

**Report of the
Marine Chemistry Working Group**

**Berlin, Germany
4–8 March 2002**

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

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

TABLE OF CONTENTS

Section	Page
1	1
2	1
3	2
4	2
4.1	2
4.2	2
4.3	2
4.4	3
4.4.1	3
4.4.2	3
4.4.3	3
4.4.4	4
5	4
6	4
7	4
7.1	4
7.2	4
7.3	5
7.4	5
7.5	6
7.6	6
7.7	7
8	7
8.1	7
8.1.1	7
8.1.2	8
8.1.3	9
8.1.4	9
8.1.5	9
8.1.6	9
8.1.7	9
8.1.8	9
8.2	10
8.2.1	10
8.2.2	10
8.2.3	10
8.2.4	10
8.2.5	11
8.2.6	12
8.3	12
8.3.1	12

Section	Page
8.3.2	Review new information on <i>tris</i> (4-chlorophenyl)methanol (TCPM) and <i>tris</i> (4-chlorophenyl)methane (TCPMe) in flatfish 13
8.3.3	Review new information on the analysis of PAH metabolites in bile, and critically review the robustness of the methods 14
8.3.4	Review new information on the use of membrane systems for sampling 15
8.3.5	Review new information on the monitoring and analysis of toxaphene 16
8.3.6	Review new information concerning polybrominated diphenylethers (PBDEs) 17
8.3.7	Propose data products that could be developed for organic contaminants in marine organisms in relation to environmental state indicators, based on OSPAR monitoring data [OSPAR 2002/5.1] 18
8.3.8	Review and comment on the outcome of an OSPAR pilot assessment integrating input data, and data on organic contaminants in biota and sediments [OSPAR 2002/2.1] 18
8.3.9	Review specific text in Annexes 7, 8 and 9 of the draft report of SGQAC 2002 18
8.3.10	Review new information regarding dioxins and dioxin-like PCBs 19
8.3.11	Review new information concerning polycyclic aromatic hydrocarbons 20
8.3.12	Review information on new contaminants, and consider the need for new overviews of contaminants 20
8.4	Chemical Oceanography Subgroup 21
8.4.1	Review present knowledge about total nitrogen, total phosphorus, and total organic carbon in sea water, their speciation, and arguments for their use in monitoring programmes 21
8.4.2	Review studies under way in OSPAR on ecological quality objectives for the North Sea with regard to nutrients and eutrophication effects 21
8.4.3	Review recent developments in production and availability of suitable reference material for analysis of chemical oceanographic variables in sea water 22
8.4.4	Discuss OSPAR activities regarding the assessment of eutrophication, nutrient concentrations and trends, and how ICES might contribute to this process 22
9	PLENARY DISCUSSION OF SUBGROUP WORK 23
10	ANY OTHER BUSINESS 23
11	RECOMMENDATIONS AND ACTION LIST 23
12	DATE AND VENUE OF THE NEXT MEETING 23
13	CLOSURE OF THE MEETING 23
	ANNEX 1: LIST OF PARTICIPANTS 24
	ANNEX 2: AGENDA 27
	ANNEX 3: EDITED EXCERPTS FROM 2001 IOC ASSEMBLY REPORT OF RELEVANCE TO MCWG 30
	ANNEX 4: WEIGHTING PROCEDURES FOR ASSESSING TREND DATA OF VARIABLE ANALYTICAL QUALITY 31
	ANNEX 5: OSPAR LIST OF CHEMICALS FOR PRIORITY ACTION 38
	ANNEX 6: ACTION LIST 39
	ANNEX 7: RECOMMENDATIONS 40

1 OPENING OF THE MEETING

The Chair, Robin Law, opened the meeting of the Marine Chemistry Working Group (MCWG) following an address by the Head of the Water Division of the Umwelt Bundesamt, Dr Christiane Markerd, at 10.00 hrs on 4 March 2002. MCWG participants introduced themselves and briefly described their main area(s) of interest. The list of participants is given in Annex 1. The Chair passed on greetings from absent members.

2 ADOPTION OF THE AGENDA

The terms of reference for this meeting of the Marine Chemistry Working Group:

2E01 The **Marine Chemistry Working Group** [MCWG] (Chair: R. Law, UK) will meet in Berlin, Germany, from 4–8 March 2002 to:

A. Chemical Oceanography Subgroup

- a) review present knowledge about total nitrogen, total phosphorus, and total organic carbon in sea water, their speciation, and arguments for their use in monitoring programmes;
- b) review studies under way in OSPAR on ecological quality objectives for the North Sea with regard to nutrients and eutrophication effects;
- c) review recent developments in production and availability of suitable reference material for analysis of chemical oceanographic variables in seawater.

B. Organics Subgroup

- a) critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations;
- b) review new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in flatfish;
- c) review new information on the analysis of PAH metabolites in bile, critically review the robustness of the methods;
- d) review new information on the use of membrane systems for sampling;
- e) review new information on the monitoring and analysis of toxaphene;
- f) review new information concerning polybrominated diphenylethers (PBDEs);
- g) propose data products that could be developed for organic contaminants in marine organisms in relation to environmental state indicators, based on OSPAR monitoring data [OSPAR 2002/5.1];
- h) review and comment on the outcome of an OSPAR pilot assessment integrating input data, and data on organic contaminants in biota and sediments [OSPAR 2002/2.1];

C. Trace Metals Subgroup

- a) critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations;
- b) review information on estuarine transport of trace metals, relevant measurement techniques available, and the comparability of their results;
- c) review new information on the use of membrane systems for sampling;
- d) propose data products that could be developed for trace metals in marine organisms in relation to environmental state indicators, based on OSPAR monitoring data [OSPAR 2002/5.1];
- e) review and comment on the outcome of an OSPAR pilot assessment integrating data on inputs of trace metals and concentrations of trace metals in biota and sediments [OSPAR 2002/2.1];

D. Plenum

- a) review the mechanism for generating an updated list of relevant certified reference materials for use in marine monitoring programmes, and consider their availability via the ICES website;
- b) review how a presentation of the long-term performance of a laboratory can be standardised taking the information from the 2000 report of the Working Group into account and report the outcome;
- c) review any new ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea Annexes on Quality Assurance and report the outcome;
- d) discuss matters referred to from the three subgroups, as necessary.

MCWG will report by 24 March 2002 for the attention of the Marine Habitat and Oceanography Committees and ACME and ACE.

All of these items had been incorporated into the agenda. The annotated agenda, circulated before the meeting and subsequently updated at the meeting, is provided in Annex 2.

3 REPORT OF THE 89TH ICES STATUTORY MEETING

The Chair informed the group that all tasks referred to the MCWG at the 89th ICES Annual Science Conference had been incorporated into the agenda.

4 REPORTS ON RELATED ACTIVITIES

4.1 OSPAR and HELCOM

Any official requests from OSPAR or HELCOM which arose prior to the meeting have been included.

4.2 Intergovernmental Oceanographic Commission (IOC)

Harry Dooley, ICES Oceanographer, had provided a summary of relevant topics within IOC, which is appended as Annex 3. These include:

- i) the activities of the SCOR-IOC Ocean Carbon Advisory Panel, which is advocating the development of additional programmes for ocean carbon reference materials;
- ii) the establishment of a new joint SCOR-IOC Advisory Panel on Ocean CO₂, which is contributing to studies of ocean carbon cycles;
- iii) increased attention within the IODE system to data which are not routinely exchanged, such as remotely sensed, biological, chemical, pollution and coastal data. A group of experts has been established.

4.3 Laboratory Performance Study QUASIMEME

David Wells provided a summary of recent activities within the QUASIMEME programme. A model based on this experience was put forward for consideration by MCWG, as described below.

The evaluation of laboratory performance made by the MCWG should be based on the quality assurance data from those institutes, which provide data to the ICES databases.

An indicator of performance provides information on the number of laboratories, which can provide reliable measurements. It is also a useful guide to identify those areas where improvement is required.

This indicator may be expressed as:

“The number of laboratories, as a percentage, which achieve more than 75 % of $|Z| < 2$ for a specific group of determinands, over a specified time period.”

A second indicator of performance is the long-term bias of the measurement. This may be calculated using the Rescaled Sum of Z-scores (RSZ), which is given by:

$$\Sigma Z / \sqrt{n}$$

where ΣZ is the sum of Z-scores over a specified number of rounds (n). The variance of Z-scores can be obtained from the Z-scores.

However, the overall magnitude of RSZ and the variance of the value can be affected considerably by a small number of extreme values (outliers). From inspection of the QUASIMEME database, and from information subsequently received from participants, the extreme values are caused by a limited number of known events, for instance, reporting concentrations in wrong units.

Therefore, in assessing the long-term bias of laboratories, it is appropriate to consider the magnitude and variance of the RSZ *without* extreme values (those for which $|Z| > 6$) as well as the unabridged data set. When the extreme values are removed, then there is a clearer indication of the *analytical* bias of the laboratory. For the effective evaluation of RSZ, a laboratory should have contributed data in six or more rounds of the same scheme.

These indicators are only designed to provide an overview of the overall performance of a group of laboratories and not for specific data assessment. The evaluation of QA data in support of any environmental data assessment should be made by the assessors at the time of assessment.

The outcome of the plenary discussions is recorded in Section 10, below.

4.4 Other Activities

4.4.1 Criteria for screening data for analytical accuracy in contaminant trend studies

This was considered under Section 8.1.5, below.

4.4.2 Review of GESAMP working group document on risk assessment

Following discussions at MCWG 2001, Bo Jansson had agreed to attend the scoping meeting for this GESAMP Working Group, which was held in December 2001. In the event he was unable to do so due to other commitments at that time. The original intention of this work was to address hazard/risk assessment, but the aim of the current work is towards exposure only. The MCWG was somewhat sceptical that some of the claims made in the draft document could be realised in practice, and also of the indication that modelling would entail much less work than determining seafood contaminant concentrations directly. Regarding the choice of contaminants, MCWG felt that PBDEs were to be preferred over PBBs, as considerably more data are available for these compounds. PAHs are also important contaminants in seafood, and of concern for the potential health effects on human consumers.

The underlying assumption in this project is that it is difficult to determine seafood contaminants, and that modelling and prediction of them is a more cost-effective approach. However, in order to effectively model uptake and bioaccumulation, you need a good knowledge of topics such as the ecology of the species studied, and migration patterns, and concentration data for the contaminants in water, sediments, and the local food webs (the primary uptake source).

Overall, the intention of modelling bioaccumulation as a tool to predict and assess seafood contamination is a good one, but a very large amount of data will be needed to successfully develop and validate the models, and it may not be a straightforward matter to transfer a model validated at one location and for one species, to other species and areas.

4.4.3 Global POPs monitoring network

An update on the UNEP Global Monitoring Network was presented by Bo Jansson. The Stockholm Convention seeks to eliminate or restrict the production and use of all POPs. Initially, it is focused on twelve substances or groups of substances. There is an article in the Convention on "Research, development and monitoring" which states that Parties shall encourage and/or undertake research, development and monitoring of POPs and their alternatives, and of candidate POPs. They should also support and further develop international programmes, networks and organisations aimed at defining, conducting, assessing and financing research, data collection and monitoring. The results of these activities

shall be made accessible to the public. Another article defines the need for an effectiveness evaluation, calling for comparable global monitoring data on the presence of the twelve POPs. This should be implemented on a regional basis based on existing programmes, and may have to be supplemented where necessary.

UNEP has recently begun a project called “Regional assessment of persistent, bioaccumulating and toxic substances” with support from the Global Environmental Facility. This project is trying to collect as much information as possible on these substances for twelve regions in the world, possibly also including more compounds than the twelve covered by the Convention. It is already clear that information is very sparse for several of the regions, and there is an obvious need to establish new monitoring activities. UNEP has therefore started another project called “Global Network for the Monitoring of Chemicals in the Environment”, which aims at linking together national, regional and global organisations, laboratories and individuals responsible for, or involved in, monitoring of chemicals in man and the environment. This project is hosting a website www.chem.unep.ch/gmn, which links to programmes and resources on environmental monitoring. It is also setting up several Internet-based discussion groups on monitoring issues. These will be accessible via the website.

4.4.4 New chemicals policy in the EU and the technical guidance document

Bo Jansson presented an update on the development of this programme, and other relevant initiatives. Currently there are different legislative requirements for new and existing chemicals. It has been decided that a large proportion of the more than 100,000 existing chemicals will be risk assessed. Around 140 substances have been given a high priority in this process and, of these, some 60 have already been assessed. The resulting reports, which can be downloaded from the website <http://ecb.jrc.it>, are of a generally good quality and they are proving useful for many other purposes in addition to risk management. The protocols for the assessments are described in a “Technical Guidance Document”, which is also available on the ECB website above. These protocols have been used in almost all of the assessments completed to date. Based on the experiences gained in this process this document is currently being revised, and the new version will also include a section on marine risk assessment, something that is missing from the present version. This chapter has been developed in cooperation between the EC and OSPAR.

It is clear that, at the present speed, it will take generations to complete the assessment of the existing chemicals. This was one of the reasons which led the European Commission to propose a new chemicals policy in a white paper published last year. This was supported by both the Council and the Parliament, and currently six working groups with representation from the member states, industry, and NGOs are working to develop a proposal for new legislation. This will shift the responsibility for conducting risk assessments from the governments to the producers/importers and users of the chemicals. The proposal will be completed shortly, but it is difficult to foresee how long negotiations within the Commission will take before it can be forwarded to the Council and Parliament for a decision.

5 REPORTS OF PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES

No additional items were included under this heading.

6 REQUEST FROM ACME AND REGULATORY AGENCIES

Requests from ACME which arose prior to the preparation of the agenda have been included.

7 PLENARY PRESENTATIONS

7.1 Wiebke Schwarzbach: Selection and prioritisation procedure for hazardous substances within the OSPAR Convention—the OSPAR DYNAMEC procedure

Dr Schwarzbach outlined the process by which OSPAR is developing its strategy on hazardous substances. This primarily adopts the PBT (Persistence, Bioaccumulation, Toxicity) approach for the initial compound selection, but also includes a safety net procedure for other properties such as endocrine disruption. This is of great relevance to discussions within MCWG, as the hazardous substances selected in this manner will feed through into future monitoring and assessment needs under OSPAR programmes.

7.2 Erik Evers: The quality of organotin determinations in sediment

In the Netherlands, it is necessary to dredge and dispose of 20–30 million m³ of sediment annually in order to maintain adequate water depths in harbours and waterways. The current testing protocol used for licensing purposes, established 20–30 years ago, utilises data for a range of chemical analytes including metals, PCBs, PAHs, and organochlorine

pesticides. A revised and improved testing protocol (the Chemistry Toxicity Test, CTT) will be implemented as of January 2002. Organochlorine pesticides which are no longer relevant have been deleted, whilst toxicity testing and analyses for tributyltin have been added. In addition, the protocol includes new guideline values for specific compounds. The concentrations of tributyltin (TBT) and its decomposition products have increased in Dutch coastal sediments, and data from recent monitoring studies have demonstrated that this substance is widespread along the Dutch coast, as in other North Sea states. Erik Evers presented recent findings on the current status of analytical quality, precision, and reproducibility for the determination of TBT. This drew upon:

- the results of the last intercomparison study on organotins of the QUASIMEME proficiency testing scheme;
- the results of the certification of reference material BCR 646;
- the performance of the organotin methods of two Netherlands institutes (IVM and RIKZ);
- sediment sampling and pre-treatment;
- an assessment of the quality of an analytical testing laboratory conducting organotin analysis of dredged materials;
- the relation of detection limits to Dutch water quality objectives and action levels for dredged materials.

In general, intralaboratory agreement was considerably better than interlaboratory agreement in analyses of marine and freshwater sediments. However, in analyses of a certified sample, agreement within labs and between labs improved considerably. Quality criteria (saltwater maximum tolerable risk, MTR) for tributyltin and triphenyltin are below the detection limits of most laboratories. However, the proposed criterion for TBT within the CTT, $100 \mu\text{g Sn kg}^{-1}$ dry weight, is well above the detection limits of most laboratories. Although analytical methods and performance seem to be improving, there is a need for further improvements in repeatability, within-sample homogeneity, analytical precision, and reproducibility of results, so as to attain high quality and reliable data. Also, TBT is rarely distributed uniformly vertically through the sediment column because it often occurs as paint chips, especially close to shipyards.

The RIKZ intends to organise a workshop on the further improvement of analytical methods, laboratory performance in intercomparison exercises, and other developments on this subject. This will be conducted in cooperation with QUASIMEME in July 2002 in Amsterdam.

7.3 Lars Føyn: Monitoring nutrients in the North Sea—the very last monitoring of this kind?

The Institute of Marine Research (IMR) in Bergen, Norway, has monitored the distribution of nutrients in the North Sea, Skagerrak, and Kattegat during November–December for more than twenty years. Due to changed priorities, and the fact that less shiptime will be available in the coming years, the monitoring cruise in 2001 may be the last time that IMR undertakes such a broad and thorough survey in its monitoring of nutrients in the North Sea.

This presentation dealt primarily with measurements of nutrients for the use of nutrient data in characterising water masses, the distribution of nutrients as a basis for primary production, and examination of nutrient data in the various water masses for detection of possible trends due to increased or reduced anthropogenic contributions. In other words, this paper dealt with parts of the field of chemical oceanography.

Some examples of the distribution, both vertical in cross-section and horizontal for the whole area, were presented. The figures present some characteristics in the nutrient distributions, which have hardly changed during the more than 20 years that the monitoring has been conducted. Anthropogenic contributions are apparent only in nearshore waters, in particular in the German Bight. No particular trends have been observed, but the data will allow for more thorough calculations to be made at a later date.

7.4 Uli Claussen: Assessment of the eutrophication status within the OSPAR Convention Area

This presentation described work undertaken mainly within OSPAR and under the EC Water Framework Directive to adopt a new harmonised approach. It underpins the OSPAR strategy to achieve and maintain a healthy marine environment, where eutrophication does not occur, by 2010. In the identification of problem areas for eutrophication, the OSPAR system adopts a two-stage approach, the OSPAR Common Procedure. This involves firstly a screening procedure which identifies non-problem areas. The comprehensive procedure is then applied to reclassify the other areas as either problem areas, potential problem areas, or non-problem areas, based upon more detailed study. Areas subject to the comprehensive procedure will be assessed during 2002, and the assessments will be presented during 2003. Within 5 years of the initial assessment, potential problem areas must be reclassified to either problem or non-problem areas, in order that remedial measures might be implemented in problem areas.

7.5 Peter Lepom: Polybrominated diphenylethers—activities at the German Federal Environmental Agency (UBA)

In his presentation, Dr Lepom initially described research funded by the UBA in this area. The studies included the possible substitution of PBDEs by other compounds, emissions of flame retardants from consumer goods and building materials, the analysis of penta-BDE for compliance testing purposes, and the occurrences of BDEs in breast milk, blood, and in biota samples from marine and freshwater ecosystems. Ongoing monitoring studies include the measurement of PBDEs in emissions from consumer goods, in air and airborne particulates, and on the degradation of BDE209 in the environment. Research projects under way at the Laboratory for Water Analysis include studies of PBDEs in sediments, and of higher brominated BDEs in biota and sediments from Germany and Italy, and in sediments from the Danube. This has yielded the first data showing the presence of BDEs in sediments from Eastern Europe, 100 km south of Budapest, with BDE209 predominating. BDEs have also been shown to accumulate to high concentrations in the blood of adult raptors, such as the white-tailed eagle, osprey, sparrowhawk, goshawk, and peregrine falcon. Two different patterns are seen in these birds, related to species but not to the diets of the species. One is the classic pattern seen also in marine mammals, with BDE47 dominating, whilst the other has BDEs 99, 100, and 153 as the major components, and BDE183 as significant a peak as BDE47. This may be related to metabolic differences between species. Finally, PBDEs have been determined in bream and eel from the River Elbe. Higher concentrations were seen in bream than in eel (up to 700 ng g⁻¹ lipid), and BDE209 was also detected in bream tissue.

7.6 Jan Boon: The influence of hydrographic factors on transport processes of contaminants in the North Sea

Jan Boon outlined three examples of how hydrographic conditions can affect the transport of dissolved and particle-associated contaminants (polybrominated diphenyl ether flame retardants and organotins). Very specific hydrographic conditions are needed for the formation of a good sediment core (one which exhibits layers of deposition, often annual). These are: a high sedimentation rate, a layer of stagnant anaerobic bottom water which inhibits the degradation of natural organic material and bioturbation, and relatively sheltered and deep water which prevents erosive wave action during storms. Norwegian fjords can fulfil such conditions. Analysis of a sediment core from the Drammenfjord, a branch of the Oslofjord, showed that tetra- to hexa-brominated diphenyl ethers from the industrial penta-BDE formulation were present from 1970 onwards, whereas BDE209, constituting about 97 % of the deca-BDE formulation, first appeared around 1980. This tallies with the production data for these formulations compiled by the Bromine Science Environmental Forum.

Clear geographical gradients existed for the concentrations of BDE congeners from the penta-BDE mixture in invertebrates (sea stars, hermit crabs and whelks) caught in the North Sea in 1999. The River Tees (NE England) has been shown to be a dominant source for these compounds, which are then transported with the residual currents in that area. These residual currents differ seasonally due to vertical stratification of the waters in summer; from May–October a jet-current along the 25 m depth contour leaves the UK coast near Flamborough Head and flows towards the Dogger Bank. In winter, the currents continue southwards along the UK coast. BDE183, a marker compound for the octa-BDE formulation, was not detected in the North Sea. Also, although BDE209 is often the dominant congener in sediments, it was not found at concentrations clearly above the LOQ in the North Sea food web. For the congeners derived from the penta-BDE formulation, the major biomagnification step occurred from fish to marine mammals, coinciding with the change from gill-breathing to lung-breathing animals.

During the same cruise, samples of whelks were taken for the analysis of organotin compounds (TBT, TPT and metabolites) and measurement of the associated effect of imposex (the development of a penis in females). In the Southern Bight of the North Sea, where the waters are always homogeneously mixed, proximity to shipping traffic resulted in higher tissue concentrations of butyltins and phenyltins and imposex in benthic snails (*Buccinum undatum*). In contrast, in waters which become vertically stratified during the summer season (the deeper parts of the open North Sea) or which are stratified all year round (such as the Skagerrak), much lower concentrations and incidence of imposex were seen. This is because in vertically stratified waters the thermocline forms a barrier, which separates the upper and lower layers of the water column. Thus, there will be much more dilution through advection in the upper layer before dissolved compounds can penetrate into the bottom layer and affect benthic animals, than in homogeneously mixed waters.

In general, these results showed that currents are an important vector of contaminant transport on the scale of the North Sea basin. This also indicates that the global transport of contaminants occurs within both the atmosphere and the oceans.

7.7 David Wells: Cofino statistics: an alternative approach to the analysis of data

Interlaboratory studies play a key role in analytical chemistry by assessing the robustness of a method, and the quality of laboratory performance, and by providing data which may be used to certify reference materials. Sound statistical evaluation underpins these studies.

The original statistical tests used for this purpose provided a series of outlier tests for performance study data. However, this approach assumes an equal within-laboratory variance and a Normal distribution of values, which is often not found in practice.

Over the past 10 years, robust statistics have been applied to data from interlaboratory studies in an attempt to overcome these difficulties. With this technique, extreme values are not discarded as outliers, but *downweighted* to minimise the effect on the data set as a whole. This works well with up to about 10 % of extreme values, even when the data are highly skewed. However, the robust means are affected when there is a larger proportion of extreme values and when the evaluation is on a small number of values (ca. < 10). Until now QUASIMEME has used the robust statistical approach to assess the data from its Laboratory Performance Studies. The extreme values can result from calculation or transcription errors, use of incorrect units, wrong calibration, analytical errors, or contamination. In practice, many of these problems can be overcome by inspection of the data, bringing in an element of subjectiveness, which the application of robust statistics intended to avoid.

Cofino Statistics (developed by Wim Cofino, a former MCWG Chair) are intended to solve many of these difficulties. In addition to their use within laboratory performance studies, they are also applicable to other data sets where information on the underlying distributions is required. Cofino Statistics, derived from quantum mechanical wave functions and matrix algebra, are considerably more robust when applied to asymmetrically distributed data than existing techniques. They also provide both numerical and graphical methods for assessing data distributions. The principles and application, with examples, are outlined in a recent publication (Cofino *et al.*, 2000).

One example is taken from a recent study of PAH metabolites including chrysene 1,2 diol. The data for one set of measurements was 61.7, 65.3, 67.4, 75.2, 83.3, 519.2, 561.7 $\mu\text{g kg}^{-1}$, showing two high values and a skewed distribution for the remaining 5 values. When robust statistics were used the resultant robust mean was 224 $\mu\text{g kg}^{-1}$ which clearly falls between the two modes of the data. Using Cofino Statistics, the mean of the first mode was 70.1 $\mu\text{g kg}^{-1}$ with 65 % probability, and of the second mode 540 $\mu\text{g kg}^{-1}$ with 23 % probability. Clearly, the Cofino Statistics yield a better estimate of the most likely expected value.

Cofino, W.P., van Stokkum, I.H.M., Wells, D.E., Ariese, F., Wegener, J.M., and Peerboom, R.A.L. 2000. *Chemometrics and Intelligent Laboratory Systems*, 53: 37–55.

8 SUBGROUP ACTIVITIES AND DISCUSSIONS

Justification 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 the three subgroups is supported by plenary discussions, which add value to the work undertaken within the subgroups.

8.1 Plenary activities and those common to all subgroups

8.1.1 Review the mechanism for generating an updated list of relevant certified reference materials for use in marine monitoring programmes, and consider their availability via the ICES website

Information received from Marilynn Sørensen of ICES prior to the meeting had indicated that the advice of MCWG 2001, that information on certified reference materials (CRMs) should be made available automatically via the ICES website, had been agreed. The implementation of this procedure had been delayed by resource constraints, but would proceed as soon as possible. MCWG agreed that each subgroup should provide a list of recent marine CRMs for inclusion in the report of MCWG 2002, for information.

Two new BCR certified reference materials (CRMs) for PCBs have been made available recently: CRM 718 – CBs in herring and CRM 719 – non-*ortho* CBs in chub. The CRM 718 includes 12 di- and mono-*ortho* CBs, and CRM 719 includes the non-*ortho* CBs 77, 81, 126 and 169. The latter is the first material available worldwide for non-*ortho* PCBs in fish, and the uncertainties are relatively small.

Two fish bile materials certified for PAH metabolites, CRM 720 and 721, are expected to become available from BCR at the end of the year (see Section 8.3.3).

Until now, few reference materials exist for chemical oceanographic variables. The following can be mentioned:

- *Salinity standards*: Initially developed by ICES (the Copenhagen seawater), they are presently produced by Ocean Scientific International (UK).
- *Inorganic carbon species*: A certified reference material for total inorganic carbon has been available for a number of years from Dr A. Dickson at the Scripps Institute of Oceanography. The alkalinity of the samples is also given, but it is not known whether the samples are certified for alkalinity.
- *Dissolved organic carbon and dissolved organic nitrogen*: In 1998, the National Science Foundation (NSF, USA) awarded a grant to the Bermuda Biological Station for Research (BBSR) to support development of a reference material programme for DOC analyses. Two forms of reference material have been produced for DOC analyses. One is deep-ocean water containing biologically refractory DOC at a concentration of 43–45 mol l⁻¹; the other is a low-carbon water containing DOC at a concentration of roughly 2 μmol l⁻¹. Both reference materials are available in 10 ml ampoules. The reference waters have been certified for DOC by a number of laboratories in both the USA and other countries. The concentration of Total Nitrogen has been tested by a smaller number of laboratories using high-temperature combustion. Laboratories interested in obtaining DOC reference material should contact Dr Wenhao Chen at the University of Miami's Rosenstiel School of Marine and Atmospheric Science.

Despite the high priority given by the GESREM (Group of Experts on Standards and Reference Materials, UNESCO) in 1991 and 1992 to developing reference material for nutrients in seawater, no material is commercially available as yet. The CSK standards developed in the 1960s and 1970s are no longer produced.

Various other bodies are presently dealing with reference material issues. The SCOR-IOC Ocean Carbon Advisory Panel is advocating programmes for the development of ocean carbon reference materials (mainly inorganic carbon). Also, a symposium was organised in September 2001 on behalf of the National Research Council's Ocean Studies Board and the NRC Committee on Reference Materials for Ocean Science to promote the development of reference materials for ocean science. The report will be available in November 2002 (pre-publication April 2002).

David Wells advised the group that QUASIMEME and DHI Denmark are producing reference materials for nutrients, which are expected to be commercially available in October 2002. Two types of sample will be produced: one with open ocean salinity (S ~35), and one with a low salinity (Baltic type, S ~10–12). Two types of samples are in the process of certification for the following determinands: one containing nitrate, nitrite, ammonia, and total nitrogen (glass bottles), and the other containing phosphate, total phosphorus, and silicate (plastic bottles).

8.1.2 Review how a presentation of the long-term performance of a laboratory can be standardised taking the information from the 2000 report of the Working Group into account and report the outcome

Gert Asmund outlined a method for treating data from laboratory proficiency tests. The relative deviations from the assigned values are assumed to be Normally distributed and to be composed of two components, a constant error E_c (independent of the concentration in the sample) and a proportional error E_p . An Excel spreadsheet is used to calculate the values for E_c and E_p which result in the best fit to three criteria: 95 % of the data should have an error smaller than 2 standard deviations, 68 % of the data should have an error less than one standard deviation, and 50 % of the data should have an error less than 0.67 standard deviation.

The advantage of this method is that the proficiency data from a number of rounds can be condensed to only two numbers in an objective manner. It is, however, realised that this cannot be done for all laboratories and for all determinands, as in some cases data are not distributed according to the assumption of a constant and a proportional error.

A small working group was formed composed of Gert Asmund, David Wells, and Patrick Roose to investigate whether this method can be applied successfully to data from QUASIMEME, and to report to MCWG 2003.

Action: Gert Asmund to report the findings to MCWG 2003.

8.1.3 Review any new ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea Annexes on Quality Assurance and report the outcome

The draft report of the 2002 meeting of SGQAC was received by the Chair immediately prior to the meeting. Three draft annexes were included for MCWG comment, all of which were relevant only to the Organics Subgroup. These have been incorporated into the subgroup agenda in Section 8.3.9, below.

8.1.4 Screening contaminant data submitted to the ICES database

Following a request from the ICES Secretariat, MCWG agreed that the primary contacts list for contaminant groups established during MCWG 2001 was still valid. In order to solve the difficulty with the assignment of maximum values for each chemical group and matrix, MCWG recommends the following procedure: for each of these combinations, the maximum valid value recorded in the database will act as the trigger value under the SCREEN program. Values submitted which are higher than these will be returned to the data originator for validation.

8.1.5 Weighting procedures for assessing trend data of variable analytical quality

A paper on this subject, numbered MCWG 2002 8.1.5/2 by Mike Nicholson and Rob Fryer, was presented by Robin Law. (The paper is appended as Annex 4.) MCWG accepted the aim of the paper, to aid data assessment within, e.g., OSPAR, by maximising the utility of historic data. However, the group still felt that the approach was fraught with problems. In particular, for years for which QA are absent, and which tend primarily to be the early years of the data sets, there are also likely to be methodological differences, which can alter the comparability of the data (for instance, following the change from packed GC columns to capillaries). These cannot be accounted for in any way, and their effect on the overall trend is not obvious. As the highest values occur in these early years, they are critical to the determination of any trend, and are still not well controlled following this statistical treatment. One final comment regarding the discussion on weighting data: Why not use the value of the reciprocal of the variance as the weighting factor, as this is standard practice in other areas?

8.1.6 ICES database issues

In response to requests from the ICES Secretariat, two other database topics were discussed. Firstly, concerning limits of detection and of determination. After some discussion, the group agreed that in order to avoid confusion, an alternative in common use was preferred and they should be termed "limit of detection (LOD)" and "limit of quantification (LOQ)". The LOD is already defined as "that concentration of analyte which yields an analytical response equal to three times the standard deviation of the complete procedural blank". MCWG would add to this, "or a sample with a very low concentration of the analyte" as sometimes spiking is necessary in order for a response to be detectable. The definition for LOQ would be the same, except that a multiplication factor of ten would be applied. MCWG also recommends that, in the text below, the phrase "worst case" should be replaced by "best case". LODs and LOQs are sample-dependent to a degree, and this requirement may be causing more, rather than fewer, values to be correctly reported as positive when they are below the apparent LOD (or, in the future, LOQ). Secondly, the interpretation that new fields from the SGQAC QA form given as Annex 8 in the MCWG 2001 report should be added to the ICES database is correct.

8.1.7 Discuss the preparation of guidelines for integrated chemical and biological effects monitoring, covering as many CEMP parameters as are relevant

Initiatives are under way within a number of countries in order to meet the needs of their own national programmes for guidelines of this type. Robin Law, Erik Evers, Michael Haarich, and Patrick Roose will endeavour to take this forward interessionally, in conjunction with members of WGBEC, and will report to MCWG 2003.

8.1.8 Discuss matters referred from the three subgroups, as necessary

MCWG encouraged the development and use of environmental indicators. Firstly, however, the aims of such indicators need to be clear. They might be intended, for instance, to inform environmental managers of the effects of controls, inform the wider public of the efficacy of regulations intended to control pollution, or for other purposes. For each aim, differently derived indicators may be appropriate. Similar approaches have been implemented successfully in other areas of the world, and we should learn from the experiences of others. One example specifically mentioned during the discussions was the joint USA/Canada studies undertaken in the Great Lakes area, where indicators have been developed over the past 25 years. The development of these indicators, and the means to represent them took time, but

they have proved useful. Further development of these indicators is under way, and existing indicators are being maintained and updated. For further information, there is a website: www.ijc.org.

Additional examples which would merit study include the report no. 5052, “Coasts and Seas”, prepared by the Swedish EPA, and the programme “Water Mondrian” being developed by the Rijkswaterstaat in the Netherlands (contact Erik Evers).

Within OSPAR and the EEA there is a desire to link input data with environmental data on the concentrations and/or effects of chemicals, but it seems to the MCWG that there needs to be some more focus on processes and the development of a holistic approach in order to facilitate this. For instance, input data are not always comprehensive and, currently, environmental sampling is not yet targeted towards those locations which would most directly reflect changes in inputs over time. The design of such a targeted monitoring strategy would benefit from discussions between the environmental managers, process modellers and oceanographers, as well as biologists, chemists and sedimentologists, to promote the exchange of ideas and to develop indicators which apply to both spatial and temporal scales, and are likely to provide a rapid response to changes. The whole process of the development of each indicator should be transparent, and data should carry information on the quality assurance and a statement of the associated uncertainties. It should be clearly stated which data have been used in preparing the indicators, whether there are gaps in these spatial and/or temporal data, and what process has been applied in order to generate the indicators from the data. It is also important to clearly demonstrate the environmental relevance of the indicators being reported, for instance, in relation to eutrophication and ecosystem effects.

This will require concerted action between ICES and OSPAR, and should include workshop(s) at which the development can progress.

Action: All MCWG members to supply information on examples of existing environmental indicators to Robin Law for onward transmission to the ICES Environment Adviser.

8.2 Trace Metals Subgroup

8.2.1 Critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations

This was conducted in conjunction with the Organics Subgroup – see Section 8.3.1 and Annex 5.

8.2.2 Review information on estuarine transport of trace metals, relevant measurement techniques available, and the comparability of their results

No new information was available on this topic.

8.2.3 Review new information on the use of membrane systems for sampling

No new information was available for metals, but the latest information on passive sampling devices was presented under Section 8.3.4, below.

8.2.4 Propose data products that could be developed for trace metals in marine organisms in relation to environmental state indicators, based on OSPAR monitoring data [OSPAR request 2002/5.1]

The subgroup could understand the need to develop indicators of environmental status in order to present complex data in a more accessible and understandable way for the public and politicians, and was generally in favour of such an approach. It was, however, stressed that it is important that the indicators are done in an “intelligent” manner, so that they represent the actual status and development in a certain area, both in time and space. It is also important that the indicators are not too overly simplistic, so that the message is not misunderstood or misinterpreted.

A number of papers from the OSPAR MON 2001 meeting and the EEA were discussed in detail. The subgroup thought that the indicators presented in the EEA paper (YIR 02) on hazardous substances (cadmium, mercury, lead, zinc, and PCB₇) in blue mussels and cod in the Northeast Atlantic (including the North Sea) and the Mediterranean in the period 1990–1999 (MCWG 2002 8.2.4/6) did not meet these criteria. Data for one of the indicators presented (concentrations in mussels) were aggregated in space across the whole North Sea. This led to a misleading conclusion, because the number of data sets used in the calculation of the time trends were very unevenly distributed geographically, as most of

the data sets were from Norway. The trend for some countries was only represented by a single data set. The overall trend shown is therefore only valid for Norway, and not for the North Sea as a whole. Also, no information about the uncertainties is given for the trends presented. A more relevant presentation of the trends could have been obtained by dividing the information into sub-areas, and by using colours to indicate trend directions (up, down, or no apparent trend). It should also be borne in mind that, when concentrations are simply summed, a clear upward trend in one area could be cancelled by a clear downward trend in another area, giving no trend as a result. To a large extent, the persons producing the indicators are aware of the above-mentioned drawbacks, as this is discussed in a special section concerning the Quality of Information. The subgroup felt, however, that this information was not really used and integrated into the graphs that were presented, thus presenting the risk that the caveats regarding data quality would be lost at later stages.

In discussion of the paper MON 01/4/3-E (MCWG 2002 8.2.4/1) "Development of an indicator on marine sediment" prepared by the EEA, it was noted that the authors felt that the development of an indicator based on concentrations in sediment should be postponed. The subgroup felt, however, that it is just as difficult to develop indicators for biota as for sediment. A sediment indicator to describe the spatial distribution could, however, create a special problem until relevant normalisation procedures to account for differences in the sediment structure are agreed upon. Aggregation of data for spatial or temporal trend assessment should be avoided, where the comparability and reliability of data had not been verified. The subgroup felt that OSPAR should be encouraged to cooperate with EEA so that indicators were developed in an intelligent manner.

The subgroup also discussed the paper MON 01/3/5-E (MCWG 2002 8.2.4/3) "Developing An Effective Temporal Monitoring Assessment Protocol Using Environmental Indicators". This paper presents information on the temporal trend of mercury concentrations in plaice muscle from Liverpool Bay, UK. The subgroup felt that this was an example of a good and effective indicator for temporal data. The good points about this paper were:

- the careful selection of compatible data sets;
- taking the variance in the data into account;
- effective statistical treatment;
- the condensed figures and ratios also display uncertainties;
- reference concentrations are shown;
- a map shows the region of the evaluation.

Such evaluations, prepared by experts that understand the data and the local situation, can provide the basis for more summary evaluations for either a larger region and/or for a wider range of contaminants. This paper could provide a framework for national reports on temporal trends in local regions.

The subgroup also discussed the paper (YIR01HS01) "Input of hazardous substances (cadmium, mercury, lead, zinc, lindane and PCB₇) into the North East Atlantic (including the North Sea) in the period 1990–1998" (MCWG 2002 8.2.4/7) from the European Environmental Agency. Within this paper, the EEA has included data from Belgium, Denmark, France, Germany, Ireland, the Netherlands, Norway, Portugal, Spain, Sweden, and the UK. The subgroup found that the quality of these data was of a very inhomogeneous character. Often, data were missing and in the calculations were assumed to be zero. In other cases, it was felt that there were orders of magnitude errors; e.g., the input of cadmium, riverine + direct, to the marine environment from Denmark is stated to be 50 grams. Several of these shortcomings are acknowledged in the report, but we must stress once again the importance of reliable data inputs to the indicator process. Within the report, an average trend for the four elements and the two groups of organic compounds are shown. The MCWG does not think that it is scientifically justified to present averages of substances that are so different in their chemical characters, and does not recommend this approach.

This report also shows how important it is to harmonise the data reporting system in order to be able to produce meaningful overview curves. Experience from the Baltic countries has shown that this is possible:

HELCOM. 1998. Third Baltic Sea Pollution Load Compilation 1998. Baltic Sea Environment Proceedings, No. 70. ISSN 0357–2994. 134 pages.

8.2.5 Review and comment on the outcome of an OSPAR pilot assessment integrating data on inputs of trace metals and concentrations of trace metals in biota and sediments [OSPAR request 2002/2.1]

The subgroup discussed a number of OSPAR documents in relation to this agenda item. Concerning MON 01/4/1-E (MCWG 2002 8.2.5/2) "Danish sediment data: availability and normalisation", the paper is an introduction to the

comprehensive sediment monitoring programme begun in 2000. The results of the first year's monitoring data for heavy metals and organic contaminants are presented. As normalisation parameters, the fraction < 63 µm, the lithium and aluminium concentrations, the TOC content, and the loss on ignition were determined. The main conclusion was that further work is needed to decide on the most appropriate normalisation procedure.

Regarding the paper MON 01/4/2-E (MCWG 2002 8.2.5/3) "Evolution of trace metal concentrations in sediments (fraction <20 µm) at selected sites in the German North Sea EEZ over a period of 15 to 25 years", the paper presents available data for temporal trend monitoring of heavy metals in sediments. Data are compiled according to general outlines presented at the MON meeting and discussed also by the Trace Metals Subgroup (MON 01/4/4-E; MCWG 2002 8.2.5./4). The paper contains all necessary information for an overall assessment of the temporal trends. To evaluate the comparability of the data with other monitoring stations or national reports, data on quality assurance and statements regarding the uncertainty of the data would be valuable. Additionally, a map could be provided for an easy overview of the locations of the sampling stations investigated, and a discussion of the temporal variation of heavy metal concentrations determined in sediments would be a useful addition to the text presented.

In general, the subgroup agreed with proposals for a mechanism for assessing temporal trends in contaminant concentrations in sediments, but felt that the reports should include the following information as an aid to interpretation:

- 1) information on total organic carbon content and other normalising parameters;
- 2) additional information on the grain size distribution, particularly the proportion of the fraction < 2 microns;
- 3) concentration levels from pre-industrial time, as reference values;
- 4) sedimentation rate at the different sites and age of the sediment layers (where undisturbed sediments were available).

Finally, the subgroup discussed the report MON 01/3/7-E (MCWG 2002 8.2.5/5) "Long term trends in mercury, cadmium and lead in the Forth". This paper illustrates the response of concentrations in biota (mussels and fish) and sediment to the reduction of inputs of Hg, Cd, and Pb to the Forth estuary. The biota show a clear response to the reduction in inputs that occurred primarily between 1981 and 1991. Hg and Cd in mussels and fish show a clear downward trend in these elements in the period 1983–2000. There is no clear trend for Pb. The subgroup would also recommend the inclusion of information on the uncertainties associated with the data and on quality assurance.

8.2.6 Discuss the need for the determination of the speciation of trace elements, particularly for lead, arsenic, tin, cadmium, chromium and mercury, where the behaviour and toxicity of the trace elements can vary dramatically between chemical species

It seems that additional information on the importance of chemical speciation is needed if the significance of environmental concentrations of trace elements in the marine environment is to be properly assessed. The subgroup also requested that QUASIMEME consider the inclusion of speciated metal determinations within their programme.

This topic was not discussed in detail during the meeting, but will be added to the agenda for MCWG 2003.

Action: All members of TMSG to bring relevant information on the speciation of the trace elements listed above to MCWG 2003, and its effects on behaviour and toxicity, to aid the development of future work programmes in this area.

Action: Jan Boon to seek information from his NIOZ colleagues regarding their work on iron in the ocean for MCWG 2003.

8.3 Organics Subgroup

8.3.1 Critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations; consider draft SIME request regarding OSPAR list of priority substances and how this might be addressed

MCWG has informally been asked by OSPAR (a formal request is expected at a later stage) to comment on "Substances on the OSPAR List of Chemicals for Priority Action". Patrick Roose, the Chair of SIME, presented the background. The request asks for advice on whether there are suitable analytical methods available to allow the measurement of environmental concentrations or effects of these substances, and whether any information exists on the presence of these chemicals in the environment. The Organics Subgroup, in consultation with the TMSG, has considered the list

provided, and an initial response is given in Annex 5. This reflects the knowledge and experience of subgroup members at the meeting rather than including the results of literature searches, and it may be possible to refine this at a later date.

The subgroup also briefly discussed other priority lists from international or regional organisations. The UNEP POPs list is now included in the Stockholm Convention, which was signed last year. A possible priority among those twelve substances, or groups of substances, was discussed without any conclusions being reached.

The same thing was done for the list of priority substances in the Water Framework Directive. A recent meeting of an EU working group (AMPS – Analysis and Monitoring of Priority Substances and Chemical Pollutants) at which analytical techniques and monitoring strategies for the measurement of these 33 substances in the aquatic environment were discussed, was also mentioned.

The present EU legislation requires the analysis of those compounds included in the Dangerous Substance Directive in surface waters. Several member states have not as yet fulfilled this requirement, and members in the subgroup exchanged information on ways to improve that, e.g., noting laboratories that are able to conduct these analyses.

Recommendation: In view of concerns amongst members that inappropriate analytical methods may become mandatory for work in support EU Directives (under CEN/ISO and in relation to the Water Framework Directive, for example), the Chair of MCWG should approach the Chair of the AMPS group for reassurance that all validated methods that meet the criteria and are fit for purpose will be accepted.

Recommendation: The Chair of MCWG, on behalf of ICES should approach the Chair of the AMPS group with a view to establishing a liaison between the two groups in areas of common interest regarding contaminant monitoring in the marine environment in which MCWG has considerable experience.

8.3.2 Review new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in flatfish

Michel Lebeuf gave an overview of data that he has generated for TCPM and TCPMe for samples supplied by other subgroup members. These compounds have been shown to bioaccumulate in biota, but their origin is, as yet, unknown. Levels of TCPM are generally higher than those of TCPMe. However, data are sparse, especially for fish, and the toxicology of these compounds is largely unknown. One possible source, which has been suggested, is the production and/or use of DDT, as traces of these compounds have been found in technical DDT formulations. Co-occurrence could, however, be due simply to a similarity in properties and behaviour. The results of an intercomparison exercise were presented at MCWG 2001, and showed that comparable data can be produced at least by a selected group of laboratories. The work within the subgroup focused specifically on the concentrations of these compounds in flatfish, both from Canada and Europe. Flatfish was chosen as a species occupying a lower level in the food chain, so as to be able to compare concentrations without the complication of the substantial bioaccumulation which occurs between fish and marine mammals. Detectable levels were found in all of the various species analysed, and concentrations in the liver were both generally higher than those found in the muscle tissue and were clearly related to the lipid content of the tissue. All in all, the results show no clear correlation with DDT levels. Concentrations in Canada are generally lower than those in Europe and there is no real difference between concentrations in flatfish from the Baltic Sea and in those from the North Sea. Unfortunately, it is not possible to establish whether a similar pattern applies to sediments due to the general lack of data. Another possibility which was raised is that these could be natural compounds. One way of evaluating this would be to determine the ¹⁴C content of these compounds, as it has been shown that synthetic man-made compounds do not contain detectable levels of ¹⁴C unless made from natural products. In practice this could, however, turn out to be very difficult to achieve. Moreover, a clear gradient from the port of Antwerp to the open sea was shown in sediments from the Western Scheldt, which seems to rule out natural sources. Another possibility is that both compounds were present in the earlier technical grade batches of DDT (used in Europe during the Second World War) and not in the later, more refined formulations. Again, the previously mentioned gradient in sediments of the Western Scheldt seems to rule out this possibility as well. Further useful information relating to these questions could be obtained by analysis of time trends of the concentrations in undisturbed sediment cores. A further suggestion was their possible presence as contaminants in Dicofol, a pesticide which is still used in Europe. As was mentioned before, very little is known of the toxicological properties of these compounds. A Japanese study (Minh *et al.*, 2001) was described, in which the concentrations of TCPM and TCPMe in human tissues (adipose tissue, liver and bile) were determined, and in which the authors observed age-dependent accumulation. The concentrations reported in this study are a fraction of those observed for PCBs, but their mere general presence seems to warrant further study. It is therefore recommended that the MCWG keeps these compounds on its agenda and gives a yearly update on the available information. Further research on this topic is also encouraged.

Action: All members of the Organics Subgroup should bring new information on TCPM and TCPMe to MCWG 2003.

Minh, T.B., Watanabe, M., Tanabe, S., Yamada, T., Hata, J., and Watanabe, S. 2001. Specific accumulation and elimination kinetics of *tris*(4-chlorophenyl)methane and *tris*(4-chlorophenyl)methanol, and other persistent organochlorines in humans from Japan. *Environmental Health Perspectives*, 109: 927–935.

8.3.3 Review new information on the analysis of PAH metabolites in bile, and critically review the robustness of the methods

Two fish bile candidate reference materials, CRM 720 and CRM 721, have been produced for the first time, and certification of four PAH metabolites was attempted in these samples. Twelve laboratories participated in the certification, one of which used two independent techniques. For each CRM, six replicate measurements were made of each analyte, which was measured on two different days in two different ampoules. Spiking experiments (three levels in triplicate) to a “blank” bile sample were conducted in order to estimate the recoveries. If necessary, the final results were corrected for recovery.

The feasibility of exposing flatfish to petroleum-derived or pyrogenic PAHs in a controlled fashion in mesocosms was demonstrated. No mortality was observed and the fish appeared to be in good health throughout. The petroleum/water mixing system was shown to provide a steady dose of petroleum micro-droplets to the mesocosm used for the crude oil exposure.

Three PAH metabolites (3-hydroxy benzo[*a*]pyrene (3-OH BaP), 1-hydroxy pyrene (1-OH pyrene) and 1-hydroxy phenanthrene (1-OH phenanthrene)) showed no sign of degradation during a period of 13 months, not even when held at room temperature. Nevertheless, for long-term stability, storage of the CRMs at -20°C or a lower temperature is recommended. No stability data could be obtained for 2-hydroxy naphthalene (2-OH naphthalene) in these samples, although there is no reason to assume that that compound would be significantly less stable than the other PAH metabolites. Long-term stability tests, and a test aimed at studying the short-term stability (e.g., during shipment) and the effects of repeated opening of the transport container have shown that shipment on ice is feasible.

An inhomogeneity was found in the case of 3-OH BaP in CRM 720, and this must be added to the overall uncertainty of the certified value. 1-OH pyrene and 1-OH phenanthrene passed the homogeneity test in both CRMs. No homogeneity data could be obtained for 2-OH naphthalene.

The calibrants and test samples were prepared in a solvent mixture of ethanol/water 80:20 v/v and are not suitable for direct injection into a gas chromatographic column. Extraction into a volatile non-polar solvent is, of course, possible, but could introduce additional errors. Different solvents and more volatile anti-oxidants were tested, but the preparation of calibrants from crystals *in situ* in the participating laboratories is preferred. Ascorbic acid can be used to preserve standard solutions if they are to be used for HPLC analysis, but they are wholly unsuitable for use with GC-MS analysis.

The preparation of good, reliable calibrants is an essential analytical step, however, an effective anti-oxidant suitable for use with both HPLC and GC analysis was not found. The main problem with shipping PAH metabolites in solution is that the presence of oxygen promotes degradation. The metabolites in natural samples are not subject to the same problem since they exist as conjugates rather than free compounds.

The compound 1-OH chrysene was not included in the certification, as it was found to be only a minor metabolite even in chrysene-injected fish. Alternative chrysene metabolites such as chrysene-1,2-diol were considered, but these were also excluded as they, too, were only minor components in the bile.

The pyrene glucuronide conjugate was used in tests of the efficiency of the enzymatic hydrolysis step. This was generally found to be straightforward and not critical to the analysis as long as the batch of enzyme used was within its expiry date.

The intercomparison exercise showed satisfactory results for the unknown standard solutions, both at the 50 ng g^{-1} and at the 100 ng g^{-1} level (nominal).

Following the technical discussion with the participating institutes and with the EC, the following PAH metabolites were recommended for certification:

1) CRM 720 Flounder bile from fish exposed to contaminated sediment:

- 1-OH pyrene
- 1-OH phenanthrene
- 3-OH benzo[*a*]pyrene

for 2-OH naphthalene, only a table of raw data will be presented.

2) CRM 721 Plaice bile from fish exposed to oil:

- 1-OH pyrene

for 1-OH phenanthrene, only a table of raw data will be presented.

For the other PAH metabolites, 3-OH benzo[*a*]pyrene in the plaice bile and the 1-OH phenanthrene in the flounder bile, there was insufficient reliable data either to propose certification or provide an indicative value.

Details on the actual concentrations of the PAH metabolites in these CRMs will be available once the EC has certified the candidate materials.

8.3.4 Review new information on the use of membrane systems for sampling

Ton von der Zande presented further developments and new results from a collaborative research project on the first phase of implementation of semi-permeable membrane devices (SPMDs) into routine monitoring programmes in the Netherlands. After a short recapitulation of the samplers and passive media used previously (such as semi-permeable membranes of low-density polyethylene filled with triolein lipid or used as empty polyethylene tubing), the new design of silicone rubber sampler was presented. It was stressed that most of the samplers, when used for highly hydrophobic compounds ($K_{ow} > 5$), are still in the linear uptake phase when removed from the environment at the end of the sampling period because the equilibration time for these compounds is very long. This makes proper calibration and the establishment of uptake rates for passive samplers essential. The influence of environmental conditions such as hydrodynamics, temperature, and fouling of the samplers on uptake rates were discussed. In order to compensate for uptake rate variations, the use of performance reference compounds (PRCs) spiked onto the sampling devices before deployment was also presented. These compounds (fully deuterated PAHs provide a typical example) are spiked at known concentrations and their residual concentrations are determined after recovery, thereby allowing the kinetics of reverse diffusion (and so of uptake) to be estimated.

The new system, known as a solid phase sampling device (SPSD), consists of silicone film (0.5 mm thick) held in stainless steel containers for deployment. A programme of preparation, conditioning, spiking, laboratory and field testing were conducted with this sampler. The results of this testing indicate the importance of proper storage due to possible contamination of the sampler, both before and after sampling, as well as during storage and transport. The deployment undertaken during summer time in the Marsdiep, near Texel, indicated very intense biofouling of a sampler. The use of different PRCs showed that, for instance, lower molecular weight compounds such as anthracene-*d*₁₀ reached equilibrium after 6 weeks' exposure. An acceptable repeatability of uptake for CB153 was also demonstrated.

The first deployment conducted within an active Mussel Watch Programme with caged mussels was carried out at eight locations over more than 40 days' exposure time. The results showed higher uptake rates for lower molecular weight compounds in the SPSP than for mussels. In contrast, higher molecular weight compounds were taken up to a greater degree by the mussels, probably due to their uptake from suspended particulate material as well as from the dissolved phase. Therefore, the distribution patterns differ between the two types of samples, but nevertheless the contamination ranges can be established using the SPSP. The use of SPSP for the uptake of brominated flame retardants was also demonstrated.

In conclusion, the silicone film SPSP samplers appear relatively easy to handle. However, further developments need to be made, and some constraints such as biofouling and variable kinetic rates of uptake must be overcome. The use of silicone films seem to be a good alternative diffusive media to polyethylene, as the equilibrium is reached more quickly and a wider range of organic compounds could eventually be monitored. Passive samplers offer a number of advantages over conventional techniques, and can also supplement "mussel watch" type studies where these animals are not available naturally.

The discussion revealed a general interest in passive samplers and their *in situ* deployments. These samplers provide simple, inexpensive, and readily available equipment for environmental monitoring of chemical contamination in the

water column. Their use for the sampling of contaminants in air was also reported. The discrimination (lower uptake rates) seen for higher molecular weight compounds may also be due in part to partitioning of these compounds to organic colloids and humic substances. It was mentioned that this technique, once fully standardised, could eventually become a global monitoring alternative for organic contaminants, generating comparable, mutually acceptable data, and aiding harmonisation within relevant EU and international programmes.

Huckins, J.N., Tubergen, M.W., and Manuweera, G.K. 1990. Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavailability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere*, 10: 533–552.

Booij, K., Sleiderink, H.M., and Smedes, F. 1998. Calibrating the uptake of semipermeable membrane devices using exposure standards. *Environmental Toxicology and Chemistry*, 17: 1236–1245.

Booij, K., Smedes, F., and van Weerlee, E.M. 2002. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere*, 46: 1157–1161.

Booij, K., van Weerlee, E.M., Fischer, C.V., and Hoedemaker, J. 2000. Passive sampling of organic contaminants in the water phase. Netherlands Institute for Sea Research, 16 pp.

Action: Ton van der Zande to report new information concerning the development and use of these sampling devices to MCWG 2003.

8.3.5 Review new information on the monitoring and analysis of toxaphene

Michel Lebeuf presented work undertaken by himself and his colleagues on toxaphene in seals in eastern Canada. Data for six toxaphene congeners, P26, P40/41, P44, P50 and P62, were presented for grey, harp, and hooded seals from the Gulf of St. Lawrence, for harbour seals from the St. Lawrence Estuary, and for ringed seals from northern Quebec. Clear differences in concentrations between species were evident, with hooded seals being more contaminated than ringed seals (mean value 595 ng g⁻¹ wet weight and 15.6 ng g⁻¹ wet weight, respectively). Levels of toxaphene in seals in eastern Canada were, however, not higher than those reported for seals in the northern hemisphere in general. Species differences were also evident from the congener patterns observed, especially P50/P62 ratios which reached a value of 20 for harp seals, compared to about 2 in ringed seals.

During the discussion, it was noted that *in vitro* studies using microsomes from harbour seals had indicated the elimination of the congener P62, which was not observed using those from cetaceans. This supported the idea that P62 may be metabolised more easily than P26 or P50 in some seal species. It is also likely that chirality is important in this congener metabolism. Further research on the metabolism of toxaphene congeners in marine biota is warranted. Other current toxaphene research activities being undertaken by Michael Oehme's group at the University of Basle, and by Hester Kramer at the University of Utrecht were also noted.

Gert Asmund presented new data on toxaphene in terrestrial and marine biota collected in Greenland as part of the Arctic Monitoring and Assessment Programme (AMAP). For marine biota, particularly high levels were found for narwhals from northern Greenland, and in walrus from east and northwest Greenland. This is an important finding as these animals form an important part of the diet for the indigenous people. It was suggested that the risk assessment model presented in the recent EU Fair-funded MATT project (2000 MCWG report) may assist in assessing the potential risk to the local population.

Data for toxaphene concentrations in a range of animals from Greenland are given in Table 8.3.5.1, below. This includes information for mussels, fish (cod), birds (murre, Eider ducks, ptarmigan, and guillemot eggs), narwhal, walrus, and three species of terrestrial animals (lamb, musk ox, hare).

Table 8.3.5.1. Examples of toxaphene concentrations in Greenland animals ($\mu\text{g kg}^{-1}$).

	% lipid	Total toxaphene	P26	P50	P62	$\Sigma(\text{P26}+\text{P40}+\text{P41}+\text{P44}+\text{P50}+\text{P62})$
Blue mussel	2					0.21
Murre liver		53	0.11	0.16	< 0.05	
King Eider liver		14	0.02	0.19	0.05	
Common Eider liver		12	0.09	0.32	< 0.05	
Ptarmigan liver		0.75				
Ringed seal blubber		265	11	11	3.2	
Ringed seal blubber	92					49
Ringed seal muscle	5.5	8.6				
Cod liver	35					41
Black guillemot egg	10					58
Walrus blubber East Greenland	84	1,610				
Walrus blubber Northwest Greenland	85	292				
Narwhal blubber	96	4,260				
Lamb, musk ox, hare muscle		< 0.1				

Action: Michel Lebeuf to report on relevant studies on toxaphene currently under way in Canada under the Toxic Substances Research Initiative to MCWG 2003.

8.3.6 Review new information concerning polybrominated diphenylethers (PBDEs)

Jacob de Boer presented data for polybrominated diphenylethers (PBDEs) in the aquatic environment from a recent BSEF-funded study, which involved three European research groups (RIVO, NIOZ and CEFAS) (see also Section 7.6, above, for complementary information on the same topic). It was shown that PBDEs, in particular tri- to hexa-BDEs, are accumulating in food chains with biomagnification factors (BMFs) ranging from 5 to 20. BDE209 was not found in biota samples, and if this compound bioaccumulates at all, then its BMF must be very low. PBDEs were also found in surface sediments, and some river surface sediments (from the Mersey, Clyde, and the Western Scheldt) showed concentrations of BDE209 above 1 mg kg^{-1} dry weight. As part of a mass balance study, it was shown that penta-mix formulation-related congeners were higher in the western part of the North Sea than elsewhere, suggesting an input from the UK east coast. The PBDE input from UK estuaries was estimated to be 0.3 to 2 tonnes per annum (tpa) for BDE209 and 0.06 to 0.2 tpa for the sum of the other BDE congeners. Roughly 50–70 % of that input derives from dredging and disposal activities, and the remainder from natural transport. Recent trend studies indicated that environmental levels of penta-mix related congeners in Europe are tending to decrease, but exceptions are found in several UK rivers and in cod liver from the central North Sea. Concentrations of BDE209 have increased by 50–100 % in sediments at specific locations over the past six years, and sediment core analyses confirm the increase. A parallel increase of tetra- to hexa-BDE congeners was not seen. Consequently, it is unlikely that tetra- to hexa-BDE congeners are being formed in significant amounts from BDE209 in the environment. Sediment core analyses show a time trend relationship in line with production data, and consequently it is unlikely that natural production is a major source of PBDEs.

Two recent papers described the method development and intercomparison studies included within the BSEF-funded project described above:

de Boer, J., and Cofino, W.P. 2002. First world-wide interlaboratory study on polybrominated diphenylethers (PBDEs). *Chemosphere*, 46: 625–633.

de Boer, J., Allchin, C., Law, R., Zegers, B., and Boon, J.P. 2001. Method for the analysis of polybrominated diphenylethers in sediments and biota. *Trends in Analytical Chemistry*, 20: 591–599.

A second round of the interlaboratory study, involving more than 40 laboratories from Europe and North America, is presently under way. In addition, two reference materials (one fish and one sediment) are in preparation and are expected to be available within the next few years. A workshop on analytical methods for the determination of PBDEs will be held during October 2002 in Barcelona alongside the QUASIMEME Conference. A new European project on flame - integrated risk assessment (FIRE) will start in September 2002, and will focus primarily on toxicological studies of PBDEs but will also include a large monitoring programme in both the marine and freshwater environments.

It was recommended that brominated flame retardants should be included in international monitoring programmes, beginning with the PBDEs, since validated analytical methods and quality assurance programmes are available. If one-off surveys are to be conducted, then the programme should be expanded to include other similar compounds now in use, such as tetrabromobisphenol-A (TBBPA) and hexabromocyclododecane (HBCD).

Action: Michel Lebeuf should report on relevant studies on PBDEs currently under way in Canada to MCWG 2003.

Action: Jacob de Boer should report on progress within the FIRE project to MCWG 2003.

Recommendation: MCWG recommends to OSPAR that PBDEs should be considered for inclusion within the JAMP programme, as fully validated methods for their determination are now available.

8.3.7 Propose data products that could be developed for organic contaminants in marine organisms in relation to environmental state indicators, based on OSPAR monitoring data [OSPAR 2002/5.1]

Following discussions in all subgroups, this topic was considered in plenary (see Section 8.1.8).

8.3.8 Review and comment on the outcome of an OSPAR pilot assessment integrating input data, and data on organic contaminants in biota and sediments [OSPAR 2002/2.1]

The idea is to link input data to environmental concentrations of contaminants, such as CBs, organochlorine pesticides, PAHs and organotin compounds, in sediments and biota. This is the so-called “joint” or “integrated” assessment requested by OSPAR. This is a substantial task which we did not feel could be carried out simply within the framework of the MCWG meeting.

It is known that transport models for contaminants are currently being developed for regional areas, such as the Seine estuary in France. Data about, for example, topography, hydrogeology (river flows, ocean water flows), contaminant levels in the different environmental compartments: water (dissolved and particle-associated fractions), sediments, biota and air should be known or should be estimated, together with the respective contaminant transfer rates between the different ecological compartments or systems, the volumes of the compartments and the breakdown rates of each contaminant in each compartment of a given system. The relationship between contaminant levels in biota and sediment at one side, and the various inputs at the other, is not straightforward. Also, there is doubt about the quality of the input data that have been collected until now. At specific locations there may be a shortage of data on contaminant concentrations in the environment. Also, temporal trend data may be insufficient in some cases.

A concerted international action would be necessary to develop relationships between input data and environmental levels, and collaboration between ICES and OSPAR on a broader scale than just marine chemistry would be required.

8.3.9 Review specific text in Annexes 7, 8 and 9 of the draft report of SGQAC 2002

The subgroup reviewed the annexes and a first general recommendation for the introduction of all annexes was to clearly state that the guidelines are purely advisory, and by no means constitute operational procedures. Users of the guidelines should be encouraged to make a thorough study and validation of the procedures that they intend to use.

Considering the annexes in turn, the following comments were made:

There were no major comments on Annex 7, as the text is, to a large extent, based on a previous publication by de Boer and Smedes (1998), also reviewed by this subgroup.

Smedes, F., and de Boer, J. 1998. Chlorobiphenyls in marine sediments: Guidelines for determination. ICES Techniques in Marine Environmental Sciences, No. 21.

In Annex 8, the subgroup pointed out that alkaline saponification is not mentioned as an extraction method for PAHs in sediments, although it is a commonly used and very efficient method. Not only does it eliminate organic sulphur, but also other interfering compounds such as lipids, resulting in an extract that is very easy to clean up. Also, polyethylene is not considered to be a suitable sample container for samples for PAH analysis, due to the presence of phthalate plasticisers which can leach into the samples and cause interference in chromatograms. Freeze-drying is also not recommended as back streaming of the oil from the rotary pump generating the vacuum may contaminate the sample and, in addition, the more volatile PAHs (such as naphthalene) can easily be lost during the process. Similarly, concentrating the extract by evaporation, e.g., in a rotary evaporator, can easily result in losses of PAHs. Care should be taken that the extracts are never evaporated to dryness and the water bath temperature should be carefully controlled (< 30 °C). In the guidelines, both the HPLC-fluorescence and GC-MS methods are considered to be equally valid approaches. Although this may be the case for the parent PAHs, it is certainly not the case for alkylated species, as this range of compounds cannot be satisfactorily analysed using HPLC. This is particularly relevant for the future as additional PAHs, including both additional parent compounds of 5- and 6-rings, and the alkylated PAHs, gain more and more interest. Similar considerations apply to analysis by GC-FID, and this technique should not be recommended either. Moreover, the guidelines refer to GC-MS in the SIM mode as the preferred way of quantifying PAHs. Full-scan MS using an ion trap, which operates with the same sensitivity as SIM, is a much more powerful technique and should, at least, be mentioned. The GC column diameter and length are also discussed in the paper. Although it is indeed true that longer columns, or columns with a smaller internal diameter, will generally yield better resolution, such changes will not yield any practical benefit in terms of resolving critical pairs of determinands. The use of several deuterated PAHs spanning the entire MW range as internal (surrogate) standards should also be encouraged, as well as the use of a deuterated recovery standard.

In the guidelines, MCWG was invited to comment on a series of specific questions (printed in italics in the SGQAC report) and these are dealt with in the following text:

For Annex 8 on PAHs in sediments in the draft SGQAC report:

Paragraph 5.1. The contact time required for desorption of PAHs from sediments may vary with sediment type, although if alkaline saponification is used, 1.5 h under reflux is sufficient. Other extraction techniques, such as solvent extraction, may require much longer time periods (up to 24 h). If there is any doubt, a second extraction step should be performed and the quantities of PAHs in the two extracts compared.

Paragraph 5.2. A recovery during the first extraction step of over 90 % would be considered adequate.

Paragraph 6.1. Using HPLC and measuring concentrations using peak height, a 50 % valley should be adequate.

Paragraph 6.2.4. For GC-MS, peak area is generally used, and a 10 % valley would represent a good separation. Less resolved peaks may also be quantified (for instance, by dropping perpendiculars to the baseline), but increasing errors may result.

Paragraph 6.2.5. The use of GC-FID is not recommended.

Paragraph 6.3. Using GC-MS on a modern instrument, retention times should be reproducible to within ± 0.05 minutes, and additionally there are deuterated analogues of many of the parent compounds present for comparative purposes. For HPLC, reproducibility of retention times may be less good, but should certainly be within ± 1 minute.

In Annex 9, the subgroup felt that some updating of the text should be recommended, so as to take account of new extraction techniques, for instance microwave-assisted solvent extraction, which are now being applied to PAH analysis.

8.3.10 Review new information regarding dioxins and dioxin-like PCBs

Information was provided by Jacob de Boer on new tolerance levels for polychlorinated dibenzo-*para*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (PCBs) in foodstuffs.

Two new EC Council Regulations setting maximum levels of PCDDs and PCDFs (“Dioxins”) in foodstuffs (Regulation No 2375/2001), including fish, and in animal nutrition (Regulation No. 2001/102/EC) have been adopted by the European Commission, and will apply from 1 July 2002.

In 2001, the European Scientific Committee on Food (SCF) recommended a tolerable weekly intake (t-TWI) of 14 pg WHO-PCDD/F-TEQ per kg body weight (bw), which has been used as a basis for these new standards in foodstuffs.

The maximum limit value for fish muscle meat, fishery products and products thereof has been set at 4 pg WHO-PCDD/F-TEQ g⁻¹ fresh weight. The maximum limits also apply to crustaceans (excluding the brown meat of crabs), and to cephalopods without viscera. Due to a repeated deficiency in the availability of data (some countries do not have methods available for CB123 and CB114, although CB105, CB118, and CB126 can be measured properly), dioxin-like PCBs are still excluded from inclusion in these calculations of total-TEQ values. The supposed inclusion of dioxin-like PCBs in the limits to be set will be reviewed for the first time by December 2004. In general, however, the PCB contribution to the total-TEQ is higher than the contribution of the PCDDs and PCDFs together. It is therefore recommended to include PCBs in these maximum limit values as soon as possible.

In order to establish baseline values for dioxins in wild and farmed fish, the Food Safety Authority of Ireland and the Irish Marine Institute have determined the concentrations of dioxins and dioxin-like CBs in salmon and trout. Levels of PCDD/Fs in both wild and farmed fish were all well below the new EU regulatory limit value. They found that dioxin levels in farmed salmon appeared to be higher than levels in (proven) wild salmon caught in NW Ireland. Farmed salmon contained 13 to 38 pg g⁻¹ WHO-PCDD/Fs+PCBs-TEQ lipid weight (n = 15), whereas the concentrations in wild salmon varied from 5 to 14 pg g⁻¹ WHO-PCDD/Fs+PCBs-TEQ (n = 15). PCB levels in these fish were on average 2.3 times higher than dioxin levels in wild fish and 3.6 times higher than dioxin levels in farmed salmon. Findings for farmed trout were similar, and they contained 3.4 times higher PCB levels than wild trout.

Furthermore, the concentration of CB153 correlated well with the concentration of dioxin-like PCBs (TEQ) and could therefore be used as a potential indicator for dioxin-like PCB contamination in some species.

Jacob de Boer announced the start of two new European research projects: DIAC (DIOXIN Analysis by Comprehensive multi-dimensional gas chromatography) in October 2001, and DIFFERENCE (Dioxins in Food and Feed – Reference methods and new certified reference materials) in February 2002. Both projects will focus on new, alternative methods for the analysis of dioxins and CBs in food and animal feed. The proposed methods include two bio-analytical methods: the Calux bioassay and the DELFIA immunoassay, and two chemical analytical methods: Comprehensive multi-dimensional GC and low-resolution GC/MS-MS.

More information can be obtained from a newsletter, and the website: www.dioxins.nl.

Action: Jacob de Boer should provide an update on progress within the DIFFERENCE project at MCWG 2003.

8.3.11 Review new information concerning polycyclic aromatic hydrocarbons

Patrick Roose gave a presentation of the results from an OSPAR INPUT pilot study on riverine inputs of PAHs to the marine environment. The study included method development, surveys, and calculations of fluxes from selected river systems in Europe. The final report “International Pilot Study for the determination of Riverine Inputs of Polycyclic Aromatic Hydrocarbons (PAHs) to the Maritime Area on the basis of a harmonised methodology” can be obtained by contacting Patrick Roose.

8.3.12 Review information on new contaminants, and consider the need for new overviews of contaminants

Action: Norbert Theobald and Jacek Tronczynski will prepare a review note on phenylurea compounds (diuron and isoproturon) in the marine environment for MCWG 2003.

Bo Jansson mentioned the possible presence of mirex in marine environmental samples.

Action: All Organics Subgroup members should check their chromatograms for the presence of mirex and report their findings to Bo Jansson during the intersessional period. Bo Jansson will report the findings to MCWG 2003.

Finally, Jacob de Boer stood down as Chair of the Organics Subgroup and Evin McGovern was appointed to take his place. Both the subgroup and MCWG thanked Jacob for the substantial effort that he has put into his role as Chair, and wished Evin well for the future.

8.4 Chemical Oceanography Subgroup

In the unavoidable absence of Stig Carlberg, Alain Aminot acted as Chair of the subgroup for this meeting.

The subgroup felt it appropriate to note that chemical oceanography is defined as using chemical measurements to describe and understand processes, including biological production and physical processes, taking place in the marine environment. The complexity of this is demonstrated, for example, when trying to distinguish between anthropogenically derived and naturally occurring nutrients. In the context of Ecological Quality Objectives (EcoQOs) and nutrients, this means that such objectives may differ considerably depending on the ecosystem in question. In the text below, considerable caution has been exercised because of this complexity.

8.4.1 Review present knowledge about total nitrogen, total phosphorus, and total organic carbon in sea water, their speciation, and arguments for their use in monitoring programmes

The total amount of an element or a class of compounds in the water is the sum of the concentrations of all forms of these elements. These “total amounts” include inorganic and organic as well as particulate and dissolved components, all of which undergo different fates and behaviours.

It may be worthwhile, for the characterisation of aquatic ecosystems, to have some information about the total amounts of nitrogen, phosphorus, and carbon present in the system. However, it is questionable whether one can expect dramatic changes in concentrations of total nitrogen (TN), total phosphorus (TP), or total organic carbon (TOC) within short time scales, as the total amounts of these elements are not affected by turnover processes within the system. In open systems such as coastal waters, total amounts are altered by continental inputs (from rivers and the atmosphere), sedimentation of particulate material, and biological processes including nitrogen fixation and denitrification.

In marine ecosystems, the concentrations of inorganic nutrients limit the growth of phytoplankton. Nevertheless, it is well documented that, even if concentrations of inorganic nutrients are below detection limits, remineralisation of dissolved and particulate organic material can occur to support primary production. Moreover, the speciation data from the Bay of Seine (English Channel, France), showed that the labile fraction of organic matter (i.e., that which can be remineralised within the productive season) accounted for only a low proportion of the total dissolved organic material. Most of the dissolved organic material is therefore composed of refractory material which is not involved in the carbon cycle on seasonal time scales.

If a better understanding of marine ecosystem cycles is required, it is more useful to determine specific components such as dissolved organic nitrogen, phosphorus and carbon, as well as particulate phosphorus, organic nitrogen and carbon (PP, PON, POC), or even additional parameters (e.g., labile and refractory fractions of these). It is under discussion whether these parameters may be necessary to define ecological quality objectives to characterise the status of aquatic ecosystems. It is also important to note that QUASIMEME results showed that laboratories could not determine TN and TP as well as they could determine the inorganic species. If these parameters are required for special purposes, then we need better quality control on the data.

The subgroup therefore does not recommend the routine determination of TN, TP, or TOC in monitoring programmes unless local studies have previously shown a reason for measuring these parameters. In general, a good knowledge of the system can be obtained by the determination of dissolved inorganic nutrients and particulate matter (POC, PON, PP) resulting from their consumption. These separate parameters can be measured with an acceptable reliability. However, it should be kept in mind that the interpretation of particulate matter data may also be difficult in areas where the contribution of continental or resuspended materials is not negligible. In such instances, chlorophyll *a* is probably a better marker of the biomass produced from nutrient consumption.

8.4.2 Review studies under way in OSPAR on ecological quality objectives for the North Sea with regard to nutrients and eutrophication effects

The discussion in the subgroup was mainly based on the paper, “Current status of Ecological Quality Objectives for the Greater North Sea with regard to Nutrients and Eutrophication Effects” (EcoQOs-eutro, EUC 01/5/3 – Rev 1).

The subgroup agreed in principle that it was necessary to have objective criteria for assessing nutrient enrichment and ecological quality objectives. However, some of the “Agreed Harmonised Assessment Criteria” require clarification and may not be relevant to all sites at all times.

The OSPAR region—in common with other coastal areas—is subject to large natural temporal and spatial variations in nutrient concentrations. One of the major deficiencies of the proposed criteria is that transboundary nutrient transports are not adequately taken into account. This is particularly important for inorganic nutrients, since the natural fluxes in the North Sea are many orders of magnitude greater than the anthropogenic fluxes, which are also likely to be localised in space and time. Care must therefore be used in interpreting nutrient data, since misleading or inappropriate conclusions may be drawn. For example, “winter concentrations” of nutrients are only appropriate for the description of phytoplankton development in summer if it is confirmed that transboundary effects are not significant over the intervening period. Moreover, the definition of “winter concentrations” is too broad, as this parameter is defined by the status of the ecosystem (maximum accumulation of nutrients and minimum primary productivity) and not by a specific time of the year. The start of the phytoplankton spring bloom may not necessarily occur at the same time for all stations.

The subgroup was also concerned that the criteria listed as “Assessment Criteria” are not necessarily universally applicable and recommended that the listed criteria be checked for relevance to local conditions. For example, natural perturbations such as wind-induced mixing or upwelling need to be considered before deciding whether critical values have been exceeded. The rationale for assigning values to “background concentrations” and “elevated concentrations” is not always clear since we have limited information as to how the ‘spatial/historical background concentrations’ were fixed. The relevant information needs to be readily available. In addition, if the normal concentration of a nutrient is low, an increase of >50 % may not be environmentally significant. It is also not clear from the document what criteria will be used to define the boundaries of problem areas (PA). Given these concerns, it is surprising that, in Document EUC 01/5/2-Add.1-E, Item 9), no comments are included under the heading *Remaining problems and suggested actions*.

The scientific background behind the Ecological Quality Objectives, strategies to support their evaluation, and information on their proper use need more clarification and ongoing discussion.

8.4.3 Review recent developments in production and availability of suitable reference material for analysis of chemical oceanographic variables in sea water

This information has been incorporated into Section 8.1.1 (see above).

8.4.4 Discuss OSPAR activities regarding the assessment of eutrophication, nutrient concentrations and trends, and how ICES might contribute to this process

Discussions of agenda items 8.4.4 and 8.4.5 were merged since their overall content is complementary and no document was available for discussion under item 8.4.5. Many documents from OSPAR and the EEA were provided for item 8.4.4 just prior to the meeting and some time was therefore required to review these documents. It should be mentioned that discussion under this item is, to some extent, connected with that under Section 8.4.2, above.

The documents from the EEA concerned indicator fact sheets and dealt with nitrogen, phosphorus, and chlorophyll *a* concentrations in rivers and coastal waters. The assessment of concentration trends is achieved using indicators which have been selected to give an answer to policy issues as follows:

EEA Indicator	EEA Policy issue
River nutrients	Are nutrient reduction policies resulting in lower levels of nutrients?
Nutrients in coastal waters	Are nutrient reduction policies resulting in lower levels of nutrients?

The subgroup examined the relevance of the policy issues and of the corresponding indicators.

With regard to nutrients in rivers, there is an obvious direct influence of a reduction of inputs from agricultural or urban sources on water concentrations of nutrients. Thus, the policy and the indicator are both consistent.

With regard to nutrients in coastal waters, the problem is more complex. Contrary to the situation for anthropogenic contaminants, nutrients are natural compounds present at significant concentrations in marine systems and they undergo a variety of processes, which can induce large natural variations. These variations in seawater concentrations, in addition to the dilution factor due to the mixing of river water and sea water, may mask any reductions in concentration in the freshwater source. It is therefore questionable whether the policy issue stated for nutrients in coastal waters is relevant. Since eutrophication is the main problem, and nutrients are not contaminants by themselves, the subgroup wondered whether the policy issue relating to nutrients in the coastal waters depends strongly on local conditions.

The subgroup agreed with the EEA statement concerning phosphate and nitrate concentrations in coastal waters that "...trends in nutrient concentrations as such cannot be directly related to measures taken". This does, however, appear to contradict the stated policy issue. The subgroup also considered that it is not possible to make meaningful statements about changes in nutrient concentrations by aggregating data from multiple stations with widely different hydrographic conditions. Presentation of data should always take this aspect into account and, at least, be accompanied with a map showing the location of the stations.

The OSPAR documents under consideration dealt with the assessment of inputs and concentrations. The document from Germany shows that despite a significant reduction of inputs measured in rivers (~30 % over 15 years), no similar trend can be identified in the German Bight. On the contrary, the documents from Denmark, Belgium, and the Netherlands mention a connection between reduction of inputs and concentrations in the medium. However, these countries assess concentration trends in estuaries (Denmark) or at a salinity of 20 (the Netherlands). Hydrographic conditions, residence times, and freshwater proportions obviously differ significantly from one area to another in these examples. This again points out the major effect of local conditions on trend assessments. Therefore, the subgroup call the attention of the bodies in charge of trend assessments to the risk of misinterpretations and biased conclusions that could result from non-comparable data or data products.

9 PLENARY DISCUSSION OF SUBGROUP WORK

No additional discussions at this stage.

10 ANY OTHER BUSINESS

The statements regarding the assessment of laboratory performance supplied by David Wells in Section 4.3 (see above) were presented and discussed. Members of MCWG felt that they were unable to fully endorse them at this stage, as the time for discussion and reflection were not sufficient for them to fully judge the outcome in the future. It was agreed that this suggested model would be adopted for MCWG 2003, and reviewed at that meeting.

11 RECOMMENDATIONS AND ACTION LIST

These are appended to the report as Annexes 6 and 7.

12 DATE AND VENUE OF THE NEXT MEETING

MCWG discussed the venue and dates of the next meeting. One of the members, Anne Talvari, kindly offered to host the 2003 meeting of the MCWG at the Estonian Environmental Research Centre in Tallinn. MCWG acknowledged the invitation with appreciation. It was decided to plan the meeting for week 10 (3–7 March 2003), subject to confirmation by the host institute.

13 CLOSURE OF THE MEETING

The members of the MCWG expressed their appreciation to Peter Woitke, and to Sabine Guenther, who had assisted Peter so effectively in making arrangements for the meeting. The Chair thanked the participants for all their hard work and support during his second meeting as Chair, and closed the meeting at 12.30 hrs on 8 March 2002.

ANNEX 1: LIST OF PARTICIPANTS

Name	Address	Telephone	Telefax	E-Mail
Alain Aminot (Acting COSG Chair)	IFREMER-Brest P.O. Box 70 29280 Plouzané France	+33 2 98224361	+33 2 98224548	aaminot@ifremer.fr
Gert Asmund (TMSG Chair)	National Environmental Research Institute Department of the Arctic Environment Frederiksborgvej 399 DK-4000 Roskilde Denmark	+45 46301925	+45 46301114	gas@dmu.dk
Victoria Besada (TMSG)	Instituto Español de Oceanografía Centro Oceanográfico de Vigo Apartado 1552 E-36280 Vigo Spain	+34986 492111	+34986 492351	victoria.besada@vi.ieo.es
José Biscaya (OSG)	Instituto Hidrográfico Rua das Trinas, 49 1293-049 Lisbon Portugal	+351 213914103 +351 213914000	+351 213914199	quimica@hidrografico.pt
Jacob de Boer (OSG)	Netherlands Institute for Fisheries Research P.O. Box 68 Haringkade 1 1970 AB IJmuiden The Netherlands	+31 255564736	+31 255564644	j.deboer@rivo.wag-ur.nl
Jan Boon (OSG)	Royal Netherlands Institute for Sea Research (NIOZ) P.O. Box 59 1790 AB Den Burg / Texel The Netherlands	+31 222 369466	+31 222 319674	boon@nioz.nl
Erik Evers (OSG)	National Institute for Coastal and Marine Management/ RIKZ P.O. Box 20907 2500 EX The Hague The Netherlands	+31 70 3114312	+31 70 3114600	h.g.evers@rikz.rws.minvenw.nl
Lars Føyn (COSG)	Institute of Marine Research P.O. Box 1870 Nordnes N-5817 Bergen Norway	+47 55238501	+47 55238584	lars@imr.no
Hannu Haahti (COSG)	Finnish Institute of Marine Research Asiakkaankatu 3A P.O. Box 33 Fin-00931 Helsinki Finland	+359 9613941	+358 961394494	haahti@fimr.fi
Michael Haarich ¹ (OSG)	Bundesforschungsanstalt für Fischerei Institut für Fischereiökologie Palmaille 9 D-22767Hamburg Germany	+49 410251128	+49 4102898207	haarich.ifo@bfa-fisch.de

¹ Address and telephone/fax will change in summer 2002.

Name	Address	Telephone	Telefax	E-Mail
Uwe Harms (TMSG)	Bundesforschungsanstalt für Fischerei Institut für Fischereiökologie Palmaille 9 D-22767 Hamburg Germany	+49 4038905289		Harms.ifo@bfa-fisch.de
Bo Jansson (OSG)	Institute of Applied Environmental Research Stockholm University S-106 91 Stockholm Sweden	+46 86747220	+46 87581360	bo.jansson@itm.su.se
Jarle Klungsoyr (OSG)	Institute of Marine Research P.O. Box 1870 Nordnes N-5817 Bergen Norway	+47 55 238498	+47 55 238584	Jarle.Klungsoyr@imr.no
Robin Law (MCWG Chair)	CEFAS Burnham Laboratory Remembrance Avenue Burnham on Crouch Essex CM0 8HA, UK	+44 1621787271 (Direct)	+44 1621784989	r.j.law@cefas.co.uk
Michel Lebeuf (OSG)	Institut Maurice-Lamontagne C.P. 1000 850 Route de la mer Mont-Joli, Quebec Canada G5H 3Z4	+1 4187750690	+1.4187750542	lebeufm@dfo-mpo.gc.ca
Denis Mackey (COSG)	CSIRO Marine Research P.O. Box 1538 Hobart, Tasmania 7001 Australia	+61 3 62325280	+61 3 62325123	denis.mackey@csiro.au
Evin McGovern (OSG Chair)	Marine Institute Marine Environment and Health Services Division Abbotstown, Castleknock Dublin 15 Ireland	+353 1 8228200	+353 1 8205078	evin.mcgovern@marine.ie
Klaus Nagel (COSG)	Institut für Ostseeforschung Seestr. 15 18119 Rostock – Warnemünde Germany	+49 3815197331	+49 3815197302	klaus.nagel@io-warnemuende.de
Solveig Olafsdottir (TMSG)	Marine Research Institute Skulagata 4 121 Reykjavik Iceland	+354 5520240	+354 5623790	solveig@hafro.is
Britta Pedersen (TMSG)	National Environmental Research Institute Frederiksborgvej 399 DK-4000 Roskilde Denmark	+45 46 301209	+45 46 301114	bpe@dmu.dk
Anna-Liisa Pikkarainen (OSG)	Finnish Institute of Marine Research Asiakkaankatu 3A P.O. Box 33 Fin-00931 Helsinki Finland	+358 9613941	+358 961394494	pikkarainen@fimr.fi

Name	Address	Telephone	Telefax	E-Mail
Marc Raemaekers (OSG)	Sea Fisheries Department Ministry of Agriculture Ankerstraat 1 8400 Oostende Belgium	+32 59342268	+ 32 59330629	mraemaek@yucom.be
Patrick Roose (OSG)	Management Unit Mathematical Model of the North Sea 3° en 23° Linierregimentsplein 8400 Oostende Belgium	+3259242054	+3259704935	p.roose@mumm.ac.be
Anne Talvari (OSG)	Estonian Environmental Research Centre Marja 4 D Tallinn 10617 Estonia	+37 26112913	+37 2611290	talvari@klab.envir.ee
Norbert Theobald (OSG)	Bundesamt für Seeschifffahrt und Hydrographie Bernhard – Nocht Str. 78 D–22305 Hamburg Germany	+49 4031903350	+49 4031905033	norbert.theobald@bsh.de
Jacek Tronczynski (OSG)	IFREMER Centre de Nantes DEL/PC B.P. 21105 Rue de l'Île d'Yeu 44311 Nantes France	+33240374136	+33240374075	jtronczy@ifremer.fr
David Wells (OSG)	QUASIMEME Project Office Marine Laboratory P.O. Box 101 Victoria Road Aberdeen AB11 9DB, UK	+44 1224876544 +44 1224295368 (Direct)	+44 1224295511	wellsd@marlab.ac.uk
Peter Voitke (TMSG)	Federal Environmental Agency FG II 3.5 P.O. Box 33 00 22 D-14191 Berlin Germany	+49 3089032566	+49 3089032285	peter.voitke@uba.de
Ton van der Zande (OSG)	National Institute for Coastal and Marine Management/RIKZ ITL P.O. Box 207 NL 9750 AE Haren The Netherlands	+31 505331301	+31 505340772	a.e.vdzande@rikz.rws.minve.nl

ANNEX 2: AGENDA

ICES Marine Chemistry Working Group: 24th meeting

Berlin, Germany, 4–8 March 2002

1. OPENING OF THE MEETING
2. ADOPTION OF THE AGENDA
3. REPORT OF THE 89th ICES STATUTORY MEETING
4. REPORTS ON RELATED ACTIVITIES
 - 4.1 OSPAR AND HELCOM
Any official requests from OSPAR or HELCOM which arose prior to the production of the agenda have been included.
 - 4.2 Intergovernmental Oceanographic Commission (IOC)
An update on relevant IOC programmes will be given.
 - 4.3 Laboratory Performance Study QUASIMEME
Dr Wells has been asked to provide an update on recent studies.
 - 4.4 Other Activities
All members who wish to make a presentation under this item should prepare a note for MCWG.
 - 4.4.1 Criteria for screening data for analytical accuracy in contaminant trend studies.
 - 4.4.2 Review of GESAMP Working Group scoping document on risk assessment. [MCWG 2002 4.4.2/1]
 - 4.4.3 Global POPs monitoring network.
 - 4.4.4 New chemicals policy in the EU and the technical guidance document.
5. REPORTS ON PROJECTS AND ACTIVITIES IN MEMBER COUNTRIES
All members who wish to make a presentation under this item should prepare a note for MCWG.
6. REQUESTS FROM ACME AND REGULATORY AGENCIES
Requests from ACME which arose prior to the preparation of the agenda have been included.
7. PLENARY PRESENTATIONS
 - 7.1 Wiebke Schwarzbach
Selection and prioritisation procedure for hazardous substances within the OSPAR Convention—the OSPAR DYNAMEC procedure.
 - 7.2 Erik Evers
The quality of organotin determinations in sediment.
 - 7.3 Lars Føyn
Monitoring nutrients in the North Sea—the very last monitoring of this kind?
 - 7.4 Uli Claussen
Assessment of the eutrophication status within the OSPAR Convention Area.
 - 7.5 Peter Lepom
Polybrominated diphenylethers —activities at the German Federal Environmental Agency (UBA).

7.6 Jan Boon
The influence of hydrographic factors on transport processes of contaminants in the North Sea.

7.7 David Wells
Cofino statistics.

8. SUBGROUP ACTIVITIES AND DISCUSSIONS

Justification 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 the three subgroups is supported by plenary discussions, which add value to the work undertaken within the subgroups.

8.1 Plenary activities and those common to all subgroups.
(See also agenda item 9).

8.1.1 Review the mechanism for generating an updated list of relevant certified reference materials for use in marine monitoring programmes, and consider their availability via the ICES website.

8.1.2 Review how a presentation of the long-term performance of a laboratory can be standardised taking the information from the 2000 report of the Working Group into account and report the outcome.

8.1.3 Review any new ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea Annexes on Quality Assurance and report the outcome.

8.1.4 Screening contaminant data submitted to the ICES database.

8.1.5 Weighting procedures for assessing trend data of variable analytical quality.

8.1.6 ICES database issues.

8.1.7 Discuss the preparation of guidelines for integrated chemical and biological effects monitoring, covering as many CEMP parameters as are relevant.

8.1.8 Discuss matters referred from the three subgroups, as necessary.

8.2 Trace Metals Subgroup

8.2.1 Critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations.

8.2.2 Review information on estuarine transport of trace metals, relevant measurement techniques available, and the comparability of their results.

8.2.7 Review new information on the use of membrane systems for sampling.

8.2.8 Propose data products that could be developed for trace metals in marine organisms in relation to environmental state indicators, based on OSPAR monitoring data [OSPAR request 2002/5.1].

8.2.5 Review and comment on the outcome of an OSPAR pilot assessment integrating data on inputs of trace metals and concentrations of trace metals in biota and sediments [OSPAR request 2002/2.1].

8.2.6 Discuss the need for the determination of the speciation of trace elements, particularly for lead, arsenic, tin, cadmium, chromium, iron and mercury, where the behaviour and toxicity of the trace elements can vary dramatically between chemical species.

8.3 Organics Subgroup

8.3.1 Critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations. Consider draft SIME request regarding OSPAR list of priority substances and how this might be addressed.

8.3.2 Review new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in flatfish.

8.3.3 Review new information on the analysis of PAH metabolites in bile, and critically review the robustness of the methods.

8.3.4 Review new information on the use of membrane systems for sampling.

8.3.5 Review new information on the monitoring and analysis of toxaphene.

8.3.6 Review new information concerning polybrominated diphenylethers (PBDEs).

8.3.7 Propose data products that could be developed for organic contaminants in marine organisms in relation to environmental state indicators, based on OSPAR monitoring data [OSPAR 2002/5.1].

8.3.8 Review and comment on the outcome of an OSPAR pilot assessment integrating input data, and data on organic contaminants in biota and sediments [OSPAR 2002/2.1].

- 8.3.9 Review specific text in Annexes 7, 8 and 9 of the draft report of SGQAC 2002.
- 8.3.10 Review new information regarding dioxins and dioxin-like PCBs.
- 8.3.11 Review new information concerning polycyclic aromatic hydrocarbons.
- 8.3.12 Review information on new contaminants, and consider the need for new overviews of contaminants.

8.4 Chemical Oceanography Subgroup

- 8.4.1 Review present knowledge about total nitrogen, total phosphorus, and total organic carbon in sea water, their speciation, and arguments for their use in monitoring programmes.
- 8.4.2 Review studies under way in OSPAR on ecological quality objectives for the North Sea with regard to nutrients and eutrophication effects.
- 8.4.3 Review recent developments in production and availability of suitable reference material for analysis of chemical oceanographic variables in sea water.
- 8.4.4 Discuss OSPAR activities regarding the assessment of eutrophication, nutrient concentrations and trends, and how ICES might contribute to this process.

9. PLENARY DISCUSSION OF SUBGROUP WORK

10. ANY OTHER BUSINESS

11. RECOMMENDATIONS AND ACTION LIST

12. DATE AND VENUE OF THE NEXT MEETING

13. CLOSURE OF THE MEETING

ANNEX 3: EDITED EXCERPTS FROM 2001 IOC ASSEMBLY REPORT OF RELEVANCE TO MCWG

- 1) The SCOR-IOC Ocean Carbon Advisory Panel is advocating the development of additional programmes for ocean carbon reference materials. The IOC has been invited to serve as a liaison to the Ocean Studies Board of the U.S. National Research Council in their 18-month programme to investigate the needs, existing programmes, and best approaches for the development of future production of reference materials. The IOC has also been approached by international groups and agencies such as the International Bureau of Weights and Measures about potential collaborations for oceanographic standards. In addition, there are a number of organizations within or affiliated with IOC programmes that are already actively addressing many issues of standards, guidelines, and reference materials, such as IODE, GIPME, the Ocean Carbon Panel, and JCOMM.

It was agreed that, as in the past, these activities should be carried out in collaboration with relevant on-going programmes and agencies including IODE, JCOMM, WMO, UNEP, ICES, ICSU, SCOR, IAEA, and IAPSO, and should include relevant training programmes.

- 2) Membership for the new joint SCOR-IOC Advisory Panel on Ocean CO₂ was established shortly after the latest Executive Council (33rd session, June 2000) and the first meeting was held in September 2000. The IOC hosted and participated in the international JGOFS EC-US Ocean Carbon Cycle Science Research Workshop in September 2000 with the goal of establishing international community consensus on ocean carbon research, observation requirements and priorities. This meeting was linked with the SCOR-IOC CO₂ programme activities and the IGBP-IHDP-WCRP initiative to develop a framework for a decade of carbon cycle research.
- 3) There are two new reports on critical issues in marine environmental protection produced by GESAMP, one of which targets the decision makers and public at large and the other targets land-based sources and activities affecting the quality and uses of the marine, coastal and associated freshwater environment. The IOC Atlantic Open Ocean Baseline Study is ongoing, and there is a new initiative for a baseline study in the western Pacific.
- 4) It is planned to restructure the Ocean Science Section of the IOC Secretariat into the following three interactive lines of work:
 - i) Oceans and Climate;
 - ii) Ocean Ecosystems Science; and
 - iii) Marine Science for Integrated Coastal Area Management.

Concern was expressed that the proposed structure might not adequately emphasize the important and continuing role the Ocean Science Section must play in areas of the protection of the marine environment. It was suggested that the Ocean Ecosystems Science programme area could be renamed Science for Ocean Ecosystem and Marine Environmental Protection (SOEMEP) in order to increase the visibility of marine pollution science activities.

- 5) Increased attention in the IODE system for 'not routinely exchanged data' such as remotely sensed, biological, chemical, pollution and coastal data is to be given. An IODE Group of Experts on biological and chemical data management and exchange practices has been established, and requested the Group to maintain close relations with GIPME, OSLR and other relevant programmes.
- 6) Dr Scott Parsons, past President of the International Council for Exploration of the Sea (ICES), informed the Assembly about the ICES activities that are pertinent to those of IOC. Attention was drawn to the existing Memorandum of Understanding between ICES and IOC, which should be used to strengthen and increase the existing collaboration between the two organizations. The Assembly welcomed the calls for increased and enhanced cooperation between IOC and PICES and ICES, as well as with other regional international organizations, such as the Permanent Commission for the South Pacific (CPPS), and requested the Executive Secretary to take appropriate measures to this effect.

ANNEX 4: WEIGHTING PROCEDURES FOR ASSESSING TREND DATA OF VARIABLE ANALYTICAL QUALITY

Mike Nicholson and Rob Fryer

1 Introduction

In a paper presented to the 2001 meeting of the Marine Chemistry Working Group (MCWG), Nicholson *et al.* (2001) reviewed the implications for contaminant trend assessments of using data filters to remove data not supported by evidence of satisfactory analytical quality. They considered an alternative approach, where information about analytical performance is used to weight the trend data according to its accuracy.

Broadly, their conclusions were:

- 1) Although intuitive interpretation of P and Z scores relative to fixed values such as 2 provide a useful, informal guide to performance within Quality Assurance (QA) exercises, a more formal approach should be used for filtering data from monitoring programmes. Reference values should reflect the numbers of observations used to calculate P and Z so that p -values for rejecting data remain constant between years and between laboratories.
- 2) In practice, given the levels of sampling and environmental variability observed for temporal monitoring data within the current OSPAR JAMP, analytical variability tends to have only a small effect on the ability to detect trends.
- 3) Data-filtering criteria for the OSPAR JAMP programme could be less stringent, allowing more data to be assessed.
- 4) In terms of the ability to detect a linear trend, comparisons of four potential weighting strategies gave rankings: 1 *optimum*-; 2 *intuitive*-; 3 *equal*-; and 4 *zero-weighting* (i.e., deletion of *Poor* data). However, strategy 4 was by far the least efficient.
- 5) Since these different weighting strategies were demonstrated using synthetic data generated using defined levels of *Good* and *Poor* analytical performance, an example using real data should be presented.

In Section 2, we present an example using QA and trend data for PCBs generated at the UK Burnham Laboratory. The example is very realistic, reflecting that historic information about analytical performance is often incomplete. Consequently, the QA weights in some years need to be estimated. For comparison, a simpler approach using intuitive weights is also applied.

Any practical solution to this problem will be a compromise between the need to develop and maintain good analytical practice, the needs of assessment groups to make the best use of submitted data, and for the correct application of statistical methods. In Section 3 we propose a simple solution that attempts to satisfy all of these.

2 QA Weighting Applied to Trends in PCBs in Cod from the North Sea

Table A4.1 summarises the available ICES-7 PCB data for the period 1982–2000. As we see, the series of available QA data is very short relative to the trend series, with little overlap between them. Although it is statistically irresponsible, we will estimate values for the missing QA data, to show that it is possible and to demonstrate how this might be done.

Optimum-Weighted Analysis of Trend Data

The missing QA data can be estimated by assuming a simple model for between-year variation (bias) and within-year variation (precision). Bias is assumed to consist of both a systematic and random component. Both of these may change with time. Precision is also allowed to change with time. A formal description of this model and the method of estimating its parameters is given in the Technical Annex, and in Nicholson and Fryer (2001).

The results for the data in Table A4.1 are summarised in Figures A4.1a and A4.1b. Figure A4.1a shows the QA annual means with their 95 % confidence intervals (vertical lines). Superimposed is the change in systematic bias (solid line) projected back to the start of the trend data (dashed line). For simplicity, the random bias component was assumed to be constant, and estimated to be 4 %. Similarly, Figure A4.1b shows the QA annual variances with their corresponding trend.

The results of the trend assessment are shown in Figure A4.2.

Intuitive-Weighted Analysis of Trend Data

For comparison, we consider a simpler analysis using intuitive down-weighting of data with poor performance or missing QA data and a different plotting symbol to signify the status of data in each year.

The following convention was adopted:

- satisfactory QA (closed circles): weight =100 %
- unsatisfactory QA (crossed open circles): weight =50 %
- missing QA (open circles): weight =10 %.

Using simplistic targets for bias and precision of ± 12.5 %, only the data for 1993 were considered to have unsatisfactory QA (Table A4.1). The resulting trend assessment is shown in Figure A4.3.

3 Conclusions and Recommendation

The problem discussed here brings together three issues that are inextricably linked, but which are invariably treated separately. These are:

- 1) analytical performance, i.e., how well contaminants are measured;
- 2) monitoring performance, e.g., how well trends are detected; and
- 3) statistical assessment methodology, e.g., survey design and how trends are assessed.

Ideally, a monitoring programme would develop by first defining targets for, e.g., trend detection. For a particular survey design and method of trend assessment, this would imply a maximum level of variability in observed contaminant concentrations. In turn, this would identify a suitably small component of analytical variability, which laboratories would demonstrate in interlaboratory comparisons.

This tidy progression tends not to occur. Here, a statistical method is trying to accommodate data with unknown or variable analytical performance. Further, in the past these data have been filtered using criteria relevant to good laboratory practice independently of monitoring requirements.

The problem we must tackle is how to move closer to the ideal, making sensible analyses of the maximum amount of data.

We have demonstrated how missing and variable analytical QA data could be incorporated into contaminant trend assessments. However, we feel that estimating the optimum weights could not be recommended as a general procedure within a large assessment programme. The method may not be reliable when there are few QA data, and may give a spurious implication of statistical correctness. Also, from an analytical viewpoint, there is a point at which data stop being *variable* and become *meaningless*.

However, with sensible statistical guidance, we could employ a sub-optimal weighting system that:

- allows historic trend data (where QA data are missing) to be included in assessments;
- is statistically reliable; and
- responds to the need to maintain good analytical quality.

We propose:

- 1) a simple four-tier system for analytical quality corresponding to, e.g., *Good*, *Poor*, *Unknown*, and *Unacceptable*. Within the trend assessment, corresponding data would be given weights w_{good} , w_{poor} , w_{unknown} and zero (i.e., deleted);
- 2) that a procedure for identifying QA performance as *Good*, *Poor* or *Unacceptable* should be a compromise between analytical, assessment, and statistical issues; and
- 3) similarly that the values of w_{good} , w_{poor} , and w_{unknown} are determined taking account of the analytical, assessment, and statistical implications of this compromise.

Acknowledgements

Our thanks to Colin Allchin at the CEFAS Burnham Laboratory for providing the PCB QA data.

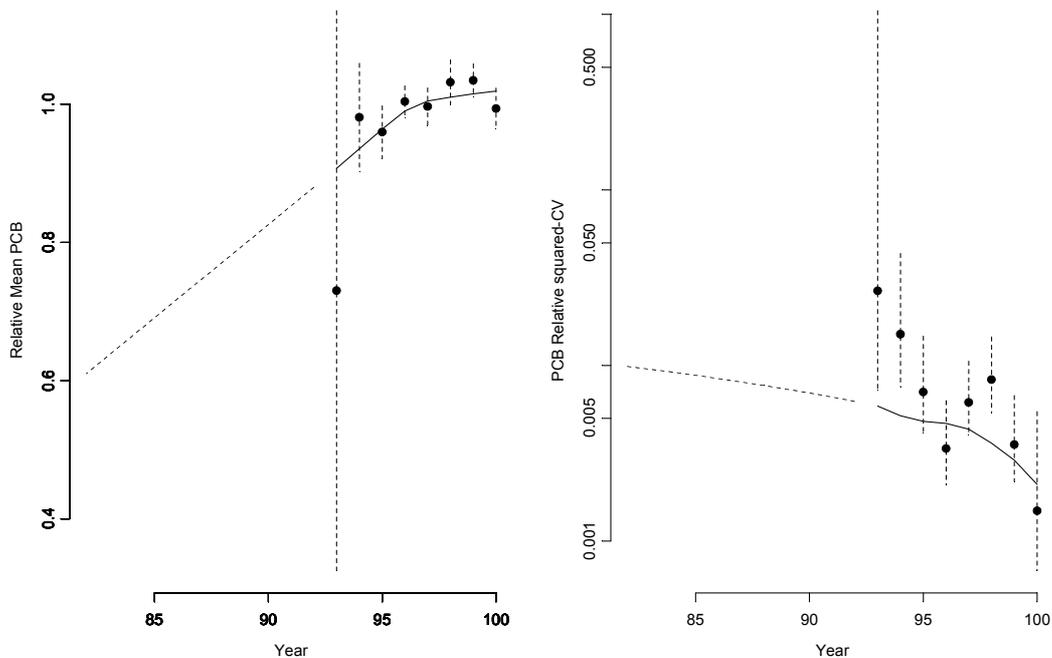
References

Nicholson, M.D., and Fryer, R.J. 2001. Weighting Procedures for Assessing Trend Data of Variable Quality. ICES Working Group on the Statistical Aspects of Environmental Monitoring, 2001.

Nicholson, M.D., Fryer, R.J., and Law, R. 2001. Criteria for Screening Data for Analytical Accuracy in Contaminant Trend Studies. ICES Marine Chemistry Working Group. 2001.

Table A4.1.

Year	QA data			Monitoring Data
	Replicates	Relative Mean %	Relative Standard Deviation %	Annual PCB Index (mg kg ⁻¹)
1982	-	-	-	14.4
1983	-	-	-	12.6
1984	-	-	-	-
1985	-	-	-	6.67
1986	-	-	-	7.62
1987	-	-	-	5.26
1988	-	-	-	8.00
1989	-	-	-	7.94
1990	-	-	-	4.36
1991	-	-	-	5.09
1992	-	-	-	-
1993	3	73	16.3	2.73
1994	12	98	12.3	6.25
1995	21	96	8.4	-
1996	27	100	5.8	2.98
1997	35	100	7.8	-
1998	33	103	9.1	-
1999	26	103	6.0	-
2000	9	99	3.9	-



Figures A4.1a and A4.b.

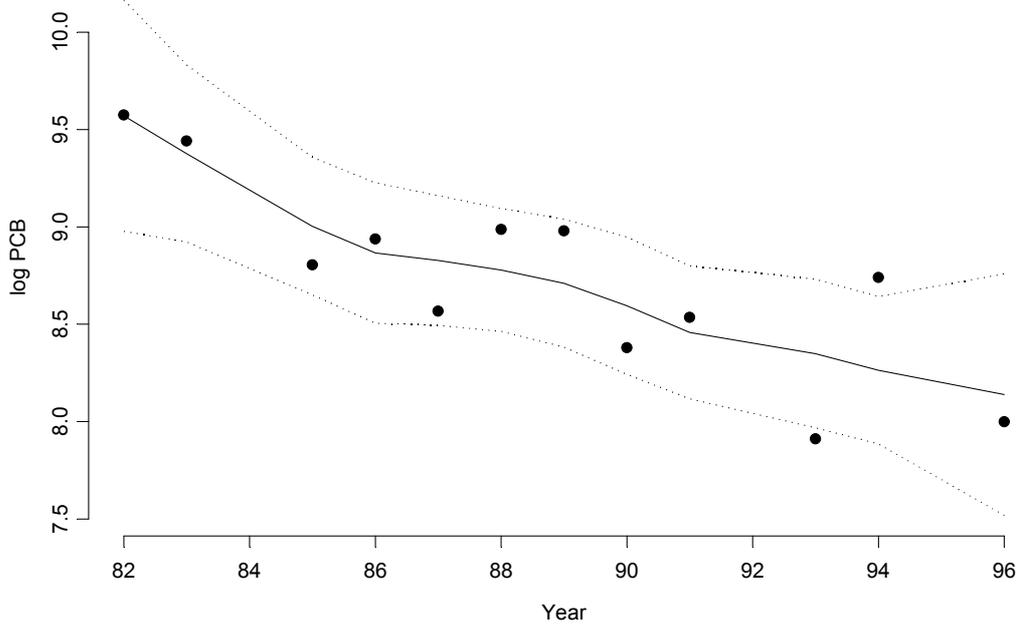


Figure A4.2. Weighted trend in PCBs using estimated optimum weights.

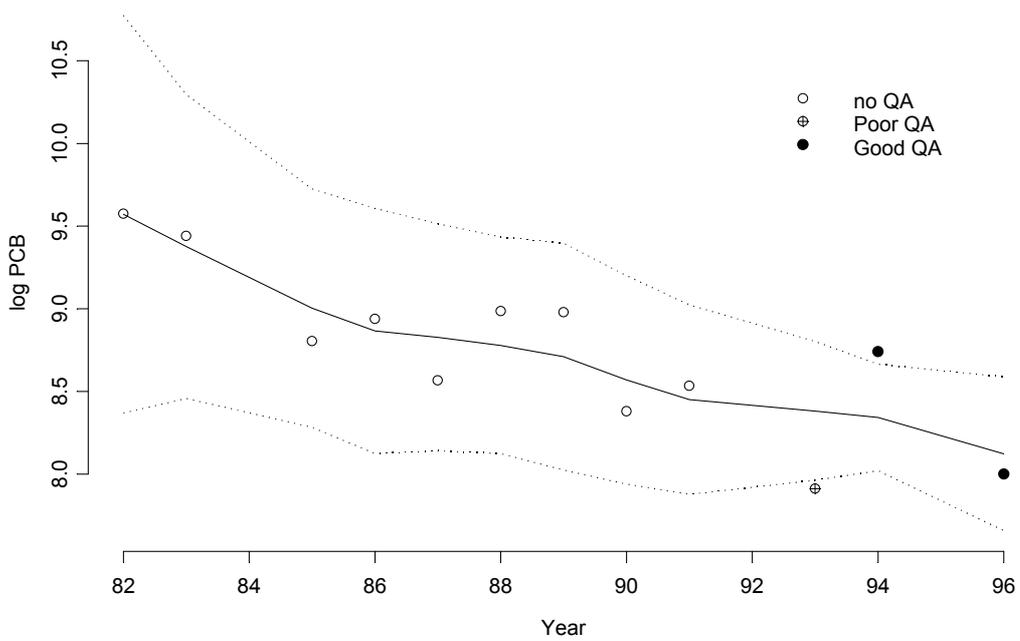


Figure A4.3. Weighted trend in PCBs using intuitive weights.

Weighting Procedures for Assessing Trend Data of Variable Analytical Quality

Technical Annex

Analysis of QA data

A simple model for the observed mean (m_y) and variance (v_y) estimated from n_y replicates in year y is:

$$m_y = f(y) \times \mu + \varepsilon_y$$

where ε_y is a random component of bias in year y with zero mean and variance given by:

$$V[\varepsilon_y] = g(y) \times \sigma_b^2 + h(y) \times \sigma_w^2 / n_y$$

where $g(y)$ represents the trend in the between-year variance σ_b^2 . The mean for v_y is given by:

$$E[v_y] = h(y) \times \sigma_w^2$$

where $h(y)$ represents the trend in the within-year variance σ_w^2 .

For simplicity here, we will assume that $g(y) = 1$, i.e., there is no trend in σ_b^2 .

The true mean μ is estimated by the overall mean. The trend in the bias, $f(y)$, and the between-year variance, σ_b^2 , are estimated using the EM-algorithm described in Nicholson and Fryer (2001) for a weighted smoother of m_y on y with weights estimated by:

$$w_y = \frac{1}{\sigma_b^2 + v_y / n_y}.$$

The trend in the within-year variance, $h(y)$, is estimated using a weighted smoother of v_y on y with weights estimated by:

$$w_y = \frac{n_y - 1}{2v_y^2}.$$

Analysis of Trend Data

Having estimated the annual components of analytical variance, these were used to construct the component of analytical variance in the annual trend index (assuming individual analyses of an annual sample of 25 fish), i.e.,

$$\sigma_{ay}^2 = \hat{\sigma}_b^2 + \hat{h}(y) \hat{\sigma}_w^2 / 25$$

with total variance given by:

$$\psi^2 v_t = \sigma_e^2 + \sigma_{at}^2$$

where σ_e^2 is the unknown and constant environmental variance (including sampling variability), and σ_{at}^2 is the (now assumed known) total analytical variance. Equating

$$\psi^2 = \sigma_e^2$$

and

$$v_t = 1 + \frac{\sigma_{at}^2}{\sigma_e^2}$$

the optimum weights are given by:

$$w_t = v_t^{-1} = \frac{\sigma_e^2}{\sigma_e^2 + \sigma_{at}^2}$$

The variance components are again estimated using the EM-algorithm.

ANNEX 5: OSPAR LIST OF CHEMICALS FOR PRIORITY ACTION

An immediate response from the Organics Subgroup of the MCWG to the OSPAR request for views on the possibility to analyse the compounds on the “Substances on the OSPAR List of Chemicals for Priority Action”, and whether there are levels of these substances reported from the marine environment, is provided in this table.

Chemical (CAS or name)	Analysis ^a	Presence ^b	Comment
85-22-3	1	-	
36065-30-2	1	-	
732-26-3	1	-	Blank problems
98-51-1	1	-	
Brominated flame retardants	3	+	For PBDE
	2	+	For HBCD and PBB
77-47-4	2	+	
Certain phthalates	2	+	Blank problems
115-32-2	2	+	
115-29-7	3	+	
2104-64-5	0	-	
70124-77-5	0	-	
28680-45-7	1	-	Not a major Toxaphene comp.
HCH-isomers	3	+	For α -, β - and γ -isomers
107-46-0	1	-	Blank problems
465-73-6	2	-	Environmental levels very low
Organic lead compounds	2	+	For tetraalkyllead
Organic mercury compounds	3	+	
72-43-5	3	+	
Musk xylene	2	+	
Chlorinated naphthalenes	2	+	Individual isomers should be measured
51000-52-3	0	-	
NP/NPEs	2	+	
140-66-9	2	+	
Organic tin compounds	3	+	For trialkyl- and triphenyltin
1825-21-4	2	+	
PCP	3	+	
603-35-0	0	-	
PAHs	3	+	
PCBs	3	+	
PCDD/Fs	3	+	
SCCP	2	+	
79-94-7	?	?	Unclear structure
2227-13-6	2	+	
87-61-6	2	+	
120-82-1	2	+	
108-70-3	2	+	
55525-54-7	0	-	
Cadmium	3	+	
Lead	3	+	
Mercury	3	+	
Organic mercury compounds	2 – 3	+	
Organic tin compounds	2 – 3	+	

^a The Organics Subgroup knows that 3) there are good validated methods available; 2) there are methods described in the literature; 1) it is possible for some laboratories to analyse the compound; or 0) no methods are known to the subgroup.

^b The Organics Subgroup knows that there are environmental levels reported (+), or the subgroup does not have knowledge of any environmental data (-).

ANNEX 6: ACTION LIST

Gert Asmund	to report on intersessional studies concerning the presentation of long-term laboratory performance to MCWG 2003.
Michael Haarich Patrick Roose Erik Evers Robin Law	to prepare draft guidelines for integrated chemical and biological effects monitoring, covering as many CEMP parameters as are relevant, in liaison with WGBEC, and to report progress to MCWG 2003.
All members of MCWG	to supply information on existing environmental indicator systems to Robin Law for onward transmission to the ICES Environment Adviser.
All members of TMSG	to bring relevant information on the speciation of the trace elements listed in Section 8.2.6, above, to MCWG 2003, and its effects on behaviour and toxicity, to aid the development of future work programmes in this area.
Jan Boon	to seek information from his NIOZ colleagues regarding their work on iron in the ocean for MCWG 2003.
All members of the Organics Subgroup	to bring new information on TCPM and TCPMe to MCWG 2003.
Ton van der Zande	to report new information concerning the development and use of these sampling devices to MCWG 2003.
Michel Lebeuf	to report on relevant studies on toxaphene currently under way in Canada under the Toxic Substances Research Initiative to MCWG 2003.
Michel Lebeuf	to report on relevant studies on PBDEs currently under way in Canada to MCWG 2003.
Jacob de Boer	to report on progress within the FIRE project to MCWG 2003
Jacob de Boer	to provide an update on progress within the DIFFERENCE project at MCWG 2003.
Norbert Theobald and Jacek Tronczynski	to prepare a review note on phenylurea herbicides (diuron and isoproturon) in the marine environment for MCWG 2003.
All Organics Subgroup members	to check their chromatograms for the presence of mirex and report their findings to Bo Jansson during the intersessional period. Bo Jansson will report the findings to MCWG 2003.
Gert Asmund, David Wells and Patrick Roose	to investigate a method to calculate the constant and proportional errors in data from QUASIMEME, and to report the findings to MCWG 2003.

ANNEX 7: RECOMMENDATIONS

The Marine Chemistry Working Group recommends that:

- 1) in view of concerns amongst members that inappropriate analytical methods may become mandatory for work in support of EU Directives (under CEN/ISO and in relation to the Water Framework Directive, for example), the Chair of MCWG should approach the Chair of the AMPS group for reassurance that all validated methods that meet the criteria and are fit for purpose will be accepted.
- 2) the Chair of MCWG, on behalf of ICES, should approach the Chair of the AMPS group with a view to establishing a liaison between the two groups in areas of common interest regarding contaminant monitoring in the marine environment in which MCWG has considerable experience.
- 3) ICES recommends to OSPAR that PBDEs should be considered for inclusion within the JAMP programme, as fully validated methods for their determination are now available.

2E02 The **Marine Chemistry Working Group** [MCWG] (Chair: R. Law, UK) will meet in Tallinn, Estonia, from 3 to 7 March 2003 to:

A. Chemical Oceanography Subgroup

- a) provide advice and assistance relating to the development a series of data products to illustrate eutrophication status within the ICES area;
- b)

B. Organics Subgroup

- a) advise on the availability of suitable analytical methods to allow the determination of environmental concentrations of the substances listed on the OSPAR list of chemicals for priority action, and review the data which are available to date, and report the outcome;
- b) review new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in flatfish, 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 polybrominated diphenylethers (PBDEs) and report the outcome;
- g) consider a review note on phenylurea herbicides (diuron and isoproturon) 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 trace metal speciation and its effects on behaviour and toxicity, and report the outcome;
- c) review new information on the use of membrane systems for sampling and report the outcome;

D. Plenum

- a) review the mechanism for generating an updated list of relevant certified reference materials for use in marine monitoring programmes, and their availability via the ICES website;
- 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 any new SGQAC Annexes on Quality Assurance and report the outcome;
- d) consider draft guidelines for integrated chemical and biological effects monitoring, and report the outcome;
- e) discuss matters referred to from the three subgroups, as necessary.

MCWG will report by 24 March 2003 for the attention of the Marine Habitat and Oceanography Committees and ACME.

Supporting Information

Priority:	
Scientific Justification:	<p>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.</p> <p>A. Chemical Oceanography Subgroup</p> <ol style="list-style-type: none">a) Data available in the ICES databanks will be used to prepare illustrative data products under the OSPAR Common Procedure.b) <p>B. Organics Subgroup</p> <ol style="list-style-type: none">a) This is related to an OSPAR request [ASMO 02/13/1-E Annex 15].b) This project was initiated several years ago among MCWG members on the basis of concerns regarding these contaminants in the marine environment.c) This is part of the work of MCWG in reviewing and evaluating methods for measuring chemical properties in marine and estuarine environments. In addition, 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.d) These systems are being reviewed for application to monitoring contaminants in the marine environment.e) 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.f) This is to evaluate information on the distribution and potential effects of these contaminants in the marine environment.g) These compounds are widespread contaminants in the aquatic environment. <p>C. Trace Metals Subgroup</p> <ol style="list-style-type: none">a) Given the varied sources and applications of trace elements and organometallic compounds, it is important to develop a means to determine which may be potentially serious contaminants of the marine environment.b) The speciation of trace metals is of great importance in determining

	<p>their behaviour, fate and effects in the environment..</p> <p>c) These systems are being reviewed for application to monitoring contaminants in the marine environment.</p> <p>D. Plenum</p> <p>a) MCWG has maintained a current listing of CRMs for organic compounds available for use in marine monitoring; at MCWG2001 recommendations were made to ICES regarding an improved mechanism by which information could be made available to users in marine monitoring programmes and updated, and this needs to be reviewed.</p> <p>b) QA systems, QA data, reporting of QA data to a database and the assessment of these data (data filter) in order to ensure the quality of the environmental data used in the assessments are topics of major concern for monitoring agencies.</p> <p>c) This item addresses the interests of HELCOM.</p> <p>d) This is the subject of a request from OSPAR [ASMO 02/13/1-E Annex 15].</p> <p>e) Plenary discussions add value to the work in the subgroups.</p>
Relation to Strategic Plan:	Most of the items on the MCWG agenda are related to Objective 2 for achieving the strategic goals (Understand and quantify human activities on the marine environment, including living marine resources) and Objective 1 (Understand the physical, chemical, and biological functioning of marine ecosystems.), as well as Objective 3d, Development of monitoring techniques.
Resource Requirements:	No extra resources are needed from ICES
Participants:	MCWG members. Based on earlier experience, there will be a great advantage if a person from the ICES Secretariat participates in the meeting in order to improve the cooperation between MCWG and ICES.
Secretariat Facilities:	The 2003 meeting will be held at the offices of the Estonian Environmental Research Centre in Tallinn, Estonia, so no extra Secretariat facilities are needed in relation to the meeting. Support to the MCWG mailbox to keep this up-to-date is needed as this has been proven to be an efficient tool in the communication between MCWG members.
Financial:	
Linkages to Advisory Committees:	ACME
Linkages to other Committees or Groups:	MHC, OCC
Linkages to other Organisations:	HELCOM, QUASIMEME