemistry, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands
[§]Current address: Management Unit Mathematical Models of the North Sea, Royal Belgian Institute for Natural Sciences, 3e & 23e Linieregimentsplein, B-8400 Oostende, Belgium

## ABSTRACT

The concentration levels of 12 priority volatile organic compounds (VOCs) were determined in two species of vertebrates and four species of invertebrates from sampling stations in the southern North Sea, using a modified Tekmar LSC 2000 purge and trap system coupled to GC-MS. In general, concentration levels of VOCs found in this study were of the same order of magnitude as those previously reported in the literature. The concentrations of the chlorinated hydrocarbons (CHCs), with the exception of chloroform, tended to be lower than those of the monocyclic aromatic hydrocarbons (MAHs). The experimental data were statistically evaluated using both cluster and principal component analysis (PCA). From the results of cluster analysis and PCA, no specific groups could be distinguished on the basis of geographical, temporal or biological parameters. However, based on the cluster analysis and the PCA, the VOCs could be divided into three groups, $C_2$-substituted benzenes, CHCs and benzene plus toluene. This division could be related to different types of sources. Finally, it was shown that organisms can be used to monitor the presence of VOCs in the marine environment and the observed concentration levels were compared with proposed safety levels.

Keywords: VOCs, marine organisms, southern North Sea

## INTRODUCTION

The potential threat of large-production chemicals to the marine environment has caused considerable concern since the deleterious effects of some of these, such as p,p′-DDT, the drins and polychlorinated biphenyls (PCBs), became evident. Much research has since been dedicated to the study of transport mechanisms, environmental distribution, prediction and measurement of fluxes, and adverse environmental effects of important classes of pollutants such as PCBs, aromatic hydrocarbons and heavy metals (Baker and Eisenreich, 1990; Clark *et al.*, 1990; Södergren *et al.*, 1990; Mackay and Paterson, 1991; Walker and Livingstone, 1992). Much less is known, however, about the fate of more volatile chemicals, even though volatile organic compounds (VOCs) are well-known atmospheric contaminants that are frequently determined in air, drinking water, fresh water, effluents and soils (Sweet and Vermette, 1992; Bellar *et al.*, 1974; Anderson *et al.*, 1991; Jungclaus *et al.*, 1978). Most representatives of the group are important industrial compounds with a high annual production. The annual production of tetrachloromethane, for instance, is estimated at about 300 000 tonnes (Howard, 1990). In Belgium, the emissions of the chlorinated hydrocarbons (CHCs) chloroform, 1,1,1-trichloroethane, tri- and tetrachloroethylene, exceed those of, e.g., lead, lindane, and atrazine. Annual production, together with log $K_{ow}$ data, toxicity and persistence, was one of the main criteria used by the Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) (GESAMP, 1990) to select potentially harmful substances for the marine environment. The resulting list contained, amongst others, chloroform, tetrachloromethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene. The same compounds are also found on the high-priority compounds list of the Ministerial Declarations of the International Conferences of the North Sea (Ministerial Declaration of the Third International Conference on the Protection of the North Sea, 1990; Ministerial Declaration of the Fourth International Conference on the Protection of the North Sea, 1995) and are recognised as compounds that present an environmental problem by the Norwegian Pollution Control Authority (Dons and Beck, 1994). For other important VOCs such as the monoaromatic hydrocarbons (MAHs) benzene, toluene, ethylbenzene and the xylenes, the need to investigate their presence in the marine environment has been formulated in the Ministerial Declarations of the International Conferences of the North Sea (Ministerial Declaration of the Third International Conference on the Protection of the North Sea, 1990; Ministerial Declaration of the Fourth International Conference on the Protection of the North Sea, 1995).

Despite the potential hazards posed by VOCs, relatively little is known about the abundance or presence of these compounds in the marine environment, especially in biota, and their behaviour in the marine ecosystem. In addition, there are no on-going monitoring programmes for VOCs, in contrast to other organic pollutants such as PCBs (Oslo and Paris Commissions, 1990). Levels reported in the literature are therefore mostly the result of once-only surveys. Pearson and McConnell (1975) were among the first to report concentrations of trichloroethylene, tetrachloroethylene, trichloroethane, tetrachloromethane and chloroform in various marine organisms from sampling locations along the

British coast. The results showed that chlorinated VOCs were present at all trophic levels. The concentrations ranged from 0.02 to 180 ng $g^{-1}$ wet weight. Since that time, similar concentrations have been reported for different organisms from various marine locations (Pearson and McConnell, 1975; Dickson and Riley, 1976; Ferrario *et al.*, 1985; Yasuhara and Morita, 1987; Gotoh *et al.*, 1992). An overview of the reported concentrations for the different trophic levels is given in Table A8.1. Recent findings agree with these earlier observations (Roose and Brinkman, 1998). Generally speaking, the concentrations are of the same order of magnitude as those of other important organic contaminants such as individual PCBs, chlordanes and individual PAHs (North Sea Task Force, 1993).

The effects of these levels on organisms are at present unknown. Most VOCs can be considered as narcotic chemicals, i.e., non-electrolyte chemicals that, in the absence of specific effects, have only a minimum of toxicity (van Leeuwen *et al.*, 1992). However, halogenated aliphatic compounds in general are considered to be potent immunotoxic agents. Suppression of humoral and cellular immunity as well as host resistance to infections has been observed both in laboratory animals and humans (Wong *et al.*, 1992). Also, trichloroethylene has been shown to produce tumours in rodents and is a suspected human carcinogen (WHO Working Group, 1985). Benzene is also a well-documented immunotoxic substance. Reported adverse effects on the immune system are decreases in lymphoid organ weights, antibody production, cell-mediated immunity, and host resistance to infections and to tumours (Wong *et al.*, 1992). Benzene is also a known leukemic agent in humans (Sittig, 1980; Kalf *et al.*, 1987; WHO Working Group, 1993). Finally, benzene and its metabolites inhibit both nuclear and mitochondrial replication and transcription in mice (Kalf *et al.*, 1987). Moreover, during metabolisation both benzene and its metabolites are converted to reactive species that covalently bind to macromolecules like DNA, RNA and proteins (Kalf *et al.*, 1987). The potential danger of VOCs to marine organisms therefore lies mainly in chronic exposure to low levels, which may result in immunosuppression and carcinogenesis.

Once it has been established that a given chemical poses a threat, it remains to be determined what levels of contamination are acceptable in the marine environment. Van Leeuwen *et al.* (1992) used Quantitative Structure Activity Relationships (QSARs), extrapolation of toxicity data, and equilibrium partitioning for the assessment of the effects of narcotic industrial pollutants. The extrapolation of toxicity data generated by QSARs was used to derive safe levels for water, sediment, and biota. Another, more pragmatic, approach is described by Matthiessen *et al.* (1993) who applied a safety factor of 100 to acute toxicity data to establish safe levels of chronic exposure. Whereas the latter approach results in safety levels for the water column, the former model allows the calculation of internal toxic concentrations (ITCs) in fish tissues, which is useful for the interpretation of biomonitoring data. However, the usefulness of the model hinges on the applicability of the equilibrium-partitioning theory and its relation with octanol-water partitioning.

The present study aims at determining concentration levels of a number of priority VOCs in organisms from the southern North Sea and at studying their possible relation to geographical, temporal and/or biological parameters. In addition, the use of organisms to monitor these compounds in the marine environment will be discussed and the observed contamination levels will be compared with proposed safety levels.

## MATERIALS AND METHODS

### *Sampling*

Samples were taken on board the Belgian oceanographic vessel "*Belgica*" at six different locations (Figure A8.1) using beam-trawling over a period of one year (five campaigns: April, May, June, October and December). Two sampling points (120 and 780) were situated near the coast (4–15 km), two (421 and 435) were situated further away from the coast (35–40 km), one sampling station (B07) was situated in the mouth of the Scheldt estuary and one (800), at 80 km from the coast, was selected as a reference point. Samples were processed as swiftly as possible to avoid contamination and losses. Sampling was done in accordance with the guidelines of OSPARCOM (Oslo and Paris Commissions, 1990). Immediately after sampling, the undissected fish and shellfish were stored at –28 °C in closed containers and in the absence of organic solvents. Upon their arrival at the institute the samples were transported to an airtight freezer located in a solvent-free area.

### *Analytical methodology*

A detailed description of the analytical methodology is given elsewhere (Roose and Brinkman, 1998). Briefly, biological tissue is first homogenised (at 0 °C) using an ultra-turrax blender and transferred to a 25-ml EPA vial. After addition of 15 ml of water and the internal standard (1,1,1-trifluorotoluene), the homogenate is treated in an ultrasonic bath (20 min at 0 °C) to further disrupt the tissue. The glass vessel is then connected to a Tekmar (Tekmar, Cincinatti, USA) LSC 2000 purge and trap apparatus coupled to a gas chromatograph-mass spectrometer (GC-MS). The volatiles are forced out of the tissue by purging with a stream of helium gas while heating at 70 °C and trapped onto a Vocarb

4000 sorbent trap. After purging, the trap is backflushed while being rapidly heated to 250 °C and the analytes are desorbed and, next, trapped in a cryofocusing module (-120 °C) connected to the analytical column (Restek, RTx-502.2, 60 m, 0.32 mm i.d., 1.8 µm film). The analytes are injected into the column by rapidly heating the module from –120 °C to 200 °C in 0.75 min. Temperature programming of the GC and data acquisition were started simultaneously. The temperature of the GC oven was held at 40 °C for 2 min and then linearly increased from 40 °C to 200 °C at 10 °C $min^{-1}$. This temperature was then held for 5 min. Helium with an inlet pressure of 16 psi was used as the carrier gas.

The target compounds were identified on the basis of their retention times and mass spectra, and quantified using the total mass of selected ions (Figure A8.2). The ion trap detector was operated in the electron ionisation (EI) mode with the multiplier voltage set at 2400 V, the axial modulation (A/M) amplitude at 3.5 V and the emission current at 12 µA. The manifold temperature was set at 220 °C. The mass range was 50–250 amu and the scan rate, 1000 ms. The filament delay was 180 s, and a mass defect of 50 mmass / 100 amu and a background mass of 55 amu were selected. Detection limits varied between 0.005 ng $g^{-1}$ wet weight (1,2-dichloroethane, 1,1-dichloroethane and tetrachloromethane) and 0.2 ng $g^{-1}$ wet weight (chloroform) depending on the background levels and the amount of sample (Roose and Brinkman, 1998).

***Statistical analysis***

For the statistical analysis, samples were separated according to species, tissue, sampling date and sampling location. Here, the present data set was combined with a previous one, which contained concentration data for dab and whiting from two sampling stations (120 and 800) (Roose and Brinkman, 1998). For values below the detection limits, values equal to half these limits were used. A total of 237 statistical cases (a unique combination of concentrations, sampling time, location, species and tissue type) was considered for all 12 individual VOCs (statistical variables). Occasionally, in order to perform statistical tests that require a normal distribution, a logarithmic transformation of the original data set was used.

The Kolmogorov-Smirnov test (KS test) was used to determine whether a distribution was normal. The P value of the test was obtained with the Dallal and Wilkinson's approximation to Lilliefors' method (Motulsky, 1995). In addition, normal probability plots (NPPs) were used to study the distribution of the data.

To distinguish specific groups of samples, a cluster analysis was performed. This was done by an average-linkage clustering (unweighted-pair group average) with between-group linkage based on squared Euclidian distances. To study underlying relationships between samples, a principal component analysis (PCA) was executed. Principal components were extracted when Eigenvalues were greater than one.

**RESULTS AND DISCUSSION**

***Levels of VOCs***

***CHCs***

The concentrations of the CHCs, with the exception of chloroform were, in general, lower than those of the MAHs (Figure A8.3). The 75 percentiles (75P) of all CHCs, with the exception of chloroform, were below 2 ng $g^{-1}$ wet weight and the medians were below 1 ng $g^{-1}$ for all the species and tissues that were analysed. Tetrachloromethane and 1,1-dichloroethane could not be detected (< 0.005 ng $g^{-1}$ wet weight) in a significant number of samples. For the other CHCs, except chloroform, the 75Ps varied between 0.02 ng $g^{-1}$ for trichloroethylene and 1.5 ng $g^{-1}$ for tetrachloroethylene, with concentrations generally increasing in the order 1,1-dichloroethane < tetrachloromethane < trichloroethane < trichloroethylene < tetrachloroethylene < 1,2-dichloroethane. The 75Ps for chloroform, on the other hand, varied between 0.9 and 3.6 ng $g^{-1}$ wet weight. Pearson and McConnell (1975), Dickson and Riley (1976), Ferrario *et al*. (1985) and Gotoh *et al.* (1992) also found that the levels of chloroform were generally higher than those of the other CHCs. The only exceptions were eggs of marine birds from the Irish Sea, where the concentrations of the other CHCs were equal to or even higher than those of chloroform (Pearson and McConnell, 1975). The higher concentrations of chloroform in organisms are most likely related to higher concentrations in the water. This hypothesis is supported, for the Belgian continental shelf, by the findings of Dewulf *et al.* (1998). These authors indeed found higher water concentrations of chloroform and suggested that this could be the result of biogenic production of chloroform by marine algae. However, in contrast to the other CHCs, chloroform is also (inadvertently) formed during chlorination of drinking water, municipal sewage and cooling water (Howard, 1990). Therefore, both its use in the chemical industry and the above inadvertent formation may well dominate the natural sources in an industrialised region, as is the case for the North Sea.

For the other CHCs, concentration levels found in this study are similar to those reported in the literature (Table A8.1). There appear to be no large differences in the concentrations on a species or tissue type basis with two exceptions: the concentrations of tetrachloroethylene and 1,2-dichloroethane are significantly higher in the liver of dab than in muscle tissue. The cause of this dependence is not clear but is probably related to the intrinsic properties of the chemicals and the tissues concerned, and the way in which the organism was exposed. For instance, 1,2-dichloroethane showed a preference for liver and adipose tissue after oral administration but not after inhalation exposure (WHO Working Group, 1987). Tetrachloroethylene, on the other hand, shows a tendency to accumulate in lipid-rich tissues such as the liver; this uptake is proportional to the exposure levels (WHO Working Group, 1984). However, in general, the concentrations of CHCs are thought to be related to those in the water column through a process of physico-chemical partitioning and to be, therefore, directly related to the chemical properties of the compound of interest (see below).

***MAHs***

For the MAHs, the 75Ps varied between 0.4 ng $g^{-1}$ for benzene in shrimp and 28 ng $g^{-1}$ for toluene in *Mactra stultorum*, and the median values varied between 0.08 ng $g^{-1}$ wet weight for benzene and 22 ng $g^{-1}$ for toluene for the same species, respectively (Figure A8.3). That is, the concentrations were at least an order of magnitude higher than those of the CHCs. The concentrations of the $C_2$-substituted benzenes in Figure A8.3 show closely related patterns. This suggests that they are correlated, i.e., have a common source (see below). No such similarity was found for benzene and toluene, which have concentrations that are sometimes higher, and sometimes lower, than those of the $C_2$-substituted benzenes. The concentrations of MAHs in fish liver were consistently higher than in muscle tissue, especially for dab. These differences are probably related to metabolisation, because MAHs are known to be readily metabolised in organisms (ECETOC Working Group, 1986; Anon., 1988; Slooff, 1988; Crookes *et al.*, 1993). Furthermore, elimination of MAHs from organisms appears to be fairly rapid once exposure has ceased (ECETOC Working Group, 1986; Anon., 1988; Slooff, 1988; Crookes *et al.*, 1993).

As with the CHCs, the observed MAH concentrations in biota are related to the concentrations in the water column, as will be discussed below. Literature data on concentrations of MAHs in marine organisms are rather sparse. Ferrario *et al.* (1985) reported concentrations of benzene, toluene and ethylbenzene in clams (*Rangia cuneata*) and oysters (*Crassostrea virginica*) from the Lake Ponchartrain estuary (USA). Benzene exhibited the highest concentrations in both clam (260 ng $g^{-1}$ wet weight) and oyster (220 ng $g^{-1}$ wet weight). The concentrations of toluene and ethylbenzene were significantly lower (maximum, 18 ng $g^{-1}$ wet weight). No explanation was given for these differences, but the authors assumed that the contaminants were from anthropogenic origin. Since the concentrations in sediment were also higher for benzene, the higher concentrations in the invertebrates were explained by a higher environmental load. Yasuhara and Morita (1987) reported concentrations of benzene, ethylbenzene, *o*-xylene, *p*-xylene and *m*-xylene in *Mytilus edulis* (blue mussel) from two coastal locations in Japan. The concentrations ranged from 7.34 µg $g^{-1}$ wet weight for benzene to 0.25 µg $g^{-1}$ wet weight for ethylbenzene. The concentrations reported in the literature are high compared to those found in the present study. We observed at least 20-fold lower concentrations for benzene in the different species of marine clams and the concentrations of the other MAHs generally were about 10-fold lower.

***Statistical analysis***

The data from the original set did not show a normal distribution, as was determined by the KS test and the NPPs. However, after logarithmic transformation and resubjection of the transformed data set to the KS test, the data sets for all MAHs and chloroform passed the test. Further evaluation of the distribution with NPPs showed that for trichloroethane, trichloroethylene and tetrachloroethylene, deviations from the normal distribution were primarily caused by a few outliers (Figure A8.4) and that the distributions for 1,2-dichloroethane and tetrachloromethane were mainly biased because of a large number of undetectable levels. However, since earlier observations showed that VOCs tend to be normally distributed for species from one batch (Roose and Brinkman, 1998), a normal distribution was generally assumed. The data for 1,1-dichloroethane were omitted from the data set as too few results were above the limits of detection.

Cluster analysis was performed both case-wise and variable-wise. The variable-wise analysis resulted in two large clusters, one containing the MAHs and chloroform and the other, the rest of the CHCs (Figure A8.5). The clustering is most probably the result of different concentration levels, as is suggested by the higher levels of chloroform compared to the other CHCs. Nevertheless, within this cluster there is a clear distinction between chloroform and the MAHs. The latter clustered in two separate groups, benzene and toluene, and the $C_2$-benzenes. The distances for these groups were small which certainly suggests a common source. Furthermore, a correlation analysis of both clusters revealed that the concentrations of *m*- and *p*-xylene and *o*-xylene correlated significantly with each other ($r = 0.87$) and with ethylbenzene ($r = 0.86$ and $r = 0.82$, respectively). The same was true for benzene and toluene ($r = 0.63$). For the cluster representing the rest of the CHCs, only trichloroethylene and tetrachloroethylene appeared to cluster and even so not to

the same extent as, for instance, the $C_2$-benzenes. For the rest, analysis of this group was hampered by a rather large number of undetectable levels; this was especially true for tetrachloromethane.

The case-wise analysis did not allow specific groups to be distinguished on the basis of species type, tissue type, sampling station or sampling date. A picture similar to the above was obtained with the PCA. Here, three factors were identified with Eigenvalues greater than 1. They contributed for 40 %, 16 %, and 12 %, respectively, of the total variance of all samples. From the factor loading plot after varimax rotation (Figure A8.6) it was clear that Factor 1 was mainly determined by the $C_2$-substituted benzenes, Factor 2 by tetrachloromethane, trichloroethylene and 1,1,1-trichloroethane, and Factor 3 mainly by chloroform, tetrachloroethylene and 1,2-dichloroethane. Benzene contributed to each factor to approximately the same extent, while toluene contributed mainly to Factors 3 and 1. This means that all individual VOCs, except toluene and benzene, were closely related to only one factor. Furthermore, the largest variability in the database (40 %) can be attributed to differences in concentrations of, especially, ethylbenzene and the xylenes and, to a lesser extent, benzene and toluene. This first principal component further allows making a distinction between MAHs and CHCs, since the latter hardly contribute to this factor.

When the factor scores of all samples are considered (Figure A8.7), no distinct clusters of samples could be distinguished on the basis of species type, tissue type, sampling location or sampling time. As for the cluster analysis, the only explanation of the observed differences was concentration differences of the three groups identified above. For instance, the encircled cluster in Figure A8.7 (cases 112–115) with a high score for Factor 2 is characterised by high concentrations of tetrachloromethane, trichloroethylene and, to a lesser extent, 1,1,1-trichloroethane. These are liver tissue samples of whiting from the same location and the same date. Although they cluster because of the high concentrations mentioned above, they do not cluster with other samples that have the same characteristics (species type, tissue type, sampling location and sampling time).

At the outset of this study, we assumed that a number of causes could result in differences between the samples. Among these were distance to the coast (influence of land-based emissions), the vicinity of point sources (such as the Scheldt Estuary), seasonal variations (such as the increased use of fossil fuels in winter) and biological parameters (such as preferential accumulation in certain tissues, metabolisation, food-web effects). Somewhat surprisingly, despite the large number of data, neither the cluster analysis nor the PCA allowed the samples to be distinguished. However, the correlation analysis and both ordination analyses show that the concentrations of $C_2$-substituted benzenes are closely related to each other. The largest emission source of ethylbenzene and the xylenes is gasoline (ECETOC Working Group, 1986; Howard, 1989, 1990; Crookes *et al.*, 1993) and the correlation observed for these chemicals can possibly be related to this common source. This would also mean that the principal source of ethylbenzene and xylenes in marine organisms is the use of fossil fuel. The latter is also a known source of benzene and toluene and more than likely explains the grouping observed in the cluster analysis and the PCA. Another possible source is suggested by Dewulf *et al.* (1998). The authors observed higher levels of MAHs, compared to the CHCs, in water and air samples from the same region and attributed this to anthropogenic emissions from oil transport in this coastal area. In addition, the fossil fuel source is also one of the main differences between the MAHs and the CHCs. Chloroform is, in this context, an exceptional compound as it is inadvertently formed during chlorination of water (see earlier) and has known natural sources. Chlorination of water is potentially the largest source of chloroform for the environment (Howard, 1990). Finally, the lack of differences between the various sampling stations allows us to suggest that, for all practical purposes, the part of the Belgian and Dutch continental shelf considered in this study can be regarded as one zone, i.e., an area that is influenced by the same sources, as far as VOC concentrations are concerned. The absence of seasonal differences suggests that the area, and therefore the organisms, is subjected to the same sources all year round and that the sources are essentially constant in nature.

***Bioconcentration and hazard assessment***

In order to evaluate the possible consequences of the VOC concentrations found in marine organisms, described in the previous sections, one can use the hazard assessment proposed by van Leeuwen *et al*. (1992). However, as was mentioned earlier, the model hinges on the applicability of the Equilibrium Partitioning Theory (EPT). According to the EPT, concentrations of chemicals, such as VOCs, in organisms originate from those in the water column through a process of physico-chemical partitioning. That is, the EPT assumes a passive partitioning of a chemical compound between the aqueous phase and a lipid or a lipid-like organic phase (van Leeuwen *et al*., 1992). The resulting partition coefficient, which is equal to the ratio of the concentrations in the organism ($C_{org}$) and the water ($C_w$), is called the Bioconcentration Factor (BCF):

$$BCF = C_{org} / C_w \quad [1].$$

This coefficient is supposed to be an intrinsic property of the chemical and can, as a result, be related to its octanol-water partition coefficient, $K_{ow}$. Neely *et al*. (1974) and, subsequently, several other authors (Isnard and Lambert, 1988;

Connell and Hawker, 1988; Banerjee and Baughman, 1991) demonstrated that BCF and $K_{ow}$ are linearly related according to:

$$Log\ BCF = a + log\ K_{ow}\ [2].$$

The data obtained during the present study were compared with the average water concentrations reported by Dewulf *et al.* (1998) for the southern North Sea and BCFs were calculated for all VOCs. Plotting the logarithm of these BCFs against log $K_{ow}$ indeed resulted in the linear relationship (r = 0.42) predicted by Eq. 2. This becomes especially evident when the data for higher $K_{ow}$ values reported by Neely *et al.* (1974) are included in the picture (Figure A8.8). The larger number of data points, spread over a larger $K_{ow}$ range, results in a much better correlation (r = 0.94). Moreover, the observed slope is essentially the same as the one reported by these authors. However, plotting the average of the BCFs reported in the literature (10) resulted in a slope that is lower than those obtained with our data and those of Neely *et al.* (1974) (Figure A8.8). This suggests that the BCFs reported in the literature are somewhat too low, especially for the VOCs with a log $K_{ow}$ of less than 2.8. A possible explanation for this could be the use of nominal instead of actual concentrations. BCFs reported in the literature are often the results of laboratory experiments in open systems and nominal concentrations can easily be too high due to the high volatility of the compounds of interest (Crookes *et al.*, 1993). Even so, the observed relationship indicates that VOC concentrations in the water column are indeed reflected in the organisms and suggests that the EPT can be applied.

On the basis of the above observations, one may conclude that the hazard assessment of van Leeuwen *et al.* (1992) can be used. These authors used QSARs, the extrapolation of toxicity data, and equilibrium partitioning to assess the effects of narcotic industrial pollutants such as the target compounds of this study. The extrapolation of toxicity data generated by QSARs was used to derive safe levels for water. The QSARs in their study were expressed as:

$$log\ NOEC = a\ log\ K_{ow} + b\ [3]$$

where NOEC is the no-observed-effect concentration. These concentrations were derived from literature data or, if no chronic toxicity data were available, estimated from acute toxicity data using acute/chronic ratios. The safety level was arbitrarily set at 95 %. This implies that a threshold concentration is calculated which is unlikely to cause harm to 95 % of the aquatic community. This calculated concentration, HC5, is the hazardous concentration that will affect, at most, 5 % of the species. The $HC5_w$ for the water column was calculated from:

$$HC5_w = C_w \times (1+1.85 \times 10^{-6}\ K_{ow}) \qquad [4]$$

where $HC5_w$ is the total concentration in the water phase, including suspended matter. The internal tissue concentration, ITC or $HC5_{org}$, for the organisms was calculated from

$$HC5_{org} = 0.05 \times HC5_w \times K_{ow}\ [5]$$

where a lipid content of about 5 % by weight in the organism is assumed. Table A8.2 compares the calculated $HC5_{org}$ values and the average concentrations in the different organisms and tissues. The results show that the $HC5_{org}$ for the MAHs and CHCs was not exceeded, in any case. Most probably, this would have been true also for ethylbenzene if an $HC5_{org}$ had been available. Moreover, the observed averages are several orders of magnitude lower than the $HC5_{org}$. However, the present results still cause concern because the hazard assessment does not take into account synergistic and, thus, more damaging effects. Despite the often high results, no definite statements can, as yet, be made concerning long-term effects such as carcinogenicity or immunosuppression. The number of data is too limited and the calculation of the HC5 is one approach amongst several and needs to be further evaluated. What is clear, however, is that additional research, especially with regard to the long-term consequences of small doses of VOCs, is urgently required.

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**Figure A8.1.** Sampling stations along the Belgian and Dutch continental shelfs.

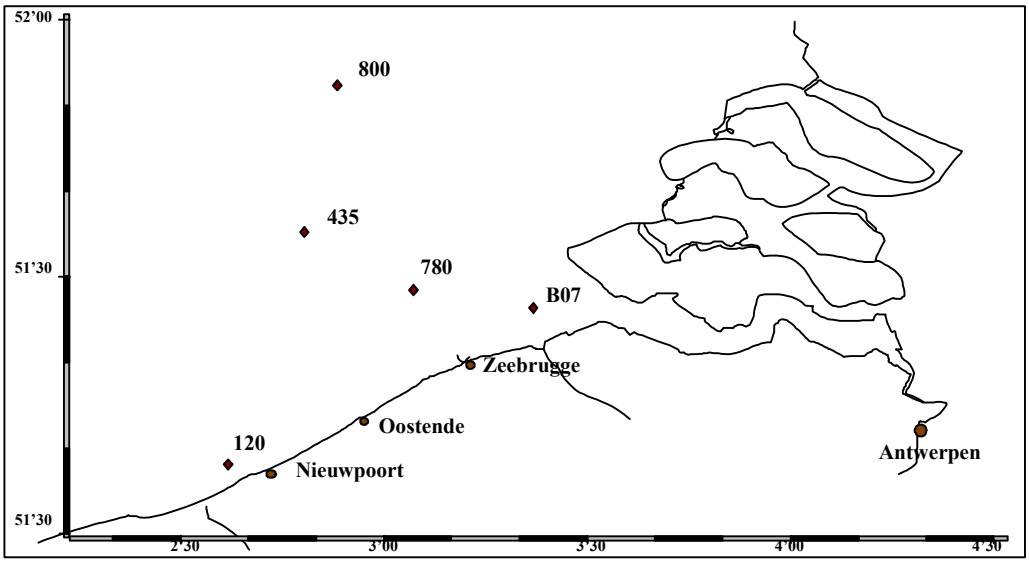


**Figure A8.2.** Representative total ion chromatogram of VOCs in a shrimp (*Crangon crangon*) sample with the mass spectrum of toluene (insert a) and the selected ion chromatogram of tetrachloroethylene (insert b).

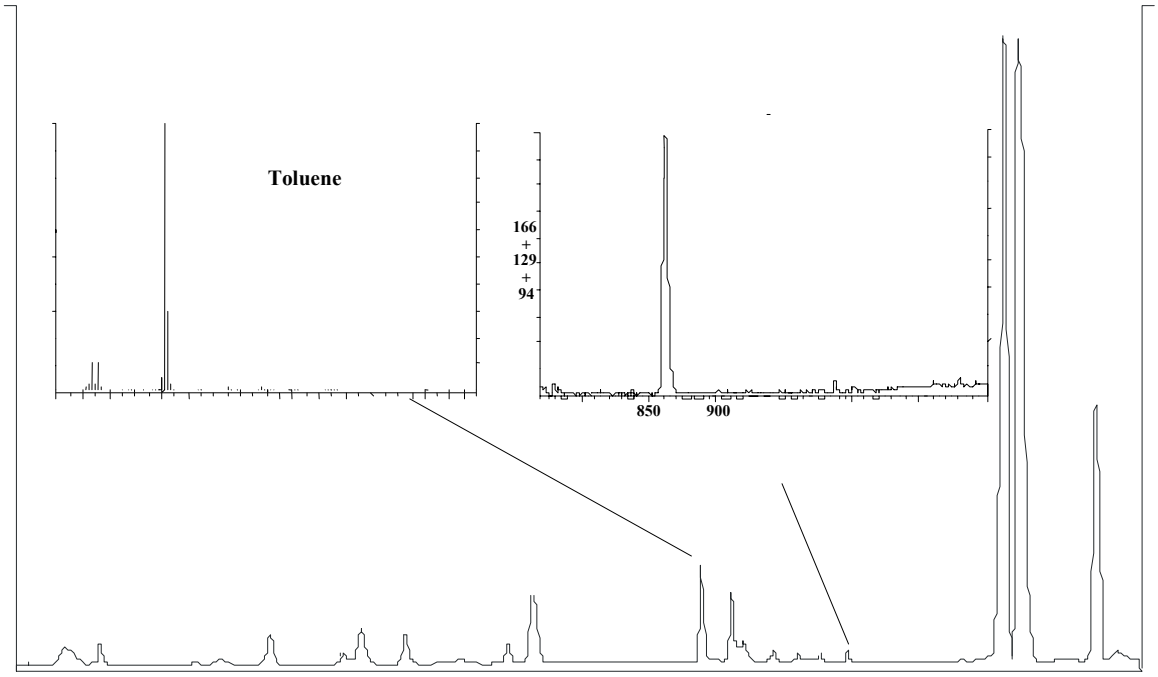
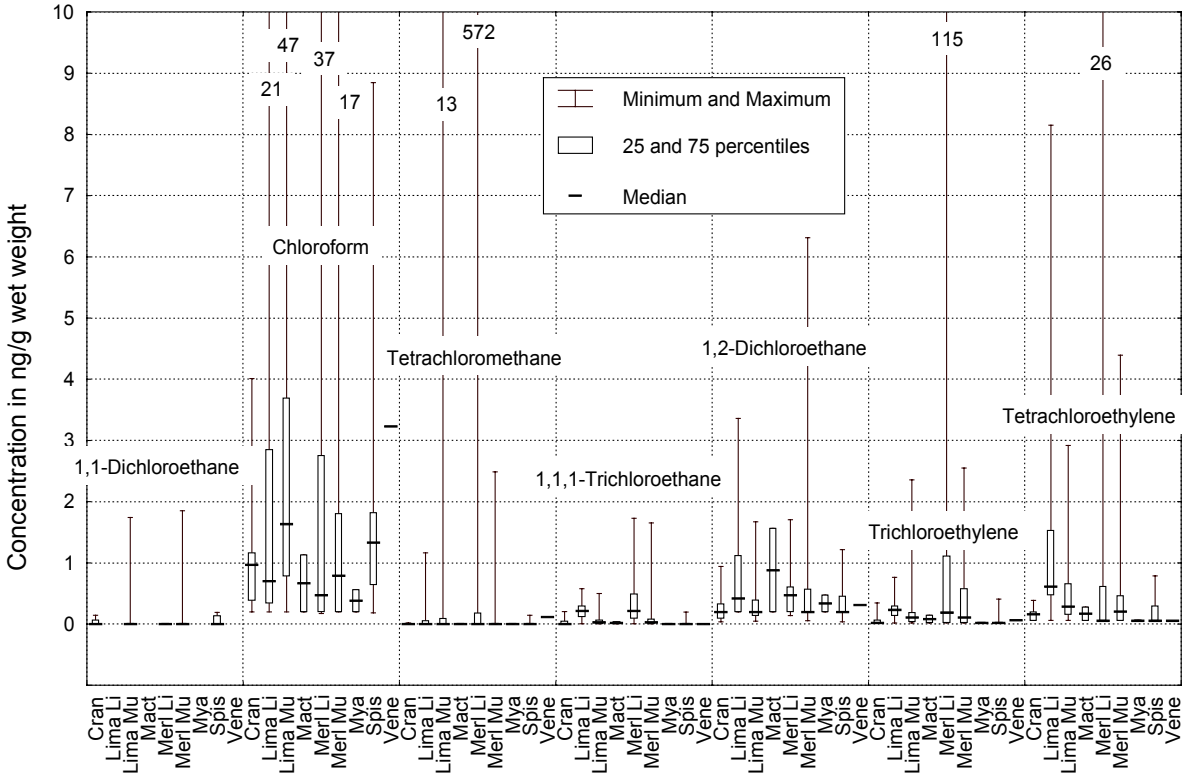


**Figure A8.3.** Concentrations in ng g-1 wet weight of CHCs (top) and MAHs (bottom) in Crangon crangon (Ccran), Limanda limanda liver (LimaLi), Limanda limanda muscle (Lima Mu), Mactra stultorum (Mac), Merlangius merlangus liver (MerlLi), Merlangius merlangus muscle (MerlMu), Mya truncata (Mya), Spisula subtruncata (Spis) and Venerupis pullastra (Vene).



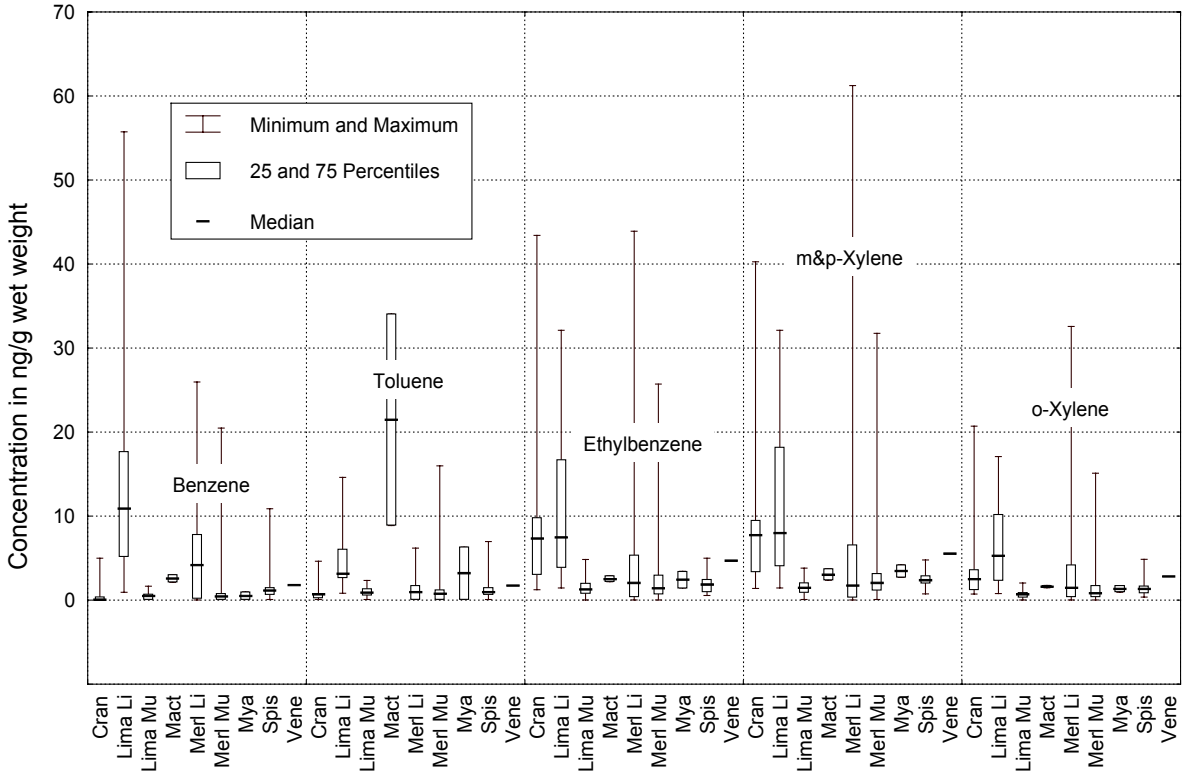



**Figure A8.4.** Normal probability plot for the trichloroethylene data of the present study.

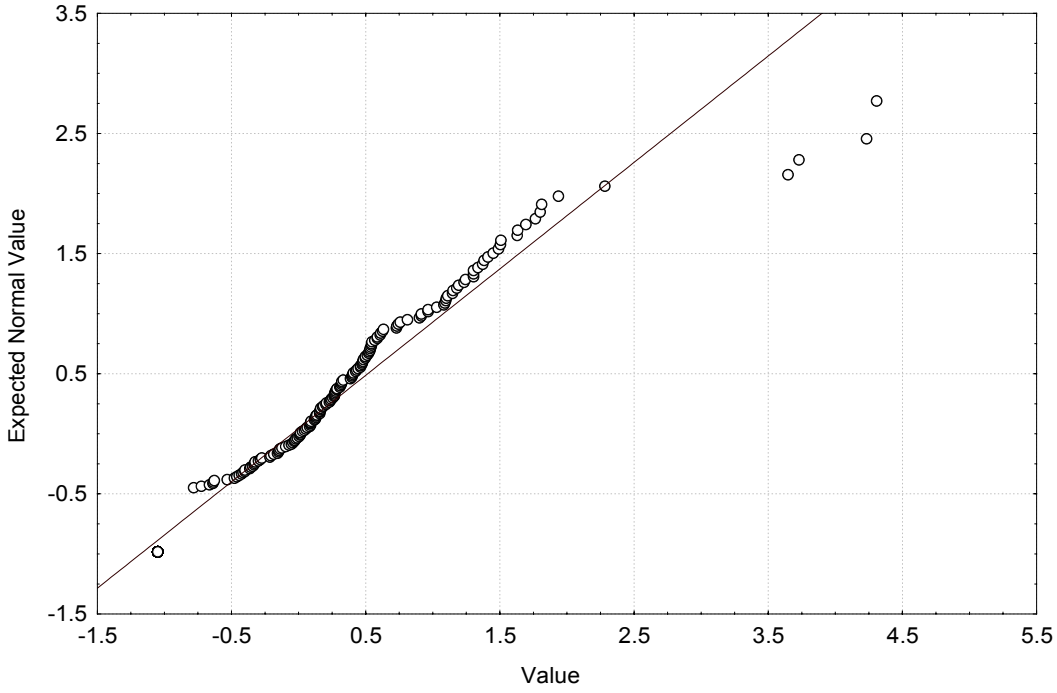


**Figure A8.5.** Horizontal hierarchical tree-plot representing the variable-wise cluster analysis of VOCs in marine organisms. (BENZ = benzene, TOL = toluene, EBEN = ethylbenzene, MPBEN = *m&p*-xylene, OBEN = *o*-xylene, CHCL3 = chloroform, CCL4 = tetrachloromethane, DCE12 = 1,2-dichloroethane, TCE = trichloroethylene, TECE = tetrachloroethylene and TRCE = trichloroethylene).

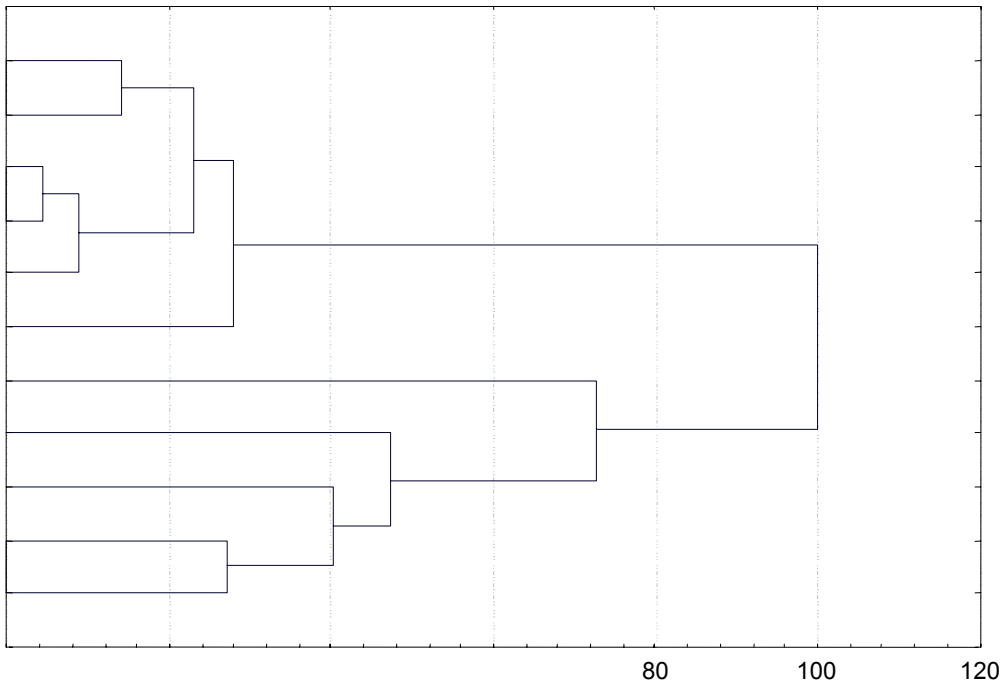


**Figure A8.6.** Three-dimensional plot of the factor loadings for the different VOCs after varimax rotation.

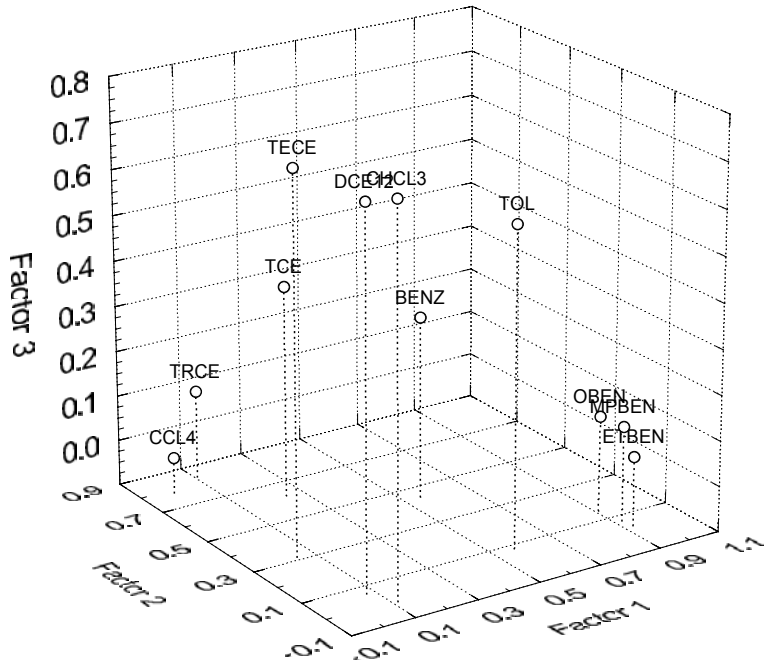


**Figure A8.7.** Factor scores for all samples (Factor 1 vs. Factor 2), with a distinct cluster of samples encircled.

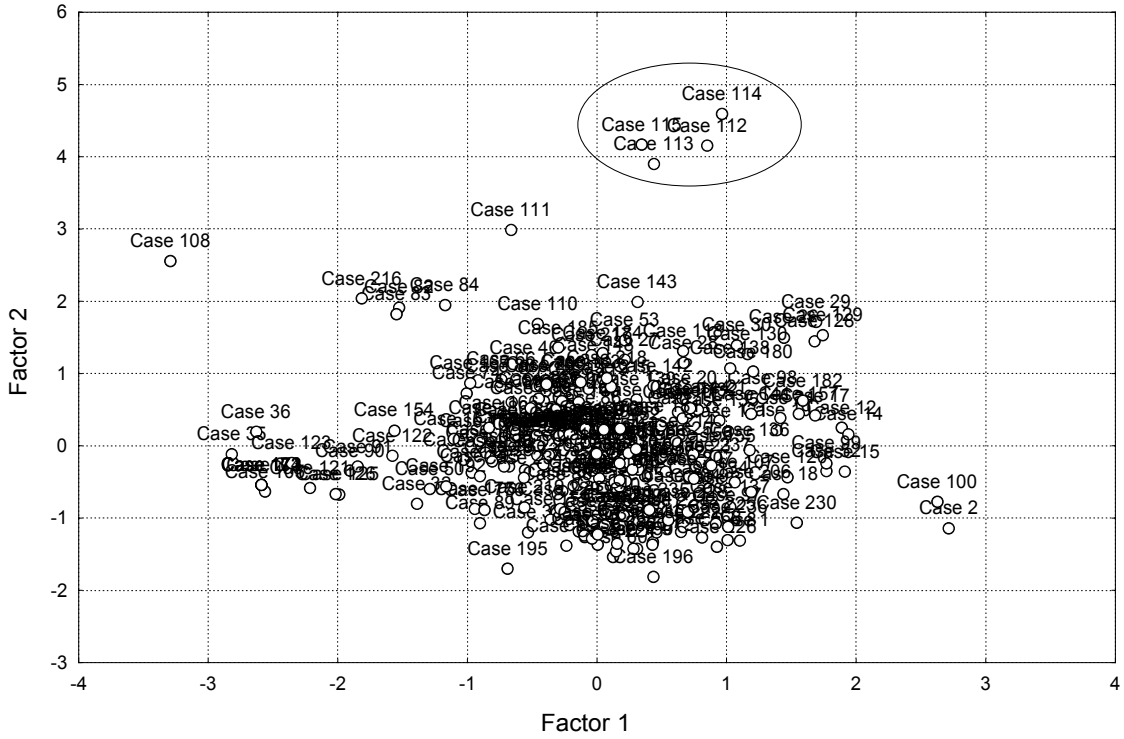


**Figure A8.8.** Relationship between the calculated BCFs and $K_{ow}$, and comparison with literature data. The data from the present study were within the range indicated by the barred line.

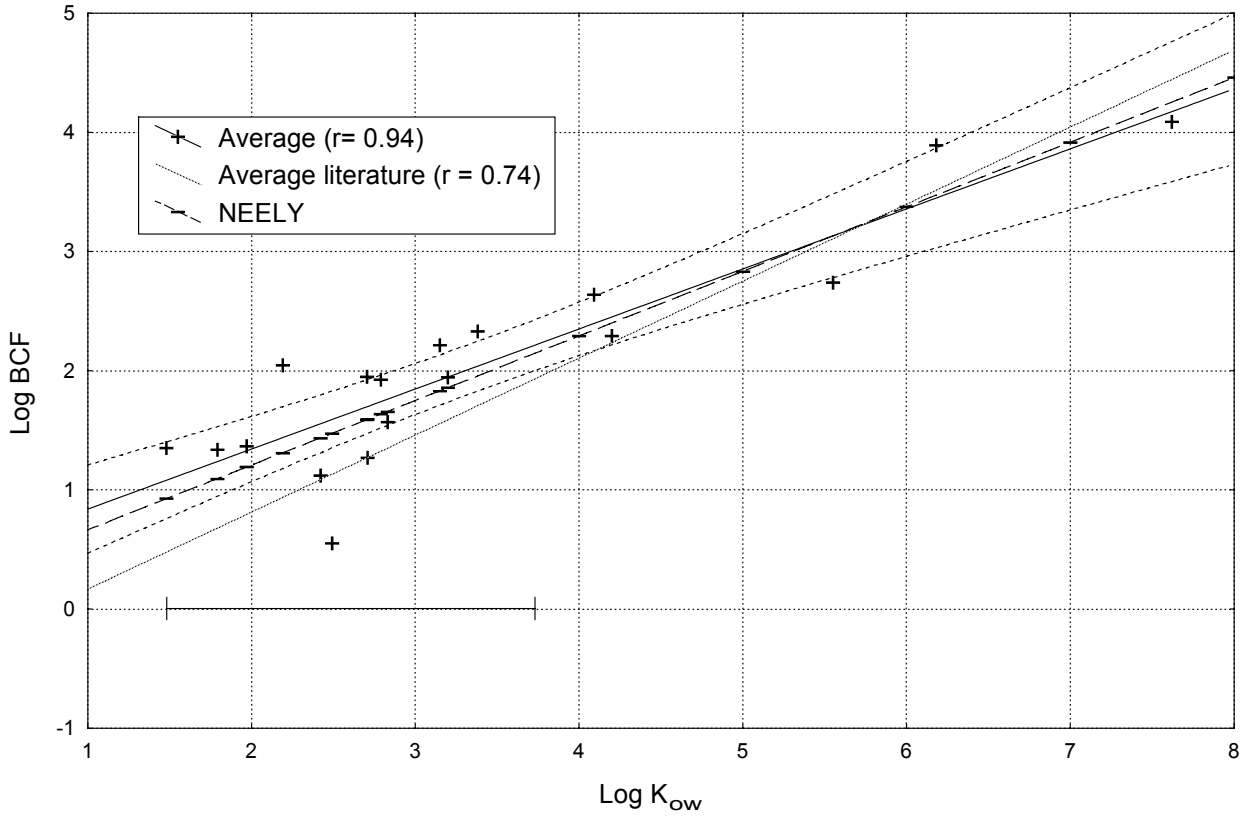


**Table A8.1.** Concentrations in ng $g^{-1}$ wet weight of VOCs in various marine organisms (10,16–21).

| **Organisms** | **CHCs** | | | | | |
|---|---|---|---|---|---|---|
| | **$CHCl_3$** | **$CCl_4$** | **DCE** | **TCE** | **TRCE** | **TECE** |
| Invertebrates | 0.02–1040 | 0.04–114 | 1–4080 | 0.03–310 | 0.05–250 | 0.05–176 |
| Marine algae | | | | | 17–236 | 13–22 |
| Fish | 2–851 | 0.3–209 | 730–3200 | 1–26 | 0.8–479 | 0.3–176 |
| Seabirds | 1.9–65 | | | | 2.4–29 | 1.5–39 |
| | | **14.1** | **MAHs** | | | |
| | | **BENZ** | **TOL** | **EBEN** | **MPBEN** | **OBEN** |
| Shellfish | | 220–7000 | 3.4–18 | 0.8–250 | 100–360 | 520 |
| Fish | | 700–1000 | | | | |

$CHCl_3$ = chloroform, $CCl_4$ = tetrachloromethane, DCE = 1,2-dichloroethane, TCE = 1,1,1-trichloroethane, TRCE = trichloroethylene, TECE = tetrachloroethylene, BENZ = benzene, TOL = toluene, EBEN = ethylbenzene, MPBEN = *m&p*-xylene, OBEN = *o*-xylene.

**Table A8.2.** Comparison of the average tissue concentrations in pg $g^{-1}$ of the present data set and the proposed safety level (HC5).

| **Compound** | ***Crangon crangon*** | ***Mactra stultorum*** | ***Mya truncata*** | ***Spisula species*** | ***Limanda limanda* liver** | ***Limanda limanda* muscle tissue** | ***Merlangius merlangus* liver** | ***Merlangius merlangus* muscle tissue** | **HC5** |
|---|---|---|---|---|---|---|---|---|---|
| MAHs | | | | | | | | | |
| Benzene | 700 | 2500 | 550 | 2000 | 14000 | 500 | 5800 | 800 | $5.2 \times 10^6$ |
| Toluene | 900 | 21000 | 3200 | 1600 | 4800 | 950 | 1500 | 1000 | $5.9 \times 10^6$ |
| Ethylbenzene | 9800 | 2500 | 2400 | 2200 | 11000 | 1500 | 5200 | 2600 | na |
| *m&p*-Xylene | 9700 | 3000 | 3500 | 2500 | 11000 | 1500 | 6300 | 3200 | $6.4 \times 10^6$ |
| *o*-Xylene | 4100 | 1600 | 1300 | 1600 | 6000 | 700 | 3600 | 1500 | $6.5 \times 10^6$ |
| CHCs | | | | | | | | | |
| 1,1-Dichloroethane | 40 | nd | nd | 60 | nd | 140 | 5 | 100 | $6.7 \times 10^6$ |
| Chloroform | 1100 | 700 | 400 | 2600 | 3200 | 5400 | 2800 | 2000 | $8.1 \times 10^6$ |
| Tertrachloromethane | 8 | 5 | 5 | 20 | 200 | 450 | 43000 | 70 | $9.8 \times 10^6$ |
| 1,2-Dichloroethane | 300 | 900 | 300 | 400 | 900 | 300 | 550 | 500 | $6.7 \times 10^6$ |
| 1,1,1-Trichloroethane | 40 | 20 | 6 | 30 | 200 | 50 | 400 | 100 | $8.8 \times 10^6$ |
| Trichloroethylene | 70 | 80 | 20 | 60 | 200 | 200 | 13000 | 400 | $8.7 \times 10^6$ |
| Tetrachloroethylene | 200 | 200 | 60 | 200 | 1200 | 500 | 1300 | 350 | $9.7 \times 10^6$ |

nd = not detected, na = not available

## ANNEX 9: SOLVENTS IN WATER AND FISH FROM LAKE MÄLAREN IN SWEDEN

Tomas Alsberg, Anna Winberg and Bo Jansson

Stockholm University, Sweden

### 1 Samples

- Water from under the "språngskiktet"
- Fish, smelt, 10–20 individuals depending on size (10–15 cm)
- Field blank, boiled water following the sampling procedure
- Lab blank, freshly boiled water

### 2 Analysis

- Solid Phase Micro Extraction (SPME)
- 4 ml water in a 22 ml bottle, deuterated styrene + bromobenzene as internal standards, 50 °C, 15 minutes
- 4 g fish muscle from 3 to 6 fish, 10 ml water in a specially designed 85 ml container, homogenisation, 50 °C, 15 minutes

### 3 Investigated compounds

| | |
|---|---|
| 1,2-dichloroethane | tetrachloroethylene |
| benzene | ethylbenzene |
| chloroform | *m*,*p*-xylene |
| dichloromethane | *o*-xylene |
| 1,1,1-trichloromethane | styrene |
| toluene | 1,4-dichlorobenzene |
| 1,2-dibromoethane | 1,2-dichlorobenzene |
| trichloroethylene | hexachloroethane |

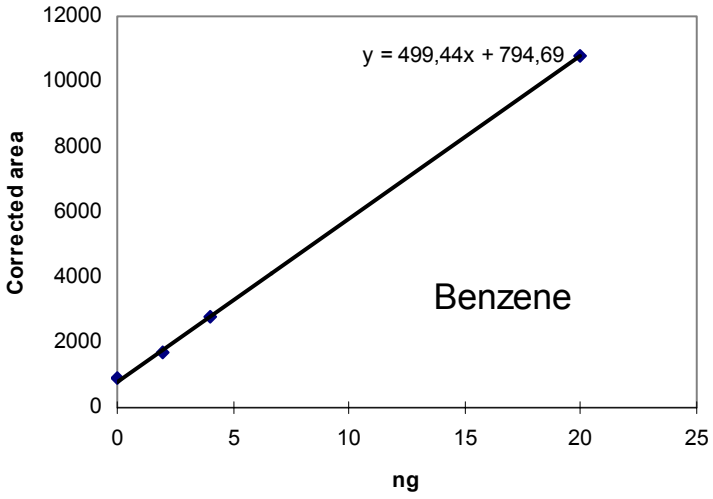
### 4 Calibration of fish analysis

- $K_{fw} = (A_{f+st+w} - A_{f+w}) / (A_{st+w} - A_w)$
- K = "partition coefficient"
- f = fish
- st = added standard
- w = blank water

## 5 "Partition coefficients"

| | | | |
|---|---|---|---|
| 1,2-dichloroethane | 0.51 | tetrachloroethylene | 0.86 |
| benzene | 0.89 | ethylbenzene | 0.39 |
| chloroform | 0.71 | *m*,*p*-xylene | |
| dichloromethane | | *o*-xylene | 0.38 |
| 1,1,1-trichloromethane | 0.74 | styrene | 0.36 |
| toluene | 0.78 | 1,4-dichlorobenzene | 0.27 |
| 1,2-dibromoethane | 0.46 | 1,2-dichlorobenzene | 0.55 |
| trichloroethylene | | hexachloroethane | 0.22 |

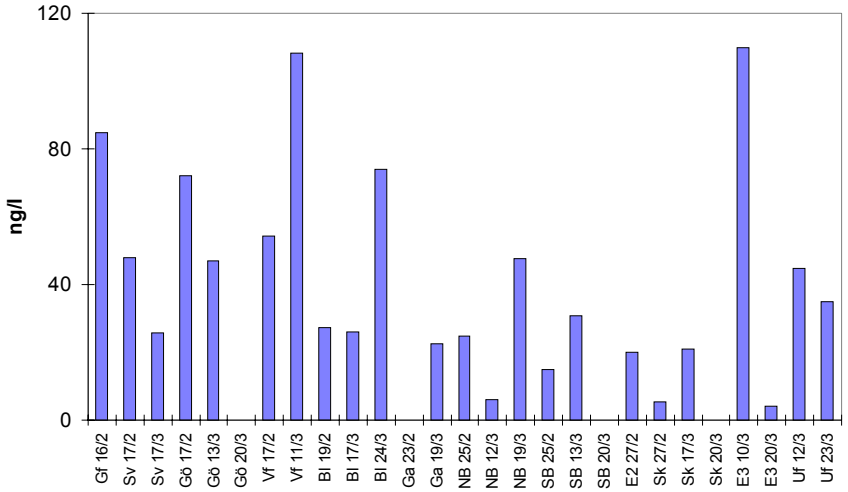
## 6 Calibration curve for benzene in fish samples



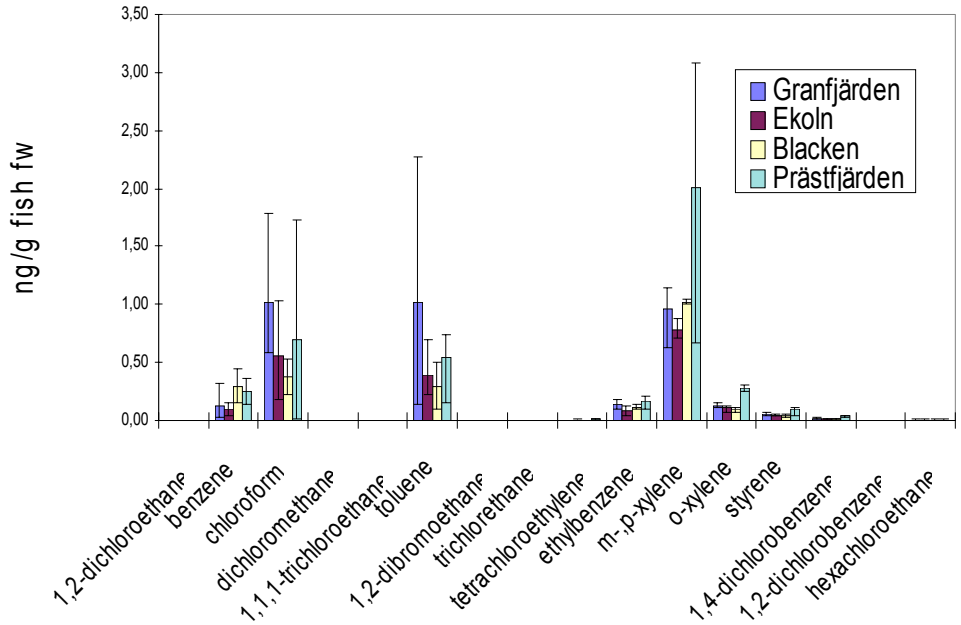

## 7 Background problems

- Our laboratory is not normally analysing solvents, and several of them are used in large volumes for extractions of pollutants from different samples.
- Consequently, most of the analysed solvents were found at variable levels in the laboratory background samples.
- Dichloromethane was not possible to analyse due to laboratory interferences.

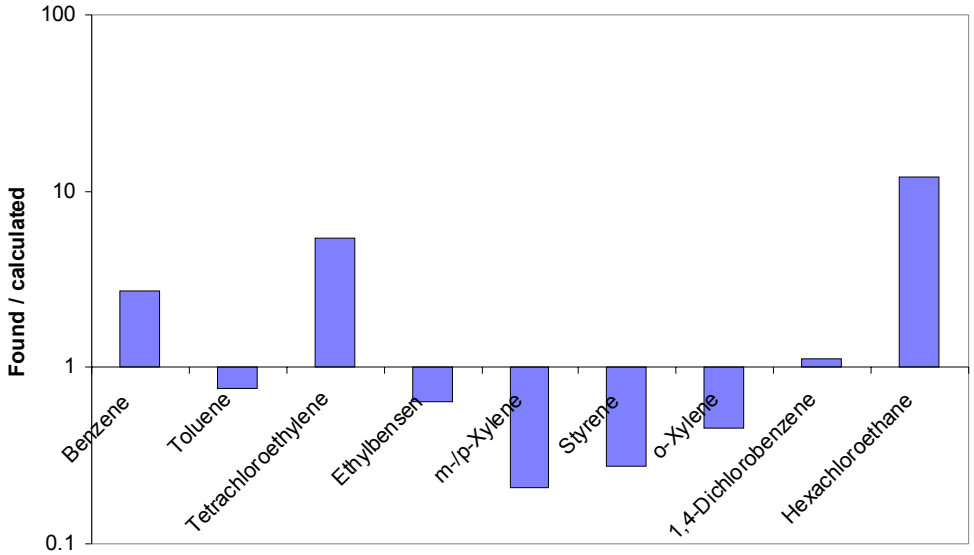
## 9 Toulene in water samples




## 10 Solvents in fish from Lake Mälaren



## 11 Found water concentrations compared to water concentrations calculated from fish concentrations




## 12 Sovents used in Sweden in 1996 (tonnes)

| | Industry | Products | | Industry | Products |
|---|---|---|---|---|---|
| 1,2-dichloroethane | 100000 | | tetrachloroethylene | ? | 9 |
| benzene | | | ethylbenzene | | |
| chloroform | 25 | <0.01 | *m*,*p*-xylene | 460000 | 10788 |
| dichloromethane | 116 | 2 | *o*-xylene | | |
| 1,1,1-trichloromethane | ? | 2.5–6.5 | styrene | 76376 | 8786 |
| toluene | 520000 | 5551 | 1,4-dichlorobenzene | | ~ 1 |
| 1,2-dibromoethane | | | 1,2-dichlorobenzene | | ~ 1 |
| trichloroethylene | 1770 | 9 | hexachloroethane | 10 | |

## 13 Conclusions

- The SPME technique is useful for the determination of solvents in both water and biological samples.
- Internal standards have to be extreemly pure.
- Background contamination is difficult to avoid in the laboratory, and may also emanate from ambient air.
- The overall levels of solvents in both water and fish from Lake Mälaren are low.
- *m*-xylene and/or *p*-xylene showed the highest levels, followed by chloroform and toluene.

# ANNEX 10: TOXAPHENE IN STANDARD SOLUTIONS AND CLEANED BIOTA EXTRACTS— RESULTS OF THE FIRST QUASIMEME INTERLABORATORY STUDIES

Jacob de Boer*, Michael Oehme[a], Kieren Smith[b] and David E. Wells[b]

*Netherlands Institute for Fisheries Research, P.O. Box 68, 1970 AB IJmuiden, The Netherlands

[a]University of Basel, Institute for Organic Chemistry, St. Johannsring 19, CH-4056 Basel, Switzerland

[b] FRS Marine Laboratory, P.O. Box 101, AB 11 9 DB Aberdeen, United Kingdom

## ABSTRACT

Two interlaboratory studies on individual toxaphene congeners have been organised by the project QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe). Fifteen laboratories analysed two standard solutions in the first study and 13 laboratories analysed a standard solution and two cleaned biota extracts in the second study. The coefficients of variation obtained for the standard solutions were 6–21 % and for the cleaned extracts 16–39 %. Although the results were comparable to those of other studies, further improvement in the level of agreement between the participating laboratories was considered possible.

## INTRODUCTION

Two toxaphene interlaboratory studies were organised as developing exercises by QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe). QUASIMEME has an ongoing programme for laboratory performance studies in the marine environment. Relevant compound classes that are added to the testing scheme of routine analyses are often first introduced through developing exercises. Toxaphene is an example of such a class of compounds. Until now, little attention has been paid to testing and improving the mutual comparability of laboratories' performance of toxaphene analysis. Two interlaboratory studies have been organised in recent years [1,2].

In the first exercise (QUASIMEME nr. 333) the participants were asked to determine the congeners 26 (B[12012]-(202)), 32 (B30012]-(111)), 50 (B[12012]-(212)) and 62 (B[30030]-(122)) in two standard solutions [3–5]. In the second exercise (nr. 379) three congeners, CHBs 26, 50 and 62, were asked to be determined in a standard solution and in a cleaned-up hake liver extract and a cleaned-up pilot whale extract. CHB 32 was left out this time because this CHB is normally not present in biological samples. The congeners mentioned above are identified by two nomenclature systems. For convenience, only the Parlar number [3] will be used in this study. The analysis of total toxaphene was not undertaken because of the errors which can occur due to the lack of calibration standards which have a pattern comparable to that in biological samples and to different methods used by the participating laboratories. Although information on total toxpahene is often required for some monitoring purposes, information on specific congeners is essential for toxicological impact assessments and for legislative purposes [6].

## MATERIALS AND METHODS

In the first exercise the participants were given three standard solutions of toxaphene congeners in *iso*-octane. The standard solutions used in this exercise was prepared by dilution from 5 mg $l^{-1}$ solutions, obtained from Promochem, Wesel, Gerrmany. One of them contained the congeners 26, 32, 50 and 62 in known concentrations (150–200 µg $l^{-1}$). The second one (2SS) contained the same congeners in unknown contrations (70–130 µg $l^{-1}$), and the third solution (3SS) contained the same congeners in undeclared concentrations (70–130 µg $l^{-1}$), but with the further addition of the congeners 25, 31 and 51, all at 70 µg $l^{-1}$. These congeners were added because they may co-elute with the congeners 26, 32 and 50, respectively, increasing the complexity of the GC separation. All glassware used for the preparation was carefully washed with detergent solutions, followed by rinsing with de-ionised water, drying, rinsing with *iso*-octane and heat treatment at 300 ˚C. Blank tests did not show any measurable signals within the elution range of the compounds of interest. The participants were asked to determine the concentrations of the congeners 26, 32, 50, and 62 in solutions 2SS and 3SS.

The second exercise focused on the determination of the congeners 26, 50 and 62 in clean biota extracts. One standard solution (4SS) with these congeners in unknown concentrations (110–160 µg $l^{-1}$) was given to the participants as well, to test the participant's own calibration. This solution was made from crystals, obtained from Promochem, Wesel, Germany. All glassware used for the preparation was cleaned and tested as before.

Hake liver was used to prepare the fish extract, coded 5BT. The liver (61.3 g) was extracted with 500 ml dichloromethane/*n*-pentane, concentrated using a rotary evaporator and diluted with *n*-pentane. The extract (35.7 g fat

in 100 ml *n*-pentane) was cleaned up by the repetitive addition of concentrated sulphuric acid. The extract was divided over ten centrifuge tubes and each tube was diluted with 20 ml of pentane. Subsequently, 15 ml of concentrated sulphuric acid was added to each tube. The next day, the pentane layers were quantitatively collected, pooled and concentrated on the rotary evaporator to approximately 30 ml. Again, 10 ml of concentrated sulphuric acid was added and, again, a brown layer appeared. The 30 ml of pentane extract was transferred quantitatively over anhydrous sodium sulphate and concentrated under nitrogen to 20 ml. Anhydrous sodium sulphate was added and the extract was divided into two parts of ca. 10 ml and eluted over two 25 g aluminium oxide columns (6 % $H_2O$) with 250 ml *n*-pentane. The eluates were combined and concentrated on the rotary evaporator to 10 ml. This volume was divided into ten parts of 1 ml each and eluted over 2.5 g silica columns (2 % $H_2O$) eluted with 12 ml *iso*-octane to retain the PCB fraction and 12 ml 20 % diethyl ether/*iso*-octane to retain the fraction containing the toxaphene congeners. The diethyl ether/*iso*-octane fractions were pooled and concentrated on the rotary evaporator to 55 ml before ampouling. Twenty-five ampoules were filled with 2 ml of the cleaned-up extract. Approximately 30 % of CHB 26 was collected in the PCB fraction with this method. This means that the CHB 26 concentrations in the cleaned-up extracts were lower than those in the original material. However, this did not interfere with the purpose of this test.

Pilot whale blubber (27.9 g) was used to prepare the marine mammal extract, coded 6BT. The whale blubber was heated gently and 17.3 g of free-flowing oil was collected and diluted to 50 ml with *n*-pentane. Subsequently, ten times 3 ml was transferred to ten centrifuge tubes and diluted with 20 ml *n*-pentane. The rest of the clean-up procedure was similar to that described for the hake liver extract. Twenty-five ampoules were filled with 2 ml of the cleaned-up extract. All test materials were tested by GC/ECD and GC/MS-NCI to determine the concentrations of the toxaphene congeners and to check if the biological extracts were free from PCBs prior to ampouling.

The participants were requested to use more than one GC column for the determination of the toxaphene congeners. However, only the best estimate of the concentration, according to the judgement of the participant, was reported.

Z-scores and robust statistics were used for the evaluation of the data [7]. The allowable error was based on a proportional error (12.5 % for the biota extracts in exercise 379 and for the unknown solutions in exercise 333, and 6 % for the unknown solutions in exercise 379) and a constant error, set by the concentration of the analyte [8]. The assigned values in exercise 333 were based on the nominal values given by the University of Basel, where the solutions were prepared. These concentrations had been checked by an independent laboratory (BgVV, Berlin, Germany). The maximum deviations found were 5 %, which is comparable to the precision of the method. The assigned values in exercise 379 were obtained from the robust mean of the data from all the laboratories excluding those laboratories submitting data which were extreme (i.e., $|Z|>6$).

**RESULTS AND DISCUSSION**

The assigned values, total allowable errors and other information on the determinands are shown in Table A10.1 for the first exercise and in Table A10.2 for the second exercise. Fifteen laboratories participated in the first exercise and 13 laboratories participated in the second exercise.

The Between-Lab CV % values (6–21 %) of the standard solution are somewhat higher than those obtained in exercise 333 (7–14 %). This seems mainly to be caused by three new participants, who had particular difficulties with the determination of CHB 50. High or low biased values for the CHBs in the standard solution were not translated to a similar bias in the cleaned-up extracts (Figure A10.1). This indicates that the errors are due to sample handling and/or dilution problems rather than to calibration.

The Between-Lab CV % values of the cleaned-up sample extracts are between 16 % and 39 %. These values are higher (27–39 %) in the hake liver (5BT), which has a lower toxaphene concentration (7–29 µg $l^{-1}$), than in the pilot whale sample (6BT) (16–21 %, concentration range 45–188 µg $l^{-1}$). In both samples CHB 62 showed the highest Between-Lab CV % value. This CHB is known to be sensitive for contamination of the liner in splitless injection and any small variations in the NCI-MS conditions. The Between-Lab CV % values are considerably better than those obtained in two previous interlaboratory studies, although it should be emphasised that in those studies uncleaned samples (fish oils) were used. Andrews [1] reported a range of 68–133 % as CV values for the CHBs 26, 32, 50 and 62 in cod liver oil and Alder *et al*. [2] reported a range of 9–50 % for the CHBs 26, 50 and 62 in cod liver oil and corn oil. On the other hand the results of the German study were obtained from laboratories which basically all used the same clean-up method [2].

**Table A10.1.** Summary statistics for all QUASIMEME participants in exercise 333.

| Matrix / Determinand | Assigned Value | Allowable Error % | n | Median Value | Robust Mean | Between-Lab. s.d. | Between-Lab. CV% |
|---|---|---|---|---|---|---|---|
| **Solution 2SS** | | | | | | | |
| CHB26 | 100 | 12.67 | 15 | 97.29 | 97.15 | 10.52 | 11 |
| CHB32 | 80 | 12.72 | 15 | 75.21 | 75.13 | 7.66 | 10 |
| CHB50 | 70 | 12.75 | 15 | 69.00 | 68.83 | 4.87 | 7 |
| CHB62 | 130 | 12.63 | 15 | 133.17 | 131.74 | 10.92 | 8 |
| **Solution 3SS** | | | | | | | |
| CHB26 | 80 | 12.72 | 15 | 80.73 | 80.70 | 11.30 | 14 |
| CHB 32 | 70 | 12.75 | 15 | 68.31 | 68.12 | 8.25 | 12 |
| CHB50 | 100 | 12.67 | 15 | 94.12 | 93.90 | 6.71 | 7 |
| CHB62 | 130 | 12.63 | 15 | 133.86 | 131.04 | 14.79 | 11 |

n = total number of observations; s.d. = standard deviation; CV = coefficient of variation.

**Table A10.2.** Summary statistics for all QUASIMEME participants in exercise 379.

| Matrix / Determinand | Assigned Value | Allowable Error % | n | Median Value | Robust Mean | Between-Lab. s.d. | Between-Lab. CV% |
|---|---|---|---|---|---|---|---|
| **Solution 4SS** | | | | | | | |
| CHB26 | 160.92 | 6.16 | 13 | 160.74 | 158.40 | 9.49 | 6 |
| CHB50 | 142.40 | 6.18 | 13 | 146.00 | 147.89 | 30.36 | 21 |
| CHB62 | 112.63 | 6.22 | 13 | 106.00 | 107.74 | 13.81 | 13 |
| **Hake liver 5BT** | | | | | | | |
| CHB26 | 7.77 | 15.72 | 13 | 8.00 | 8.34 | 3.01 | 36 |
| CHB50 | 28.84 | 13.37 | 13 | 29.00 | 29.28 | 7.99 | 27 |
| CHB62 | 6.93 | 16.11 | 13 | 6.60 | 7.49 | 2.91 | 39 |
| **Pilot whale 6BT** | | | | | | | |
| CHB26 | 84.07 | 12.80 | 13 | 86.00 | 84.07 | 13.46 | 16 |
| CHB50 | 187.98 | 12.63 | 13 | 186.00 | 187.98 | 30.93 | 16 |
| CHB62 | 45.87 | 13.05 | 13 | 44.30 | 45.87 | 9.69 | 21 |

n = total number of observations; s.d. = standard deviation; CV = coefficient of variation.

Figure A10.2 shows the correlation between results and GC columns used for CHB 26. It is known that coelution of CHBs may be a problem on certain GC columns, particularly for CHB 26.

**Figure A10.1.** Correlation between results (Z-scores) of solution 4SS and extract 6BT.

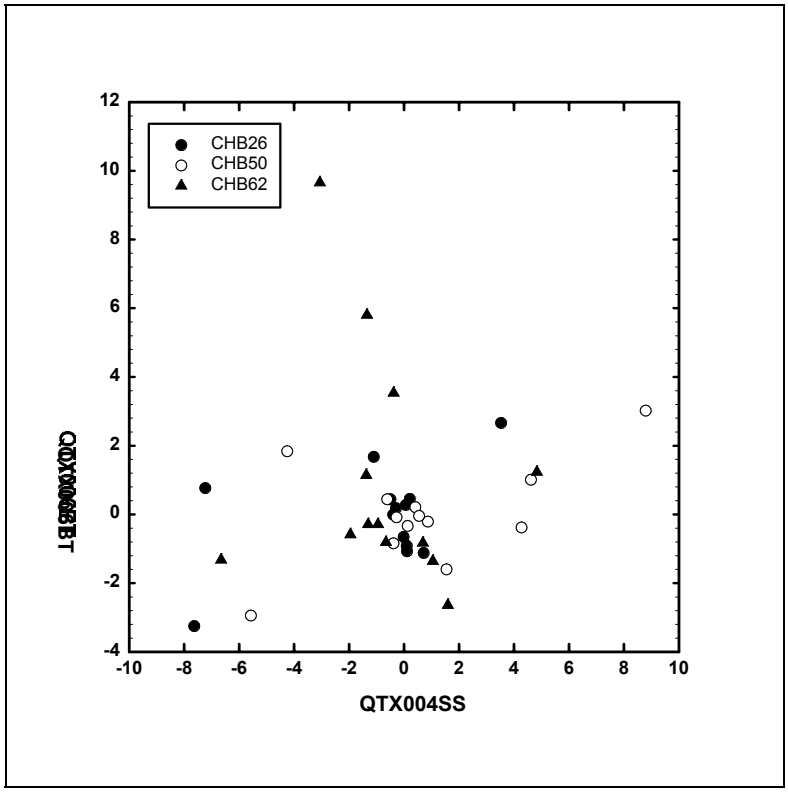
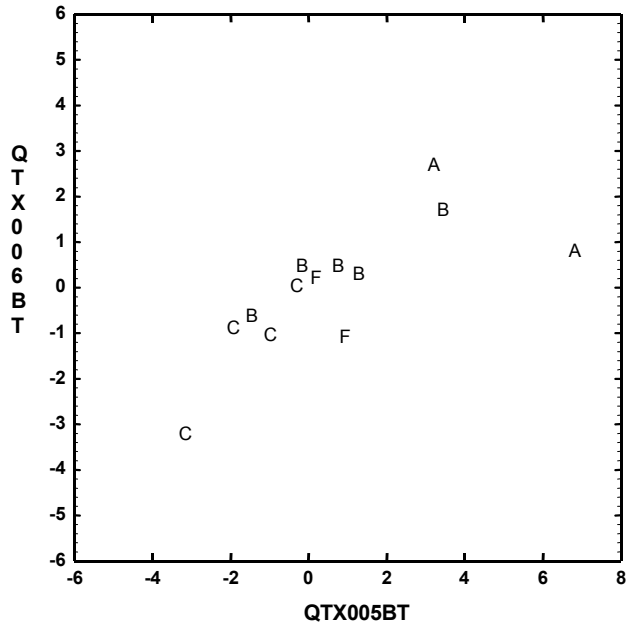



**Figure A10.2.** Results in the two cleaned extracts 5BT and 6BT, correlated to the type of column used. A: CP Sil 5 type, B: CP Sil 8 type, C: and F: other columns.



Higher CHB 26 values were obtained on non-polar columns such as CP Sil 5 and CP Sil 8, which tends to confirm the difficulties reported by de Geus *et al*. [9] due to co-elution.

All participants except one used splitless injection, although it is known that degradation of CHBs may take place during splitless injection. This may have influenced the robust means of the data set. Five laboratories used ECD for detection, five used LR-NCI-MS, one used LR-EI-MS and one used LR-EI-MS. No specific influence of the detection technique used on the data was found.

## CONCLUSIONS

- Most participants do not have a problem to calibrate with CHBs 26, 50 and 62 and to measure these congeners in a standard solution.
- The between-laboratory agreement of the participants in the analysis of the cleaned-up biological extracts is generally satisfactory compared to earlier exercises. However, improvement of the comparabiltiy is possible, and is desirable both for routine monitoring and research studies into biological effects of these contaminants. The analysis of CHB 62 is more critical than that of the other two CHBs.
- Co-elution of target CHBs, particularly of CHB 26, with other CHBs and possible degradation effects during splitless injection may have biased the results obtained by the participants and, hence, robust mean values of the data set.
- The results justify proceeding to uncleaned extracts in a next exercise.

The results reported in this paper are part of an ongoing series of development exercises for the determination of toxaphene congeners in biological tissue. The data were discussed with the participants at a workshop held at the University of Basel organised by the authors within the framework of the QUASIMEME project. The programme is projected to develop into a routine series of laboratory performance studies within this project and participation in future exercises is open to any laboratory which requires external quality assurance support for these analyses by contacting QUASIMEME.

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## ANNEX 11: RECOMMENDED EQUATIONS FOR THE CALCULATION OF SOLUBILITY OF DISSOLVED OXYGEN IN MARINE WATERS

**prepared by Alain Aminot**

### INTRODUCTION

When only physical processes are involved, dissolved oxygen (DO) concentration in water is governed by the laws of solubility, i.e., it is a function of atmospheric pressure, water temperature, and salinity. The corresponding equilibrium concentration is generally called solubility. It is an essential reference for interpretation of DO data. Precise solubility data, tables and mathematical functions were established (Carpenter, 1966; Murray and Riley, 1969; Weiss, 1970) and adopted by the international community (UNESCO, 1973). However, Weiss (1981) drew attention to an error in the international tables in which the values are low by 0.10 % since they are based on ideal gas molar volume instead of actual dioxygen molar volume. Later, the Joint Panel of Oceanographic Tables and Standards recommended that the oxygen solubility equation of Benson and Krause (1984), which incorporated improved solubility measurements, be adopted and the tables updated (UNESCO, 1986). However, the UNESCO paper only referred to the equation that gives concentrations in the unit "micromole per kilogram".

The present document repeats the equations which should currently be used for the computation of solubility values of dissolved oxygen, in various units, according to the UNESCO recommendation. These equations (so-called B&K equations) are taken directly from the paper of Benson and Krause (1984) who provided two equations for calculation either in "micromole per kilogram"or"micromole per litre", and the conversion factors for data in "milligram per litre" and "millilitre per litre".

### B&K SOLUBILITY EQUATIONS (micromole per kilogram and micromole per litre)

Two equations of the same type have been established for DO solubility, to obtain concentrations either in "micromole per kilogram" or in "micromole per litre". Two points should be clear:

- in these equations, the species under consideration is dioxygen ($O_2$), therefore "micromole" means "micromole of $O_2$";
- 1 litre = 1 cubic decimetre, exactly.

The following symbols are used:

t: Celsius temperature (°C),

T: Kelvin temperature (K), T (K) = t (°C) + 273.15,

S: salinity on the Practical Salinity Scale 1978 (PSS78),

Cs: DO solubility concentration (the unit is mentioned using subscripts).

The equations can be expressed as follows:

$$\ln Cs_{(\mu mol/kg)} = A + B/T + C/T^2 + D/T^3 + E/T^4 - S \times (F + G/T + H/T^2),$$

and

$$\ln Cs_{(\mu mol/l)} = I + J/T + K/T^2 + L/T^3 + M/T^4 - S \times (N + P/T + Q/T^2),$$

Constants A to Q are the following:

| **Unit: micromole per kilogram** | | | **unit: micromole per litre** | |
|---|---|---|---|---|
| A = | – 135.299 96 | | I = | – 135.902 05 |
| B = | + 1.572 288 × $10^5$ | | J = | + 1.575 701 × $10^5$ |
| C = | – 6.637 149 ×$10^7$ | | K = | – 6.642 308 × $10^7$ |
| D = | + 1.243 678 × $10^{10}$ | | L = | + 1.243 800 × $10^{10}$ |
| E = | – 8.621 061 × $10^{11}$ | | M = | – 8.621 949 × $10^{11}$ |
| F = | + 0.020 573 | | N = | + 0.017 674 |
| G = | – 12.142 | | P = | – 10.754 |
| H = | + 2 363.1 | | Q = | + 2 140.7 |

Application domain: t = 0–40 °C; S = 0–40).

Cs is obtained as: Cs = exp (ln Cs), i.e., when developing the equation:

$$Cs_{(\mu mol/kg)} = \exp [-135.299\,96 + (1.572\,288 \times 10^5) / (t + 273.15) - (6.637\,149 \times 10^7) / (t + 273.15)^2 + (1.243\,678 \times 10^{10}) / (t + 273.15)^3 - (8.621\,061 \times 10^{11}) / (t + 273.15)^4 - S \times (0.020\,573 - 12.142 / (t + 273.15) + 2\,363.1 / (t + 273.15)^2)].$$

and

$$Cs_{(\mu mol/l)} = \exp [-135.902\,05 + (1.575\,701 \times 10^5) / (t + 273.15) - (6.642\,308 \times 10^7) / (t + 273.15)^2 + (1.243\,800 \times 10^{10}) / (t + 273.15)^3 - (8.621\,949 \times 10^{11}) / (t + 273.15)^4 - S \times (0.017\,674 - 10.754/ (t + 273.15) + 2\,140.7 / (t + 273.15)^2)].$$

**SOLUBILITY DATA IN "milligram per litre" and "millilitre per litre"**

Solubility in **milligram per litre** is obtained from a value in micromole per litre by multiplying by the molar mass of dioxygen ($O_2$) and $10^{-3}$ for unit consistency, that is:

$$Cs_{(mg/l)} = Cs_{(\mu mol/l)} \times 0.0319988.$$

Solubility in **millilitre per litre** is obtained from a value in micromole per litre by multiplying by the molar volume of the gas at standard temperature and pressure (STP; 0 °C, 1 atmosphere). For that conversion, some data previously published refer to the molar volume (STP) of dioxygen ($O_2$; 0.022 3916 ml per micromole), like those of Weiss (1970), while others refer to that of an ideal gas (0.022 414 ml $\mu mol^{-1}$), like those of the UNESCO tables and Benson and Krause (1984). Refering to exact $O_2$ molar volume:

$$Cs_{(ml/l)} = Cs_{(\mu mol/l)} \times 0.022\,3916.$$

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## ANNEX 12: ACTION LIST

| | |
|---|---|
| G. Asmund | Act as Chair of Trace Metals Subgroup intersessionally and for MCWG 2001. |
| J. de Boer | Act as Chair of the Organics Subgroup intersessionally and for MCWG 2001. |
| S. Carlberg | Act as Chair of the Chemical Oceanography Subgroup intersessionally and for MCWG 2001. |
| E. McGovern, (organic), Peter Woitke (metals) and Elisabeth Sahlsten (nutrients) | Update the list of relevant certified reference materials for organic compounds, trace metals, and nutrients for use in marine monitoring in advance of MCWG 2001. |
| G. Asmund and G. Audunsson | Gert Asmund to contact Jørgen Nørrevang Jensen at the ICES Secretariat concerning permission to use ICES data and with the view of writing a paper on supplementary work to the Icelandic cod study together with J. Nørrevang Jensen and G. Audunsson. |
| J.F. Chiffoleau + All members of the Trace Metals Subgroup | All members of the group to inquire whether relevant information on estuarine transport of trace metals, and relevant measurement methodologies exists in their countries and, if so, to send it to J.F. Chiffoleau who will present an updated note on the subject at the next MCWG meeting (decision from the 1999 MCWG meeting). |
| B. Jansson + all members of MCWG | Review and report on any new information on priority contaminants in relevant regional and international organizations |
| J. de Boer | Coordinate an interlaboratory study on TCPM and TCPMe and present results at MCWG 2001. |
| P. Roose, M. Lebeuf and M. Haarich (+ possibly M. Reamaeker and J. Klungsøyr) | Participate in the interlaboratory study on TCPM and TCPMe. |
| M. Lebeuf | Coordinate work on TCPM and TCPMe in flatfish and present results of this study at MCWG 2001. |
| J. de Boer, P. Roose, M. Lebeuf and M. Haarich | Participate in the study on TCPM and TCPMe in fish. |
| D. Wells | Inform MCWG at its 2001 meeting about progress in the European project on the certification and analysis of PAH metabolites in bile. |
| All members of MCWG | All members to send information on booster pesticides to Robin Law by 1 July 2000. |
| R. Law | Present a review note on booster pesticides at MCWG 2001. |
| J. de Boer | Inform the MCWG at its meeting in 2001 on progress in the work on PBDEs and present the results of the running BSEF PBDE interlaboratory study. |
| J. de Boer | Present a summary of recent data on dioxins, furans and dioxin-like PCBs in fish at the next MCWG meeting. |
| E. Evers | Present any new results on the use of membrane systems |
| All members of MCWG | All members to send information on halogenated PAHs to Bo Jansson before 1 July 2000. |
| B. Jansson | Present a review note on halogenated PAHs at MCWG 2001. |
| M. Lebeuf | Prepare for a presentation at the 2001 MCWG meeting concerning toxaphene in eastern Canada. |
| J. Tronczynski, R. Law | Prepare a theme session concerning oil spills, their effects and associated protocols for incident response. |
| P. Roose | Review and report from a multiship experiment of sampling and determination of chemical variables in sea water. |
| P. Roose | Review and report oxygen determinations in sea water by Winkler titration and membrane electrodes. |

| | |
|---|---|
| K. Nagel and A. Aminot | Review and report on the present knowledge about total nitrogen, total phosphorus, and total organic carbon in sea water, their speciation, and arguments for their use in monitoring programmes. |
| J. Ólafsson | Review and report on progress in the modelling of marine biogeochemical processes. |
| J. Ólafsson | Review and report on progress in the studies of estuarine behaviour of nutrients. |
| A. Aminot to give some examples from monitoring | Joint activity with WGSSO to discuss and report on the requirements on chemical data, particularly nutrients and oxygen, for use in numerical modelling as well as the use of models in optimization of monitoring programmes, and report the outcome. |
| P. Woitke, J. Klungsøyr, B. Pedersen, M. Cleemann, and P. Roose (last name to be confirmed) + one person from ICES | Prepare a note to be discussed at the MCWG 2001 meeting regarding QA criteria for data filtering of monitoring data. |
| Chairs of the Subgroups + D. Wells (last name to be confirmed) | Prepare a note regarding how a presentation of the analytical performance of one or a group of laboratories can best be standardized. |
| L. Føyn, V. Besada, M. Haarich + C. Pohl (last name to be confirmed) | Prepare a note regarding ways of setting background and/or reference values. |

## ANNEX 13: RECOMMENDATIONS

**Recommendation 1**

MCWG recommends that ICES express its concern to IMO about the increasing number of oil spills occurring in recent years.

**Recommendation 2**

The Chair of MCWG (B. Pedersen) should make the necessary preparations to hold the next MCWG meeting at the Insitut Maurice-Lamontagne in Quebec, Canada from 26 February to 2 March in 2001 to:

A. Chemical Oceanography Subgroup

a) review and report oxygen determinations in sea water by the Winkler titration and membrane electrodes;
b) review a report from a multiship experiment on sampling and determination of chemical variables in sea water;
c) review and report on progress in the modelling of marine biogeochemical processes;
d) review and report on progress in the studies of estuarine behavior of nutrients;
e) review and report on the present knowledge about total nitrogen, total phosphorus, and total organic carbon in sea water, their speciation, and arguments for their use in monitoring programmes;
f) joint activity with WGSSO: to discuss and report on the requirements on chemical data, particularly nutrients and oxygen, for use in numerical modelling as well as the use of models in optimization of monitoring programmes, and report the outcome;

B. Organics Subgroup

a) critically evaluate the lists of priority contaminants prepared in relevant regional and international organizations and report the outcome;
b) review new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in fish, including the results of the TCPM and TCPMe interlaboratory study, second phase, and report the outcome;
c) review new information on the analysis of PAH metabolites in bile, critically review the robustness of the methods, and report the outcome;
d) review new information on the use of membrane systems for sampling and report the outcome;
e) review new information on the monitoring and analysis of toxaphene and report the outcome;
f) review new information concerning oil spills, their effects and associated protocols for incident response and report the outcome;
g) review recent data on dioxins, furans, and dioxin-like PCBs in fish and report the outcome;
h) review new information concerning polybrominated diphenylethers (PBDEs) and report the outcome;
i) review new information concerning new contaminants in the marine environment (new booster pesticides and chlorinated and/or brominated PAHs) and report the outcome;

C. Trace Metals Subgroup

a) critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations and report the outcome;
b) review information on estuarine transport of trace metals and relevent measurement techniques available and the comparability of their results and report the outcome;
c) review new information on the use of membrane systems for sampling and report the outcome;
d) review new information concerning the supplementary work to the Icelandic cod study on the relationship between trace element concentrations in cod liver and various co-factors and report the outcome;

D. Plenum

a) review the updated list of relevant certified reference materials for organic compounds for use in marine monitoring, including also metal and nutrient compounds;

b) review how a presentation of the long-term performance of a laboratory can be standardized taking the information from the 2000 MCWG meeting into account and report the outcome;

c) review which QA data should be submitted to the database together with environmental data and how a data filter could be organized and operated and report the outcome;

d) review any new SGQAC Annexes on Quality Assurance and report the outcome;

e) discuss matters referred from the three subgroups, as necessary.