Marine Habitat Committee

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REPORT OF THE

MARINE CHEMISTRY WORKING GROUP

Mont-Joli, Canada

26 February–2 March 2001

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

Palægade 2–4 DK–1261 Copenhagen K Denmark

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1 OPENING OF THE MEETING

The Chair, Mr Robin Law, opened the meeting of the Marine Chemistry Working Group (MCWG) following an address by the Director of the host institute presented by telephone link from Victoria, BC at 10.30 hrs on 26 February 2001. MCWG participants introduced themselves and briefly described their main area(s) of interest. The list of participants is given in Annex 1. It transpired that the MCWG was this year depleted in membership and consequently in some areas of expertise, particularly in relation to trace metals and chemical oceanography. 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 were:

2E02 The **Marine Chemistry Working Group** [MCWG] (Chair: R. Law, UK) will meet in Mont-Joli, Quebec, Canada, from 26 February to 2 March 2001 to:

A. Chemical Oceanography Subgroup

a) review and report oxygen determinations in sea water by the Winkler titration and membrane electrodes;

b) review a report from a multiship experiment of sampling and determination of chemical variables in sea water;

c) review and report on progress in the modelling of marine biogeochemical processes;

d) review and report on progress in the studies of estuarine behaviour of nutrients;

e) review and report on the present knowledge about total nitrogen, total phosphorus, and total organic carbon in sea water, their speciation, and arguments for their use in monitoring programmes.

B. Organics Subgroup

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

b) review new information* on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in fish, including the results of the TCPM and TCPMe interlaboratory study, second phase and report the outcome;

c) review new information on the analysis of PAH metabolites in bile, critically review the robustness of the methods, and report the outcome;

d) review new information on the use of membrane systems for sampling and report the outcome;

e) review new information on the monitoring and analysis of toxaphene and report the outcome;

f) review new information* concerning oil spills, their effects and associated protocols for incident response and report the outcome;

g) review recent data* on dioxins, furans, and dioxin-like PCBs in fish, with particular reference to Baltic fish, and report the outcome (initially to WGBEC);

h) review new information* concerning polybrominated diphenylethers (PBDEs) and report the outcome;

i) review new information* concerning new contaminants in the marine environment (new booster pesticides and chlorinated and/or brominated PAHs) and report the outcome;

j) as a follow up to work conducted in 2000 on volatile organic contaminants, provide an evaluation of the significance* of these compounds in the marine environment;

k) prepare material that can be used by WGSAEM relevant to the development of models for the relationship between the concentration of a contaminant in an organism and the ambient concentration.

* = submit results of discussion to WGBEC

C. Trace Metals Subgroup

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

b) review information on estuarine transport of trace metals, relevant measurement techniques available, and the comparability of their results, and report the outcome;

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

d) review new information concerning the supplementary work to the Icelandic cod study on the relationship between trace element concentrations in cod liver and various co-factors and report the outcome;

e) prepare material that can be used by WGSAEM relevant to the development of models for the relationship between the concentration of a contaminant in an organism and the ambient concentration.

D. Plenum

a) review the updated list of relevant certified reference materials for organic compounds for use in marine monitoring including also trace metals and nutrient compounds, and in this connection consider the mechanism for the review and updating of these tables;

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

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

d) in association with SGQAC, prepare guidelines containing criteria for data screening and evaluation prior to assessment of chemical monitoring data [HELCOM 2001/2];

e) review any new SGQAC Annexes on Quality Assurance and report the outcome [HELCOM 2001/1];

f) review contaminants in the ICES contaminants database to:

    i) establish and define new classifications for compound identification to clarify types of compounds based on isomers, size, and active sites, and preliminary identification when CAS numbers are not available;

    ii) set criteria for acceptability for inclusion in the database (e.g., need for isomer specifications);

    iii) review currently used ranges of detection and contamination;

g) establish a network of contacts for the ICES data manager with an expert for each current chemical group;

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

MCWG will report by 30 March 2001 for the attention of the Marine Habitat and Oceanography Committees and ACME.

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.

The work outlined in the agenda was (unusually) carried out entirely in plenary, due to the limited representation at this meeting of the Trace Metals and Chemical Oceanography Subgroups.

3 REPORT OF THE 88TH ICES STATUTORY MEETING

The Chair informed the group that all tasks referred to the MCWG at the 88th ICES Annual Science Conference had been incorporated into the agenda.

4 REPORTS ON RELATED ACTIVITIES

4.1 OSPAR and HELCOM

There were no official requests from OSPAR. Official requests from HELCOM have been incorporated into the agenda.

4.2 Intergovernmental Oceanographic Commission (IOC)

A summary of the current work within IODE (International Oceanographic Data and Information Exchange) was provided by Harry Dooley (ICES representative) and is appended to this report as Annex 3. Most aspects are currently being addressed within the ICES Working Group on Marine Data Management, but MCWG noted that in time they wish to become involved in the management of pollution data. This is likely to be taken forward within the IOC Global Investigation of Pollution in the Marine Environment (GIPME), and under GOOS-related initiatives such as the Rapid Assessment of Marine Pollution (RAMP).

4.3 QUASIMEME

Dr Wells had agreed to present an update on recent studies, but in the event he was unable to attend the meeting. The MCWG Chair contacted Dr Wells who agreed to provide a summary document by e-mail, and this was received towards the end of the meeting. A short summary is provided below.

Agreement was reached on the new style and structure of the reports that would be submitted to OSPAR (SIME) and HELCOM, and the initial report was made available in this format for the 2001 SIME meeting. This report included a summary of the data for the last full QUASIMEME year (1999/2000) which included rounds 18 and 20 in the scheme. The overall performance of all laboratories for the last four years whilst the subscription scheme has been in operation, 1996/1997 to 1999/2000, was reported at a conference held in Egmond-aan-Zee in the Netherlands in October 1999. Throughout this period and during the initial pilot phase the data assessment used to obtain the assigned values was based upon the robust statistics developed by the Royal Society of Chemistry in the UK. An alternative approach using quantum statistics developed by Wim Cofino has now been applied to the QUASIMEME Laboratory Performance Studies on a routine basis. QUASIMEME has conducted a series of quality control checks on these methods, comparing them with data obtained from robust statistics. Very good agreement was obtained for analyses under control, but the Cofino statistics were better able to separate the effects due to the application of different analytical methods on the results obtained. Details of these comparisons will be published in due course.

For MCWG2002 David Wells agreed to provide overviews of (a) the QUASIMEME Laboratory Proficiency Studies during the last 6 years, and (b) the PAH metabolite studies (see Agenda item 8.3.3), which will have been completed by then.

4.4 Other Activities

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

A paper was submitted under this agenda item, numbered MCWG2001 4.4.1/1. The main point of discussion was that instead of rejecting data outright when they fail criteria developed for analytical and intercomparison purposes, such as those developed within the QUASIMEME Laboratory Proficiency Scheme, it may for the purposes of trend assessment be preferable to down-weight them but retain those data within the assessment process. The MCWG were overall sceptical of this approach. Whilst the down-weighting of valid though old (and therefore not fully quality controlled to today's standards) data was regarded as a valid treatment for inclusion, the process was regarded as presenting a dubious message. Ideally, clear criteria for data acceptability should be established within each collaborative monitoring programme at inception so as to ensure that all data are “fit for purpose”, and so all data accepted should be equally valid. If this is not the case (as for most international programmes to date) then such an approach, whilst valid statistically, poses risks. For instance, there is a danger that trends due to the improvement of analytical methods may be interpreted as environmental changes. Also, if this approach is to be applied, then clear criteria for data acceptability within this process should be established in advance. Our suggestion is that in place of the theoretical example presented within the paper a real scenario for such an approach should be constructed using data from the ICES database, so as to make clearer the potential application of such a procedure. This paper is also being submitted to WGSAEM at their next meeting, and is appended to this report as Annex 4.

4.4.2 Other activities

Bo Jansson reported on some European and global activities that may be of interest to the members of MCWG.

The Scientific Committee on Toxicology, Ecotoxicology and Environment (SCTEE), which is an advisory body of the European Commission, is presently reviewing the risk assessments being undertaken within the European Union. During this work it was realised that the exposure assessment is often the weakest part of these assessments. A subgroup has therefore been preparing a report highlighting the problems and suggesting improvements to the process. The report will soon be finished, and copies will then be distributed to the members of the MCWG for information.

The report will also be sent to relevant groups working on the revision of the Technical Guidance Document (TGD), which outlines the process for risk assessments in the EU. One of these groups is working to develop guidance for marine risk assessments, a topic that is not included in the present version of the TGD. This part of the work is being conducted in cooperation with OSPAR.

UNEP is planning to establish a global network for monitoring of chemicals in the environment. This will probably start with the twelve POPs included in the Stockholm convention, but the aim is to widen it to include other chemicals in the future. The aim is to build an effective channel for communication between people professionally active in the monitoring society. After a consultation meeting in May 2001, a pilot phase is planned to investigate the interest for such a network, and if the outcome is positive a longer term operative phase may follow.

The network project will be undertaken in close cooperation with another UNEP/GEF project, the Global Assessment of Persistent, Bioaccumulating and Toxic (PBT) Chemicals. This project is compiling data for the PBT chemicals in twelve regions, including the Arctic, North America, Northern and Eastern Europe, and Southern Europe and the Mediterranean countries. The data compiled within this project will be very useful in helping to identify essential items for inclusion in the Global POPs network.

5 REPORTS ON PROJECTS AND ACTIVITIES IN ICES MEMBER COUNTRIES

No submissions were made under this agenda item.

6 REQUESTS FROM ACME AND REGULATORY COMMISSIONS

All requests from ACME were included in the agenda.

7 PLENARY TOPICS

7.1 Charles Gobeil

"Recent changes in organic carbon flux to Arctic Ocean deep basins: Evidence from acid volatile sulfide, manganese and rhenium discord in sediments".

Dr Gobeil from the Canadian Department of Fisheries and Oceans gave a talk on the influence of climate change on the organic carbon flux at the sea floor in the Arctic Ocean. Dr Gobeil reported that evidence of recent large-scale change in redox conditions in Arctic Ocean basin sediments is found in profiles of solid phase acid volatile sulfide (AVS), manganese, and rhenium. He showed that AVS occurs at 2.5–5.5 cm in sediment cores collected from all of the Arctic basins, implying that there is presently a sufficient supply of organic matter to deplete oxygen to the point of forming sulfide. However, rhenium, which precipitates under suboxic or anoxic conditions, is not found enriched in these same sediments. The absence of rhenium enrichment suggests that the AVS has been produced recently under enhanced organic carbon fluxes. Estimated diffusion rates suggest that such enhanced organic fluxes must have occurred within the past 50 years. The most likely origin for such widespread change is the ice climate. The reduction in ice observed over the past several decades in the Arctic Ocean has been accompanied by enhanced organic carbon fluxes to the sea floor.

7.2 Kenneth Lee

"Biodegradation of petroleum hydrocarbons stranded in low-energy shoreline environments".

Dr Lee described the results of a large-scale oil spill experiment to determine natural recovery rates and the efficacy of potential remediation strategies in wetland ecosystems. A controlled oil spill experiment with a weathered light crude oil (Mesa) was initiated in June 1999 at a site dominated by *Scirpus pungens* situated on the St. Lawrence River, Canada. Remediation treatments of the oiled plots included: natural attenuation (no treatment); nutrient amendment with granular ammonium nitrate and super triple phosphate; a similar treatment with plants continuously cut back (to evaluate the influence of plant growth on remediation); and a nutrient amendment treatment with sodium nitrate instead of ammonium nitrate. To elucidate the effect of nutrient amendments alone, four unoiled plots were fertilised with ammonium nitrate and triple super phosphate. Sediment samples were routinely recovered for chemical and toxicological analyses over a 21-week period that effectively covered the natural growth season of the plants. GC/MS analysis could not resolve significant changes in the composition of the residual oil as a result of experimental treatments. In contrast, significant changes in biological measures of habitat recovery were observed. *S. pungens,* the dominant plant species, was tolerant to the oil, and its growth was significantly enhanced above that of the unoiled control by the addition of nutrients. Time-series bio tests (acute and chronic endpoints) on sediments recovered from the experimental enclosures provided evidence of both habitat recovery and potential detrimental effects. This discrepancy in the detection of treatment efficacy between the chemical and biological methods was attributed to induced tolerance to the contaminant hydrocarbons, changes in the bioavailability of the residual oil, and detrimental effects of the type and quantity of bioremediation agents used. This study has identified the utility of using toxicity tests to define operational endpoints in oil spill response operations.

7.3 Jacek Tronczynski

"Contamination by PAH of intertidal and subtidal compartments after the *Erika* oil spill".

For this agenda item a plenary presentation was given by Jacek Tronczynski on the chemical surveys and studies conducted by IFREMER following the *Erika* oil spill. On 12 December 1999, the tanker *Erika* broke into two parts about 40 km from the Brittany coast of France, releasing about 25,000 tonnes of heavy fuel oil. Oil slicks were stranded ashore several days after the catastrophe, resulting in contamination of more than 400 km of coasts from south Finistere to the Vendée.

The PAH levels and composition were studied in the stranded oil on the rocks. The results indicate little change in concentrations and composition of PAHs during the first ten months of the survey. Studies of contamination in the water phase showed heavy contamination by dissolved PAHs in coastal waters persisting for several months after the accident. Oil slicks buried in the sediments and stranded on the rocks constitute probable chronic sources of contamination to the water phase.

PAH concentration levels have been surveyed in marine molluscs and crustaceans during the first year after the *Erika* oil spill. The results show a rapid increase of PAH concentration levels after the arrival of the spilled fuel oil on the shorelines. The mean Σ16PAH concentrations calculated over the one-year survey (December 1999 to December 2000) were between 231 ng g^{-1} and 623 ng g^{-1} depending on the sites. These concentration levels are 2 to 4 times higher than mean concentrations recorded for data from the French Mussel Watch programme. The maximum concentration levels (889 ng g^{-1} to 5195 ng g^{-1}) expressed as Σ16 PAHs were from 5 to 18 times higher in bivalves collected after the spill than maximum levels recorded in these areas before the spill. The spatial distribution of the levels of contamination of marine molluscs by PAHs was quite heterogeneous over the entire area impacted by the *Erika* oil. One year after the accident, PAH concentrations still exhibit high levels, especially in the Loire Atlantique and Vendée areas. The concentrations recorded in December 2000 are in most cases still above reference concentration levels determined before the spill and from data obtained from the French Mussel Watch programme. Thirty-two of the 43 sites still surveyed in December 2000 showed concentration levels above the mean reference concentration recorded before the spill, among them are 13 located in Loire-Atlantique and 9 in Vendée. The PAH distribution patterns in the organisms are characterised by high concentrations of alkylated PAHs (especially methyl phenanthrenes, methyl pyrenes and methyl chrysenes), high chrysene concentrations and low fluoranthene/pyrene ratios. These patterns are indicative of contamination by the *Erika* fuel oil.

8 SUBGROUP ACTIVITIES AND DISCUSSIONS

Whilst MCWG usually works in three subgroups relating to Chemical Oceanography, Trace Metals, and Organic Contaminants, the reduced attendance at the meeting (and the lack of representation within the first two topics) made this impractical, and the MCWG met in plenary throughout the meeting.

8.1 Plenum Activities and those Common to all Subgroups

8.1.1 Review the updated list of relevant certified reference materials for organic compounds for use in marine monitoring including also trace metals and nutrient compounds, and in this connection consider the mechanism for the review and updating of these tables

Documents

Jacob de Boer and Evin McGovern provided tables of updated lists of certified reference materials (CRMs) for organic contaminants for use in monitoring of the aquatic environment (see Annex 5). This information has recently been published (de Boer and McGovern, 2001). Peter Woitke has provided tables of updated lists of CRMs for trace metals in sea water, marine biota and sediments (see Annex 6), and Elisabeth Sahlsten (SMHI, Sweden) has provided tables of updated lists of CRMs for nutrients in surface sea water and waste water (Annex 7). The tables provided are for information and do not necessarily infer that listed CRMs are of an appropriate quality for marine monitoring. Laboratories should evaluate CRMs to ensure that they are fit for the purpose, given their individual circumstances and programmes.

Discussion

Many new certified materials are prepared on a commercial basis each year, and stocks of other previously listed materials may become exhausted so that they are no longer available. The information on these materials is made available by their producers, but there is no specific database identifying CRMs relevant to the marine environment. The MCWG considers such a specific database of CRMs for marine environmental monitoring to be very useful for the potential users within monitoring and marine research laboratories. The information needed for the database is presented in the following table:

Code	
Organization	
Country of origin	
Matrix	
UNITS	
AS	
[±] *expressed as*	
UNITS OF ISSUE	
FORM	
Analytes (concentration)*	

* indication should be given if the concentration is a certified value or tentative

It was noted during the discussion that ICES should consider whether a section of the ICES website could be devoted to a database for marine CRMs, with direct links to the websites of the producers of these materials for additional information. The MCWG considers also that this database could be continuously updated directly by the producers themselves, thereby providing the most up-to-date information in a more timely manner than can be given following the annual meetings of MCWG.

Additional information on the on-going projects

Jacob de Boer informed MCWG of new BCR materials both available now and planned. CRM 682 (in mussels) and CRM 718 (in herring) certified for chlorobiphenyls (CBs) are now available. The CRM 719 for non-*ortho* CBs in chub (a freshwater fish) is in preparation. In addition, a new project will address a two-year feasibility study for new CRMs for PBDEs in sediments and fish, organochlorine pesticides in fish, and PAH in mussels. Tentatively these materials will be available by 2005, following a full-scale preparative project to be undertaken if the feasibility studies are successful.

8.1.2 Review how the presentation of the long-term performance of a laboratory can be standardised taking the information from MCWG2000 into account

This topic was not considered due to the absence of Dr Wells. It will be considered again for MCWG2002.

8.1.3 QA data in the ICES database and data screening

8.1.4 Criteria for data screening and evaluation

These two topics, item 8.1.3 from ICES and item 8.1.4 from the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), were taken together as they represented many common features. SGQAC had prepared a draft template for QA information, which attracted many comments from MCWG members. After discussion and compilation of a list of suggested amendments, it was decided that the most effective way forward would be to redraft the template (see Annex 8). This also forms the basis for the response to the ICES request for advice on which QA data should be stored in the ICES database, as it should be the same as that requested by SGQAC. Where ICES codes for this information exist already, they are given in the new template; where they do not appear, then they will need to be created anew.

8.1.5 Review any new SGQAC annexes on QA and report the outcome

Peter Woitke, member of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (SGQAC), introduced some new annexes to the COMBINE Manual for Monitoring of the Baltic Sea from the 2001 SGQAC meeting for review by MCWG.

There were no comments to the Update on the Note on Contaminants in Fish (Annex 10, SGQAC Draft Report (ICES CM 2001/ACME:04)), nor to the Annex on Estimation of Measurement Uncertainty based on Results of Intercomparison Exercises (Annex 12, Attachment 1, SGQAC Draft Report). The latter should be passed to ICES WGSAEM for review and discussion.

MCWG took note of the Technical Note on the Determination of Organic Carbon in Sea Water (Annex 7, SGQAC Draft Report). Some doubt was expressed on the usefulness of determining dissolved organic carbon (DOC) in sea water. This matter had been discussed at the MCWG meeting in 1997 with the conclusion that the usefulness of determining DOC and consequently also total organic carbon (TOC) for oceanographic purposes is limited. The outcome of the discussion has been annexed to the 1997 ACME report (ICES Advisory Committee on the Marine Environment, 1997, ICES Cooperative Research Report, 222: 125–128). Contrary to the difficulties in reliable determinations of TOC/DOC in sea water, the determination of particulate organic carbon (POC) as well as of particulate organic nitrogen (PON) is based on a well-defined method. The MCWG, however, pointed out that there is a need for CRMs for POC and PON. MCWG recommended to HELCOM/SGQAC to check the development of intercomparison exercises for these parameters.

Regarding the Update on the Technical Note on Units and Conversions (Annex 11, SGQAC Draft Report), MCWG recommended to substitute the chapters on dissolved oxygen and oxygen saturation by the comprehensive paper of Alain Aminot, which was discussed at last year’s MCWG meeting and has been annexed to the 2000 ACME report (Report of the ICES Advisory Committee on the Marine Environment, 2000, ICES Cooperative Research Report, 241: 199–200).

8.1.6 Valid codes for selected parameters

MCWG was asked by the ICES Secretariat to comment on the lists of codes for organic contaminants, their units and CAS numbers on the home page of ICES.

As a general rule, the Group does not recommend that the number of contaminants for which data are submitted to and stored on the ICES database should be limited, only that in a few cases contaminants might be deleted from the list if no data for these contaminants exist in the database. A detailed list of changes is given in Annex 9.

8.1.7 Establish a network of contacts for the ICES data manager with an expert for each current chemical group

A network of primary contacts was proposed as follows:

Gert Asmund - trace metals.

Lars Føyn - nutrients and major organic constituents.

Robin Law - total hydrocarbons, monocyclic and polycyclic aromatic hydrocarbons.

Bo Jansson - organobromine compounds, chlorobiphenyls, cyclodienes, DDTs, dioxins, general organochlorines, and hexachlorocyclohexanes.

Michael Haarich - organometallic compounds.

Jacek Tronczynski - organophosphorus pesticides and triazine herbicides.

Contact details are given in the list of participants (appended as Annex 1).

8.1.8 Storage of information on both limits of detection and limits of determination in the ICES database

This topic was considered along with the other database and QA issues under agenda items 8.1.3 and 8.1.4. MCWG agreed that the provision of both limits of detection and limits of determination in the database would be appropriate.

The new code for limit of determination should also carry a flag “detected but not quantified” to identify values falling between the limit of detection and the limit of determination.

8.2 Trace Metals Subgroup

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

MCWG was asked to consider:

1) the issue of risk assessment methodologies in relation to marine contaminants and how MCWG could contribute to ICES work in this area;
2) whether ICES should co-sponsor a new GESAMP working group on hazard assessment of contaminants in the marine environment in relation to both the quality of seafood for human consumption and also risk to the marine ecosystem;
3) whether one or two members of the MCWG might be interested in participating in this GESAMP group on behalf of ICES.

MCWG realised that its major competence is in the exposure assessment. The method presently used in the EU risk assessment is based on both model-predicted and measured data for exposure. The models are developed for certain types of compounds (mainly lipophilic substances) and the prediction of the distribution for other types of chemicals is more uncertain. The importance of using measured data is therefore stressed by MCWG as a means of validation.

MCWG was not able to fully review the SIME document “Report on developing a Common EU/OSPAR Approach on Risk Assessment Methodology for the Marine Environment”, provided for the meeting. Some comments were made on the section “2.1 Monitoring” under Marine Exposure Assessment. Table x (page 6) describes what can be expected for data from extended monitoring programmes, but these only exist for a few contaminants and the risk assessors will be facing situations where such high quality data do not exist. It is therefore essential that the assessor makes the best use of other measured data so as to validate the model predicted data. The filtering of outliers described on page 7 can also be dangerous, as an increasing concentration of a pollutant often first becomes apparent from the presence of elevated values—in that case indistinguishable statistically from apparent “positive outliers”. Some members of the Group also expressed their fear that strict guidelines may imply that specific properties of the individual chemicals are overlooked in the risk assessment.

The conclusion reached was that MCWG would be willing to comment on the EU/OSPAR marine risk assessment document at a later stage. It was also recommended that the interest of WGBEC, WGSAEM and SGEAM in this process be investigated. If ICES decides to co-sponsor the new GESAMP group on marine risk assessment, it would bring the work to a global scale. Bo Jansson is interested to participate in such a group if it is formed. Jacek Tronczynski will also test the interest of relevant individuals within IFREMER to be represented in this group.

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

No material was provided under this agenda item, and the Group had insufficient expertise to take this topic forward. The subject will be taken forward to the agenda for MCWG2002.

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

No material was provided under this agenda item, and the Group had insufficient expertise to take this topic forward. The subject will be taken forward to the agenda for MCWG2002. Jacek Tronczynski also agreed to solicit further information on recent investigations on this topic from his colleagues in IFREMER.

8.2.4 Review new information concerning the supplementary work to the Icelandic cod study on the relationship between trace element concentrations in cod liver and various co-factors, and report the outcome

No material was provided under this agenda item, although it has now been requested on a number of occasions, and so the Group was unable to take this topic forward. This subject will now be removed from the agenda of the Trace Metals

Subgroup.

8.2.5 Prepare material that can be used by WGSAEM relevant to the development of models for the relationship between the concentration of a contaminant in an organism and the ambient concentration

The Chair of MCWG had tried to contact the Chair of WGSAEM, Dr Steffen Uhlig, in order to clarify his group's request. This was however unsuccessful. Our feeling is that probably what is needed is to direct WGSAEM towards data from the scientific literature, e.g., from uptake and loss experiments. The MCWG Chair contacted Dr Uhlig and the WGBEC Chair, Ketil Hylland, after the meeting to take this forward. The topic will be added to the agenda of WGBEC2001 as they will have the best access to experimental data from studies undertaken generally for ecotoxicological purposes, and these were thought to be initially more suitable for modelling purposes than field data.

8.2.6 Use of Certified Reference Materials (CRMs) in laboratories accredited after ISO 17025

This issue was raised by MCWG and is not in response to any request from ICES.

Gert Asmund presented a document highlighting difficulties experienced in gaining ISO 17025 accreditation for trace metal analysis, when using National Research Council of Canada (NRC) CRMs for quality assurance. In this case the assessor was not satisfied with the traceability and the level of information supplied with the CRMs. However, it was not clear what additional information the assessor required. As yet, other members of the MCWG have not experienced this problem. NRC CRMs are regarded as eminently suitable for use in support of marine environmental monitoring programmes and are indeed widely used in this context. Should the difficulties experienced by NERI be encountered on a wider scale, this could create problems for laboratories engaged in such monitoring. Whilst the accreditation of CRM producers should satisfy ISO 17025 requirements with respect to traceability, the difficulties this presented were recognised. MCWG also agreed that the information provided in NRC certification reports was currently quite limited. Note was taken of the paper by de Boer and McGovern (2001) providing information on available CRMs for monitoring organic contaminants in the aquatic environment (see agenda item 8.1.1 and Annex 5; also the reference below).

It was concluded that NRC should be encouraged to include more information in the certification reports, possibly along the lines of BRC and NIST models. MCWG did not feel it was appropriate, or, indeed, possible, for this group to recommend what information should be included to satisfy the requirements of ISO 17025 assessors.

Reference

de Boer, J., and McGovern, E. 2001. Certified reference materials for organic contaminants for use in monitoring of the aquatic environment. Trends in Analytical Chemistry, 20 (3): 140–159.

8.3 Organics Subgroup

8.3.1 Critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations and report the outcome

This item was considered with item 8.2.1 above.

8.3.2 Review new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane (TCPMe) in fish, including the results of the TCPM and TCPMe interlaboratory study, second phase and report the outcome (initially to WGBEC)

Jacob de Boer presented the results from an interlaboratory study in which 6 laboratories participated. Two fish samples (flounder and dab) and one standard solution were analysed. The differences in the analytical procedures used by the participants were not large. As a consequence of practical problems one analyst used a much smaller sample intake, which yielded higher determination limits. Different detection techniques (ECD, quadrupole-MS and ion-trap-MS) were used successfully. Except for one laboratory that reported technical problems, the results for the fish samples were in good agreement with each other, although the levels in many cases were close to the limit of determination. The standard deviations were higher for TCPMe which was present at lower concentrations than TCPM. Taking the good agreement for the samples into consideration, the results for the standard solution showed some inexplicably large differences. Overall, the results from this exercise were satisfying and showed that the results from these laboratories in North America and Europe are comparable.

Michel Lebeuf presented recent results from the analysis of fish (plaice, sole, halibut, herring, and eel) samples from Europe and Canada that were analysed by Michel Lebeuf, Michael Haarich and Jacob de Boer. Where quantifiable amounts were found in these fish samples, in all cases the samples from Europe showed higher concentrations than those from Canada. Although the results are not representative for the fish stocks from both continents (because only a small number of samples was analysed), levels of TCPM and TCPMe seem from these data to be higher in fish samples from Europe than in those from North America. Similar differences were found earlier in marine mammals from both continents. The hypothesis that the occurrence of TCPM and TCPMe is somehow related to the production of DDT could not be confirmed, as the ratios of TCPM and TCPMe to DDT seem to be different in samples from North America and Europe. To substantiate these findings more samples, focusing on flatfish (sole, dab, flounder and halibut), will be analysed during the next year by Michel Lebeuf, Michael Haarich, Patrick Roose and Jacob de Boer. They will also supply Michel Lebeuf with concentrations of TCPM, TCPMe and DDTs determined in these same samples within their own laboratories before the end of January 2002 so that he can report the results at next year's meeting.

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

During MCWG2000 the group was informed about a European project then under way with the aim of developing a fish bile reference material certified for PAH metabolites. At that time an intercomparison exercise had been held, and a second was planned. Dr Wells agreed at that time to present the results of these studies at this meeting. In his absence, however, the Chair presented a summary report provided by Dr Freek Ariese of IVM, the project coordinator. It seems from this report that the intercomparison exercises must have met with some success, as preliminary storage trials were under way and the certification process had also begun for 2 bile materials (one containing oil-derived and the other combustion-derived PAH metabolites). Insufficient data were however provided to allow an assessment of the robustness of the methodology and the degree of comparability. Further information was sought from Dr Ariese. He advised that the determination of PAH metabolites provides an insight into recent PAH uptake, and that in his experience neither GC/MS nor HPLC/UVF chromatograms are subject to interferences from other compounds (ie., that there are no false positive results). PAH metabolite concentrations depend to some extent on the feeding status, and fish that have fed very recently and have emptied their gall-bladders will show lower metabolite levels. This effect will add to the inter-individual spread, and the representativeness of the group average will depend on the group size. However, one positive aspect of using PAH metabolites as a biomarker of exposure is that the measured parameter is linearly dependent on the uptake (or dose) over several orders of magnitude. This means that even if the inter-individual spread may be as large as 50 %, the group average of a low-exposure population will still be easily distinguishable from that of a high-exposure population. Monitoring should however be carried out during the same season so as to avoid bias due to temperature differences.

The more abundant PAH metabolites can be measured without great difficulty using either HPLC/UVF or GC/MS. The analytical uncertainty (within-laboratory) will in most cases be lower than the inter-individual spread. However, for comparison of data obtained in different institutes, the between-laboratory comparability must also be assessed.

Regarding the repeatability/reproducibility:

Some laboratories have carried out sufficiently large series of determinations to compile long-term control charts, mostly focusing on 1-hydroxy pyrene. At the RIKZ laboratory in Middelburg, NL, an internal reference material was prepared by homogenising a pool of ten fish bile samples, and storing single-shot quantities of 10 microlitres in separate vials at –70 °C. The Shewhart control chart produced for the period from March 1999 to December 1999 (24 measurements on different days) showing an average of 312 ng ml^{-1}, and 2-sigma warning levels at 280 ng ml^{-1} and 344 ng ml^{-1} (sigma = 16 = 5.1 %). Of the 24 data points, 19 are within 1 sigma from the average, 3 data points are within 2 sigma and 2 data points are within 3 sigma of the average. During the latest intercomparison held within the EU-SMT project, repeatabilities of the order 2–8% were obtained for standard solutions and for the major components in real samples.

These results appear comparable to those obtained for other chromatographic procedures. Extraction and/or hydrolysis do not seem to be very critical. However, analysts should be aware of the risk of degradation of standard solutions.

Regarding accuracy: since there is no "absolute method", information regarding the accuracy or "trueness" of the results can only be obtained by comparing results from different laboratories or results obtained in the same laboratory using different methods. The current level of interlaboratory comparability can be improved and this is an aim of the current EU-SMT project. During the latest intercomparison, the between-lab CV for 1-OH pyrene was 28 % and 34 % in the oil-exposed and sediment-exposed fish bile samples, respectively (10 labs, two measurements each). Between-laboratory CVs were higher for the other compounds, which in some cases could be traced back to co-elution or other technical problems. It is expected that by organising further intercomparisons, through better contacts between laboratories, and with the availability of (certified) reference materials, most systematic errors will be identified and overcome in the near future.

A summary of the conclusions from the final report of this intercomparison study will be presented to MCWG2002 by David Wells.

8.3.4 Review new information on the use of passive sampling systems and report the outcome

Ton van der Zande presented results from a collaborative research project undertaken within the Netherlands (NIOZ/RIKZ) into the utility of passive sampling devices for sampling a wide range of non-polar to moderately polar organic contaminants in the water phase in the North Sea and Western Scheldt. The passive sampling media tested consisted of Semi-permeable Membrane Devices (SPMDs), Low-Density Polyethylene (LDPE) membranes and silicone tubing. New and positive results were obtained with silicone tubing. With proper calibration (so as to take account of differences in water flow and ambient temperature during deployment) and with the use of Performance Reference Compounds (PRCs), these devices yield time-weighted average concentrations of dissolved chemicals in the water column, which may be used for monitoring the exposure of biota to dissolved chemicals.

Also, the implementation of *in situ* passive sampling devices can provide a simple, inexpensive and readily available means of monitoring chemical contaminants in the water column, providing data that are capable of theoretically sound interpretation. The current practice in environmental monitoring of organic contaminants in the aquatic environment is often limited to measurements of the bulk concentration in biota or sediments. Typically, the concentration in the water phase is considered too low or too variable over time, and the collection of representative samples for monitoring purposes is not practically feasible. The determination of concentrations of hydrophobic organic compounds using conventional techniques such as liquid-liquid extraction or solid phase extraction is difficult, and often requires the collection of large volume samples. In the marine environment, data for dissolved organic contaminants are relatively sparse and these determinations are generally not included within marine monitoring programmes. Passive sampling using SPMDs offers a number of advantages over conventional techniques, and can also supplement “mussel watch” type studies where these animals are not available. This technique could eventually provide a standardised method for water column monitoring, generating comparable, mutually accepted data, and ensuring harmonisation within relevant EU and international programmes.

It was agreed to follow developments regarding this topic and report back to MCWG2002 if there is any new information available and to provide more information on passive samplers for metals.

8.3.5 Review new information on the monitoring and analysis of toxaphene and report the outcome

Jacob de Boer gave a presentation on the outcome of the EU FAIR-funded MATT (Monitoring, Analysis and Toxicity of Toxaphene) project, which was completed during 2000. Participants included institutes in the Netherlands (2), Norway, Ireland and Germany. The project resulted in the proposal of a tentative tolerable daily intake (TDI) of 0.41 mg for total toxaphene per day for a person of 60 kg. This is considerably higher than the Canadian TDI of 12 µg per day per person of 60 kg. Baseline data collected in this project indicated that the levels of toxaphene (measured as CHB 26, CHB50 and CHB62) in fish from European waters were well below the proposed TDI and for the most part also considerably below the Canadian TDI.

Jean-Pierre Gagné (Institut des Sciences de la mer de Rimouski) outlined the ongoing Canadian research project “Toxaphene in the St. Lawrence marine ecosystem; concentration, ecotoxicology and human health” which is part of the Canadian Toxic Substance Research Initiative (TSRI). The aims of this project are:

- determination of toxaphene levels in biotic and abiotic compartments in the St. Lawrence;
- extraction of toxaphene residues from fish;
- assessment of toxic effects of environmentally weathered toxaphene in fish;
- study of toxic effects of toxaphene on human immune system.

This project will provide complementary information to the MATT project for the following reasons:

- information on toxaphene levels obtained on both sides of the North Atlantic;
- different toxicological studies were employed in each project;

- different approach for isolation of environmentally weathered toxaphene for use in toxicity testing (isolation of toxaphene following cod (*Gadus morhua*) dosing experiments – MATT; isolation, of naturally incurred toxaphene from Atlantic tomcod (*Microgadus tomcod*) from St. Lawrence estuary, Canada).

It was agreed that a further update on the occurrence of toxaphene in marine mammals, comparing data from Canada and from the Arctic Monitoring and Assessment Programme (AMAP), should be presented to MCWG 2002. An update on the TSRI studies will also be presented.

8.3.6 Review new information concerning oil spills, their effects and associated protocols for incident response and report the outcome (initially to WGBEC)

Agenda items 7.2 and 7.3, above, are also relevant to this topic. MCWG was informed that the European Standards Institution CEN is looking to develop a new standard procedure for the fingerprinting and identification of spilled oil. The CEN/BT Task Force 120: Oil Spill Identification held its first meeting in Helsinki in November 2000. The next meeting is scheduled for June this year. Its task is to develop standard(s)/guidance for the characterisation and identification of waterborne oil spills.

8.3.7 Review recent data on dioxins, furans, and dioxin-like PCBs in fish, with particular reference to Baltic fish, and report the outcome (initially to WGBEC)

Jacob de Boer presented a paper entitled "Dioxins and dioxin-like CBs in fish and feed and the current status of legislation in the EU". This paper includes two annexes with data derived from (i) the SCOOP project, which was a European study of literature data on dioxins in food, and (ii) a Dutch study on dioxins and PCBs in (mainly) Dutch fishery products. These annexes also include mean dioxin data for samples of Baltic fish. These data were not essentially different from the data in the paper coded MCWG2001 8.3.6/2, entitled "Annex 6: Use of Baltic clupeoids to make fish meal (protein) for the manufacture of fish feed". Therefore, the data cited in that paper (for the maximum levels of dioxins in Danish industrial fish landings) should be considered as correct.

The WHO advice for a tolerable daily intake (TDI) for dioxins and dioxin-like CBs has been set at 1–4 pg kg^{-1} body weight (bw). This advice was adopted by the European Committee on Food (SCF) and transferred into a temporary tolerable weekly intake (t-TWI) of 7 pg kg^{-1} bw. The current intake of dioxins by the general European population is above this t-TWI. In the Netherlands the intake is 1.8 pg kg^{-1} bw / day^{-1}, of which 0.25 pg kg^{-1} bw (14 %) is contributed by fishery products, with the remainder from other dietary items. This demonstrates that simply setting tolerance levels for dioxins and dioxin-like CBs in fish and fishery products will not result in a substantial reduction of the dioxin intake by the population of the Netherlands. Even a total ban on fish consumption would not reduce the dioxin intake to below the t-TWI of 7 pg kg^{-1} bw. Nevertheless, in the near future statutory tolerance levels might be set in Europe. Recently, a tolerance level of 8 pg g^{-1} for dioxin only was set for eel in the Netherlands. A Dutch tolerance level for fishery products in general, including dioxin-like PCBs, is also in preparation.

The level of dioxins and dioxin-like CBs in farmed fish can be controlled by selection of the feed. Recent data from the European Scientific Committee on Animal Nutrition (SCAN) show that Pacific fish oil and fish meal have an approximately eight-fold lower dioxin and dioxin-like PCB contamination than that found in European fish oil and fish meal. Therefore, by using Pacific fish oil and fish meal, lower dioxin and PCB concentrations in farmed fish can be obtained. Other options are the removal of dioxins and PCBs from the fish oil and meal by specific techniques such as distillation or carbon treatment, or a partial administration of vegetable oils in the place of fish oils. Treatment of the fish prior to consumption (baking, frying, smoking, etc.) may also lead to some reduction of the dioxin and PCB concentrations in the products as consumed. The paper by van Leeuwen and de Boer (see Annex 10) includes an overview of the available literature on this aspect. However, given the limited amount of information available and the large variations in the treatment methods, firm conclusions cannot be drawn.

The sources of dioxins were discussed. Forest fires were suggested as a possible (natural) source. However, these cannot be considered as the major source as most of the dioxins in the environment originate from combustion processes, amongst which municipal waste burning is one of the more important sources.

In fish, PCBs make a larger contribution to the total toxic equivalent (TEQ) values than do the dioxins. Generally the CB-TEQ is higher than the dioxin-TEQ by a factor of 2 to 3 times, but in some cases this ratio has been up to 10 times or more. This means that the dioxin "problem" in fish is in reality more of a "PCB problem". MCWG agreed with the approach of including dioxin-like CB-TEQs in the derivation of TDIs and possible tolerance levels. Laboratories conducting dioxin analyses will soon be able to analyse mono-*ortho* CBs in addition to the non-*ortho* CBs, dioxins and furans. Given the advice of WHO and the SCF, which is based on a total TEQ, and the logical structure of the TEF concept, the non-inclusion of dioxin-like CBs would hinder the overall risk assessment of dioxin-like compounds. The inclusion of other compounds which show dioxin-like effects and for which TEF factors can be derived, such as polychlorinated naphthalenes (PCNs), should also be considered in the future.

The limited information available on time trends suggests a decreasing trend of TEQ values in fish, mainly as a result of decreasing levels of PCB contamination. In several countries, dioxin and PCB monitoring was terminated at the beginning of the 1990s, partly as a result of financial constraints, and partly because the decreasing values suggested that PCBs were a problem solved. The further development of toxicological knowledge has, however, led to a new situation in which dioxin and PCB concentrations in fish are now much closer to the new, lower, levels of concern. MCWG emphasised the risk of an early termination of monitoring programmes in general, which, as in this case, can easily lead to gaps in knowledge and can seriously hinder decision-making processes.

Finally, a recent publication of S. van der Plas *et al.* (Toxicology and Applied Pharmacology, 169: 255–268 (2000)) was discussed. One of the conclusions of this publication was that the majority of the tumour-promoting potential of PCB mixtures resides in the non-dioxin-like fraction, which is not taken into account in the TEQ approach for risk assessment of PCBs and dioxins. This is then likely to result in an underestimation of the tumour-promoting potential of environmental PCB mixtures. MCWG concluded from this information that given the apparent tumour-promotion potential and other known toxic effects (e.g., neurotoxic effects) of the di-*ortho* PCBs, monitoring of these di-*ortho* PCBs should be continued in addition to the monitoring of dioxins and non-*ortho* and mono-*ortho* substituted PCBs.

The paper of van Leeuwen and de Boer was considered to be complete enough to serve as a basis for advice to ICES and WGBEC on the presence of dioxins and dioxin-like PCBs in fish, and it is appended to this report as Annex 10.

8.3.8 Review new information concerning polybrominated diphenylethers (PBDEs) and report the outcome

On this subject, Jacob de Boer presented (a) an overview of the results of the first world-wide interlaboratory study on polybrominated diphenylethers (PBDEs), and (b) a report on the outcome of a national study on measurements of PBDEs and polybrominated biphenyls in different matrices.

(a) The first interlaboratory study on PBDEs involved eighteen laboratories from nine countries. Seven different materials and a standard solution were analysed, comprising biota (eel, mussels, cormorant liver, harbour porpoise liver and blubber oil) and two sediment samples. The laboratories were asked to determine the concentrations of congeners BDE 47, BDE 99 and BDE 209 in all samples, and some additional congeners including BDE 100, BDE 153 and BDE 154 on a voluntary basis.

The results for BDE 47 showed good agreement between the laboratories for seven of the eight samples. Also the results for BDE 100 were acceptable, whereas the analysis of BDE 99, BDE 153 and BDE 154 requires further improvement. The analysis of BDE 209 gave unsatisfactory results and was obviously not under control in the laboratories, neither for biota nor sediments, with relative standard deviations (RSD) not better than 48 % and 78 %, respectively. But even the analysis of the standard solution showed problems for BDE 209, demonstrated by the RSD of 44 %, as compared with RSDs for BDE 47 (20 %) and BDE 99 (28 %). One reason may be the temperature sensitivity of BDE 209, which may cause losses due to deterioration in the injection system as well as on the column of the analytical system. Although improvement is needed, particularly for the determination of BDE 209 as well as for the calibration of all congeners, this study was a successful first step towards comparable results for the analyses of PBDEs. The main subjects of a short discussion were related to technical details, particularly the clean-up procedure for sediments, injection conditions for BDE 209 and MS-identification. Further guidance will be given to participants in a future study, which is currently in preparation.

(b) In the second part of the presentation, the results of a Dutch national study on PBDEs and PBBs in suspended particulate matter (SPM), sediments, sewage treatment plant (STP) influents and effluents, and biota from the Netherlands were presented. PBBs were not found in any of the samples. Detected concentrations and ratios between BDE congeners differed greatly for different matrix types: e.g., BDE 47 was highest in fish samples and STP effluent residues, whereas BDE 209 could not be determined in any of the biota samples, but was high in SPM, sediments, STP influent filtrate, waste water and particularly in STP effluent residues. For BDEs in SPM it was shown that the highest concentrations were detected in samples originating from the Western Scheldt area.

In discussion, some additional information was given: although the dioxin-like effects of PBDEs are less than for PCBs, particular concern was expressed as some congeners are accumulated in the brain. Concentrations of tetra- and penta-BDEs are apparently increasing in marine mammals from North America, but not in samples from the Netherlands. On the other hand, tetra- and penta-BDE concentrations have increased recently in human milk from Sweden. One possible reason for the lack of data for BDE 209 may be analytical problems (see first part of the presentation) combined with low or zero concentrations in biota.

Detailed descriptions are given in: (a) Jacob de Boer (2000): First world-wide Interlaboratory Study on Polybrominated Diphenylethers (PBDEs). Organohalogen Compounds, 45: 118–121.

(b) Jacob de Boer, Aschwin van der Horst, and Peter G. Wester (2000): PBDEs and PBBs in Suspended Particulate Matter, Sediments, Sewage Treatment Plant In- and Effluents and Biota from the Netherlands. Organohalogen Compounds, 47: 85–88.

8.3.9 Review new information concerning new contaminants in the marine environment and report the outcome, and submit results of discussions to WGBEC

Under this item, the Group considered a report "The Aquatic Fate and Effects of Antifouling Paint Booster Biocides" prepared by Dr Kevin Thomas of the CEFAS Burnham Laboratory. Jacek Tronczynski drew MCWG's attention to an ongoing EU programme ACE which involves studies of the same group of compounds as those covered in the paper (Irgarol 1051, diuron, Sea Nine 211, TCMTB, dichlofluanid, chlorothalonil, TCMS pyridine and copper/zinc pyrithione). More environmental data will also be forthcoming from that programme, and within the next few months a website and database will also become accessible. Oestrogenic testing of these compounds has also been undertaken within the ACE programme, and estuarine data suggest that Irgarol 1051 and diuron have other uses in addition to antifoulings. New data are available on the biological availability and uptake of either the biocides themselves or their degradation products. Finally, our understanding of the fate of these compounds when associated within particulate paint waste is poor. Additional studies are under way to address these issues, and allow the risks posed by each of these compounds to be assessed, and so to determine whether they offer a safe alternative to organotin antifoulants. During discussion, Bo Jansson asked a question relating to the reduced half-life of Sea Nine 211 in synthetic sea water with algae—is this due to attachment or do the algae break down this compound? Michel Lebeuf asked whether Irgarol 1051 was used in the USA and Canada, as no data on environmental occurrence were presented for these countries. Jacek Tronczynski felt that it was likely that the major biocide used in North America was Sea Nine 211. MCWG commended Dr Thomas for preparing a very nice overview, and recommended that, after the incorporation of comments from members of MCWG and WGBEC (to which it has already also been submitted), it be revised and submitted to ACME2001.

8.3.10 Evaluation of the significance of volatile organic compounds to the marine environment

During MCWG2000, two presentations had been given concerning the presence of volatile organic compounds (VOCs) in the marine environment. At the time it was already mentioned that VOCs were unlikely to present a significant hazard for organisms and the marine environment as a whole. As a follow-up, a short presentation and paper were presented by Patrick Roose that contained the most important findings of a recently published paper by Roose and Brinkman (2001) (summarised in Annex 11). The authors used a hazard assessment procedure proposed by van Leeuwen *et al.* (1992) that ultimately results in the calculation of a threshold concentration that is unlikely to cause harm to 95 % of the aquatic community. This calculated concentration, HC5, is the hazardous concentration that will affect, at most, 5 % of the species. The concentrations that were found in the environment were generally a factor 10 or more below these HC5 values. However, the authors qualified their findings by stating that no information was available concerning possible long-term effects of these contaminants in the marine environment. Even though the conclusions of the paper were based on a large and robust data set, they only relate to a relatively small region and no information is available for other areas. It is not therefore possible to extrapolate these findings to the marine environment as a whole. During the discussion a Norwegian study on the effect of the volatile fraction of oil on fish larvae was mentioned. Benzene is a major constituent of this fraction and the study demonstrated that effects were observed at low concentrations (possibly comparable to those found in the study described above).

Roose, P., and Brinkman, U.A. Th. 2001. Volatile organic compounds in various marine organisms from the southern North Sea. Marine Pollution Bulletin (to be published in 2001).

van Leeuwen, C.J., Van Der Zandt, P.T.J., Aldenberg, T., Verhaar, H.J.M., and Hermens, J.L.M. 1992. Application of QSARS, extrapolation and equilibrium partitioning in aquatic effects assessment. I. Narcotic industrial pollutants. Environmental Toxicology and Chemistry, 11: 267–282.

8.3.11 Prepare material that can be used by WGSAEM relevant to the development of models for the relationship between the concentration of a contaminant in an organism and the ambient concentration

This was taken with agenda item 8.2.5, above.

8.3.12 Review new information on polyfluorinated substances

Bo Jansson gave a presentation on the environmental occurrence and toxicity of polyfluorinated compounds. During the last few decades a lot of attention has been paid to the environmental presence of chlorinated compounds. More recently, the brominated compounds, predominantly brominated flame retardants, have received more attention within environmental research laboratories. However, until now little work has been conducted regarding fluorinated compounds, in spite of the fact that fluorinated compounds are being used frequently and in relatively high quantities in products used in our daily lives. Some specific applications of these compounds are the surface treatment of textiles, leather, carpets and fabric/upholstery to protect these materials against soil, oil and water; paper protection against grease, oil and water, such as in food contact materials; and their use in fire fighting foam, floor polish and shampoos. On 16 May 2000 the 3M Corporation, the main producer of fluorinated chemicals, announced a phase-out of all products "based on perfluorooctanyl chemistry". This includes compounds as perfluorooctylsulfonate (PFOS), perfluorooctylsulfonamide (PFOSA) and perfluorooctanoic acid (POAA). The reasons for this phase-out were given as the possible risks that these compounds presented to humans and the environment.

PFOS has been reported to be present in the environment in relatively high concentrations. It has to date been found in cormorant liver, sea otter blood, striped dolphin, chinook salmon liver, herring gull plasma and in several other organisms. The presence of PFOS in polar bear livers indicates that this compound is present at locations far removed from its sources. Therefore, the presence of PFOS in the environment should be considered as being of concern. Mean PFOS concentrations in eagle blood were 4-fold higher than the DDT concentrations and 2-fold higher than PCB concentrations in the same samples. Fluorinated compounds are generally very stable. The C-F bond is stronger than both the C-Cl bond and the C-Br bond. PFOS is very stable in human tissues, having a half-life of ca. 4 years. Mean levels of 30–44 $\mu g\ kg^{-1}$ in adult blood and of 54 $\mu g\ kg^{-1}$ in that of children have been reported. The acute toxicity of PFOS is not particularly high, but various serious chronic toxic effects have been reported. In a second generation rat study, all pups were killed at a dose of 3.2 mg kg^{-1} body weight day^{-1}. A relatively high toxicity was also found in ecotoxicity tests.

Because of the polar character of these compounds, LC/MS with negative chemical ionisation is the preferred method for their determination. MCWG emphasised the need for further development of analytical methods for fluorinated substances and the need for the collection of more data on the environmental presence of these compounds.

8.4 Chemical Oceanography Subgroup

8.4.1 Review and report oxygen determinations in sea water by the Winkler titration and membrane electrodes

Patrick Roose presented a paper "Comparing oxygen determinations in sea water by Winkler titration and membrane electrodes". These comparisons were made for a series of sampling stations situated along the Belgian coast and in the Scheldt estuary. The conclusion of this study was that, in general, the methods compared very favourably. It was noted however that the comparability was poor for anoxic waters, and that there was also higher variability in samples which were oversaturated. It is recognised that the Winkler method can be accurate even at low concentrations of oxygen (< 0.5 ml l^{-1}). It should also be noted that there is an inherent time-lag when using electrodes, and this should be considered when making vertical profiles. It was suggested that calibration of the electrodes at 0 % DO in addition to saturation may improve the performance of the electrode determinations at low DO concentrations, and that any further information available on this procedure should be presented at MCWG2002.

For seawater monitoring in Belgium henceforth, routine determinations of DO will be carried out using the electrode method, and the Winkler method will be used occasionally as an independent control.

8.4.2 Review and report from a multiship experiment of sampling and determination of chemical variables in sea water

Patrick Roose reported on a project which involved the comparison of data from four research vessels (MS "Argus", MS "Cygnus", MS "Mitra" and RV "Belgica"). Sampling at a depth of 3 metres was carried out in two different zones (comprising four stations in all) in the Scheldt estuary, on two consecutive days. The aim was to compare the results of *in situ* measurements, and to evaluate the variability caused by sampling. Samples were analysed by two different labs (MUMM and RIKZ), operating under strict QA/QC protocols. Filtration of water samples was conducted on board the vessels, immediately after sampling. Samples for nutrient analysis were stored at –20 °C. Lars Føyn referred to an earlier project which had demonstrated that unreliable results were obtained if samples were stored frozen prior to analysis. For samples collected within the Arctic monitoring programmes, the storage of samples prior to analysis currently involves the addition of chloroform (in order to inactivate metabolism) and sample storage in a refrigerator at a temperature around +4 °C. Patrick Roose will describe the sample storage experiment undertaken to validate storage at –20 °C at MCWG2002.

Results for the following parameters were presented: suspended particulate matter (SPM) content, nitrate, nitrite, ammonia, phosphate, silicate. Averages, relative standard deviations (%) and Z-scores were calculated for all these parameters. For the RIKZ and the MUMM laboratories, 98 % and 86 % respectively of the results were within $Z = \pm 2$, and the results obtained for the same samples were never significantly different from one another. Nevertheless, after carefully analysing the SPM data it was concluded that the Mitra pump system had a technical problem; this was resolved later. Nutrient results that were highly variable for samples collected from two of the vessels were ascribed to improper sampling or sample handling techniques. In conclusion, this exercise demonstrated that it was possible to identify a number of problems in both sampling and analysis and to resolve them. Sampling by a qualified team using well-documented procedures resulted in the generation of reliable and comparable data.

8.4.3 Review and report on progress in the modelling of marine biogeochemical processes

No progress has been made with this subject as the new ICES Study Group on the Modelling of Physical and Biological Interactions has not met to date. The agenda item will be carried forward to the MCWG2002 meeting.

8.4.4 Review and report on progress in the studies of estuarine behaviour of nutrients

No material was provided under this agenda item, and the group had insufficient expertise to take this topic forward. The subject will be taken forward to the agenda for MCWG2002.

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

No material was provided under this agenda item, and the group had insufficient expertise to take this topic forward. The subject will be taken forward to the agenda for MCWG2002.

9 PLENARY DISCUSSION OF SUBGROUP WORK

This was unnecessary during this meeting of MCWG as all topics were considered in plenary.

10 ANY OTHER BUSINESS

A series of comments were submitted to MCWG by Dr Chiffoleau regarding a recent QUASIMEME intercomparison exercise concerning dissolved trace metals in sea water. He commented that there were apparent shortcomings in the way in which the samples were prepared and presented to participants. MCWG considered this and prepared the following advice:

a) *The samples for dissolved trace metals were not wrapped with any plastic bag, although it has been known for many years now, and especially after previous ICES intercomparison exercises, that seawater samples can be dramatically contaminated by dust, even in relatively clean environments like chemistry laboratories, and/or by the hands of the operators. Metal-enriched dust may settle on the top of the bottle necks or on the lips of the caps, parts that come into contact with the liquid to be analysed when shaking or pouring. Please note that seawater CRMs are always covered with plastic bags.*

This has been the subject of previous advice from the Trace Metals Subgroup and it was agreed that "best practice" is to wrap sample bottles in plastic bags before distribution. Samples distributed within the later ICES exercises also carried a cautionary note to the effect that bottles should only be opened in a clean area so as to further guard against possible contamination.

b) *The bottles containing dissolved mercury samples are of glass. It is now known that adsorption phenomena occur on such a material, and thus Teflon bottles would be preferred.*

MCWG felt that acidified samples, stored in glass and wrapped in plastic, would be suitable for these analyses.

c) *It is not judicious to produce an artificial estuarine water by mixing sea water and milli-Q water, because the particulate content, in addition to the levels of contaminants, are often more elevated than those of sea water. Also, the dissolved organic matter content of the artificial product would be much lower than that normally present in estuarine water, and as this can present difficulties in the pre-concentration steps (due to strong associations with some trace metals) this is not representative of the true situation facing the analyst.* [NB last sentence slightly expanded by MCWG for clarity].

MCWG agreed that if it were possible to collect an estuarine water sample, then this would be preferable.

d) *It is not helpful to provide the laboratories with spiked water: the techniques of determination of seawater-dissolved trace metals are highly specific (e.g., work in clean rooms, pre-concentration steps, control of contamination in each step of the procedure…) when these requirements are not necessary when analysing highly contaminated water. The best way to help labs to improve their proficiency is to put them under real conditions.*

MCWG recognised the validity of this opinion, and it has previously been recorded in advice given by the Trace Metals Subgroup. However, in the last QUASIMEME exercise, two spiked samples were distributed along with one unspiked sample, and the levels of spiking were not unrealistic.

e) *Finally, seawater samples highly concentrated in trace contaminants can dramatically contaminate the analytical operating systems, when it is already difficult to maintain them at their cleanest.*

The Trace Metals Subgroup has previously advised that samples spiked at high concentrations should carry a warning notice to that effect, and MCWG noted that in the QUASIMEME exercise referred to an indication of the range within which the spiked value fell was given for each such sample.

QUASIMEME is invited to note these concerns and to take them into account in future exercises of this type.

11 RECOMMENDATIONS AND ACTION LIST

The action list and the recommendations are given in Annexes 12 and 13, respectively.

12 DATE AND VENUE OF THE NEXT MEETING

MCWG discussed the venue and dates of the next meeting. One of the German members, Peter Woitke, kindly offered to host the 2002 meeting of the MCWG at the Federal Environmental Agency in Berlin. MCWG acknowledged the invitation with appreciation. It was decided to plan the meeting for week 10 (4–8 March 2002).

13 CLOSURE OF THE MEETING

The members of MCWG expressed their appreciation to Michelle Noel, who had assisted Michel Lebeuf so effectively in making arrangements for the meeting. The Chair thanked all the participants for all their hard work and support during his first meeting as Chair, and closed the meeting at 12 noon on 2 March 2001.

ANNEX 1: LIST OF PARTICIPANTS

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ANNEX 2: AGENDA.

ICES Marine Chemistry Working Group: 23rd meeting
Mont-Joli, Canada, 26 February – 2 March 2001

1. OPENING OF THE MEETING

2. ADOPTION OF THE AGENDA

3. REPORT OF THE 88TH ICES STATUTORY MEETING

4. REPORTS ON RELATED ACTIVITIES

4.1 OSPARCOM AND HELCOM
Any official requests from OSPARCOM 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.

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 Charles Gobeil
Recent change in organic carbon flux to Arctic Ocean deep basins: Evidence from acid volatile sulfide, manganese and rhenium discord in sediments.
7.2 Kenneth Lee
Biodegradation of petroleum hydrocarbons stranded in low-energy shoreline environments.
7.3 Jacek Tronczynski.
Contamination by PAH of intertidal and subtidal compartments after the ERIKA oil spill.

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 Plenum activities and those common to all subgroups. (see also agenda item 9).
8.1.1 review the updated list of relevant certified reference materials for organic compounds for use in marine monitoring including also trace metals and nutrient compounds, and in this connection consider the mechanism for the review and updating of these tables;

8.1.2 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.

8.1.3 review which QA data should be submitted to the database together with environmental data and how a data filter could be organised and operated and report the outcome.

8.1.4 in association with SGQAC, prepare guidelines containing criteria for data screening and evaluation prior to assessment of chemical monitoring data. *(This item is a request from HELCOM: [HELCOM 2001/2]).*

8.1.5 review any new SGQAC Annexes on Quality Assurance and report the outcome. *[HELCOM 2001/1].*

8.1.6 review contaminants in the ICES contaminants database to:

   i) establish and define new classifications for compound identification to clarify types of compounds based on isomers, size, and active sites, and preliminary identification when CAS numbers are not available;
   ii) set criteria for acceptability for inclusion in the database (e.g., need for isomer specifications);
   iii) review currently used ranges of detection and contamination;

8.1.7 establish a network of contacts for the ICES data manager with an expert for each current chemical group.

8.1.8 Storage of information on both limits of detection and limits of quantification on the ICES database.

8.2 Trace Metals Subgroup

8.2.1 critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations and report the outcome.

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

8.2.3 review new information on the use of membrane systems for sampling and report the outcome.

8.2.4 review new information concerning the supplementary work to the Icelandic cod study on the relationship between trace element concentrations in cod liver and various co-factors and report the outcome.

8.2.5 prepare material that can be used by WGSAEM relevant to the development of models for the relationship between the concentration of a contaminant in an organism and the ambient concentration.

8.2.6 use of certified reference materials in laboratories accredited after ISO 17025.

8.3 Organics Subgroup

8.3.1 critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations and report the outcome.

8.3.2 review new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in fish, including the results of the TCPM and TCPMe interlaboratory study, second phase and report the outcome (initially to WGBEC).

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

8.3.4 review new information on the use of membrane systems for sampling and report the outcome.

8.3.5 review new information on the monitoring and analysis of toxaphene and report the outcome.

8.3.6 review new information concerning oil spills, their effects and associated protocols for incident response and report the outcome (initially to WGBEC).

8.3.7 review recent data on dioxins, furans, and dioxin-like PCBs in fish, with particular reference to Baltic fish, and report the outcome (initially to WGBEC).

8.3.8 review new information concerning polybrominated diphenylethers (PBDES) and report the outcome (initially to WGBEC).

8.3.9 review new information concerning new contaminants in the marine environment (booster biocides) and report the outcome, and submit results of discussion to WGBEC.

8.3.10 as a follow up to work conducted in 2000 on volatile organic contaminants, provide an evaluation of the significance of these compounds in the marine environment, and submit results of discussion to WGBEC.

8.3.11 prepare material that can be used by WGSAEM relevant to the development of models for the relationship between the concentration of a contaminant in an organism and the ambient concentration.

8.3.12 review new information on polyfluorinated substances.

8.4 Chemical Oceanography Subgroup

8.4.1 review and report oxygen determinations in sea water by the Winkler titration and membrane electrodes.
8.4.2 review a report from a multiship experiment of sampling and determination of chemical variables in sea water.
8.4.3 review and report on progress in the modelling of marine biogeochemical processes.
8.4.4 review and report on progress in the studies of estuarine behaviour of nutrients.
8.4.5 review and report on the present knowledge about total nitrogen, total phosphorus, and total organic carbon in sea water, their speciation, and arguments for their use in monitoring programmes.

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: IODE OBSERVER'S REPORT

XVIth Session of the IOC's Working Committee on International Oceanographic Data and Information Exchange

Lisbon, Portugal, 29 October–9 November 2000

1. ICES was represented by the ICES Oceanographer (H. Dooley) who attended part of the Session. As the coordination mechanism for international oceanographic data management practices, the session was also attended by a number of ICES Member Countries most of the representatives of which are active in the ICES Working Group on Marine Data Management and/or the Oceanography Committee. These were Belgium (who announced a formal entity in the IODE system immediately prior to the meeting), Canada, Finland, France, Germany, Netherlands, Norway, Spain, Sweden, Portugal, Russia, UK, and USA. A total of 71 countries participate in IODE and many of these attended this meeting.

2. The Working Committee was chaired by B. Searle, leader of the Australian Oceanographic Data Centre. The Chair, with the backing of his Data Centre, is instrumental in pushing IODE forward to meet currently perceived challenges presented by the developing global oceanographic programmes, in particular GOOS.

3. In his frank review of the IODE System, the Chair saw the following as currently positive aspects of the IODE system, many of which remain achievements to be sought:

- Long-term archival capabilities and experience.
- Proven capabilities of establishing and operating data management programmes.
- Existing partnerships with a large number of scientific and intergovernmental programmes and projects.
- Large number of individuals (several hundred) working on marine data management activities – developing applications, undertaking quality control, developing databases and data products.
- Broad expertise across most marine data parameters and marine information.
- Data management, Information Technology, oceanographic, climate change expertise.
- Excellent spirit of cooperation and collaboration.
- Capabilities in data management training and capacity building.

(a) His list of perceived weaknesses of this system has been apparent for a number of years. The ICES Working Group on Marine Data Management has been attempting to address some of these weaknesses for a number of years, but with limited success.
   a) Projects are predominantly driven by individuals and their success is very much dependent on the enthusiasm of the project leader.
   b) Poor performance is difficult to rectify.
   c) Volunteer basis of operation.
   d) Insufficient budget to fully fund projects – generally seed funding only.
   e) Limited cooperation between data centres on a practical or day-to-day level.
   f) Limited visibility of the IODE data management process.
   g) Each NODC operates in isolation from the others, developing similar procedures and computing systems (significant duplication of effort).
   h) Different national agendas for each NODC resulting in different views, procedures and objectives.
   i) Lack of agreed standards for data management and data exchange.
   j) Lack of commercially developed marine-specific data management software.
   k) National focus at the data centre but IODE operates as an international programme.

(b) There was considerable debate and concern about the current discussion in IOC for a revised oceanographic data policy required by the demands of, *inter alia*, the forthcoming global programmes. The Committee are very much for the *status quo*, and have recommended to IOC to revert to the original policy of completely free and open exchange, but also to respect the desires of individual groups who wished to place temporary restrictions on data. In this way it is hoped that data will flow to IODE data centres as soon as possible after their collection.

(c) The Session was informed about a number of information and metadata initiatives that are under way and which are being adopted by, or due to be adopted by, GOOS. The principle of these is GOSIC, which is an initiative of the University of Delaware and serves as the focus to sources of data in support of GOOS. In addition, the revised and updated MEDI (Marine Environmental Data and Information) system is being seen as the primary metadata information system for GOOS. To facilitate this, MEDI is being redesigned as a close interface to the online catalogues of the Global Change Master Directory system (GCMD).

(d) Following the discussion on the status of NOPs (National Oceanographic Programmes) and ROSCOP (CSRs) it was agreed that the ICES Secretariat will work closely with the Oceanic on-line system at the University of Delaware with a view to a closer integration of these important data tracking systems. It was also agreed that IOC should stop circulating hard copy NOPs, as these were not very popular as more countries were resorting to web-based programme information.

(e) GODAR (Global Ocean Data Archaeology and Rescue) remains one of the most important of IODE's projects, being the focus of global oceanographic data CD-ROMs. The Session approved the further development of this project by the establishment of the World Ocean Database Project which will give special attention to the speed of transfer of modern data in real-time into such databases for research, monitoring or establishment of quality control for oceanographic data on local, regional and global scales to support research and real time analysis of data.

(f) In a parallel initiative promoted by the French and Canadian data centres, the session approved the establishment of a Pilot Project on Underway Sea Surface Salinity. This initiative recognises the potentially very large source of such data being collected on many ships and research ships of opportunity using thermo-salinographs. It is now expected that a formal data management system will be set up along the lines of the GTSPP (Global Temperature and Salinity Profile Programme) with a view to maximising the input of these data (via the GTS) into the IODE system. ICES, as the main source of such data meantime, will play an active part in this activity, in the company of the French, Canadian, German, Greek and UK data centres and the World Data Centre for Oceanography. Although addressing only salinity initially, it is the intention that this project will move quickly towards the development of systems for a wider range of underway observations.

(g) There were a number of initiatives proposed in relation to the provision of internet-based training and information kits, as well as initiatives to promote the visibility of IODE. In particular the Netherlands will take the lead in making an electronic presentation of the virtues of the IODE and the IODE system. The session formally approved the establishment of the IODE Resource Kit project which is primarily of use to IODE training projects. This kit primarily draws on web pages downloaded from various websites, including those maintained by the ICES Secretariat. The session also learned about the IOC Secretariat's initiative in establishing an Ocean Portal and was informed additionally about portal developments in other areas. One notable development in this regard is the portal OneFish that was described by its developer, who made a presentation to the Committee, as a vertical portal (Vortal).

(h) The Committee was informed about the important need for IODE to become involved rapidly in the development of XML for the exchange of marine data. XML came into being 2–3 years ago, and its potential use in oceanographic data exchange was recognised by IODE's Group of Experts on the Technical Aspects of Data Exchange (GETADE) at its 8th session earlier this year. The immediate interest of and direct actions by a number of data centres in XML make it urgent for IODE to participate in the selection of standards for a marine XML. Consequently, the Session agreed to IODE participation in a W3 marine XML international consortium. In ICES it is expected that further development in XML applications will be focused through the ICES Working Group on Marine Data Management. However it is very likely that interest in and use of XML will spread broadly across many of the data and information systems in which ICES is directly involved.

(i) Following the initiative of Canada, IODE agreed to establish a group which would develop the means to encourage contacts with the many existing and planned international marine monitoring programmes. This proposal was based on the recognition that many international and national data management activities were being pursued and developed without IODE having the opportunity to promote its practices and principles in these programmes. Consequently, it is expected that this group, which will be led be MEDS (Canada) and BODC (UK), will facilitate future direct and/or indirect contributions of IODE to these programmes. Although seeing GOOS as a primary focus for this activity, the terms of reference for this Group cover all aspects of international research and monitoring programmes.

(j) IODE has traditionally focused on the management of physical data, but this meeting saw the first signs of recognition of the need to broaden the basis of IODE data types. A Group of Experts on chemical and biological data has now been established, although initially this will have a fairly narrow focus on plankton data. ICES Member Countries may be expected to play a major role in this. The Committee also recognised the need to become involved in Pollution data (sic), but considered it premature to propose strategies for the management of these data for the needs of, for example, GIPME, whose future focus will be on anthropogenic activities, including GOOS–related initiatives such as Rapid Assessment of Marine Pollution (RAMP). For the time being IODE will proceed by documenting the experiences within the IODE community in managing and archiving pollution (sic) data. Although not part of the IODE community, it is expected that ICES Secretariat activities in the area of marine contaminant data management will be included in this exercise.

ANNEX 4: CRITERIA FOR SCREENING DATA FOR ANALYTICAL QUALITY IN CONTAMINANT TREND STUDIES

ICES MCWG 2001 4.4 1/1

Mike Nicholson, Rob Fryer, Robin Law and Ian Davies

Summary

Although targets for laboratory QA are important, failure to meet these targets does not mean that data generated by the laboratory are worthless. In contaminant trend studies, when the level of environmental variability is low, meaningful trends can still be detected even when levels of analytical variability are high. Conversely, when the level of environmental variability is high, trend detection is poor regardless of the level of analytical variability.

A simple way to use data with poor underlying QA is to down-weight the corresponding data in the statistical analysis. Such data are easily identified in the analysis, and the analysis provides more-effective trend detection than simply rejecting the data.

The informal use of *P* and Z scores to categorise data as, e.g., *satisfactory* can be misleading, with more data than expected apparently meeting targets for precision and fewer than expected apparently meeting targets for bias. Modified rules are described which maintain a fixed probability of incorrectly concluding that targets have not been met.

1 Introduction

In its 2000 report, the Marine Chemistry Working Group commented that although laboratory QA is regarded as absolutely necessary, it is unclear how *this information … can be incorporated into, e.g., the determination of temporal trends* and questioned what is the best approach to take into account the performance of laboratories in intercomparison exercises?

They provided a review of different national criteria for signifying that performance at a particular laboratory is adequate – e.g. for the UK, that 80 % of the laboratory means are within limit value of a maximum tolerable bias as set by the organiser of the proficiency test.

However, none of these criteria were based on any quantitative justification that, in some sense, data generated by the laboratory would be fit for their purpose. Further, there was no explicit guidance on how these criteria could be used to accept/reject data submitted to international assessments.

Nicholson (1994), Nicholson and Jones (1996) and Fryer *et al.* (1999) showed that in trend studies, targets for analytical quality can be constructed based on the levels of environmental variability and the magnitude of the trend considered worth detecting. However, this approach still leaves the problem of how to deal with data submitted by laboratories that have not demonstrated satisfactory performance.

This is not a small problem, especially when assessing time series where data quality in early years may not have been measured or may have been poorer than in subsequent years. For example, in the 1998 OSPAR assessment of contaminant trends in marine organisms, a considerable amount of data was rejected on QA grounds. The following table shows the percentage of annual observations of trace metals lost for the four countries experiencing the highest losses. The table also shows the reasons the data were rejected as a percentage of the total number of losses.

	Germany	Netherlands	Norway	Iceland
% Deleted	45	41	27	24
QA absent	87	68	47	-
Poor QA (Z and/or P scores > 2)	6	30	53	100
Undocumented Reference Materials	7	2	-	-

In this paper, we will demonstrate that:

- When considered in relation to the levels of environmental variability, data that fail targets for analytical quality may still be useful for trend detection (Section 2).
- A simple strategy for dealing with variable QA is to down-weight poor-quality data in the statistical assessment of trend. This is demonstrated for trends in mercury in fish (Section 3).
- Rejection rules based on the QUASIMEME definition of *satisfactory P* and *Z* scores can be misleading. Modified rules are suggested (Section 4).

2 The Effect of Environmental and Analytical Variability on Trend Assessments

In this section we demonstrate how the relative size of environmental and analytical variation affect the detection of a temporal trend. We assume that the contaminant index constructed at time *t*, y_t, is made up of four components as follows

$$y_t = f(t) + e_t + b_t + w_t$$

where *f(t)* is the trend signal, and e_t, b_t, and w_t are noise components due to the environment (including sampling), analytical variability between time periods, and analytical variability within the time period, respectively. Further, we will assume that these noise terms are independent, and Normally distributed with mean zero and variances σ_{e}^2, σ_{b}^2 and $\sigma_{\mathrm{w}}^2 / R$, respectively. *R* is the number of replicate analyses, equal to the number of animals if analyses are made on individual animals.

The component b_t is commonly referred to as *bias*, and the standard deviation σ_{w} as *precision*. Here we assume that bias varies from time period to time period.

The following table gives some guidance on the likely values of environmental variability for mercury in fish muscle. They are taken from Nicholson *et al.* (1997), who summarised environmental variation (including sampling) seen in OSPAR assessments for three groups corresponding to *Low*, *Medium* and *High* levels of variability. The values tabled below assume that the annual index of mercury concentration is calculated as the back-transformed mean log-concentration measured individually in 25 fish.

Group	Environmental St. Dev. %	Detectable trend % analytical St. Dev. = 0 %	Detectable trend % analytical St. Dev. = 12.5 %	Detectable trend % analytical St. Dev. = 25 %
Low	*9.7*	*3.9*	*6.5*	*11.2*
Medium	*26.2*	*11*	*12*	*15*
High	*52.4*	*21*	*22*	*24*

The performance of a temporal trend programme can be measured by the detectable trend (Nicholson *et al.,* 1997), the linear trend (% change per year) that would be detected after 10 years with a power of 90 % using a test at the 5 % significance level. The final three columns of the table give the detectable trend for three levels of analytical variability: $\sigma_{\mathrm{w}} = \sigma_{\mathrm{b}} = 0$ %, $\sigma_{\mathrm{w}} = \sigma_{\mathrm{b}} = 12.5$ %, and $\sigma_{\mathrm{w}} = \sigma_{\mathrm{b}} = 25$ %.

As would be expected, the effect of increasing analytical noise is greatest for the group with *Low* environmental variation. However, in that group, even with $\sigma_{\mathrm{w}} = \sigma_{\mathrm{b}} = 25$ % (where analytical variability is about 2.5 times greater than environmental variability), trends of the order of 10% are still detectable. At *High* levels of environmental variation, the effect of increased analytical variability is small, with little change in the detectable trend.

3 Down-weighting Observations with Poorer Analytical Quality

An alternative to rejecting data with unsatisfactory QA is to down-weight them in the statistical assessment of the trend. This is demonstrated below using weighted linear regression to assess the trend.

Figure A4.1 shows a realisation of a simulated decreasing trend in the log-concentration of mercury over 10 years. The trend has been subjected to the level of environmental variation from the *Low* group defined in Section 2. The underlying trend is a decrease of 3.9 % per year, i.e., the *detectable trend* in this group when there is zero analytical noise.

In the final five years, an additional component of low-level analytical variability has been added with $\sigma_w = \sigma_b = 6.25\%$. In the first five years however, a higher level of analytical noise with $\sigma_w = \sigma_b = 25\%$ has been added. In the figure, this difference in QA status is indicated by different plotting symbols, with solid circles indicating poorer QA.

Three fitted lines are shown. The solid line is an unweighted regression line, i.e., where all the data have equal weight. The dotted line is from a weighted regression, where the first five years have been down-weighted by 50 %. The short dashed line is an unweighted regression line fitted to the data from the last five years, i.e,. where the data from the first five years have been deleted.

Judged informally, the weighted line is slightly flatter than the unweighted line, due to the higher concentrations observed in the early years being down-weighted. However, it still captures the essence of the underlying trend. There is little suggestion of any trend in the line fitted to only the last five years.

4 Identifying Analytical Quality from *P* and *Z* Scores

For any weighting strategy, including rejection, the QA status of the data must be inferred. This is commonly done using *P* and *Z* scores derived from the results of interlaboratory exercises. They are usually interpreted as indicators of *precision* and *bias,* respectively. However, as shown below, uncritical interpretation of these scores could be misleading, since both are dependent on the number of replicate analyses made in the exercise, and the *Z* score is a function of both precision and bias.

This may not matter if the scores are used informally to compare performance between laboratories within an interlaboratory exercise. However, it is important if the scores are intended to provide an objective basis for rejecting data. Formulae for deriving formal rules are derived below.

Definition of *P* and *Z* Scores

Typically, for an experiment to assess analytical performance for some determinand at concentration μ, laboratory i reports a series of n results, x_{i1}, x_{i2}, …, x_{in}, measured in a circulated sample. These can be summarised by the sample mean ($\bar{x}_i$) and standard deviation (s_i), used to define

$$P_i = {}^{s_i}\!\big/_{\sigma_{w(\text{target})}}$$

and

$$Z_i = {}^{\bar{x}_i - \mu}\!\big/_{\sigma_{b(\text{target})}}$$

where $\sigma_{w(\text{target})}$ and $\sigma_{b(\text{target})}$ are targets for σ_w and σ_b (Wells *et al.,* 1993). Alternative robust estimators are discussed by Cofino and Wells (1994).

Assessment of Data Quality on the Basis of *P*≤2 and *Z*≤2

Common assessment criteria for interpreting the significance of *P* and *Z* scores are that absolute values ≤ 2 indicate that performance is *satisfactory* (Cofino and Wells, 1994). This is based on the assumption that *Z* has a standard normal distribution when $\sigma_b = \sigma_{b(\text{target})}$ (Wells *et al.,* 1993), with the implication that the probability (significance level) of incorrectly rejecting the hypothesis of *satisfactory* analytical performance is approximately 5 %. However, it is simple to show that the actual significance levels for these rules is given by

$$\Pr[|P| \le 2] = \Pr\left[\chi^2_{n-1} \le {4(n-1)\sigma^2_{\mathrm{w(target)}}}\Big/{\sigma^2_{\mathrm{w}}}\right]$$

and

$$\Pr[|Z| \le 2] = \Pr\left[\chi^2_1 \le {4\sigma^2_{\mathrm{b(target)}}}\Big/{\sigma^2_{\mathrm{b}} + \sigma^2_{\mathrm{w}}/n}\right]$$

where χ^2_{df} is a chi-squared variate with *df* degrees of freedom. Thus, the significance of *P* scores depends on the value of *n* (in addition to σ_{w}), and the significance of *Z* scores depends on both *n* and σ_{w} (in addition to σ_{b}).

Values of *n* used in practice tend to be small, typically in the range 2 to 5 (e.g., Pedersen and Cofino, 1994; Dixon and Gardner, 1998). The following table shows how *n* affects the probabilities of getting *P* or *Z* scores greater than 2 when the underlying values of σ_{w} and σ_{b} equal their targets $\sigma_{w(\mathrm{target})}$ and $\sigma_{b(\mathrm{target})}$, and when $\sigma_{w(\mathrm{target})} = \sigma_{b(\mathrm{target})}$.

n	Pr[|P| > 2]	Pr[|Z| > 2]
2	0.05	0.10
3	0.02	0.08
4	<0.01	0.07
5	<0.01	0.07
∞	<0.01	0.05

The significance level for *P* scores decreases rapidly with *n*, so when $n > 2$, more data than expected will apparently meet the targets for precision. For *Z* scores, the significance level decreases from double the notional value of 5 % when *n*=2, to 5 % when *n*=∞, so fewer data than expected will apparently meet the targets for bias.

Another way of looking at this is to consider the values of σ_w and σ_b for which the true significance level of the criteria $|P|\le2$ and $|Z|\le2$ is 5 %. Assuming $\sigma_{\mathrm{w}} = \sigma_{\mathrm{b}}$ and $\sigma_{\mathrm{w(target)}} = \sigma_{\mathrm{b(target)}} = \sigma_{\mathrm{(target)}}$, the following table shows the approximate values of σ_{w}^2 and σ_{b}^2 that satisfy $\Pr[|P|\le2]=0.95$ and $\Pr[|Z|\le2]=0.95$ for $n = 2$ and $n=\infty$.

n	σ_{w}^2	σ_{b}^2
2	$\sigma^2_{\mathrm{(target)}}$	$\sigma^2_{\mathrm{(target)}}/2$
∞	$4\sigma^2_{\mathrm{(target)}}$	$\sigma^2_{\mathrm{(target)}}$

When $n = 2$, $\Pr[|P|\le2]=0.95$ when $\sigma_{\mathrm{w}}^2 \approx \sigma^2_{\mathrm{(target)}}$ as expected. However, $\Pr[|Z|\le2]=0.95$ when $\sigma_{\mathrm{b}}^2 \approx \sigma^2_{\mathrm{(target)}}/2$, so we are actually aiming for a more demanding target for bias. Only when *n* is very large does $\Pr[|Z|\le2]=0.95$ when $\sigma_{\mathrm{b}}^2 \approx \sigma^2_{\mathrm{(target)}}$, but then the actual target for σ_{w}^2 is too liberal.

Alternative Assessment Criteria based on *P* and *Z* Scores

Alternative criteria based on *P* and *Z* scores can be constructed which correctly control the probability of incorrectly concluding that results are not *satisfactory*. For example, it is simple to show that $\Pr[|P| \le k_P] = 0.95$ implies

$$k_P = \sqrt{\frac{\sigma_w^2}{\sigma_{w(target)}^2} \times \frac{\chi_{n-1}^2(0.95)}{n-1}}$$

whereas $\Pr[|Z| \le k_Z] = 0.95$ implies

$$k_Z = \sqrt{\frac{\sigma_b^2 + \sigma_w^2/n}{\sigma_{b(target)}^2} \times \chi_1^2(0.95)}\ .$$

Thus, assuming $\sigma_{\text{w(target)}} = \sigma_{\text{b(target)}} = \sigma_{\text{(target)}}$, we can maintain the correct 5 % significance level if we define performance to be *satisfactory* if $|P| \le k_P$ and $|Z| \le k_Z$, where

$$k_P = \sqrt{\frac{\chi_{n-1}^2(0.95)}{n-1}}$$

and

$$k_Z = \sqrt{\frac{n+1}{n}\chi_1^2(0.95)}\ .$$

The table below gives the appropriate values of k_P and k_Z for different values of *n*.

n	k_P	k_Z
2	2.0	2.4
3	1.7	2.3
4	1.6	2.2
5	1.5	2.1
∞	1.0	2.0

These rules could easily be extended to a three-tier system, e.g., with QA performance classified as *satisfactory*, *questionable*, and *unsatisfactory*. For example, suppose *unsatisfactory* corresponds to $\sigma_\text{w} > 2\sigma_{\text{(target)}}$ and $\sigma_\text{b} > 2\sigma_{\text{(target)}}$. Then if *n*=2, classifying data based on the following rules

satisfactory	*questionable*	*unsatisfactory*
$P \le 2$	$2 < P \le 4$	$4 < P$
$Z \le 2.4$	$2.4 < Z \le 5$	$5 < Z$

provides a maximum probability of approximately 5 % that standard deviations less than or equal to their targets would be mislabelled as *questionable* or *unsatisfactory*, and that standard deviations less than twice their targets are mislabelled as *unsatisfactory*.

If these extended rules were incorporated into a QA-weighted trend assessment, data classified as *questionable* would be down-weighted. Data classified as *unsatisfactory* could either be further down-weighted or rejected.

5 Discussion

We have looked at the interaction between analytical variability and environmental variability, and considered the implications of accepting or rejecting data with different levels of analytical quality. In particular, we have shown that data of poorer quality might still be useful for trend assessments. This does not, of course, imply that targets for laboratory performance should be looser. Trend detection will be most effective when analytical variability is as low as possible. However, our results have shown that although minimum targets of, e.g., 12.5 % may be useful for motivating improvements in laboratory performance, they may be excessive when used to filter out unworthy data.

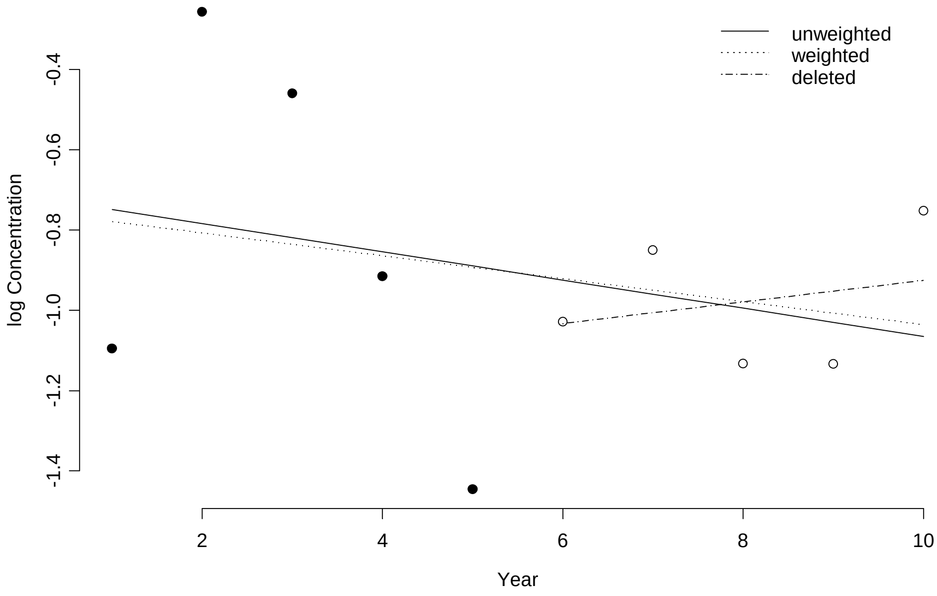
Further, our results show that informal assessments of *P* and *Z* scores can be a misleading way of rejecting data. A better solution is to define appropriate rules taking the number of replicate analyses into account.

The weighting approach appears to offer a useful compromise between ignoring high analytical variability and rejecting the data. In particular, the weighting approach is likely to have greater power than rejection because it retains more degrees of freedom. It would be simple to extend the weighting approach so that extremely poor data are rejected and questionable data are down-weighted. The visual presentation of QA status in a trend plot allows the inferior quality of some data points to be identified, and would assist in the interpretation of possible QA-related outliers.

The method of trend assessment used here for demonstration was linear regression. However, the weighting procedure could be extended to other assessment models such as smoothers (cf. Fryer and Nicholson, 1999).

The weighting used in the example was a fixed, crude approximation of the optimum weighting based on the levels of environmental variability typically observed in mercury time series. If this statistical basis was abandoned, the weighting could be seen as a simple heuristic device to reduce the contribution of questionable data to the analysis. In this case, other non-quantitative information could contribute to some index of quality. For example, Dobson *et al.* (1999) suggested an index of fitness for data generated at a laboratory based on the answers to eighteen questions concerning QA/QC. This could easily be extended to incorporate other equally important qualities, such as the extent to which sampling guidelines have been followed, climatic anomalies, or any other variations in conditions known to affect the monitored signal.

Figure A4.1. Example of trend assessment with down-weighting of data with poor QA (solid circles).



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ANNEX 5: CERTIFIED REFERENCE MATERIALS FOR ORGANIC CONTAMINANTS FOR USE IN MONITORING OF THE AQUATIC ENVIRONMENT

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Over the last three decades organic contaminants have been of increasing importance in environmental monitoring. Dioxins, furans, polychlorinated biphenyls and organochlorine pesticides have determined the environmental research agenda. This has led to an increasing demand for certified reference materials (CRMs). However, CRMs have only been made available in limited numbers, as the production and certification of CRMs is normally a relativelt slow process. This paper gives an overview of the available CRMs for biota and sediments for these contaminants and the developments in their quality.

The full document can be found in:

De Boer, J., and McGovern, E. 2001. Certified Reference Materials for Organic Contaminants for use in Monitoring of the Aquatic Environment. Trends in Analytical Chemistry 20(3): 140–159

ANNEX 6: REFERENCE MATERIALS FOR TRACE METALS IN SEA WATER, MARINE BIOTA AND MARINE SEDIMENTS

The following comments apply to these tables:

a) The compiled tables are for information. Although every effort has been made to ensure that these tables are accurate, users of CRMs should consult vendors for full and accurate information;

b) Certified calibration materials and standards are not included;

c) These tables do not purport to be complete and all the CRMs listed may not be commercially available.

Currently available marine CRMs for trace metals are listed in the table (January 2001). The following websites provide additional information:

NIST (USA):	http://ois.nist.gov/srmcatalog/
BCR (Belgium):	http://www.irmm.jrc.be/mrm.html
NRC (Canada):	http://www.cm.inms.nrc.ca/ems1.htm
IAEA (Austria):	http://www.iaea.org/programmes/nahunet/e4/nmrm/index.htm
LGC (UK):	http://www.lgc.co.uk/products/rm/environment.htm
USGS (USA):	http://minerals.cr.usgs.gov/geo_chem_stand/index.html
RTC (USA):	http://www.rt-corp.com/catalog/99solph.htm

The IAEA (see address above) provides a very comprehensive and searchable database for natural matrix reference materials.

Table A6.1. Currently available CRMs for trace metals (January 2001).

Matrix	Certified Values for	Material	Name	Manufacturer
Sediment	2 Sn-species	BCR 462	Coastal sediment	BCR (Belgium)
Sediment	2 Hg-species	BCR 580	Estuarine sediment	BCR (Belgium)
Sediment	10 Metals	MURST-ISS-A1	Antarctic sediment	BCR (Belgium)
Sediment	14 Metals	HISS-1	Marine sediment	NRC (Canada)
Sediment	20 Metals	MESS-3	Marine sediment	NRC (Canada)
Sediment	19 Metals, 3 Sn-species	PACS-2	Marine sediment	NRC (Canada)
Sediment	18 Metals	SRM 1646A	Estuarine sediment	NIST (USA)
Sediment	9 Metals	SRM 1944	Waterway sediment	NIST (USA)
Sediment	44 Metals	USGS-MAG-1	Marine sediment	USGS (USA)
Sediment	23 Metals	GBW 07313	Marine sediment	NRCCRM (China)
Sediment	9 Metals	GBW 07314	Offshore sediment	NRCCRM (China)
Sediment	56 Metals	GBW 07315	Marine sediment	NRCCRM (China)
Sediment	56 Metals	GBW 07316	Marine sediment	NRCCRM (China)
Sediment	19 Metals	LGC6137	Estuarine sediment	LGC (UK)
Sediment	20 Metals	LGC6156	Harbour sediment	LGC (UK)
Sediment	8 Metals	CRMPR-96961	Non-polluted sediment	RTC (USA)
Sediment	18 Metals	CRM015-050	Sediment	RTC (USA)
Sediment	18 Metals	CRM016-05	Sediment	RTC (USA)
Biota	9 Metals	BCR 278R	Mussel tissue	BCR (Belgium)
Biota	6 Metals	BCR 279	Sea Lettuce	BCR (Belgium)
Biota	11 Metals	BCR 414	Plankton	BCR (Belgium)
Biota	10 Metals	BCR 422	Cod muscle	BCR (Belgium)
Biota	2 Hg-species	BCR 463	Tuna fish	BCR (Belgium)
Biota	2 Hg-species	BCR 464	Tuna fish	BCR (Belgium)
Biota	3 Sn-species	BCR 477	Mussel tissue	BCR (Belgium)
Biota	3 As-species	BCR 627	Tuna fish tissue	BCR (Belgium)
Biota	10 Metals	MURST-ISS-A2	Antarctic krill	BCR (Belgium)
Biota	17 Metals and species	DOLT-2	Dogfish liver	NRC (Canada)
Biota	14 Metals, Methyl-Hg	DORM-2	Dogfish muscle	NRC (Canada)
Biota	17 Metals	LUTS-1	Lobster hepatopancreas	NRC (Canada)
Biota	15 Metals, Methyl-Hg	TORT-2	Lobster hepatopancreas	NRC (Canada)
Biota	21 Metals	SRM 1566b	Oyster tissue	NIST (USA)
Biota	6 Metals, Methyl-Hg	SRM 2977	Mussel tissue	NIST (USA)
Biota	8 Metals, Methyl-Hg	SRM 2976	Mussel tissue	NIST (USA)
Biota	Hg, Methyl-Hg	SRM 2974	Mussel tissue	NIST (USA)
Biota	25 Metals	IAEA-140/TM	Fucus (sea plant homogenate)	IAEA (Austria)
Biota	20 Metals	GBW08571	Mussel	NRCCRM (China)
Biota	19 Metals	GBW08572	Prawn	NRCCRM (China)
Biota	27 Metals	NIES-CRM-09	Sargasso seaweed	NIES (Japan)
Biota	3 Sn-species	NIES-CRM-11	Fish tissue	NIES (Japan)
Water	6 Metals	BCR 403	Seawater	BCR (Belgium)
Water	4 Metals	BCR 505	Estuarine water	BCR (Belgium)
Water	Hg	BCR 579	Coastal seawater	BCR (Belgium)
Water	12 Metals	CASS-4	Nearshore seawater	NRC (Canada)
Water	10 Metals	NASS-5	Open ocean seawater	NRC (Canada)
Water	11 Metals	SLEW-3	Estuarine water	NRC (Canada)
Water	6 Metals	LGC6016	Estuarine water	LGC (UK)

Table A6.2a. Reference materials for trace metals in marine sediments. Values preceded by an asterisk (*) are non-certified.

Code	**MURST-ISS-A1**	**HISS-1**	**MESS-3**	**PACS-2**
Organization	BCR	NRC	NRC	NRC
Country of origin	Belgium	Canada	Canada	Canada
Matrix	Antarctic sediment	Marine sediment	Marine sediment	Harbour sediment
Units	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
as	Dry weight	Dry weight	Dry weight	Dry weight
[±] expressed as	no information	Conf. interval (95%)	Conf. interval (95%)	Conf. interval (95%)
Units of issue	75 g	100 g	50 g	65 g
Form		Freeze-dried	Freeze-dried	Freeze-dried
Aluminium	6.71 ± 0.33 %	0.73 ± 0.05 %	8.59 ± 0.23 %	6.62 ± 0.32 %
Antimony		(0.13)*	1.02 ± 0.09	11.3 ± 2.6
Arsenic	4.41 ± 1.06	0.801 ± 0.099	21.2 ± 1.1	26.2 ± 1.5
Beryllium		0.129 ± 0.023	2.30 ± 0.12	1.0 ± 0.2
Cadmium	0.538 ± 0.027	0.024 ± 0.009	0.24 ± 0.01	2.11 ± 0.15
Calcium		1.14 ± 0.10 %	1.47 ± 0.06 %	1.96 ± 0.18 %
Chromium	42.1 ± 3.4	30.0 ± 6.8	105 ± 4	90.7 ± 4.6
Cobalt	6.87 ± 0.31	(0.65)*	14.4 ± 2.0	11.5 ± 0.3
Copper		2.29 ± 0.37	33.9 ± 1.6	310 ± 12
Iron	2.44 ± 0.07 %	0.246 ± 0.009 %	4.34 ± 0.11 %	4.09 ± 0.06 %
Lead	21.0 ± 2.9	3.13 ± 0.40	21.1 ± 0.7	183 ± 8
Lithium		2.83 ± 0.54	73.6 ± 5.2	32.2 ± 2.0
Magnesium		0.075 ± 0.016 %	(1.6 %)*	1.47 ± 0.13 %
Manganese	446 ± 19	66.1 ± 4.2	324 ± 12	440 ± 19
Mercury		(0.01)*	0.091 ± 0.009	3.04 ± 0.20
Molybdenum		(0.13)*	2.78 ± 0.07	5.43 ± 0.28
Nickel	9.56 ± 1.05	2.16 ± 0.29	46.9 ± 2.2	39.5 ± 2.3
Phosphorus			(0.12 %)*	0.096 ± 0.004 %
Potassium		0.332 ± 0.013 %	(2.6 %)*	1.24 ± 0.05 %
Selenium		0.050 ± 0.007	0.72 ± 0.05	0.92 ± 0.22
Silver		0.016 ± 0.002	0.18 ± 0.02	1.22 ± 0.14
Sodium		0.373 ± 0.026 %	(1.6 %)*	3.45 ± 0.17 %
Strontium		96.9 ± 11.2	129 ± 11	276 ± 30
Sulphur			(0.19 %)*	1.29 ± 0.13 %
Thallium		(0.06)*	0.90 ± 0.06	(0.6)*
Tin		(0.11)*	2.50 ± 0.52	19.8 ± 2.5
Titanium		0.076 ± 0.004 %	0.44 ± 0.06 %	0.443 ± 0.032 %
Vanadium		6.80 ± 0.78	243 ± 10	133 ± 5
Zinc	53.3 ± 2.7	4.94 ± 0.79	159 ± 8	364 ± 23

Table A6.2b. Reference materials for trace metals in marine sediments. Values preceded by an asterisk (*) are non-certified.

Code	**SRM 1646A**	**SRM 1944**	**LGC6137**	**LGC6156**
Organization	NIST	NIST	LGC	LGC
Country of origin	USA	USA	UK	UK
Matrix	Estuarine sediment	Waterway sediment	Estuarine sediment	Harbour sediment
Units	μg g^{-1}	μg g^{-1}	μg g^{-1}	μg g^{-1}
as	Dry weight	Dry weight	Dry weight	Dry weight
[±] expressed as	Conf. interval (95%)	Conf. interval (95%)	no information	no information
Units of issue	70 g	50 g	50 g	5 x 50 g
Form	Freeze-dried	Freeze-dried	Extractable metals	Extractable metals
Aluminium	2.297 ± 0.018 %	5.33 ± 0.49 %	1.90 %	1.90 %
Arsenic	6.23 ± 0.21	18.9 ± 2.8	12.4	38.3
Barium			82	
Beryllium			1.0	4.1
Cadmium	0.148 ± 0.007	8.8 ± 1.4		2.9
Calcium	0.519 ± 0.02 %		5.11	4.30 %
Chromium	40.9 ± 1.9	266 ± 24	47	111
Cobalt			13.7	28.3
Copper	10.01 ± 0.34		31.6	2400
Iron	2.008 ± 0.039 %	3.53 ± 0.16 %	3.07 %	7.20 %
Lead	11.7 ± 1.2	330 ± 48	73.0	1685
Lithium			42.5	
Magnesium	0.388 ± 0.009 %		1.11	0.9425 %
Manganese	234.5 ± 2.8	505 ± 25	665	553
Mercury			0.34	10.1
Molybdenum				19.9
Nickel		76.1 ± 5.6	31.5	61
Phosphorus	0.027 ± 0.001 %			
Potassium	0.864 ± 0.016 %		0.501	0.546 %
Selenium	0.193 ± 0.028			
Silicon	40.00 ± 0.16 %			
Sodium	0.741 ± 0.017 %		0.742	2.01 %
Sulphur	0.352 ± 0.004 %			
Tin				145
Titanium	0.456 ± 0.021 %			
Vanadium	44.84 ± 0.76		47.0	91.5
Zinc	48.9 ± 1.6	656 ± 75	231	3530

Table A6.2c. Reference materials for trace metals in marine sediments. Values preceded by an asterisk (*) are non-certified.

Code	**GBW 07313**	**GBW 07314**	**GBW 07315-3**	**GBW 07316**
Organization	NRCCRM	NRCCRM	NRCCRM	NRCCRM
Country of origin	China	China	China	China
Matrix	Marine sediment	Offshore sediment	Marine sediment	Marine sediment
Units	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
as	Dry weight	Dry weight	Dry weight	Dry weight
[±] expressed as	no information	no information	no information	no information
Units of issue	50 g	50 g	50 g	50 g
Form				
Aluminium	7.2778 %	13.070 %	6.04 %	4.08 %
Antimony	1.85	(1.4)*	2.0	1.3
Arsenic	(5.8)*	10.3	7.1	4.6
Barium	0.44	425	3100	2500
Boron	125	(73)*	125	84
Cadmium		0.2	(0.25)	(0.3)
Calcium	1.2221 %	4.3100 %	4.10 %	16.14 %
Cerium	82	(78)*	82	55
Caesium	9.4	(8.2)*	6.8	4.5
Chromium	58.4	86	59	38
Cobalt	76.7	14.2	81	53
Copper	424	31	357	231
Iron	4.602 %	5.3600 %		
Lead	29.3	25	37	22
Lithium	60		51	
Magnesium	2.0388 %	2.5000 %	1.81 %	1.22 %
Manganese	3257		4570	3099
Mercury		0.048	0.95	0.13
Molybdenum	7.2	(0.64)*	14	5.7
Nickel	150	34.3	167	108
Phosphorus	1963		2096	1441
Potassium	2.449 %	2.4800 %	1.93 %	1.34 %
Selenium		0.16		
Silicon	25.1795 %	28.9430 %	23.85 %	14.75 %
Silver				
Sodium	3.5685 %		3.29 %	2.79 %
Strontium	267	150	298	
Titanium	4 016		3660	2340
Vanadium	112	(103.1)*	101	69
Zinc	160	87	137	142

Table A6.2d. Reference materials for trace metals in marine sediments. Values preceded by an asterisk (*) are non-certified.

Code	**MAG-1**	**CRMPR-96961**	**CRM015-050**	**CRM016-05**
Organization	USGS	RTC	RTC	RTC
Country of origin	USA	USA	USA	USA
Matrix	Marine sediment	Sediment	Sediment	Sediment
Units	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
as	Dry weight	Dry weight	Dry weight	Dry weight
[±] expressed as	Uncertainty	Uncertainty	No information	No information
Units of issue	30 g		50 g	50 g
Form				
Aluminium	8.68 ± 0.17 %	(2.7896)*	0.92 %	0.892 %
Antimony	0.96 ± 0.1			
Arsenic	(9.2)*	8.0 ± 0.5	6.6	6.48
Barium	480 ± 43	(128.6)*	83	79.3
Boron	140 ± 6		(8.6)*	(13)*
Cadmium	0.20 ± 0.03	(0.3)*		0.47
Calcium	0.98 ± 0.07 %	2.3934 ± 0.1915 %	2.3463 %	2.2646 %
Cerium	88 ± 9			
Caesium	8.6 ± 0.7			
Chromium	97 ± 8	(33.3)*	14.3	14.5
Cobalt	20 ± 2	(7.4)*	6.04	5.96
Copper	30 ± 3	17 ± 1	16.1	15.5
Iron	4.8 ± 0.4 %	2.1506 ± 0.0860 %	1.7070 %	1.6831 %
Lead	24 ± 3	(15.4)*	15.04	14.1
Lithium	79 ± 4			
Magnesium	1.8 ± 0.1 %	(1.3890 %)*	1.3611%	1.3246 %
Manganese	759 ± 68	208.1 ± 12.5	183.4	180
Mercury	(0.02)*	(0.1)*	0.1	0.11
Molybdenum	(1.6)*		1.16	(0.97)*
Nickel	53 ± 8	(18.6)*	17.5	16.7
Phosphorus	700 ± 90	0.73 ± 0.04		
Potassium	2.95 ± 0.15 %	(0.4080)*	0.2074 %	0.1958 %
Selenium			(1)*	(1)*
Silicon	23.52 ± 0 %		(491)*	(347)*
Silver	(0.08)*			(0.7)*
Sodium	2.84 ± 0.09		0.0400 %	0.0292 %
Strontium	150 ± 15		(62)*	(61)*
Titanium	0.45 ± 0.04 %			
Vanadium	140 ± 6		22.1	22.5

Code	**MAG-1**	**CRMPR-96961**	**CRM015-050**	**CRM016-05**
Zinc	130 ± 7	79 ± 4	69.9	69.7

Table A6.3. Reference materials for trace metal species in marine sediments.

Code	**CRM 462**	**PACS-2**	**CRM 580**
Organization	BCR	NRC	BCR
Country of origin	Belgium	Canada	Belgium
Matrix	Coastal sediment	Harbour sediment	Estuarine sediment
Units	µg kg^{-1}	mg kg^{-1}	µg kg^{-1}
as	Dry weight	Dry weight	Dry weight
[±] expressed as	Expanded uncertainty (coverage factor k = 2)	Confidence interval (95%)	Expanded uncertainty (coverage factor k = 2)
Units of issue	25 g	65 g	50 g
Form	Air-dried	Freeze-dried	
Tributyltin (as Sn) Dibutyltin (as Sn) Monobutyltin (as Sn)	22 ± 6 35 ± 6	0.98 ± 0.13 1.09 ± 0.15 0.45 ± 0.05	
Total Mercury MeHg			132 ± 3 mg/kg 75.5 ± 3.7

Table A6.4a. Reference materials for trace metals in marine biota. Values preceded by an asterisk (*) are non-certified.

Code	**BCR 278R**	**BCR 279**	**BCR 414**	**BCR 422**
Organization	BCR	BCR	BCR	BCR
Country of origin	Belgium	Belgium	Belgium	Belgium
Matrix	Mussel tissue	Sea Lettuce	Plankton	Cod muscle
Units	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
as	Dry weight	Dry weight	Dry weight	Dry weight
[±] expressed as	Conf. interval (95%)	Conf. interval (95%)	Conf. interval (95%)	Conf. interval (95%)
Units of issue	8 g	35 g	5 g	7 g
Form	Freeze-dried		Freeze-dried	
Arsenic	6.07 ± 0.13	3.09 ± 0.20	6.82 ± 0.28	21.1 ± 0.5
Cadmium	0.348 ± 0.007	0.274 ± 0.022	0.383 ± 0.014	0.017 ± 0.002
Chromium	0.78 ± 0.06		23.8 ± 1.2	
Copper	9.45 ± 0.13	13.14 ± 0.37	29.5 ± 1.3	1.05 ±0.07
Iron				5.46 ± 0.30
Iodine				4.95 ± 0.49
Lead	2.00 ± 0.04	13.48 ± 0.36	3.97 ± 0.19	0.085 ± 0.015
Manganese	7.69 ± 0.23		299 ± 12	0.543 ± 0.028
Mercury	0.196 ± 0.009		0.276 ± 0.018	0.559 ± 0.016
Nickel			18.8 ± 0.8	
Selenium	1.84 ± 0.10	0.593 ± 0.032	1.75 ± 0.1	1.63 ± 0.07
Vanadium			8.1 ± 0.18	
Zinc	83.1 ± 1.7	51.3 ± 1.2	112 ± 3	19.6 ± 0.5
Code	**BCR 463**	**BCR 464**	**BCR 477**	**BCR 627**
Organization	BCR	BCR	BCR	BCR
Country of origin	Belgium	Belgium	Belgium	Belgium
Matrix	Tuna fish	Tuna fish	Mussel tissue	Tuna fish
Units	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
as	Dry weight	Dry weight	Dry weight	Dry weight
[±] expressed as	Conf. interval (95%)	Conf. interval (95%)	Conf. interval (95%)	Conf. interval (95%)
Units of issue	15 g	15 g	14 g	10 g
Form	Freeze-dried	Freeze-dried		
Total Mercury	2.85 ± 0.16	5.24 ± 0.10		
MeHg	3.04 ± 0.16	5.50 ± 0.17		
TBT - $Sn(C_4H_9)_3^{+}$			2.20 ± 0.19	
DBT - $Sn(C_4H_9)_2^{2+}$			1.54 ± 0.12	
MBT - $Sn(C_4H_9)^{3+}$			1.50 ± 0.28	
Arsenobetaine				52 ± 3 µmol kg^{-1}
Dimethylarsinic acid				2.0 ± 0.3 µmol kg^{-1}
Total Arsenic				4.8 ± 0.3

Table A6.4b. Reference materials for trace metals in marine biota. Values preceded by an asterisk (*) are non-certified.

Code	**MURST-ISS-A2**	**SRM 1566b**	**SRM 2977**	**IAEA-140/TM**
Organization	BCR	NIST	NIST	IAEA
Country of origin	Belgium	USA	USA	Austria
Matrix	Antarctic krill	Oyster tissue	Mussel tissue	*Fucus*
Units	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
as	Dry weight	Dry weight	Dry weight	Dry weight
[±] expressed as	Conf. interval (95%)	Uncertainty	no information	Uncertainty
Units of issue	0.5 g	25 g	10 g	14 g
Form	Freeze-dried	Freeze-dried	Freeze-dried	
Aluminium		197.2 ± 6.0		(1184)*
Antimony				0.103 ± 0.022
Arsenic	5.02 ± 0.40	7.65 ± 0.65		44.3 ± 2.2
Bromine				567 ± 96
Calcium		0.0838 ± 0.0020 %		1.2730 ± 0.1782 %
Cadmium	0.73 ± 0.06	2.48 ± 0.08	4 0.179 ± 0.003	0.537 ± 0.038
Cobalt	0.110 ± 0.010	0.371 ± 0.009		0.876 ± 0.131
Chromium				10.4 ± 0.8
Copper	65.2 ± 2.3	71.6 ± 1.6	9.42 ± 0.52	5.05 ± 0.30
Iron	56.6 ± 2.3	205.8 ± 6.8		1256 ± 38
Lithium				2.29 ± 0.34
Lead	1.11 ± 0.09	0.308 ± 0.009	2.27 ± 0.13	2.19 ± 0.64
Magnesium		0.1085 ± 0.0023 %		0.9070 ± 0.0907
Manganese	4.12 ± 0.10	18.5 ± 0.2	23.93 ± 0.29	56.1 ± 2.2
Mercury		0.0371 ± 0.0013		0.038 ± 0.006
MeHg (as Hg)		0.0132 ± 0.0007		0.000626 ± 0.000106
Molybdenum				2.65 ± 0.37
Nickel	1.28 ± 0.12	1.04 ± 0.09	6.06 ± 0.24	3.79 ± 0.42
Potassium		0.652 ± 0.009 %		3.1100 ± 0.2488 %
Rubidium		3.262 ± 0.145		16.4 ± 2.30
Selenium	7.37 ± 1.13	2.06 ± 0.15		(0.079)*
Silver		0.666 ± 0.009		(0.078)*
Sodium		0.3297 ± 0.0053 %		3.2000 ± 0.6720 %
Strontium			69.3 ± 4.2	750 ± 98
Sulfur		0.6887 ± 0.0140 %		
Thorium		0.0367 ± 0.0043		0.299 ± 0.063
Uranium				0.73 ± 0.08
Vanadium		0.577 ± 0.023		3.67 ± 0.48
Zinc	66.0 ± 2.0	424 ± 46		47.3 ± 1.9

Table A6.4c. Reference materials for trace metals in marine biota. Values preceded by an asterisk (*) are non-certified.

Code	**DOLT-2**	**DORM-2**	**LUTS-1**	**TORT-2**
Organization	NRC	NRC	NRC	NRC
Country of origin	Canada	Canada	Canada	Canada
Matrix	Dogfish liver	Dogfish muscle	Lobster hepatopancreas	Lobster hepatopancreas
Units	$\mu g\ g^{-1}$	$\mu g\ g^{-1}$	$\mu g\ g^{-1}$	$\mu g\ g^{-1}$
as	Dry weight	Dry weight	Wet weight	Dry weight
[±] expressed as	Conf. interval (95%)	Conf. interval (95%)	Conf. interval (95%)	Conf. interval (95%)
Units of issue	25 g	30 g	6 x 10 g	35 g
Form			Slurry (85% water)	Vacuum dried
Aluminium	25.2 ± 2.4	10.9 ± 1.7		
Arsenic	16.6 ± 1.1	18.0 ± 1.1	2.83 ± 0.13	21.6 ± 1.8
Calcium			203 ± 33	
Cadmium	20.8 ± 0.5	0.043 ± 0.008	2.12 ± 0.15	26.7 ± 0.6
Cobalt	0.24 ± 0.05	0.182 ± 0.031	0.051 ± 0.006	0.51 ± 0.09
Chromium	0.37 ± 0.08	34.7 ± 5.5	0.079 ± 0.012	0.77 ± 0.15
Copper	25.8 ± 1.1	2.34 ± 0.16	15.9 ± 1.2	106 ± 10
Iron	1103 ± 47	142 ± 10	11.6 ± 0.9	105 ± 13
Lead	0.22 ± 0.02	0.065 ± 0.007	0.010 ± 0.002	0.35 ± 0.13
Magnesium			89.5 ± 4.1	
Manganese	6.88 ± 0.56	3.66 ± 0.34	1.20 ± 0.13	13.6 ± 1.2
Mercury	2.14 ± 0.28	4.64 ± 0.26	0.0167 ± 0.0022	0.27 ± 0.06
MeHg (as Hg)	0.693 ± 0.053	4.47 ± 0.32	0.0094 ± 0.0006	0.152 ± 0.013
Molybdenum				0.95 ± 0.10
Nickel	0.20 ± 0.02	19.4 ± 3.1	0.200 ± 0.034	2.50 ± 0.19
Potassium			948 ± 72	
Selenium	6.06 ± 0.49	1.40 ± 0.09	0.641 ± 0.054	5.63 ± 0.67
Silver	0.608 ± 0.032	0.041± 0.013	0.580 ± 0.049	
Strontium			2.46 ± 0.28	45.2 ± 1.9
Thallium		(0.004)*		
Tin	(0.13)*	(0.023)*		(0.04)*
Vanadium				1.64 ± 0.19
Zinc	85.8 ± 2.5	25.6 ± 2.3	12.4 ± 0.8	180 ± 6
Arsenobetaine (as As)		16.4 ± 1.1		
Tetramethyl-arsonium (as As)		0.248 ± 0.054		

Table A6.4d. Reference materials for trace metals in marine biota. Values preceded by an asterisk (*) are non-certified.

Code	GBW08571	GBW08572	NIES-CRM-09	NIES-CRM-11
Organization	NRCCRM	NRCCRM	NIES	NIES
Country of origin	China	China	Japan	Japan
Matrix	Mussel	Prawn	Sargasso seaweed	Fish tissue
Units	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
as	Dry weight	Dry weight	Dry weight	Dry weight
[±] expressed as	Uncertainty	Uncertainty	Uncertainty	Uncertainty
Units of issue	12 g	8 g	10 g	20 g
Form				
Aluminium	(231)*	1310 ± 39	(215)*	
Arsenic	6.1 ± 1.2	1.42 ± 0.07	115 ± 9	
Barium		4.29 ± 0.73		
Bromine		(13.5)*	(270)*	
Calcium	1110 ± 44	3040 ± 61	13400 ± 536	
Cadmium	4.5 ± 0.6	0.023 ± 0.004	0.15 ± 0.02	
Cobalt	0.94 ± 0.07	(0.029)*	0.12 ± 0.01	
Chromium	0.57 ± 0.08	0.24 ± 0.06	(0.2)*	
Copper	7.7 ± 1.0	4.66 ± 0.28	4.9 ± 0.2	
Fluorine		5.31 ± 0.42		
Iron	221 ± 15	19.8 ± 0.4	187 ± 6	
Lead	1.96 ± 0.12	0.298 ± 0.021	1.35 ± 0.05	
Magnesium	1970 ± 217	1600 ± 48	6500 ± 325	
Manganese	10.2 ± 1.8	1.96 ± 0.16	21.2 ± 1.1	
Mercury	0.067 ± 0.008	0.201 ± 0.004	(0.04)*	
Molybdenum	(0.6)*			
Nickel	1.03 ± 0.14			
Potassium	4240 ± 212	5970 ± 119	61000 ± 183	
Ruthenium			24 ± 2	
Selenium	3.65 ± 0.18	1.52 ± 0.05	(0.05)*	
Silver			0.31 ± 0.02	
Sodium	5820 ± 175	3810 ± 114	17000 ± 850	
Strontium	12.8 ± 1.3	40.6 ± 3.7	1000 ± 30	
Tin				2.4 ± 0.1
Vanadium			1 ± 0.1	
Zinc	138 ± 11	60.8 ± 1.8	15.6 ± 1.2	
TBT (as Sn)				1.3 ± 0.1
TPhT (as Sn)				(6.3)*

Table A6.4e. Reference materials for trace metals in marine biota. Values preceded by an asterisk (*) are non-certified.

Code	**SRM 2976**	**SRM 2974**		
Organization	NIST	NIST		
Country of origin	USA	USA		
Matrix	Mussel tissue	Mussel tissue		
Units	µg g^{-1}	µg g^{-1}		
as	Dry weight	Dry weight		
[±] expressed as	Uncertainty	Uncertainty		
Units of issue	25 g	8 g		
Form	Freeze-dried	Freeze-dried		
Arsenic	13.3 ± 1.8			
Cadmium	0.82 ± 0.16			
Copper	4.02 ± 0.33			
Iron	171.0 ± 4.9			
Lead	1.19 ± 0.18			
Mercury	61.0 ± 3.6 µg/kg	176 ± 13 µg/kg		
MeHg (as Hg)	27.8 ± 1.1 µg/kg	77.3 ± 3.1 µg/kg		
Selenium	1.80 ± 0.15			
Zinc	137 ± 13			

Table A6.5. Reference materials for trace metals in sea water. Values preceded by an asterisk (*) are non-certified.

Code	**BCR 403**	**BCR 505**	**BCR 579**	**CASS-4**
Organization	BCR	BCR	BCR	NRC
Country of origin	Belgium	Belgium	Belgium	Canada
Matrix	Sea water	Estuarine water	Coastal sea water	Nearshore sea water
Units	nmol kg^{-1}	nmol kg^{-1}	ng kg^{-1}	µg l^{-1}
[±] expressed as	Conf. interval (95%)	Conf. interval (95%)	Conf. interval (95%)	Conf. interval (95%)
Units of issue	2 litres	1 litre	1 litre	500 ml
Form	Acidified	Acidified	Acidified	Acidified
Arsenic				1.11 ± 0.16
Cadmium	0.175 ± 0.018	0.80 ± 0.04		0.026 ± 0.003
Cobalt				0.026 ± 0.003
Chromium				0.144 ± 0.029
Copper	3.9 ± 0.4	29.4 ± 1.5		0.592 ± 0.055
Iron				0.713 ± 0.058
Lead	0.117 ± 0.025			0.0098 ± 0.0036
Manganese				2.78 ± 0.19
Mercury			1.85 ± 0.20	
Molybdenum	103 ± 20			8.78 ± 0.86
Nickel	4.4 ± 0.4	24.1 ± 2.0		0.314 ± 0.030
Vanadium				1.18 ± 0.16
Zinc	25.7 ± 2.9	172 ± 11		0.381 ± 0.057
Code	**NASS-5**	**SLEW-3**	**LGC6016**	
Organization	NRC	NRC	LGC	
Country of origin	Canada	Canada	UK	
Matrix	Open ocean sea water	Estuarine water	Estuarine water	
Units	µg l^{-1}	µg l^{-1}	µg kg^{-1}	
[±] expressed as	Conf. interval (95%)	Conf. interval (95%)	no information	
Units of issue	500 ml	500 ml	50 ml	
Form	Acidified	Acidified		
Arsenic	1.27 ± 0.12	1.36 ± 0.09		
Cadmium	0.023 ± 0.003	0.048 ± 0.004	101	
Cobalt	0.011 ± 0.003	0.042 ± 0.010		
Chromium	0.110 ± 0.015	0.183 ± 0.019		
Copper	0.297 ± 0.046	1.55 ± 0.12	190	
Iron	0.207 ± 0.035	0.568 ± 0.059		
Lead	0.008 ± 0.005	0.0090 ± 0.0014	196	
Manganese	0.919 ± 0.057	1.61 ± 0.22	976	
Molybdenum	9.6 ± 1.0	(5.1)*		
Nickel	0.253 ± 0.028	1.23 ± 0.07	186	
Vanadium		2.57 ±0.31		
Zinc	0.102 ± 0.039	0.201 ± 0.037	75	

ANNEX 7: LIST OF RELEVANT CERTIFIED REFERENCE MATERIALS FOR NUTRIENTS, FOR USE IN MARINE MONITORING

Table A7.1. Certified Reference Materials for nutrients in surface water. (RW= Recipient Water). Recommended also for the control of analyses of mineral nutrients in marine water samples. They are to be diluted 100 times with sea water.

Code	**QC RW1**	**QC RW2**
Organization	DHI Water & Environment (e-mail: refmat@dhi.dk)	DHI Water & Environment (e-mail: refmat@dhi.dk)
Country of origin	Denmark	Denmark
Matrix	Water	Water
UNITS	µg l^{-1}	µg l^{-1}
[±] expressed as	± 95% CI (according to ISO 5725)	± 95% CI (according to ISO 5725)
UNITS OF ISSUE	Set 10 or 50 ampoules, 10 ml/ampoule	Set 10 or 50 ampoules, 10 ml/ampoule
FORM		
NUTRIENTS		
Nitrate-N	100	
Ammonium-N	100	
Orthophosphate-P	100	
Total Nitrogen (TN)		250
Total Phosphorus (TP)		200
COD (Cr)		
BOD		
TOC (NVOC)		

Table A7.2. Certified Reference Materials for nutrients, recommended mainly for waste water (WW= Waste Water).

Code	**QC WW1A**	**QC WW2.1**	**QC WW2.2**	**QC WW3**	**QC WW4, 4A**	**QC WW5**
Organization	DHI Water & Environment (e-mail: refmat@dhi.dk)	DHI	DHI	DHI	DHI	DHI
Country of origin	Denmark	Denmark	Denmark	Denmark	Denmark	Denmark
Matrix	Water	Water	Water	Water	Water	Water
UNITS	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}
[±] expressed as	± 95% CI	± 95% CI	± 95% CI	± 95% CI	± 95% CI	± 95% CI
UNITS OF ISSUE						
FORM						
NUTRIENTS						
Nitrate-N	5.0		1.0			
Ammonium-N	1.0	10				
Orthophosphate-P	1.5	5.0				
Total Nitrogen (TN)				7.5		
Total Phosphorus (TP)				1.5		
COD (Cr)					500, 50	
BOD						200
TOC (NVOC)					200, 20	

ANNEX 8: TABLES ON NECESSARY QA INFORMATION

A. UNCERTAINTY associated with monitoring data		**ICES Field**
Laboratory Bias	…… % - …… %	
Determined using:		
(a) certified reference materials	☐	
(b) intercomparison exercises	☐	
(c) recovery experiments	☐	
(d) experience	☐	
(e) other: ……………………………………	☐	
Precision:	……	
Unit:	……	
Calculated using:		
a) control chart data	☐	
b) internal laboratory method validation	☐	
c) intercomparison exercises	☐	
d) experience	☐	
e) other : …………………………………	☐	

B. Limit of detection/Limit of determination		**ICES Field**
Concentration/Amount which is *qualitatively* detectable (Limit of detection):	……	[DETLI]
Concentration/Amount which is *quantitatively* detectable (Limit of determination):	……	
Unit:	……	
Determined using:		
a) calibration data	☐	
b) procedural blank measurements	☐	
c) other : …………………………………	☐	

C1 - Cx Control Charts		**ICES Field**
Name of Internal Laboratory QC Sample RM or CRM:	……	[CRMCO]
Provider:	……	[CONCH]
Matrix:	……	
Certified Concentration/Amount:	……	
Associated Uncertainty (mostly the 95% conf. interval):	……	
Unit:	……	
Determined Mean of Concentration/Amount:	……	[CRMMV]
Determined Precision:	……	[CRMSD]
Unit:	……	
Number of Determinations:	……	[CRMNM]
Time Period:	……	[CRMPE]

Procedural Blanks
Determined Mean of Concentration/Amount: ……
Determined Precision: ……
Unit: ……
Number of Determinations: ……
Time Period: ……

Recovery
Spiked Concentration/Amount: ……
Determined Mean of Recovery: ……
Determined Precision: ……
Unit: ……
Number of Determinations: ……
Time Period: ……

D1 - Dx Proficiency Testing Schemes/Intercomparison Exercises		**ICES Field**
Provider:	…………	[ICCOD]
Material:	……	
Assigned Value of Concentration/Amount:	……	[RBMEA]
Precision of the assigned value:	……	
Number of participants:	……	
Found Value of Concentration/Amount:	……	
Lab Precision:	……	[PSCOR]
Unit:	……	
Participant Result:		
Own Ranking (satisfactory/questionable/unsatisfactory)		
External Ranking:		
Z-score:	……	[ZSCOR]

Other: ……………………………………

ANNEX 9: COMMENTS ON ICES DATABASE CODES FOR ORGANIC CONTAMINANTS

Benzo[*a*]pyrene + Benzo[*e*]pyrene
Phenanthrene+Anthracene
Nonachlor III
Heptachlor epoxide

Some contaminants should be transferred from one category to another:

Mineral oil
From Major organic constituents to Total hydrocarbons.

1-Chloronaphthalene
Chloronaphthalene (mixture) and explain what is meant by "mixture" in a textual comment in each case.
Octachloronaphthalene
From Polycyclic aromatic hydrocarbons to Organochlorines general.

Methoxychlor
From Dichloro-diphenyl-trichloroethane to Organochlorines

Extractable persistent organically bound chlorine
From Organochlorines to Major organic constituents.

Reactive mercury
From Organometallic compounds to Metals.

Additions to the lists:

Irgarol 1051	code IRGA (suggested in each case).
Diethyl atrazine	code DEA
Diisopropylatrazine	code DIA
Terbutylazine	code TBUAZ

To be added to the list of Triazine pesticides.

***Tris* (4-chlorophenyl) methanol**	code TCPM
***Tris* (4-chlorophenyl) methane**	code TCPME

To be added to the list of Organochlorines (general).

Toxaphene congeners need to be added to the list. Remove Polychlorinated camphenes (as toxaphenes) (chlorinated bornanes), and PCC26, PCC32, PCC50, PCC62, from the list of Organochlorines and make a new category of compounds "Toxaphene congeners".

The relevant congeners are listed in the table below:

	Toxaphene congeners	
Code	**Chemical name**	**Trivial name(s)**
PECB1	2-exo,5-endo,9,9,10-PeCB	
HXSED	2-exo,3-endo,6-exo,8,9,10-HxCB	Hx-Sed
HPSED	2-endo,3-exo,5-endo,6-exo,8,9,10-HpCB	Hp-Sed
P26	2-endo,3-exo,5-endo,6-exo,8,8,10,10-OCB	T2, Parlar 26
HPCB1	2-exo,3-endo,5-exo,8,9,10,10-HpCB	
HPCB2	2,2,5,5,8,9,10-HpCB	
P32	2,2,5-endo,6-exo,8,9,10-HpCB	Tox B, Parlar 32
HPCB3	2-exo,3-endo,6-exo,8,9,10,10-HpCB	
HPCB4	2-exo,3-endo,5-exo,6-exo,8,9,10-HpCB	
P38	2,2,5,5,9,9,10,10-OCB	Parlar 38
HPCB5	2-exo,5-exo,6-endo,8,9,10,10-HpCB	
P39	2,2,3-exo,5-endo,6-exo,8,9,10-OCB	Parlar 39
P40	2-endo,3-exo,5-endo,6-exo,8,9,10,10-OCB	Parlar 40
P41	2-exo,3-endo,5-exo,8,9,9,10,10-OCB	Parlar 41
P42A	2,2,5-endo,6-exo,8,8,9,10-OCB	Parlar 42a
P44	2-exo,5,5,8,9,9,10,10-OCB	Parlar 44
OCB1	2,2,5-endo,6-exo,8,9,10,10-OCB	
P50	2-endo,3-exo,5-endo,6-exo,8,8,9,10,10-NCB	T12, Tox Ac, Parlar 50
NCB1	2,2,3-exo,5,5,9,9,10,10-NCB	
OCB2	2-endo,3-exo,6-exo,8,8,9,10,10-OCB	
NCB2	2,2,3-exo,5-endo,6-exo,8,9,10,10-NCB	
P56	2,2,5-endo,6-exo,8,8,9,10,10-NCB	Parlar 56
P58	2,2,3-exo,5,5,8,9,10,10-NCB	Tox C, Parlar 58
P62	2,2,5,5,8,9,9,10,10-NCB	Parlar 62
TTOX	Total toxaphene (with textual comment describing description of measurement basis)	

The list of Brominated compounds has also to be extended considerably. The codes for those compounds can be exactly the same as for the CB congeners, with BDE instead of CB for the brominated diphenyl ethers and BB for the brominated biphenyls.

The following list contains the most relevant organobromine compounds to date.

Code	**Brominated compounds (IUPAC number)**
BDE15	4,4′-Dibromodiphenyl ether (15)
BDE32	2,4′,6-Tribromodiphenyl ether (32)
BDE17	2,2′,4-Tribromodiphenyl ether (17)
BDE25	2,3′,4-Tribromodiphenyl ether (25)
BDE33	2′,3,4-Tribromodiphenyl ether (33)
BDE28	2,4,4′-Tribromodiphenyl ether (28)
BDE35	3,3′,4-Tribromodiphenyl ether (35)
BDE37	3,4,4′-Tribromodiphenyl ether (37)
BDE75	2,4,4′,6-Tetrabromodiphenyl ether (75)
BDE49	2,2′,4,5'-Tetrabromodiphenyl ether (49)
BDE71	2,3′,4′,6-Tetrabromodiphenyl ether (71)
BDE47	2,2′,4,4′-Tetrabromodiphenyl ether (47)
BDE66	2,3′,4,4′-Tetrabromodiphenyl ether (66)
BDE77	3,3′,4,4′-Tetrabromodiphenyl ether (77)
BDE100	2,2′,4,4′,6-Pentabromodiphenyl ether (100)
BDE119	2,3′,4,4′,6-Pentabromodiphenyl ether (119)
BDE99	2,2′,4,4′,5-Pentabromodiphenyl ether (99)
BDE85	2,2′,3,4,4′-Pentabromodiphenyl ether (85)
BDE126	3,3′,4,4′,5-Pentabromodiphenyl ether (126)
BDE105	2,3,3′,4,4′-Pentabromodiphenyl ether (105)
BDE155	2,2′,4,4′,6,6′-Hexabromodiphenyl ether (155)
BDE154	2,2′,4,4′,5,6′-Hexabromodiphenyl ether (154)
BDE153	2,2′,4,4′,5,5′-Hexabromodiphenyl ether (153)
BDE140	2,2′,3,4,4′,6′-Hexabromodiphenyl ether (140)
BDE138	2,2′,3,4,4′,5′-Hexabromodiphenyl ether (138)
BDE166	2,3,4,4′,5,6-Hexabromodiphenyl ether (166)
BDE181	2,2′,3,4,4′,5,6-Heptabromodiphenyl ether (181)
BDE183	2,2′,3,4,4′,5′,6-Heptabromodiphenyl ether (183)
BDE190	2,3,3′,4,4′,5,6-Heptabromodiphenyl ether (190)
BDE209	Decabromodiphenyl ether (209)
	Homologue groups
MBDE	Mono BDE (sum of congeners)
DBDE	Di BDE (sum of congeners)
TRBDE	Tri BDE (sum of congeners)
TEBDE	Tetra BDE (sum of congeners)
PEBDE	Penta BDE (sum of congeners)
HXBDE	Hexa BDE (sum of congeners)
HPBDE	Hepta BDE (sum of congeners)
OBDE	Octa BDE (sum of congeners)
NBDE	Nona BDE (sum of congeners)
HBCD	Hexabromocyclododecane
TBBPA	Tetrabromobisphenol-A
METBA	Dimethyl TBBP-A
CB12E	1,2 *Bis* (pentabromophenyl) ethane
DBB	Decabromobiphenyl (BB209)

Add total organic mercury to the list of Organometallic compounds.

Add Parathion-ethyl to the list of organophosphorus pesticides, after Parathion-methyl.

Better Explanations

There are some cases where it is necessary to explain in more detail the exact meaning of the text in "Parameter/Contaminant".

In the list of PAHs:

Sum of PAHs (total) Specify which PAHs are included in the sum as a textual comment.

In the list of chlorobiphenyls:

Write the structural formula for the PCB congeners in the column Parameter/Contaminant

e.g., 2,4,2′, 4′- tetrachlorobiphenyl

Polychlorinated biphenyls (formulation basis) explain in textual field which formulation was used as the basis for quantification.

In the list of organometallic compounds:

Explain that the concentrations are "gram metal/ gram" or "gram metal / litre"

Changes

In the list of dioxins:

In the next generation of this list from a revised ICES database, it should be possible to use a 10-digit code for the congeners. Also the CAS-numbers are particularly important for dioxins, as it is expected that they will be used in the future to retrieve date from the database.

In the list of Organochlorines:

Add after *cis*-heptachlorepoxide "(alpha)" and after *trans*-heptachlorepoxide "(beta)". These two compounds should also have CAS-numbers.

In the list of Hexachlorocyclohexanes:

Remove the word "delta lindane"

The Monocyclic aromatic compounds are said to be NA for biota. That is incorrect. These compounds are routinely analysed and we expect that data will be reported to ICES. These determinands should be cited as g/g.

In the list of Chlorobiphenyls:

The CAS-numbers should be available for CB77 and CB81, but are not given.

Misspellings

Dioxins should be spelled out:

e.g., heptachlorodibenzo-*p*-dioxin.

Check the list for other misspellings and be consistent with the use of capitals.

ANNEX 10: DIOXINS AND DIOXIN-LIKE CBs IN FISH AND FEED AND THE CURRENT STATUS OF LEGISLATION IN THE EU

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The term "dioxins" refers to a group of polychlorinated, planar aromatic substances with similar structures, chemical and physical properties. This group of compounds consists of dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) of which seven dioxin congeners and ten furans in particular are extremely resistant to biological and chemical degradation processes and, consequently, persist in the environment and accumulate in the food chain. A limited number of polychlorinated biphenyls (PCBs) contain similar chemical, physical and toxicological properties as the group of seventeen dioxins and are therefore referred to as "dioxin-like CBs".

Since the Belgian dioxin crisis in 1999 the European Commission has put a lot of effort into the evaluation of the potential risks of intake of dioxins (PCDDs, PCDFs) and dioxin-like CBs by consumption of food. The available data on the occurrence of these contaminants in feed and food was collected and evaluated (Anon., 2000a, 2000b). Currently, discussions on new maximum residue limits for PCDDs, PCDFs and dioxin-like PCBs are taking place at national levels and in the European Union (Liem *et al.*, 2000). Recently the EU adopted a new tolerable weekly intake (TWI) for the total intake of dioxins and dioxin-like CBs at a maximum level of 7 pg TEQ kg^{-1} bw (Anon., 2000c). This TWI is based on the WHO-TDI (Tolerable Daily Intake) of 1–4 pg kg^{-1} bw day^{-1}.

The purpose of this paper is to summarise the available information on (i) the available data on the occurrence of dioxins and dioxin-like CBs in fish and fish products, and (ii) current legislation within the EU member states on contamination of fish and fish products.

Dioxins and dioxin-like CBs in fish, fish oil and fish meal

The biochemical and toxic response to dioxins in animals and humans depends on the planar or nearly planar conformation and the geometrical size of the different congeners, with 2,3,7,8-TCDD being the most toxic compound. As the toxicity of the different congeners varies, toxic equivalency factors (TEFs) are used to express the total concentrations and exposures in toxic equivalents of 2,3,7,8-TCDD (TEQ). The I-TEQ values are based on the international TEFs (I-TEF) issued by NATO/CCMS in 1988. For dioxin-like CBs the PCB-TEFs, as published by Ahlborg *et al.* (1994), have been used. Recently the WHO has re-evaluated the toxicity of dioxins and dioxin-like CBs and established WHO-TEFs for seven dioxins, ten furans, and eleven dioxin-like CBs (van den Berg *et al.*, 1998). WHO- and I-TEFs are mentioned in Appendix 1.

Dioxins and dioxin-like CBs in fish

Concentrations of dioxins and dioxin-like CBs in fish and fish products vary considerably, which is due to the difference in fish species, fat content and the geographical differences (Anon., 2000a). Many species contain dioxins and dioxin-like CBs at levels below 1 pg I-TEQ g^{-1} and 1 pg PCB-TEQ g^{-1} wet weight, respectively (Appendix 2). In some fish species such as crab (Norway), Mediterranean tuna, eel, and cod liver higher concentrations have been found. Baltic herring shows a comparable total-TEQ to that of North Sea herring (4–6 pg g^{-1}), but Baltic salmon showed a relatively high TEQ of 16 pg g^{-1}. Serious gaps in data on the dioxin-like CBs hinder the drawing of overall conclusions on the contamination of fish with dioxin-like CBs. Time trends are rarely available. In general, the PCB contribution to the total-TEQ is higher than the contribution of PCDDs and PCDFs together. However, ratios vary strongly, depending on species and location.

In a recent Dutch study on the contamination of fish and shellfish with dioxins and dioxin-like CBs, similar results were obtained (Leonards *et al.*, 2000). Many species contain dioxins at levels below 1 pg g^{-1} WHO-TEQ but in some fish and shellfish species such as eel, mussels, cod and herring originating from Dutch fresh waters or the southern North Sea, higher levels were found (Appendix 3). Levels of dioxins of approximately 17 pg WHO-TEQ per gram of product were found in cod liver from the North Sea (Appendix 3). The total-TEQ (PCDD/Fs and CBs) ranges from 0.03 (tuna from Sri Lanka) to 88.7 (cod liver, southern North Sea) pg TEQ g^{-1} product. The level of contamination depends highly on the origin of the fish: freshwater fish were more contaminated than fish from the North Sea. Concentrations of 0.7–10.7 pg TEQ g^{-1} product (PCDD/Fs) were found in cultured fish. No consistent relation was found between the PCDD/F

TEQ and the dioxin-like CB TEQ.

Dioxins and dioxin-like CBs in fish oil and fish meal

Fish is frequently used as a raw material for the production of animal feed and can be identified as an important source of dioxins in foodstuffs. Although few dioxin analyses have been carried out, the available data are relatively consistent. The data show a clear difference in contamination levels between fish meal and fish oil originating from the (south) Pacific (Chile and Peru) and those originating from the European waters, with average concentrations in the latter being approximately eight-fold higher. Table A10.1 shows levels of dioxins and dioxin-like CBs in fish meal and fish oil from European waters and the Pacific (Anon., 2000b).

Contaminated fish meal used as fish feed can lead to an accumulation of the contaminants in the cultured fish. In particular, this can become a problem with relatively highly contaminated fish meal or oil from European waters. A reduction of the dioxin content in cultured fish may be obtained by i) the use of fish originating from clean areas such as the Pacific, ii) partly replacing fish meal and oil by vegetable feeding stuffs, or iii) applying cleaning techniques such as filtration or distillation.

Table A10.1. Levels of dioxins and dioxin-like CBs in fish meal and fish oil originating from Europe and the Pacific, expressed as the range of occurrence (low–mean–high) (Anon., 2000b).

	Europe		**Pacific**	
	Dioxin only[1]	Dioxins and PCBs[2]	Dioxin only[1]	Dioxins and PCBs[2]
Fish meal (ng WHO-TEQ kg^{-1} dry matter)	0.04–1.2–5.6	0.18–6–28.2	0.02–0.14–0.25	0.11–0.7–1.26
Fish oil (ng WHO-TEQ kg^{-1}fat)	0.7–4.8–20	3.5–24–100	0.16–0.61–2.6	0.8–3–13

[1] TEQ based on the contribution of PCDDs and PCDFs.

[2] TEQ based on the contribution of PCBs, PCDDs and PCDFs.

Effects of cooking

The actual human intake of dioxins and PCBs through the consumption of fish is influenced by the commonly used cooking practices. Removal of the toxic substances may occur by volatilisation, extraction in the cooking oil or by discarding the fat drippings and removal of the (contaminant-rich) skin.

Several studies (Zabik *et al.*, 1992, 1995, 1996; Salama *et al.*, 1998; Schecter *et al.*, 1998; Wilson *et al.*, 1998) reported reductions of PCBs and PCDD/Fs, depending on the cooking process applied. Zabik *et al.* (1996) reported a reduction of 40 % in the sum of PCBs through smoking of lake trout, whereas baked, char-boiled and salt boiled showed reductions of approximately 15 %. In an other study, the total amount of PCBs in boiled blue crab was reduced by 25–36 % compared with the raw material (Zabik *et al.*, 1992). Salama *et al.* (1998) studied reductions of PCBs in Atlantic blue fish filets and found reductions with smoking and microwave baking of 65 % and 60 %, respectively. Skin-off charbroiling, skin-on charbroiling, pan-frying and convection oven baking showed reductions of 46 %, 37 %, 27 % and 39 %, respectively.

The sum of the congeners of PCDDs and dioxin-like CBs in catfish is reduced by 43 % and 32 % wet weight, respectively (Schecter *et al.*, 1998). The amount of PCDFs, however, was increased by 67 %, caused by an increase of the congener OCDF, for which no explanation was given. Reductions are presumably an effect of the reduction of the fat in the sample. Zabik *et al.* (1995) showed PCDD reductions through cooking of skin-on fillets of about 40 % to 80 % for different species. Cooking of skin-off fillets showed increased reductions. Finally, Wilson *et al.* (1998) reviewed the available data from different studies and reported average PCB mass reductions of 28 %, 68 %, 28 %, 48 % and 30 %, respectively, for baking, boiling, broiling, frying and smoking, but data from different studies were inconsistent and showed significant ranges. Microwaving was applied in one study and reported to cause a 26 % reduction of PCBs (Wilson *et al.*, 1995).

It is rather complicated to take the effect of cooking into account when assessing the human exposure as cooking methods vary (temperature, cooking time, etc.) and differ between species and tissues. Moreover, cooking methods differ geographically and, in practice, this step is not controlled as with the laboratory experiments. Besides, the available data are not consistent and show gaps. Therefore, although a tendency towards a reduction of the PCB and dioxin content of fish due to cooking processes may be extracted from the literature, it is difficult to express a quantitative reduction for all species and cooking methods, which, for the time being, hampers the inclusion of cooking factors into an overall risk assessment.

Present regulations on dioxins and dioxin-like CBs in fish and feed

Recently, the WHO re-evaluated the toxicology of dioxins and recommended a TDI of 1–4 pg TEQ kg^{-1} body weight (including dioxin-like PCBs) (van Leeuwen *et al.*, 2000). It was stressed that the upper range of the TDI of 4 pg TEQ kg^{-1} should be considered as a maximum tolerable daily intake on a provisional basis and that the ultimate goal is to reduce human intake levels below 1 pg TEQ kg^{-1} bw / day^{-1}. Based on the WHO re-evaluation, the EU recently established a group TWI for PCDDs, PCDFs and dioxin-like CBs of 7 pg WHO-TEQ kg^{-1} bw (Anon., 2000c). The total intake of dioxins and dioxin-like CBs from the diet in the EU countries is currently equivalent to 1.2–3.0 pg WHO TEQ kg^{-1} bw day^{-1} (Anon., 2000c). A considerable proportion of the European population will exceed the above-mentioned group TWI. The contribution of fish to the daily intake of dioxins in the EU countries ranges from 2 % (Netherlands) to 63 % (Finland), depending on the composition of the diet and the contamination of the fish consumed (Anon., 2000a).

Table A10.2. Present regulations on concentrations of dioxins and dioxin-like PCBs in fish in European countries (Anon., 2000a).

Country	Dioxins (PCDDs, PCDFs)	Dioxin-like PCBs	Other CBs (non-dioxin-like)
Austria, Belgium, Denmark, Finland, Germany, Greece, Ireland, Italy, Luxembourg, Norway, Portugal, Spain, Sweden, United Kingdom	No explicit guidelines on maximum level of dioxins in fish	No explicit guidelines on maximum level of dioxin-like CBs in fish	Sweden: CB 153 0.1 mg kg^{-1} wet weight Germany: congener- specific limits for CB 28, 52, 101, 138, 153 and 180 (0.008–0.6 mg kg^{-1} fat or whole weight basis)
Netherlands	Eel: 8 pg WHO-TEQ g^{-1} product[1]	Limit for CB 118 (wet weight basis)[2], in eel: 0.40 mg kg^{-1}, in fish liver 1.2 mg kg^{-1}, in other fish: 0.08 mg kg^{-1}	Congener-specific limits for CBs 28, 52, 101, 138, 153 and 180 (0.04–2.0 mg kg^{-1} wet weight for fish and fish liver)

[1] Anon., 2000d.

[2] Anon., 1984.

Present regulations within European countries with respect to the concentrations of PCDDs, PCDFs, and PCBs in food from different origins are diverse. Several countries have not set national limits, whereas regulations in other countries are mainly in force on milk, milk products and pork, beef, poultry and eggs. Recently, the Netherlands has enforced a regulation on the maximum allowable concentrations of dioxins (only) in eel (Anon., 2000d). The Dutch Ministry of Agriculture, Nature Management and Fisheries is currently evaluating the possibilities of setting group limits on the maximum allowable concentrations of PCDD/Fs and dioxin-like CBs in fish.

In Sweden, Germany, and the Netherlands tolerance levels in fish are valid for indicator CBs. The single dioxin-like CB included in the tolerance levels in the Netherlands is CB 118 (Table A10.2). Although other European countries currently have no legislation in force on concentrations of dioxins or dioxin-like PCBs in fish (see Table A10.2), it is the intention of the EU to regulate maximum allowable concentrations in different types of food and feed, including fish and fish products, in the near future.

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APPENDIX 1: TEF-VALUES FOR DIOXINS, FURANS AND PCBS

	WHO-TEF values[1]	**I-TEF values**[2]
Dioxins (PCDDs)		
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	0.5
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	0.001
Furans (PCDFs)		
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05
2,3,4,7,8-PeCDF	0.5	0.5
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	0.001
PCBs		
Non-*ortho* CBs		
CB 77	0.0001	0.0005
CB 81	0.0001	-
CB 126	0.1	0.1
CB 169	0.01	0.01
Mono-*ortho* CBs		
CB 105	0.0001	0.0001
CB 114	0.0005	0.0005
CB 118	0.0001	0.0001
CB 123	0.0001	0.0001
CB 156	0.0005	0.0005
CB 157	0.0005	0.0005
CB 167	0.00001	0.00001
CB 189	0.0001	0.0001
Other CBs		
CB 180	-	0.00001

[1] van den Berg *et al*., 2000

[2] Nato/CCMS, 1988

APPENDIX 2. NATIONAL AVERAGE CONCENTRATIONS OF DIOXINS AND RELATED PCBS IN REPRESENTATIVE SAMPLES OF FISH AND FISH PRODUCTS (ANON., 2000A) FROM 1995 TO 1999. I-TEF VALUES HAVE BEEN USED.

Country	**Species**	***Latin name***	**PCDD/F (pg TEQ g^{-1} product)**	**PCB (pg TEQ g^{-1} product)**
Denmark	Alaska Pollack		0.01	
	Carp	*Cyprinus carpio*	0.74	
	Catfish	*Anarchinas lupus*	0.52	
	Coalfish	*Pollachius virens*	0.07	
	Cod	*Gadus morhua*	0.05	
	Eel	*Anguilla anguilla*	1.64	
	Haddock	*Melanogrammus aeglefinus*	0.04	
	Hake	*Merluccius merluccius*	0.03	
	Halibut	*Hippoglossus hippoglossus*	0.46	
	Herring	*Clupea harengus harengus*	0.79	
	Mackerel	*Scomber scombrus*	0.29	
	Plaice	*Pleuronectes platessa*	0.28	
	Redfish	*Sebastes marinus*	0.23	
	Salmon (cultured)	*Salmo salar*	0.43	
	Sardine	*Sardina pilchardus*	0.43	
	Trout	*Salmo trutta*	0.43	
	Trout (cultured)	*Oncorhynchus mykiss*	0.26	
	Tuna	*Thunnus thynnus*	0.01	
	Fish mixture	-	0.29	
	Sea fish mixture	-	0.48	
Finland	Trout (cultured)	*Oncorhynchus mykiss*	0.74	1.49
France	Sea fish mixture	-	0.63	
	Seafood mixture	-	1.41	
Italy	Anchovy	*Engraulis encrasicolus*	0.35	
	Clam		0.10	
	Mackerel	*Scomber scombrus*	0.86	
	Mussel	*Mytilus edulis*	0.17	
	Norway lobster	*Homarus gammarus*	0.12	
	Red mullet	*Mullus surmuletus*	0.44	
	Squid		0.18	
Norway	Crab		10.2	
Sweden	Cod	*Gadus morhua*	0.13	0.23
	Herring	*Clupea harengus harengus*	0.73	1.11
	Herring (Baltic)	*Clupea harengus harengus*	3.18	1.33
	Pike	*Esox lucius*	0.90	0.67
	Salmon (Baltic)	*Salmo salar*	7.04	9.12
	Salmon (cultured)	*Salmo salar*	1.04	1.16
	Trout (cultured)	*Oncorhynchus mykiss*	0.81	1.14
	Fish mixture	-	0.39	0.55
United Kingdom	Cod	*Gadus morhua*	0.03	0.07
	Dietary supplements	-	3.55	14.2
	Eel	*Anguilla anguilla*	1.55	8.39
	Haddock	*Melanogrammus aeglefinus*	0.03	0.03
	Herring	*Clupea harengus*	2.10	6.24
	Mackerel	*Scomber scombrus*	0.61	2.50
	Plaice	*Pleuronectes platessa*	0.25	0.48
	Salmon	*Salmo salar*	0.71	2.39
	Trout (cultured)	*Oncorhynchus mykiss*	0.24	0.87
	Whiting	*Merlangius merlangus*	0.03	0.11

APPENDIX 3: RESULTS OF A DUTCH STUDY ON DIOXINS, FURANS AND PCBs IN FISH AND FISH PRODUCTS FROM FRESH AND MARINE WATER SOURCES (LEONARDS *et al.*, 2000). WHO-TEF VALUES HAVE BEEN USED.

Species	**Latin name**	**Location**	**TEQ-concentrations (pg TEQ g^{-1} product)**		
			PCBs	**PCDD/Fs**	**ΣTEQ PCB+PCDD/Fs**
Anchovy	*Engraulis encrasicolus*	Italy	7.9	0.6	8.5
Bass	*Dicentrarchus labrax*	France	13.8	1.0	14.8
Blue whiting	*Micromesistius poutassou*	Atlantic Ocean	0.52	0.11	0.63
Trout (cultured)	*Oncorhynchus mykiss*	Cultured	0.7	0.2	0.9
Grey gurnard	*Eutrigla gurnardus*	North Sea	1.9	1.4	3.3
Herring	*Clupea harengus*	The Channel	1.77	1.46	3.23
Herring	*Clupea harengus*	North Sea	1.12	1.31	2.43
Herring	*Clupea harengus*	The Channel	3.9	1.8	5.7
Herring	*Clupea harengus*	The Channel	1.8	2.1	3.9
Hake	*Merluccius merluccius*	Celtic Sea	0.4	0.05	0.4
Halibut	*Hippoglossus*	Cultured	0.5	0.2	0.7
Horse mackerel	*Trachurus trachurus*	Celtic Sea	2.13	0.57	2.70
Cod	*Gadus morhua*	Silverpit	0.22	0.07	0.29
Cod	*Gadus morhua*	North Sea	0.5	0.3	0.8
Cod liver	*Gadus morhua*	North Sea	71.6	17.1	88.7
Coalfish	*Pollachius virens*	North Sea	0.8	0.1	1.0
Coalfish (black)	*Rachycentron canadum*	Northern North Sea	0.2	0.1	0.3
Dab	*Limanda limanda*	North Sea	0.84	0.54	1.38
Eel	*Anguilla anguilla*	Yssel Lake (Enkhuizen)	32.8	3.9	36.7
Eel	*Anguilla anguilla*	Yssel Lake (Staveren)	14.56	3.11	17.7
Eel	*Anguilla anguilla*	Yssel Lake (Medemblik)	7.48	2.14	9.6
Eel	*Anguilla anguilla*	Yssel Lake (Urkerhoek)	18.55	3.63	22.2
Eel	*Anguilla anguilla*	Yssel Lake (Staveren)	7.33	1.39	8.7
Eel (cultured)	*Anguilla anguilla*	Netherlands	8.18	2.54	10.7
Eel (cultured)	*Anguilla anguilla*	Italy	3.13	0.77	3.89
Eel (cultured)	*Anguilla anguilla*	Netherlands	7.2	2.2	9.4
Eel (cultured)	*Anguilla anguilla*	Italy	5.4	0.7	6.1
Haddock	*Melanogrammus aeglefinus*	North Sea	0.1	0.1	0.2
Haddock liver	*Melanogrammus aeglefinus*	North Sea	25.6	17.5	43.1
Mackerel	*Scomber scombrus*	South of Ireland	1.60	0.63	2.23
Mackerel	*Scomber scombrus*	Skagerrak	1.0	0.3	1.3
Mackerel	*Scomber scombrus*	Atlantic Ocean	1.0	0.3	1.3
Mussel	*Mytilus edulis*	Eastern Scheldt	2.03	1.47	3.50
Mussel	*Mytilus edulis*	Western Wadden Sea	1.20	1.10	2.30
Pikeperch	*Stizostedion lucioperca*	River Nieuwe Merwede, Netherlands	2.7	1.1	3.8
Pikeperch	*Stizostedion lucioperca*	River Lek, Netherlands	2.5	1.3	3.7
Pikeperch	*Stizostedion lucioperca*	River Amer, Netherlands	1.8	0.9	2.7
Pikeperch	*Stizostedion lucioperca*	River Rhine, border, Netherlands	2.3	0.8	3.1
Pikeperch	*Stizostedion lucioperca*	River Waal, Netherlands	4.0	1.5	5.5
Pilchard	*Sardina pilchardus*	The Channel	6.3	1.6	7.9

Species	**Latin name**	**Location**	**TEQ-concentrations (pg TEQ g^{-1} product)**		
			PCBs	**PCDD/Fs**	**ΣTEQ PCB+PCDD/Fs**
Plaice	*Pleuronectes platessa*	North Sea	0.23	0.25	0.48
Redfish	*Sebastes marinus*	Northern North Sea	1.6	0.8	2.4
Salmon	*Salmo salar*	Norway	2.0	1.3	3.3
Salmon	*Salmo salar*	Norway	2.94	1.36	4.31
Salmon	*Salmo salar*	Scotland	2.78	1.14	3.93
Salmon	*Salmo salar*	Scotland	2.6	1.4	4.1
Sardinella	*Sardinella uarita*	Africa	0.08	0.02	0.10
Sea devil	*Lophius piscatorius*	Northern North Sea	0.2	0.1	0.3
Shrimps	*Crangon crangon*	Wadden Sea-west, Netherlands	0.93	1.02	1.95
Shrimps	*Crangon crangon*	Wadden Sea (Sylt)	0.57	0.76	1.33
Shrimps	*Crangon crangon*	Western Scheldt	0.5	0.6	1.1
Shrimps	*Pandalus borealis*	Norway	0.1	0.1	0.2
Sole	*Solea solea*	North Sea	0.18	0.15	0.32
Sprat	*Sprattus sprattus*	North Sea	3.1	2.5	5.6
Squid	*Loligo* spp.	North Sea, Dutch coast	2.0	1.2	3.1
Swordfish	*Xiphias gladius*	Italy	3.4	0.5	3.9
Tuna	*Thunnus thynnus*	Sri Lanka	0.02	0.01	0.03
Tuna (Bonito)	*Thunnus thynnus*	Italy	9.0	0.7	9.8
Tuna	*Thunnus thynnus*	France	3.5	0.6	4.2
Turbot	*Psetta maxima*	North Sea, Dutch coast	2.4	0.8	3.3
Whiting	*Merlangius merlangus*	North Sea	0.17	0.07	0.24
Yellow gurnard	*Trigla lucerna*	North Sea	2.4	1.5	4.0
Silversmelt	*Argentina silus*	Atlantic Ocean	0.54	0.40	0.94

ANNEX 11: BIOCONCENTRATION AND HAZARD ASSESSMENT OF VOLATILE ORGANIC COMPOUNDS (VOCS)

P. Roose
(Extracted from Roose and Brinkman, 2000)

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

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

This partition coefficient is supposed to be an intrinsic property of the compound and can, as a result, be related to its octanol-water partition coefficient, K_{ow}. Neely *et al.* (1974) and, subsequently, several other authors (Isnard and Lambert, 1988; Connell and Hawker, 1988; Banerjee and Baughman, 1991) demonstrated that BCF and K_{ow} are linearly related according to:

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

with *a* the regression coefficient and *b* the y intercept. The data obtained during the present study were compared with the average water concentrations reported by Dewulf *et al.* (1998) for the southern North Sea and BCFs were calculated for all VOCs. Plotting the logarithm of these BCFs against log K_{ow} indeed resulted in the linear relationship ($r = 0.42$) predicted by Eq. 2. This becomes especially evident when the data for higher K_{ow} values reported by Neely *et al.* (1974) are included in the picture (Figure.A11.1). The larger number of data points, spread over a larger K_{ow} range, results in a much better correlation ($r = 0.94$). Moreover, the observed slope is essentially the same as the one reported by these authors. However, plotting the average of the BCFs reported in the literature resulted in a slope that is lower than those obtained with our data and those of Neely *et al.* (1974) (Figure A11.1). This suggests that the BCFs reported in the literature are somewhat too low, especially for the VOCs with a log K_{ow} of less than 2.8. One explanation could be the use of nominal instead of actual concentrations. BCFs reported in the literature are often the result of laboratory experiments in open systems and nominal concentrations can easily be too high due to the high volatility of the compounds of interest (Crookes *et al.*, 1993). Even so, the observed relationship indicates that VOC concentrations in the water column are indeed reflected in the organisms and suggests that the EPT can be applied.

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

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

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

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

where $HC5_w$ is the total concentration in the water phase (including suspended matter) and C_w the concentration in the water column for a given K_{ow} that is unlikely to harm 95 % of the population, calculated on the basis of the QSARs as given in Eq. 3. The proportionality constant, *a*', relates to the average suspended matter concentrations in the area and their organic carbon content (van Leeuwen *et al.,* 1992). The internal tissue concentration, ITC or $HC5_{org}$, for the organisms was calculated from

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

where a lipid content of about 5 % wt. in the organism is assumed. Table A11.1 compares the calculated $HC5_{org}$ values and the average concentrations in the different organisms and tissues. The results show that, in no case, is the $HC5_{org}$ for the MAHs and CHCs exceeded. Most probably, this would have been true also for ethylbenzene if an $HC5_{org}$ had been available. Moreover, the observed averages are several orders of magnitude lower than the $HC5_{org}$. However, the present results still cause concern because the hazard assessment does not take into account synergistic, and thus more damaging, effects. Despite the often high results, no definite statements can, as yet, be made concerning long-term effects such as carcinogenicity or immunosuppression. The number of data is too limited and the calculation of the HC5 is one approach amongst several and needs to be further evaluated. What is clear, however, is that additional research, especially with regard to the long-term consequences of small doses of VOCs, is urgently required.

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Figure A11.1.Plot of the log of BCFs calculated for the present study, BCFs rported in the literature, and BCFs reported by Neely et al. (1974) against log K_{ow}

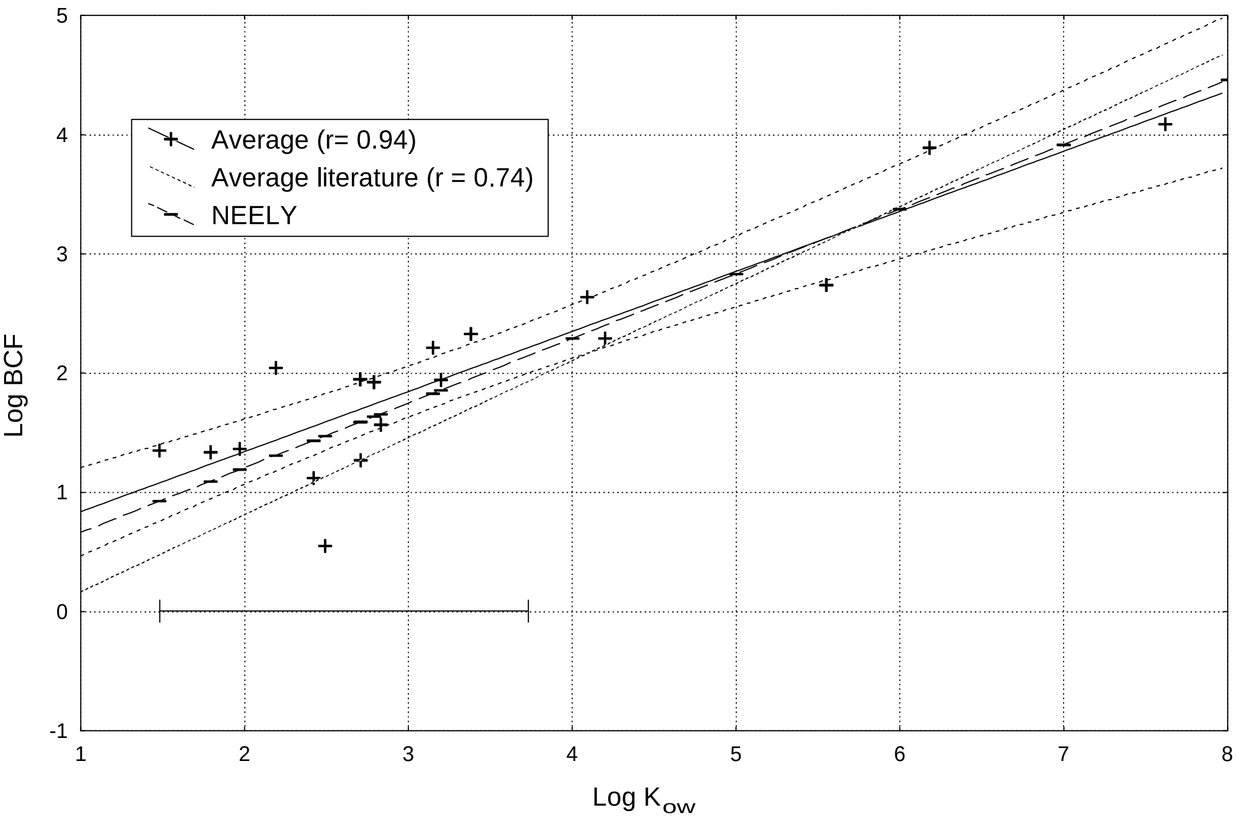

Table A11.1. Comparison of the average tissue concentrations in pg g–^{1} of the present data set and the proposed safety level (HC5).

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

nd = not detected; na = not available

ANNEX 12: ACTION LIST

David Wells	to provide an update on recent QUASIMEME studies in advance of MCWG2002.
Jacek Tronczynski	to approach colleagues in France with a view to providing information on the use of membrane systems for sampling to MCWG2002.
Jacob de Boer	to report new information on PBDEs and other brominated flame retardants to MCWG2002.
Robin Law	to transmit comments of MCWG members on the booster biocides document to Kevin Thomas, and arrange for the revised manuscript to be submitted to ACME2001.
Michel Lebeuf	to present an update on research and monitoring activities and developments in Canada regarding toxaphene in marine mammals to MCWG2002.
Michel Lebeuf	to present an update on research undertaken within the TSRI study to MCWG2002.
Gert Asmund	to present information on the monitoring of toxaphene in marine mammals within AMAP to MCWG2002.
Peter Woitke	to transmit to SGQAC the outcome of MCWG discussions based on items from their 2001 report, and also the recommendation that intercomparison exercises be undertaken for POC and PON.
Jacek Tronczynski	to ask Michel Marchand, who is involved in risk assessment within IFREMER, whether he might be interested in participating in the proposed GESAMP group on this topic.
Michael Haarich Patrick Roose Jacob de Boer Robin Law	to supply information to Michel Lebeuf on TCPM, TCPMe and DDT group compound concentrations in flatfish before the end of January 2002.
Michel Lebeuf	to report the results of the studies of TCPM, TCPMe and DDT group compounds to MCWG2002.
José Biscaya	to provide information on the utility of freezing nutrient samples prior to analysis to Patrick Roose by June 2001.
Patrick Roose	to present the results of studies on the preservation of nutrient samples in a frozen state to MCWG2002.

ANNEX 13: RECOMMENDATIONS

The Marine Chemistry Working Group recommends:

1) ICES to explore the possibility of establishing a database for information on marine reference materials, accessible via the internet, and establish a mechanism whereby this database can be continuously updated by the producers as new materials become available.
2) to SGQAC that intercomparison exercises be conducted for POC and PON, as these are mandatory determinands within the COMBINE monitoring programme.

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 and report on progress in the modelling of marine biogeochemical processes;
b) review and report on progress in the studies of estuarine behaviour of nutrients;
c) review and report on the present knowledge about total nitrogen, total phosphorus, and total organic carbon in sea water, their speciation, and arguments for their use in monitoring programmes.

B. Organics Subgroup

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

* submit results of discussion to WGBEC

C. Trace Metals Subgroup

a) critically evaluate the lists of priority contaminants prepared in relevant regional and international organisations and report the outcome;
b) review information on estuarine transport of trace metals, relevant measurement techniques available, and the comparability of their results, and report the outcome;
c) review new information on the use of membrane systems for sampling and report the outcome;

D. 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 2001 MCWG meeting into account and report the outcome;
c) review any new SGQAC 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.

Supporting Information

Priority:	
Scientific Justification:	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. A. Chemical Oceanography Subgroup a) Progress in the development and status of physical models for coastal circulation will be reviewed so as to understand the inherent accuracy, resolution, assumptions and parameterisations, etc., in relation to biological parameterisations. This is necessary to appropriately couple physics and population dynamics to provide meaningful calculations of population development. b) This study is part of the work on chemical oceanographic conditions and methods coordinated by MCWG. c) This study is also a part of the work on chemical oceanographic conditions and methods coordinated by MCWG. B. Organics Subgroup a) Given the tens of thousands of chemicals produced and used in industrial and other applications, it is important to develop a means to determine which chemicals may be potentially serious contaminants of the marine environment. 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. C. Trace Metals Subgroup 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) This is part of the MCWG work to review the distribution and transport of contaminants in the estuarine environment. c) These systems are being reviewed for application to monitoring contaminants in the marine environment. D. Plenum 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. 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. c) This item addresses the interests of HELCOM. d) Plenary discussions add value to the work in the subgroups.
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 co-operation between MCWG and ICES.
Secretariat Facilities:	The 2002 meeting will be held at the offices of the Federal Environmental Agency in Berlin, Germany, 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, OSPAR
Cost share	ICES 100 %