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Executive summary

The Marine Chemistry Working Group [MCWG] (Co-chairs Evin McGovern, Ireland, and Jacek Tronczynski, France) met at BFAFi, Hamburg, from 19–23 March 2007, alongside Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (STGQAC, 19–21 March). The Working Group on Marine Sediments (WGMS) met concurrently at BSH, Hamburg. Certain issues of common interest were discussed in joint plenary sessions with these working groups.

Highlights:

- **Perfluorinated compounds (PFCs)**: MCWG reviewed new information on concentrations of these emerging pollutants in air, biota (arctic), water and sediment. Studies on fluorotelemers, which are hypothesised as precursors of the ionic and very persistent perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), report higher air concentrations in the northern than in the southern hemisphere. A screening project in Greenland and the Faroe Islands indicated strong biomagnification of PFCs with high concentrations in polar bear liver (1300 ng/g). A time trend study on archived ringed seal liver samples (1983–2003), showed increasing concentrations.

  These substances have been detected in all compartments of the North and Baltic Seas with PFOS and PFOA the main components. These compounds have also been detected in surveys in the East Atlantic. Concentrations of PFOA and PFOS in the Greenland Sea of between 10 pg/L and 80 pg/L were higher than concentrations from the Southern Atlantic. PFOS is generally the most abundant compound in biota and sediment. These field studies suggested higher bioconcentration factors and higher biomagmifcation factors than previously reported. While these substances are classed as very persistent, very bioaccumulative (vPvB) more information is needed on their toxicity.
- **Passive Sampling**: The cooperation of MCWG and WGMS in the passive sampler trial survey has proved very successful with 13 laboratories participating and samplers being deployed at 31 locations for water and 25 for sediments. Initial results were presented and a detailed progress report is annexed. The outcome of this project will be presented at ICES Annual Science Congress 2007.
- **Advice on OSPAR requests:** MCWG responded to OSPAR requests for advice on establishing Background Concentrations for metals and PAH in biota. Due to the ubiquitous nature of contamination by these substances, MCWG expressed some reservations about using contaminant data from so-called "pristine" areas to derive background concentrations. MCWG made arrangements to collect data to try an approach using sediment cores to estimate ambient pre-industrial pollutant concentrations. This is suggested as a method for verifying the OSPAR approach.

  MCWG prepared new technical annexes on the analysis of two brominated flame retardants: Polybrominated diphenyl ethers (PBDEs) and Hexabromocyclododecane (HBCD) for inclusion in the OSPAR Joint Assessment and Monitoring Programme (JAMP) Guidelines for Monitoring Contaminants in Biota and assisted WGMS in drafting annexes for sediments. Arrangements were made to intersessionally complete Technical Annexes for the analysis of alkylated polyaromatic hydrocarbons (PAH) in biota and sediment (with WGMS) and tributyltin (TBT) in biota.

Other issues:

EU Water Framework Directive (WFD –Dir. 2000/60/EC)): MCWG considered current status of guidance for chemical monitoring for the WFD and provided comments that could be fed back to the development process through the Chair of the drafting group of the Chemical Monitoring Activity. In particular, MCWG commented on a draft EC Decision on Quality Assurance. Also as monitoring under the WFD was scheduled to commence in December

2006, MCWG compiled information on monitoring activities in different countries. Although this is not a complete overview it highlighted different approaches being taken in different countries (e.g. determinants, sampling frequency, compartments tested).

***In situ* semi-continuous nutrient analysers** are becoming more widely used in monitoring activities due to the need to collect high frequency data from dynamic and rapidly changing environments. MCWG reviewed some activities in this field and undertook to provide further information on members' experiences at MCWG 2008.

Quality Assurance: Steve Crum of the QUASIMEME project office gave an update on the QUASIMEME laboratory proficiency testing scheme. MCWG made some recommendations with a view to strengthening QUASIMEME and hopes to continue its close links with the scheme, as it is an essential service for supporting marine chemistry monitoring and research activities. MCWG made arrangements for collaboration with STGQAC through intersessional contact between the group chairs and provided some advice to STGQAC and the Steering Group on Quality Assurance of Biological Measurements (STGQAB) on HELCOM Technical Annexes following requests from these working groups.

Review of ICES structures: MCWG observe that it is important to consolidate and strengthen the discipline of marine chemistry in any new ICES structure and highlight that such data is essential to understanding fundamental processes in the marine environment. MCWG was concerned that the interaction between policy and science would be organised on an issue-by-issue basis under the new structure, and that this would undermine the longer-term progress in the field of marine chemistry. The group considered that MCWG should remain as a permanent working group of ICES. MCWG are concerned at poor participation of experts in trace metal chemistry and especially chemical oceanography in recent years. While MCWG members have undertaken to try and stimulate national participation from relevant experts, ICES should consider how best to strengthen these areas.

Mono-*ortho* and non-*ortho* CBs: MCWG provided information on the relationship between marker chlorinated biphenyls (CBs) and the mono-*ortho* and non-*ortho* CBs. While present at a lower concentrations than marker CBs these exhibit "dioxin-like" toxicity and therefore have been assigned Toxic Equivalence Factors (TEFs) (e.g. by WHO). Although there is clearly a relationship between the concentrations of marker PCBs and mono-*ortho* and non-*ortho* CBs, current information does not support a unique ratio between these. MCWG recommends that the12 non-*ortho* and mono-*ortho* congeners be monitored in biota at hot spots but suggests that, given analytical difficulties, including these congeners in monitoring of set species at fixed locations to determine temporal trends may not provide substantial additional information over and above current monitoring of marker PCBs.

1 Opening of the meeting

The Co-Chairs Evin McGovern (Ireland) and Jacek Tronczynski (France) opened the meeting at 10:00 am on Monday 19 March 2007. The participants then introduced themselves and their affiliations and described their specific interests within the field of marine chemistry. Michael Haarich welcomed MCWG to BFAFi. The List of Participants is given in Annex 1, and the Agenda in Annex 2. The Terms of Reference for MCWG 2008 is given as Annex 3. Recommendations are listed in Annex 4, and the MCWG Action List is appended as Annex 5.

2 Adoption of the agenda

The agenda was adopted with one addition during the meeting (Agenda Item 8.16) following a suggestion by Patrick Roose.

3 Report of the 94th ICES Statutory Meeting

None of the members attended the ICES Annual Science Conference 2006. MCWG noted papers presented during Theme Session G on *human health risks and marine environmental quality*. No other items of specific interest to MCWG were identified. MCWG was made aware of two theme sessions proposed for ASC 2007 that were of specific interest: Theme Session I on *effects of hazardous substances on ecosystem health in coastal and brackish-water ecosystems: present research, monitoring strategies and future requirements*; and, Theme session (J) *Applications of passive sampling devices in environmental monitoring, assessment, research and testing*. MCWG members planning to attend ASC 2007 undertook to report back on these theme sessions to MCWG 2008.

4 Reports on Related Activities

4.1 OSPARCOM and HELCOM

All official requests from OSPARCOM or HELCOM have been included in the agenda.

4.2 Intergovernmental Oceanographic Commission

No new information from IOC has been available to MCWG in recent years. This agenda item will be removed from the MCWG standing agenda for future meetings.

4.3 Laboratory Performance Study - QUASIMEME update

Steve Crum (Quasimeme Project Office, Wageningen UR) attended the meeting and presented an update on Quasimeme activities. During the ensuing discussion a number of questions and issues were raised.

QUASIMEME already run exercises for certain contaminants in seawater and in the light of the requirements for monitoring under the Water Framework Directive (WFD - Dir. 2000/60/EC) plan to initiate new exercises for additional substances. This was welcomed by MCWG. Two views were expressed by members in relation to the appropriate concentrations for such exercises:

- concentrations should be in a range close to Environmental Quality Standards (EQS) proposed under the WFD. A problem could be that for some substances where there is a low EQS, an impractically large sample volume may be required for analysis to achieve the required Limits of Quantification.

- concentrations should reflect concentrations found in the marine environment. In this regard it was noted that the aim was for all countries to achieve good chemical status (<EQS) by 2015.

Occasionally there can be problems with assigned values. For example, for some CB congeners (e.g. CB163/138) many labs do not routinely achieve chromatographic separation so the assigned value is based on the sum of these peaks. This means that labs that do achieve separation may score poorly. This can be a problem given the importance of QUASIMEME in laboratories accreditation programmes and should be addressed. More proactive communication by QUASIMEME to highlight such issues would be welcomed.

Some previous exercises did not have enough participants to enable an assigned value to be set. QUASIMEME pointed out that they could not control how many participants in an exercise actually submitted results. In the future QUASIMEME are likely to skip exercises where poor participation is likely.

Workshops to facilitate performance improvement and transfer of experience will remain a fundamental part of QUASIMEME's *raison d'être* and the plan is to have two workshops a year. However, the level of participation in recent workshops has been close to the viable minimum.

MCWG reaffirmed that QUASIMEME is an essential pillar for quality assurance of marine environmental chemistry measurements and encouraged member's participation.

MCWG would like to maintain a close working link with QUASIMEME and would be pleased for a QUASIMEME representative to attend MCWG meetings on a regular basis as in previous years.

www.QUASIMEME.org

4.4 Other Activities

MCWG was asked by the Chair of the ICES Marine Habitat Committee (MHC) to review the plans for restructuring ICES science structure, advisory structure and a new strategic plan. Specifically a number of questions were put to the working group. After reading the plans the MCWG members could not get a clear view of the new structure and therefore were not in a position to respond to the specific questions. However this initiated a good discussion on the role of marine chemistry in the context of ICES and specifically the future of the MCWG.

Although the need for ICES to be able to respond with timely and sound scientific advice, it was unclear to us in what way the new more flexible structure could guarantee a good, broadly supported and complete scientific basis for the desired quicker responses to questions raised by ICES clients (e.g. OSPAR/HELCOM/EC). MCWG has a dual role as the group provides specific advice in response to requests from ICES clients and there is also the very important aspect of sharing and discussing scientific development, innovative techniques and emerging issues (such as new substances) that make the MCWG valuable to marine chemists in the member countries. The roles are important given new initiatives such as proposed the Marine Framework Directive. In this context ICES could strengthen key areas, such as the provision of advice on broad marine environmental issues and MCWG would have a role to play. MCWG was concerned that the interaction between policy and science would be organised on an issue-by-issue basis under the new structure, and that this would undermine the longer-term progress in the field of marine chemistry. The continuity of MCWG is vital for setting up and maintaining a strong network of marine chemical experts that share their experiences and collaborate in scientific projects, and to strengthen the awareness of regional differences. We must emphasise that the essential chemical data produced by the contributing laboratories and collected and maintained by ICES, plays a key role in understanding environmental processes

and assessing the state and changes in the marine environment. The quality of the data is dependent on a good and continuous exchange amongst marine chemists. For MCWG members to have a good understanding of the proposed changes and the consequences thereof, a direct exchange of views and opinions with a representative from ICES would probably have been better.

In recent years there has been poor participation by metals and chemical oceanography experts at MCWG undermining our abilities to deliver sound advice on these issues. ICES should consider how best to stimulate activities in this area to achieve critical mass. All MCWG members should consider at their home Institute's suitable topics for a theme session on chemical oceanography for ASC 2009. One example would be ocean acidification. MCWG noted that an ICES workshop on changing ocean CO_2 and pH will be held in the UK in May 2007 and relevant information from this could be reviewed at MCWG 2008.

5 Reports on projects and Activities in Member Countries

Harri Kankaanpää (Finnish Institute of Marine Research) presented information to MCWG on two issues in relation to the Baltic Sea.

5.1 Cyanobacterial phycotoxins in the Baltic Sea

There are extensive cyanobacterial (blue-green algae) blooms in the Baltic Sea every summer. Baltic Sea cyanobacteria blooms can cover areas of the order of 100 000 km^2.

These blooms are not only a considerable aesthetic and recreational problem, but they also pose a risk to the marine environment. A large part of the cyanobacteria community consists of *Nodularia spumigena*, a filamentous and toxic species. *N. spumigena* produces a cyclic pentapeptide, nodularin, which is a potent liver toxin and tumour promoter. Nodularin has an LD_{50} value of 50 µg/kg bw (i.p., rat).

Additionally, microcystin-LR (MC-LR), a cyclic heptapeptide closely related to nodularin, occurs in Baltic Sea phytoplankton. However, it is far (ca. 100-fold) less abundant and thus of less concern.

The major factors contributing to the high risk involved with *N. spumigena* are as follows: 1) very high biomass during the summer. 2) high concentration (ca. 0.1–1 g/kg dw) of nodularin in the phytoplankton. 3) potential of nodularin to bioaccumulate. 4) known toxicity of nodularin.

Nodularin can be found in almost every environmental matrix in the Baltic Sea – phytoplankton, mussels, different species of fish, water phase and soft sediments. Especially blue mussels and flounders (liver) contain high concentrations (of the order of 100's–1000's µg/kg dw) of nodularin. In contrast, concentrations of nodularin are significantly lower (ca. 1–10 µg/kg dw) in commercially more important fishes, herring and salmon. Nodularin bioaccumulates but does not biomagnify.

Nodularin is not part of ICES/HELCOM monitoring programmes of the Baltic Sea. It may be worthwhile to evaluate whether such monitoring would be warranted.

5.2 Recent trends in organochlorine and oil contamination in the Baltic Sea

Analysis of monitoring data on organochlorine compounds in two-year-old herring from 1985-2006 indicates that the concentrations of these compounds are steadily decreasing. This conclusion is based on results normalised to wet weight of muscle tissue. Data originates from

five fishing areas in the northern Baltic Sea. The parameters include CB congeners 28, 52, 101, 118, 153, 138 and 180, DDT, DDE, DDD, α- and γ-HCH plus HCB.

A positive development can be seen in temporal concentration trends of these compounds. Concentrations of HCHs and HCB have been below the limit of detection (0.2 µg/kg ww) since 2005.

Statistically most significant trends can be seen with the DDTs. According to the trend analysis, the rates of reduction of sum DDT concentrations are very linear and from -0.6 to −0.28 µg/kg/a (P<0.0001). Actual concentrations are at ca. 1–2 µg/kg ww. According to the estimates concentrations of sum DDTs will fall below between the limit of detection sometime in 2007-2011.

There are less significant trends in sum CB concentrations, but overall reduction in concentrations can nevertheless be seen. The sum CB burden in herrings has been declining at rates of −0.4 to −0.26 µg/kg/year (P=0.0005–0.03) with current concentrations of ca. 3–4 µg/kg ww.

Fluorescence-based analysis indicates that at several locations around the Baltic Sea total oil concentrations have declined. Rates of reduction have been −0.10 to −0.02 µg/l/year ($0.0001 < P < 0.05$) and are everywhere well below 1.0 µg/l (limit for non-contaminated water). This development has taken place in spite of increasing ship traffic.

The conclusion is that in terms of these chemical substances the chemical status of Baltic Sea is improving.

The complete report, together with other relevant Baltic Sea monitoring data, is available at http://www.fimr.fi/stc/palvelut/attachments/1_meri__59.pdf.

6 Requests from ACE, ACME and Regulatory Agencies

Requests from ACE and ACME which arose prior to the preparation of the agenda were included in the meeting agenda.

7 Plenary Presentations

7.1 Ashok Deshpande

Use of PCB fingerprints for the identification of subpopulations of young-of-the-year bluefish in the New York Bight.

Ashok D. Deshpande, Bruce W. Dockum, and Andrew F.J. Draxler

USDOC, NOAA, NMFS, NEFSC, James J. Howard Marine Sciences Laboratory, Sandy Hook, New Jersey, USA

Concentrations of polychlorinated biphenyl (PCB) congeners and organochlorine pesticides in young-of-the-year (YOY) bluefish, *Pomatomus saltatrix*, from seven nursery estuaries within the New York Bight correlated well with the known or anecdotal contamination histories of the respective habitats. Contaminant concentrations were highest in YOY bluefish from Newark Bay, and followed in decreasing order in YOY bluefish from Hudson River, Sandy Hook Bay, Great South Bay, and Navesink River. YOY bluefish from Great Bay and Delaware Bay were relatively uncontaminated. YOY bluefish from Hudson River displayed the best condition factors while YOY bluefish from Newark Bay displayed the worst condition factors. Despite the small sample size, this observation suggested that chemical contaminants might not be the sole determinants of the condition of YOY bluefish. Body

burdens of PCBs and p,p'-DDE increased with the weight of YOY bluefish. PCB and p,p,-DDE concentrations did not increase proportionate to the body weight probably due to the dilution effects related to the rapid growth of YOY bluefish during their estuarine residence. Low to moderate intra-estuarine homogeneity of PCB patterns in YOY bluefish was indicated by decrease in relative standard deviations in the concentrations of PCB congeners after PCB 153 normalization. Different patterns of prominent PCB congeners in YOY bluefish from Newark Bay and Hudson River suggested different sources of contamination in these relatively contaminated and geographically adjacent nursery estuaries. Principal component analyses of PCB and pesticide fingerprints in YOY bluefish using non-normalized and normalized data segregated various New York Bight sub-estuaries, including resolving adjacent nurseries with a distance of less than 15 kilometres. Bioenergetically profitable site fidelity behaviour of YOY bluefish, as suggested by the results of the present study and the results of tagging experiments reported in the literature can have management implications.

7.2 Katrin Vorkamp

Levels of perfluorinated compounds and toxaphene in biota from Greenland.

The information on perfluroinated compounds is presented under Agenda Item 8.11. The presentation on toxaphene was deferred to MCWG2008 due to time constraints.

7.3 Gerhard Dahlman

Oil spill identification –finding the sources of oil spills

The COSI-system (Computerized Oil Spill Identification) of the BSH was presented. This consists of a database of about 1400 samples of oils of different types, including about 300 crude oils from all over the world, and an evaluation system for the rapid identification of an unknown oil sample. Examples of real cases were shown, where the correct matching oil sample could be found within a few seconds. Computerized Oil Spill Identification adds a new dimension to forensic Oil Spill Identification: by comparing an oil sample with many hundred oils simultaneously a much stronger connection between a distinct oil spill and its actual source may be established than before. A PowerPoint presentation of this system can be found on the BSH-website:

http://www.bsh.de/de/Meeresdaten/Umweltschutz/Oelidentifizierung/Oeldatenbank.ppt

8 Main Agenda

8.1 to revisit the current accepted and proposed background concentrations for biota and to evaluate the methodology that was used to derive them with the aim of:

i) **developing proposals for deriving BCs in biota, with priority given to metals in fish and shellfish, bearing in mind that a pragmatic approach has to be identified that will be applicable for the wider OSPAR area;**

ii) **identify those parts of the OSPAR maritime area for which the proposed BCs in biota may not be applicable so that this can be taken into account during the assessments;**

iii) **for the parts of the OSPAR maritime area identified, determine how assessments of whether concentrations are of at or near background should be prepared.**

MCWG considered a document from SIME 2007 (SIME 07/5/4) outlining the history of the development of Background Concentrations (BCs) for use in OSPAR CEMP assessments. These are required to establish if the OSPAR objective of environmental concentrations of "near background" have been achieved for naturally occurring substances. BCs are required for metals and PAH to replace the current Background/Reference Concentrations (B/RCs) adopted by OSPAR in 1997. Patrick Roose introduced this request and explained the use of BCs and Background Assessment Concentrations (BACs) in Co-ordinated Environmental Monitoring Programme (CEMP) assessments. He also presented the outcome of discussions at MON 2006 where draft BCs were calculated for metals and PAH in mussels and used in a trial application during the CEMP assessment. It was noted that it was essential for agreement on BCs for application in the 2008 CEMP assessment as this would be the final assessment for the OSPAR Quality Status Report 2010.

There was little support from MCWG for the approach of MON in deriving BCs. That approach involved collecting data from "pristine" areas as identified by individual countries. A median of medians was then used as BC for the given parameters (selected PAH and metals). Some MCWG members noted that the MON proposed BCs were relatively high for PAH and that appreciably lower concentrations could be found in the marine environment of the OSPAR area. A number of points were raised by the group.

1) BCs of these contaminants could be considered as the pre-industrial concentrations. Since the industrial revolution, human activities have led to ubiquitous contamination of the marine environment. Due to, for instance, long range transport of pollutants or even transport from migratory animals even remote areas could not be considered as pristine. The relative anthropogenic and natural contributions to the contaminant load in remote areas was very difficult to discern. It is impossible to estimate true BCs solely based on contemporary data for contaminants in biota, even from remote areas.

2) MCWG considered the dataset and queried what constituted a "pristine" area as selected by data providers. It was noted that MON had not been in a position to quality check this information to determine if countries had a uniform understanding of this term. MCWG considered some basic criteria for identifying a remote area (i.e. likely to have relatively low anthropogenic inputs). Specifically, such areas should:

- Be remote from industry or large populations;
- Be subject to limited atmospheric transportation, i.e. currents and prevailing wind direction;
- Not be appreciably influenced by major riverine discharges.

Following a simple application of these criteria on a broad scale, MCWG felt that the most likely regions to have areas least impacted by anthropogenic inputs were the Atlantic arc (certain areas of Norway, Shetland Islands, Scottish west coast and, Irish west coast and certain areas of the French, and Iberian coasts.), Iceland, Greenland and the Faroe Islands. Even within these areas it is important to check individual sites to see if they fulfilled the criteria for remote areas.

3) Given the comments in point 1, some members expressed a view that the true BC for PAH probably lay between zero and the lowest observed concentration and therefore using the minimum observed value is probably the best estimate of BC. It was noted that in many instances this could equate to the Limit of Detection.

4) MCWG commented that while OSPAR require a single BC for each substance for the OSPAR area, that there is in fact no unique BC for the entire OSPAR area for metals as this depended on local geochemistry. MCWG further confirmed MONs conclusion that some BCs derived for metals in mussels were clearly not appropriate for assessing concentrations in oysters. This is specifically the case for cadmium, copper, silver and zinc as oysters accumulate higher levels of these elements.

5) There is still a limited dataset for remote areas for metals in mussel and particularly for metals in finfish. A number of members indicated they would have more data for remote areas to contribute for metals and PAHs. At SIME 2007 a number of OSPAR contracting parties indicated that they had further data to add to the database. It is important that the areas selected fulfil the general criteria for a remote area.

6) A number of alternative methods of estimating pre-industrial BCs were suggested and these may offer possibilities as a further check that any proposed BCs are in the correct range:

   a) Pre-industrial concentrations of individual contaminants in sediment determined from sediment cores could be used to calculate theoretical BCs for biota. This could be calculated using bioconcentration models;

   b) Use of data from deep ocean measurements as potentially pristine areas, for example deep ocean studies carried out by NIOZ;

   c) The magnitude of the increase in ambient concentrations of specific substances in a specific area from pre-industrial times to the present day could be estimated from sediment cores. The present day concentration for mussels in the same area could be divided by this enrichment factor to estimate the pre-industrial concentrations in mussels. This could be applicable for both metals and PAHs.

Following suggestion (c), Jacek Tronczynski prepared an illustration of how such an approach could be applied for PAH using French data for sediment cores and mussels, and this is presented in Annex 6. There was a consensus at MCWG that while there were assumptions in applying such an approach (e.g. similar bioavailability and similar partitioning between media), it nevertheless seemed the most promising methodology for estimating BCs in biota for both PAH and metals. The technique needs some refinement and individual enrichment factors would be required for each compound/element. Data from a number of areas would be useful and would help establish the natural geochemical variability for metals. A number of MCWG members undertook to investigate whether they could provide such data.

MCWG thanked Patrick Roose for his patient efforts in collecting and analysing the currently available data.

8.2 develop background concentrations for the following alkylated PAHs in sediments and biota:

a) **C1-, C2- and C3-naphthalenes;**

b) **C1-, C2- and C3-phenanthrenes;**

c) **C1-, C2- and C3-dibenzothiophenes, as well as the parent compound dibenzothiophene.**

MCWG noted ICES initial response to this OSPAR request which stated (SIME 07/5/4): "….that there may prove to be insufficient information to draw upon, for example data on alkylated PAH in biota (shellfish) in "pristine" areas would be very limited. If this is the case ICES may propose a sampling program to obtain the requested information or a combining such an approach with modelling e.g. a QSAR approach."

Notwithstanding the reservations MCWG have about using so-called "pristine areas" to establish BCs, as elaborated in Agenda Item 8.1, MCWG concur that data is limited for alkyl PAH in such areas, although French data is available. Furthermore, such data may not be comparable as JAMP guidelines are currently not available to ensure harmonised quantification in different laboratories (see 8.12b).

MCWG cannot see how a QSAR approach could enable calculation of BCs but recommends that the most promising approach is that recommended for PAH and metals in 8.1 for estimating pre-industrial concentrations.

8.3 examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring for nutrients and eutrophication parameters and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement

OSPAR have not made progress on this issue and no information was available for MCWG to examine

8.4 review the results of one-off surveys for the following chemicals identified by OSPAR for Priority Action: 2,4,6 tri-tert butylphenol (exploratory one-off survey to establish whether the substance is actually found in sediments in the OSPAR area), endosulphan, (exploratory one-off survey and a hot-spots survey to establish whether the substance is actually found, and to define "hot-spots" of the substance, in sediments of the OSPAR area), and short chained chlorinated paraffins (baseline survey to establish baseline in sediments in the OSPAR area against which to measure progress on the substance towards the goals of the OSPAR Hazardous Substances Strategy)

The progress report on these one-off surveys prepared by Sweden for SIME 2007 (SIME 07/6/3) was discussed. Little progress has been observed in implementation of the one-off surveys, although one laboratory (NILU) has been identified, offering to analyse all three substances. Germany and the Netherlands indicated that there are data available in their countries; therefore, they considered it not necessary to participate in a one-off survey. As two of the compounds are listed in the WFD priority pollutants list it can be expected that during 2007 more information will become available. Nevertheless, MCWG recognises that for time being neither a fully validated procedure for the analysis of SCCP nor suitable reference materials are available and therefore the use of a single laboratory for all analyses is recommended to ensure comparability.

8.5 report on any new annexes on Quality Assurance from the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea

MCWG (2005) had previously offered comments on ANNEX B16 of the HELCOM Combine manual, entitled "Technical note on the QA of the determination and documentation of co-factors". MCWG and STGQAC discussed this document again in plenary. STGQAC requested advice as to what was required to make this a more useful document and particularly noted that the current document included short texts on biota and water but did not include sediment.

MCWG offered the following comments:

- Sediment normalisation with key co-variables is an important tool for interpreting monitoring results. WGMS had previously considered this and provided extensive guidance on this issue.
- For biota and water the guidance given is very brief and is of limited use to potential users. Normalisation to co-variables is a complex issue and it would be very difficult to provide meaningful guidance in a short document. It was more important to provide references to available literature on this topic. A number of examples were given.

ICES. 2001. Normalization of Contaminant Concentrations in Sediment. Annex 2 form Report of the Advisory Committee of the Marine Environment . ICES Cooperative Research Report, No. 248. ICES. Copenhagen.

STGQAC undertook to take on board MCWG comments and may put forward any further amended document to MCWG for comment.

Hebert, C. E., and Keenleyside, K. A. 1995. To normalize or to not normalize? Fat is the question. Environ. Toxicol. Chem., 14 : 801–807.

Roose, P., Haarich, M., Nixon, E., and Abarnou, A. 1996. Lipids as a co-factor. Report of the Marine Chemistry Working Group. ICES CM 1996/ /Env.2 Ref: E.

8.6 review and discuss the *in situ* semi-continuous nutrients measurements and the progress and pitfalls of the use of these methods of data acquisition

Increasingly marine monitoring programmes are using moored deployments and ferry-box projects to obtain semi-continuous water quality data. Often this information is available through telemetry in near-real time. Various instrumentation is used and increasingly nutrient measurements are being incorporated in such programmes. In many marine environments the short-term temporal variability is high. Therefore spot sampling generally leads to undersampling and an inability to get a good picture of environmental state and change. Semi-continuous measurements therefore can complement spot sampling to provide a better temporal picture of rapidly changing conditions.

Two types of *in situ* nutrient analysers are currently available:

- Systems based on wet chemical techniques;
- Optical nutrient analysers (UV) primarily for nitrate.

Evin McGovern presented information on a pilot monitoring station in Dublin Bay Ireland where an *in situ* optical nitrate analyser was being trialled alongside other physico-chemical sensors (CT, DO, Fluorescence) for near real time semi-continuous monitoring alongside automated water samplers. This is being undertaken as part of the ERDF Interreg IIIa funded MATSIS project. The automated sampler collects samples for laboratory nutrient analysis and phytoplankton speciation. Samples are collected at periodic intervals or by conditional triggering on the basis of preset criteria (e.g. high fluorescence values). Initial validation of nitrate measurements by the optical analyser showed reasonable agreement with spot samples measured in the laboratory and any disagreement were generally small compared to the temporal variability observed at that site, illustrating that while the data may be less accurate than lab analysis, the overall information from high frequency measurements provides a better picture of water quality fluctuations at this site.

In discussion it was noted that there are advantages and disadvantages of the two types of analysers. Wet-chemical systems can be used to analyse a broader suite of dissolved nutrients. Furthermore, the chemistry is well known and understood. They can, however, be difficult to maintain and to operate. Optical nitrate analysers are more expensive and interference from coloured dissolved organic matter (CDOM) can be a problem, so they may not be appropriate for use at all sites. However, they require considerably less maintenance and have a broad quantification range. Whatever instrumentation is used, validation of the analytical results is essential and for optical instruments this may be site/area specific.

Patrick Roose informed the group of a Belgian ferrybox project, whereby MUMM planned to install a wet-chemical system on board their research vessel. He offered to update the group on this in the future. Attention was drawn to other programmes where wet-chemical nutrient analysers were deployed in coastal observatories:

- **UK:** Marine Environment Real-time Observation System (MEROS) operated by CEFAS www.cefas.co.uk/monitoring
- **Germany**: BSH SAMSON programme in the North Sea and Baltic Sea http://www.bsh.de/en/Marine%20data/Observations/Projects/SAMSON/samson_daten_e.jsp
- **France**: more information on Ifremer *in situ* data collection in English Channel and over an Atlantic coast may be obtained at web site http://www.ifremer.fr/dtmsi/programmes/marel/marel.htm

Johnson, K.S., Needoba, J., Riser, S.C., and Showers, W.J. 2007. Chemical Sensor Networks for the Aquatic Environment Chem. Rev., 107: 623–640.

8.7 review available information regarding the role of nutrients and organically-bound nutrient species as potential drivers for processes which can influence the uptake and distribution of contaminants in the environment and ecosystems

Klaus Nagel had undertaken to present information on this topic but was unable to attend MCWG 2007. This agenda item will be considered at MCWG 2008. Jacek Tronzcynski drew MCWGs attention to some relevant publications referenced below.

Aminot, A., and Kérouel, R. 2004. Dissolved organic carbon, nitrogen and phosphorus in the N-E Atlantic and the N-W Mediterranean with particular reference to non-refractory fractions and degradation. Deep Sea Res., 51: 1975–1999.

Savoye1, N., Aminot, A., Tréguer, P., Fontugne, M., Nauletn, N., and Kérouel, R. 2003 Dynamics of particulate organic matter δ15N and δ13C during spring phytoplankton blooms in a macrotidal ecosystem (Bay of Seine, France). Mar Ecol Prog Ser., 255: 27–41.

8.8 report on peer-reviewed paper reporting the finding of MCWG international collaborative project on new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-hlorophenyl)methane(TCPMe) in flatfish

In 2000, Michel Lebeuf and Jacob de Boer, initiated an MCWG project to analyse *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in flatfish, with an intercomparsion exercise as a first step. The dataset on TCPM/TCPMe in flatfish built-up in the following years contains data from Belgium (Marc Raemaekers), Spain (Teresa Nunes), Germany (Michael Haarich), The Netherlands (Stefan van Leeuwen and Jacob de Boer), U.K. (Robin Law) and Canada (Michel Lebeuf).

During the past year Michael Haarich (Germany) as well as Stefan van Leeuwen and Jacob de Boer (The Netherlands) provided additional TCPM and TCPMe data to Michel Lebeuf. In collaboration with the other members that have contributed to the project, Michel Lebeuf intends to complete the writing of a peer-reviewed paper reporting the finding of this MCWG international collaborative project and to present the outcome to the MCWG members at the next MCWG meeting.

Michel Lebeuf also reported that he is completing a time trend study of TCPM/TCPMe in blubber of beluga whales from the St. Lawrence Estuary (SLE), Canada and offered to present the data to the MCWG members at the next year meeting. Michael Haarich reported that his lab was still doing TPCM/Me analysis as part of their monitoring programme and that he might be able to report on temporal trends of these chemicals in fish collected from the North Sea/German Bight and the Baltic Sea.

Michel Lebeuf will present the outcome of the MCWG international collaborative study of TCPM/TCPMe flatfish and the results of a time trend study of TCPM/TCPMe in blubber of beluga whales from the SLE, Canada to the MCWG members at the next MCWG meeting in 2008. Michael Haarich might report temporal trends of TCPM/Me in fish collected from the North Sea/German Bight and also from the Baltic Sea, if sufficient data will be available, at the next MCWG meeting in 2008.

8.9 review (in collaboration with WGMS) the draft guidelines for the preparation, use and analysis of passive samplers

The protocols for the PSTS trial survey (Annex 7) can be considered as a starting point for the draft guidelines. The information and experiences from this trial survey will be used by the MCWG/WGMS PSTS coordination to compile a more complete guideline for the application of the passive samplers during the next half year. The following publications can also be consulted for information on use of passive samplers.

PSTS homepage (facilitated by Foppe Smedes, WGMS)
http://home.tiscali.nl/fsmedes/icespsts/.

Monitors of organic chemicals in the environment : semipermeable membrane devices. James N. Huckins, Jimmie D. Petty, Kees Booij. New York: Springer, 2006.

Smedes, F. 2007. Monitoring of Chlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons by Passive Sampling in Concert with Deployed Mussels. In Passive Sampling Techniques in Environmental Monitoring, 48**.** Edited By Richard Greenwood, Graham Mills, Bran Vrana. Amsterdam ;Elsevier, 2007 (in press).

8.10 critically review and report the results and findings from joint MCWG / WGMS trial-survey of passive samplers, and review any new information on the use of membrane systems for sampling, and on their incorporation within national monitoring programmes; (in plenary with WGMS)

After an introduction by Kees Booij, *Concepts in passive sampling* and a presentation by Foppe Smedes, *Status and preliminary results of the joint trial survey,* it was concluded that the survey, though not yet completed, was successful. A detailed report on the status and initial conclusions can be found in Annex 8 (also annexed to WGMS 2007 report)

When data analysis is completed later this year and presented at the annual science conference results for analysis of PS and mussels and worms will also be available. The use of a new model to calculate the sampling rate from all relevant Performance Reference Compounds (PRCs) is a definitive improvement. This makes the determination of the sampling rate more robust and a correct sampling rate is crucial for calculating water concentrations. Sampling rates varied from 4 to 10 liter/day for the 600 cm^2 silicone rubber samplers at the different locations that were used in this survey. The correct partitioning coefficients (seawater versus silicone rubber sampling material; Ksw) for each compound are also critical for calculation of the water concentrations. At RIKZ the Ksw for a number of PAHs, HCB and PCBs were determined but a collaborative effort is necessary to determine them for more individual compounds of interest. The majority of the locations were in harbours, inland waters or near coastal waters. Some locations in Norway were in or near effluent streams from aluminum smelters and show extremely high PAH concentrations in the water. At other remote locations relatively high concentrations of the some PAHs were observed, and while it is unclear which factors play a role in this, shipping, atmospheric deposition, seasonal influence and lack of absorption capacity were mentioned. For PCBs clear concentration gradient could be observed (e.g. in Western Scheldt). High HCB concentrations are observed in the Elbe, this location is a

known hotspot for this compound. The preliminary results seem to be very promising but validation by other measurements is needed. A few samplers are still to be analyzed by RIKZ and most of the data and measurements from the participating laboratories are still to come and these are essential to strengthen the intercalibration part of the trial survey. This intercalibration will then further be investigated by the development exercise that QUASIMEME plans to offer in the second half of this year. Time integrated sampling with passive samplers has advantages over spot sampling. It is recommended that the outcome of this trial survey is published as a separate report to ICES. The introduction from Kees Booij was very helpful for the MCWG members to grasp the concepts necessary for correct application and interpretation of results obtained by the use of passive samplers. Kees agreed to join the MCWG/ WGMS PSTS coordination group. Passive sampling offers potential as a WFD monitoring tool and Peter Lepom undertook to highlight this study at relevant WFD fora. To build on the momentum of this project, it is recommended to look for funding in the EU FP7 program to further develop this promising sampling approach. However the leading role of the RIKZ laboratory in this matter is insecure as their future existence and role is uncertain. The members of the MCWG thank Foppe Smedes and the staff of the RIKZ laboratory for their hard work in making this trial survey a success.

8.11 report on new information regarding perfluorinated compounds in environmental samples

The plenary presentation of Katrin Vorkamp on polyfluorinated compounds (7.2) is combined with other presentations under Agenda Item 8.11.

Presentation by Ralf Ebinghaus: Current GKSS research on Polyfluorinated compounds (PFCs) in the coastal and marine environment

The two most studied polyfluorinated compounds (PFCs) are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). There is experimental evidence that they are distributed ubiquitously despite their non-volatility and only moderate water-solubility. It is hypothesized that neutral, volatile precursor compounds of PFOS and PFOA, for instance fluorotelomer alcohols (FTOHs), could undergo long-range atmospheric transport and be degraded to those persistent, ionic PFCs in remote regions.

Jahnke *et al*. (2007a) have used a set of mass-labelled internal standards and published an optimised and validated trace-analytical protocol for a suite of neutral, volatile PFCs based on the original work by Martin *et al*. (2002). IS-corrected relative recoveries were around 100 % for most compounds however, if no proper mass labelled IS were applied recovery rates were between 50 and 300% for 4:2 FTOH and certain FOSEs respectively.

Table 8.11.1. Comparison of air concentrations of neutral, volatile PFCs with those of "classical POPs" determined at Waldhof, North Germany.

	CONCENTRATION [PG/M^3]	REFERENCE
6:2 FTOH	17–125 (mean 64)	Jahnke *et al*., 2007b
8:2 FTOH	33–112 (mean 75)	
∑FTOHs	64–311 (mean 181)	
∑FOSAs + FOSEs	14–52 (mean 34)	
γ-HCH	40–52	Jaward *et al.*, 2004
HCB	32–42	
pp-DDT	5.5–7.2	
PCB-149	6.7–8.8	
∑29 PCBs	73–96	
∑8 PBDEs	9.7–13	

Concentrations of ∑FTOHs in North German background air were significantly higher than ∑FOSAs + FOSEs. 8:2 FTOH was the dominating compound followed by 6:2 FTOH. Northern hemispheric marine background concentrations in comparison are reported to be ∑FTOHs: around 50 pg/m^3; ∑FOSAs + FOSEs: around 10 pg/m^3 (Jahnke *et al.*, 2007c).

First concentration data for the Southern hemispheric marine background air were recently published by Jahnke *et al.*, 2007c and show fairly low levels (i.e. ∑FTOHs: around 10 pg/m^3; ∑FOSAs + FOSEs: around 1 pg/m^3). FOSEs were in general not detected in the Southern hemisphere, which is in agreement with an estimated relatively short lifetime of 2 days. In all marine background air samples 8:2 FTOH was the dominating compound.

References:

Jahnke, A., Ahrens, L., Ebinghaus, R., Berger, U., Barber, J. L., and Temme, C. 2007a). An improved method for the analysis of volatile polyfluorinated alkyl substances in environmental samples, Analytical and Bioanalytical Chemistry, 387: 965–975.

Jahnke, A., Ahrens, L., Ebinghaus., and Temme, C. 2007b. Urban versus remote air concentrations of fluorotelomer alcohols and other polyfluorinated alkyl substances in Germany Environ. Sci. Technol., 41: 745–752.

Jahnke, A., Berger, U., Ebinghaus, R., and Temme, C. 2007c. Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53^o N-33^o S), in press for Environ. Sci. Technol.

Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. Environ. Sci. Technol., 2004, 38: 34–41.

Martin, J. W., Muir, D. C. G., Moody, C. A., Ellis, D. A., Kwan, W. C., Solomon, K.R., Mabury, S.A. Anal. Chem., 2002, 74: 584–590.

Presentation by Katrin Vorkamp: Polyfluorinated compounds in marine biota from Greenland

Results from a screening project of PFCs in the marine environment of Greenland and the Faroe Islands indicated biomagnification of PFOS along the marine food chain, with increasing concentrations from shorthorn sculpin *(Myoxocephalus scorpius)* to ringed seal *(Phoca hispida)* to polar bear *(Ursus maritimus)* from the same area (Vorkamp *et al.*, 2004; Bossi *et al.*, 2005a). Polar bear liver contained PFC concentrations of approximately 1300 ng/g wet weight. PFOS was the main PFC detected in the biota samples, except for minke whale *(Balanoptera acutorstrata)* and long-finned pilot whale *(Globicephala melas)* which had higher levels of PFOSA than of PFOS. Interestingly, ringed seal and shorthorn sculpin from East Greenland had higher concentrations than the same species from West Greenland, e.g. 61 ng/g ww and 9.7 ng/g ww in ringed seal from East and West Greenland, respectively.

A time trend study was performed in ringed seals from Central East Greenland and Central West Greenland, based on archived liver samples from 1982 to 2003 (Bossi *et al.*, 2005b). Increasing concentrations were found for all PFCs, from approximately 30 ng/g ww (median concentration) to 100 ng/g wet weight for ringed seals from East Greenland. The levels were significantly lower in seals from West Greenland (increases from about 10 ng/g ww to 30 ng/g ww), which confirmed preliminary results of the screening project. Higher concentrations in East Greenland than in West Greenland have also been observed for organochlorines and polybrominated diphenyl ethers and have been related to their transport pathways to Greenland. The target compounds analysed in this project had been extended to include perfluorocarboxylic acids (PFCAs), and perfluoroundecanoic acid (PFUnA) was found to be the PFC with the second highest concentration in the seals.

Based on results in ringed seal and polar bear from East Greenland (Smithwick *et al.*, 2005), a biomagnification factor (BMF) of 30 was calculated. BMFs of organochlorines available from the literature are generally lower, e.g. 7.4 for PCBs (Riget *et al.*, 2004; Dietz *et al.*, 2004). These first results indicate a strong biomagnification of PFOS. The precursor theory was presented, but more details had been given in the previous presentation by Ralf Ebinghaus.

Ongoing PFC-projects at NERI:

1) Continuation of the existing time trend for ringed seals in East Greenland and West Greenland.
2) A time trend study has been conducted on polar bear (N=170) from East Greenland.
3) Seals from Denmark, available from the specimen bank, are being analysed for PFOS.

PFOS has been included in the Danish national monitoring programme as a screening substance in mussels.

References

Bossi, R., Riget, F., Dietz, R., Sonne, C., Fauser, P., Dam, M., and Vorkamp, K. 2005a. Preliminary screening of perfluorinated surfactants in fish, birds and marine mammals from Greenland and the Faeroe Islands. Environ. Poll., 136: 323–329.

Bossi, R., Riget, F. F., and Dietz, R. 2005b. Temporal and spatial trends of perfluorinated compounds in ringed seal (*Phoca hispida*) from Greenland. Environ. Sci. Technol., 39: 7416–7422.

Dietz, R., Riget, F. F., Letcher, R., Born, E. W., and Muir, D. C. G. 2004. Seasonal and temporal trends in polychlorinated biphenyls and organochlorine pesticides in East Greenland polar bears *(Ursus maritimus)* 1990–2001. Sci. Total Environ. 331: 107–124.

Riget, F., Dietz, R., Vorkamp, K., Johansen, P., and Muir, D. 2004. Levels and spatial and temporal trends of contaminants in Greenland biota: an updated review. Sci. Total Environ, 331: 29–52.

Smithwick, M., Muir, D. C. G., Mabury, S. A., Solomon, K. R., Martin, J. W., Sonne, C., Born, E. W., Letcher, R. J., and Dietz, R. 2005. Perfluoroalkyl contaminants in liver tissues from East Greenland polar bears *(Ursus maritimus)*. Environ. Toxicol. Chem., 24: 981–986.

Vorkamp, K., Dam, M., Riget, F., Fauser, P., Bossi, R., and Hansen, A. B. 2004. Screening of "new" contaminants in the marine environment of Greenland and the Faroe Islands. NERI Technical Report No 525. http:\\technical-reports.dmu.dk.

Presentation by Norbert Theobald: Occurrence of Perfluorinated Organic Acids in the Marine Environment

Sensitive and specific analytical procedures have been developed for the investigation of PFCs in sea water, marine sediments and biota. Water samples were extracted by SPE on a reversed phase resin; sediment and biota samples were extracted with methanol. Analysis was done by HPLC-MS-MS (ESI, neg.). All target-components have been detected in all compartments of the North- and Baltic Seas. The main components are PFOA and PFOS, which are found at concentrations in the range of other pollutants such as PAH and Herbicides. The rivers Elbe, Rhine and Scheldt were identified as local/regional input sources for PFCs in sea water for the German Bight and southern North Sea. Remarkably, perfluorobutyl sulfonate (PFBuS) was observed at quite high concentrations (up to 4 ng/L) at coastal stations of the Netherlands. Surveys have been expanded into remote areas of the east Atlantic Ocean. PFOA and PFOS were detected in the North Atlantic (Greenland Sea) at concentrations between 10 pg/L and 80

pg/L. The lowest concentrations close to or below the LODs were observed in the South Atlantic Ocean (west of South Africa).

PFOS accumulates in sediments and biota more than PFOA, thus showing generally the highest concentrations of all PFCs in these matrices. Based on the observed field concentrations, enrichment factors from the water phase to sediment and fish liver were calculated and compared to classical pollutants. The enrichment factors for PFOS are in the range of HCH-isomers but lower than PCBs, DDT-metabolites or PAHs.

The results underline the importance of PFCs as an emerging group of pollutants.

Discussion

After the presentations, the following items were discussed in plenary:

1) Toxicity of perfluorinated compounds. Is PFOS the most toxic one of the perfluorinated compounds?

A comprehensive overview on the human and ecotoxicology of PFCs is not yet available: In most of the studies so far, only PFOS and / or PFOA were investigated and many of already existing reports have not been published in the peer reviewed literature. A significant number of studies are available through the US EPA public docket AR-226 (http://www.epa.gov).

Other relevant references:

Berthiaume, J., and Wallace, K.B. 2002. Perfluorooctanoate, perfluorooctane-sulfonate, and N-ethyl perfluorooctanesulfonamido ethanol; peroxisome proliferation and mitochondrial biogenesis. Toxicol. Letters, 129: 23–32.

Hu, W., Jones, P. D., Upham, B. L., Trosko, J. E., Lau, C., and Giesy, J. P. 2002. Inhibition of gap junctional intercellular communication by perfluorinated compounds in rat liver and dolphin kidney epithelial cell lines in vitro and Sprague-Dawleys rats in vivo. Toxicol. Sci. 68, 429–436.

2) Low concentrations have been detected in e.g. mussels, while the concentrations in the marine mammals from Greenland were high. Is there a geographical difference or is this difference related to the trophic levels of the animals? New data on PFCs in the same species from Europe and Greenland will contribute to answer this question. The high concentrations in polar bears from Greenland may be related to bio-magnification of PFCs, although the environmental fate of PFCs is not well-understood.

3) The bio-concentration factors in Norbert Theobald's presentation were higher than reported previously. Reasons for this difference may include differences in experimental set-ups, among others different concentrations in the water phase, as well as differences in kinetics.

4) Will we expect ongoing increases in the environmental concentrations of PFCs? It was discussed that the future development was likely to be linked to the precursor theory and the current status in industrial use of potential precursors.

5) The presentations and the discussion have shown that considerable new knowledge has become available. Still, substantial knowledge gaps exist that research and monitoring programmes will have to fill. MCWG will follow up on new developments at the next meeting in 2008.

8.12 together with WGMS, to carry out the following development work with regard to the JAMP Guidelines for monitoring Contaminants in Sediments (OSPAR agreement 2002-16) and JAMP Guidelines for monitoring Contaminants in Biota (OSPAR agreement 1992-2) to ensure that monitoring guidance is in place to support a revised Co-ordinated Environmental Monitoring Programme

8.12.1 develop draft technical annexes on monitoring of polybrominated diphenyl ethers and hexabromocyclododecane in sediments and biota following the structure of the existing technical annexes. SIME 2007 will be invited to clarify the congeners and compartments that are relevant for the development of monitoring guidance for brominated flame retardants

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD): MCWG thanks Lynda Webster for the preparation of draft technical annexes on the determination of PBDEs in sediment, HBCD in sediment, PBDEs in biota, and HBCD in biota. After a short discussion on the technical content of the four documents MCWG decided to establish a sub-group to revise the documents considering the various comments made in the plenary discussion and those received by the Working Group on Marine Sediments. The draft technical annexes were revised during the meeting and the technical annexes on biota are attached as Annexes 9 and 10. Comments on the technical annexes on sediments were forwarded to WGMS.

8.12.2 together with WGBEC and MCWG, review the existing technical annexes on polyaromatic hydrocarbons (PAHs) to see whether they are adequate for monitoring of target alkylated PAHs and, as appropriate, prepare advice on any revisions that are necessary.

The current technical annex for PAH analyses require updating as clear guidance is required to ensure comparable quantification of alkyl homologues of PAHs (C-PAHs) and alkyl substituted sulphur-heterocycle PAHs (C-SPAHs) in biota. This technical guideline contains relevant information for the selection of species, sampling techniques, sample transport and conservation, sample treatment (including extractions, clean-up, and pre-concentration) for the analyses of C-PAHs and C-SPAH in biota. These steps of the analytical protocols follow the same technical principles as for the analysis of unsubstituted parent PAHs. However, a number of specific instrumental guidelines should be considered for the analyses of alkyl homologues in biota. This includes the choice of instrumental determination of C-PAHs and C-SPAH (mostly GC-MS techniques, including use of GC-MS/MS systems, if better identification of individual isomers is needed). The alkyl homologues of PAHs are numerous individual compounds and many are not completely resolved by conventional gas chromatographic separations. The alkyl homologues may be quantified in different ways. The choice of internal and external standards and the method of integration, illustrated by the examples of alkyl homologues fingerprints obtained by the analyses of a selected reference material, must be agreed. During the meeting a subgroup identified the approach and made arrangements for completing this work intersessionally.

8.12.3 to develop a draft technical annex on monitoring of TBT and its breakdown products in biota;

MCWG discussed the specific technical issues involved in analysing TBT in biota. The OSPAR Technical Annex for Monitoring TBT in Sediment provides a starting point for developing a Technical Annex for TBT in biota, although substantial amendment is needed.

MCWG members have limited experience in this analysis and therefore there was insufficient expertise present to develop a new technical annex during the meeting. Patrick Roose undertook to approach a colleague (Els Monteyne) at MUMM to enquire whether she would be prepared to take a lead in this work intersessionally. Ton van der Zande and Katrin Vorkamp indicated they or colleagues from their Institutes could participate

8.13 report on the developments in Water Framework Directive monitoring programmes for physico-chemical parameters (priority substances, other pollutants, nutrient status) in transitional and coastal waters. This will focus on providing information on the specific parameters being measured, the approach to monitoring hazardous substances (e.g. matrices, frequency, etc.), classification tools, and the extent of surveillance and operational programmes;

Peter Lepom, Chair of drafting group on chemical monitoring of surface waters under the WFD Chemical Monitoring Activity (CMA), reported back to the group on developments with respect to priority substance monitoring under the water framework directive. This information is summarised below. A large part of compliance requirements for good chemical status of surface water bodies is based on chemical monitoring data. This means in turn that the legal basis of the overall directive will be primarily linked to reporting of data, which should be of demonstrated and comparable quality throughout the European Union. For this reason, Member States have expressed the need for more guidance on implementation details as regards the monitoring for chemical substances and quality assurance issues. In-line with previous documents under the WFD Common Implementation Strategy a draft guidance document on chemical monitoring of surface water and a proposal for a commission decision on QA/QC issues have been developed the contents of which were summarised by Peter Lepom.

While not being legally-binding the guidance document presents the common view of EU Member States on how to monitor chemical substances in the aquatic environment. It presents Member States best practices, complements existing guidance elaborated within the CIS and provides links to other relevant guidance documents (e.g. OSPAR, HELOM) and European and International standards or procedures, which have already been in place. This guidance includes the monitoring of priority substances, other specific pollutants and all other chemical parameters relevant in the assessment of the ecological or chemical status of a water body or in the assessment of programmes of measures. It focuses on chemical monitoring of surface water (inland, transitional, coastal, and territorial waters) including monitoring design, sampling, and chemical analyses of water, sediment, and biota samples. Furthermore, it covers complementary methods (e.g. passive sampling techniques, probes for measuring physico-chemical parameters, biological early warning systems) applicable to WFD monitoring and certain aspects of quality assurance. The annexes of the document provide information on standardised methods, reference materials and comprise substance guidance sheets for all the compounds/substance groups covered by the daughter directive on environmental quality standards as well as case studies from Member States. This document represents the current state of technical development in a field that is undergoing continuous changes through ongoing scientific research. This denotes that the guidance is open to continuous improvements and is planned to be updated by 2009 and 6 years thereafter.

Comparable monitoring information is necessary in order to provide a sound basis for Member States to develop river basin management plans, in particular programmes of measures aimed at achieving the objectives established under the WFD. Consequently, the quality and comparability of analytical results generated by laboratories appointed by competent authorities of the Member States to perform water chemical monitoring should be

ensured. For this reason, mandatory provisions have been proposed in a Commission Decision concerning minimum performance criteria for analytical methods used for chemical monitoring and the quality of analytical results. This draft document includes specifications on sampling and sample pre-treatment procedures as well as analytical methods, legally binding minimum performance criteria for analytical methods, legally binding requirements for laboratories involved in chemical monitoring, requirements for quality assurance and quality control, as well as treatment of data below the limit of quantification. The current proposal is now under discussion with Member States and planned to be adopted by the end of this year.

The mandate on Chemical Monitoring Activity is going to be renewed from 2007 to 2009. The activity for the period 2007-2009 will consist in 3 activities led by Member States or Stakeholder Organisations, which will develop their own work programme. It is envisaged that the activities will be undertaken with selected experts (15-20) willing to actively contribute to the drafting of documents and to participate in ad-hoc meetings. The progress of the activities will be reported and discussed at plenary meetings to be held twice a year and organised under the EU Presidency umbrella. The new CMA work programme covers the following three activities:

CMA-1 – Exchange of best practices and recommendations on monitoring programme design, sampling, selection parameters, analytical methods update, calculation methods of background concentrations, sediment and biota monitoring, case studies and organisation of field trials to test methods and exchanges experiences etc.

CMA-2 – Development of a common strategy for quality assurance and control of chemical monitoring data and of a data flow quality concept in support of the chemical monitoring of surface and ground waters

CMA-3 – Evaluation of standardisation needs and appropriate actions related to them Information on national monitoring programmes for hazardous substances in transitional and coastal waters

Members of MCWG were asked to report on national Water Framework Directive monitoring programmes for physico-chemical parameters (priority substances, other pollutants, nutrient status) in transitional and coastal waters using the provided template. Emphasis was placed on the specific parameters being measured, the approach to monitoring hazardous substances (e.g. matrices, frequency, etc.), classification tools, and the extent of surveillance and operational programmes. Information made available by the Netherlands, Ireland, Portugal, Spain, Finland, France, Germany, Belgium and Denmark (see Annex 11). In brief, the information provided is still fairly fragmentary as MCWG were not in the position to collect the necessary information from their competent authorities responsible for WFD related monitoring activities in coastal and transitional waters of their countries during the meeting. Some countries strictly interpret the Annex V of the WFD and the guidance documents developed within the Common Implementation Strategy as regards matrix selection and frequency. This denotes monitoring of priority substances in water with a sampling frequency of 12 times a year. Other countries keep their existing monitoring programmes, which often focus on sediment and biota. As regards physico-chemical parameters the definition of numerical classification tools, e.g. standards, which might be related to salinity is under development

This information will be updated at MCWG 2008 if further information is available.

Discussion on WFD monitoring and the draft commission decision implementing Directive 2000/60/EC concerning minimum performance criteria for analytical methods used for chemical monitoring and the quality of analytical results

MCWG recognises that for the analysis of total water as required by the WFD for priority substances with the exception of trace metals, there are neither standard methods, certified reference materials nor appropriate proficiency testing schemes available. Thus test methods for hydrophobic substances in whole waters cannot be validated properly and this is a particular problem for hydrophobic substances. Alternatively, the analysis can be conducted on both fractions (dissolved and particulate) separately. MCWG would be concerned that methods developed for the analysis of filtered water samples will be extrapolated to total water, for which they have not been validated and may not be appropriate.

MCWG does not see that providing reference materials or intercomparisons for hydrophobic substances in turbid waters is a practical proposition. Therefore, monitoring of hydrophobic substances in coastal water with high SPM content is difficult to standardise. In open sea water – with low SPM content – this is less of a problem. It should also be noted that sediment analysis methods are not appropriate for suspended matter.

Peter Lepom indicated that there might be a call within FP7 to address these issues. In ISO /TC147 Water Quality, there are some activities on developing methods for the analysis of PAHs and organochlorines in water samples with high SPM content by using, for example, extraction discs.

In reviewing the draft Commission Decision on Quality Assurance MCWG noted that ISO standards are recommended where available but that OSPAR guidelines can be applied where relevant, although they are currently restricted to a limited number of compounds.

Article 5 1a: MCWG suggests the wording is unclear and recommends the following proposed wording: “the relative uncertainty should be no more than 50% near the EQS level (and normally lower for higher levels)”

Article 6: LoQ taken as ½ LoQ should only be applied for calculation of annual average concentrations for compliance monitoring, and not for load estimations, for example.

Article 8: The way uncertainty is calculated is not specified. The use of results from intercomparison exercises will probably result in the highest values for measurement uncertainty. However, “bottom-up” and “top-down” approaches have been shown to provide comparable results in many cases. The coverage factor to use is k=2.

The decision requires that the uncertainty associated with sampling is determined. Presumably this refers to the uncertainty associated with the procedure of collecting and handling a sample and not an estimate of the field variance. More precise wording is recommended.

Article 9: The experience of MCWG is that different national accreditation bodies have different interpretations of what is meant by *accreditation of sampling*, i.e. sample collection and sample handling procedures or representativity of sampling.

8.14 provide expert knowledge and guidance to the ICES Data Centre as requested

At MCWG2006, Gert Asmund, Robin Law and Klaus Nagel were nominated to respond to intersessional requests from the ICES data centre. As Robin Law will not continue to participate in MCWG, Jacek Tronczynski volunteered to report on queries relating to organic determinants. It was agreed amongst the MCWG meeting participants that Gert Asmund and Klaus Nagel would carry on in their role.

Evin McGovern reported on a query received from the Data Manager of ICES regarding the term Total Petroleum Hydrocarbons and whether there was a need for a code for it. An initial response was provided before MCWG2007, highlighting that TPH is a method defined parameter which would almost certainly be measured by various methods using different detection means. The data obtained from the different methods is not comparable and therefore different codes for each method should be kept. No further comments were made.

8.15 report on relevant new annexes on Quality Assurance from the ICES/OSPAR/HELCOM Steering Group on Quality Assurance of Biological Measurements (STGQAB)

MCWG were requested by ICES to review annexes on quality assurance contained in the ICES/OSPAR/HELCOM Steering Group on Quality Assurance of Biological Measurements (STGQAB) in their 2007 report. Annexes 12-16 of the report were reviewed by MCWG. Annexes 12 and 13 provides proposals for new/rearranged structures for Quality Assurance Annexes (Part B) in the HELCOM combine manual and MCWG suggests that this is an editorial issue for HELCOM. Annexes 14-16 deal with requirements for quality systems, validation guidelines and standard operating procedures. MCWG suggests following standards and guidelines such as ISO 9000, EN/ISO/IEC 17025 (2005) and Euracham guidance on validation as already referenced in the text. The text from these guidelines might be repeated here or simply referenced. It was not clear to MCWG whether Annex 16 was presented just as an example of an SOP format. MCWG would not recommend that HELCOM be over-prescriptive and that any SOP format that meets the requirements of ISO 17025 is acceptable.

8.16 Consider the relationship between co-planar PCB and marker PCB concentrations and further consider the requirement for monitoring coplanar PCBs and provide advice on what congeners should be tested

Following MCWG 2006, it was proposed that an investigation should be undertaken into the possibility of calculating ratios of mono-*ortho* and non-*ortho* CBs ('dioxin-like' CBs) to the concentrations of the routinely monitored ICES7 CBs (marker CBs), with the aim of using these ratios to calculate the concentration of the 'dioxin-like' CBs and estimate the overall risk for the environment. This was initially suggested at the SIME meeting in February 2006.

Data was provided from a few contracting parties (Canada, Denmark, France, Ireland, Norway, Sweden). Patrick Roose gave a presentation on the data received. The major planar CBs were CB77 followed by CB126 in fish. However marine mammals showed a different pattern with CB126 being the predominant planar congener. In general, PCDD and PCDF had a much lower contribution to the toxic equivalence (TEQ) and CBs the greatest contribution. Although some biota samples gave TEQs above the WHO TEQ for humans, most were below.

Marker CBs and planar CBs were plotted to establish if there was simple ratio between the marker and 'dioxin-like' CB concentrations. This indicated that if concentrations of marker CBs were high the concentrations of planar CBs were also high, indicating a correlation between the marker and 'dioxin-like' CB concentrations. However, there was a large spread of data and there was no unique ratio between these two groups of CBs. In contrast, Evin McGovern reported that initial assessment of Irish data for 6 indicator PCBs and coplanar PCBs expressed as WHO-TEQ in fish showed a good co-relation.

A request was received from the chair of OSPAR's Assessment and Monitoring Committee (ASMO) on whether 'dioxin-like' CBs should be monitored for the Co-ordinated Environmental Monitoring programme (CEMP) and if so what congeners should be included. Concentrations of non-ortho CBs in the marine environment are generally lower than for the *ortho* CBs, however, the TEFs (toxic equivalent factors) are relatively high, and so they may

contribute substantially to the TEQ values. Techniques are available for their analysis, although this can be expensive. Determining the concentrations of the non-*ortho* CB congeners (CB77, 81, 126 and 169), which exhibit the highest dioxin-like toxicity, is less straightforward and requires specialised fractionation procedures. Moreover, as concentrations of these congeners in environmental samples tend to be very low, detection limits need to be low. This may require the use of GC-HRMS instruments or GC with low resolution MS/MS. It is also possible to analyse for CBs along with the ICES7 CBs. The planar CBs can show a different behaviour in the environment than would be expected from their K_{ow} values. It was decided that if the 'dioxin-like' CBs are to be monitored in the marine environment then all 12 congeners (non-*ortho* and mono-*ortho*) should be included in the analysis. As concentrations are considerably lower than for the marker CBs the dioxin-like CB congeners should only be monitored in areas identified as having high CB concentrations (hotspots). Monitoring should be limited to biota. It is likely that for trend monitoring where a single species is sampled periodically at a given location, the ratio of indicator PCBs to non-*ortho* and mono-*ortho* PCBs is likely to be relatively constant and therefore analysis of indicator PCBs should be sufficient.

9 Plenary discussion of draft report

This took place on Thursday 22 March and Friday 23 March.

10 Any other business

10.1 Election of Chair(s)

One of the Co-Chairs, Jacek Tronczynski is stepping down after completion of a three-year terms of office. He thanked the members of MCWG for all their help and support during this period. MCWG showed their appreciation for Jacek's contribution as Co-Chair over the period. No Co-Chair was appointed to replace Jacek and Evin McGovern will act as sole Chair for MCWG 2008.

10.2 Working Arrangements with STGQAC

MCWG 2006 had responded positively to a suggestion from STGQAC 2006 that STGQAC operates within MCWG. HELCOM subsequently indicated their preference for STGQAC to remain as a separate group. In a joint session MCWG and STGQAC agreed that while the groups would continue to collaborate on topics on mutual interest, it may not always be practical for the groups to meet concurrently at the same location to facilitate interactions. The groups made arrangements to collaborate informally through the chairs.

11 Recommendations and action list

These are given as Annexes 4 and 5.

11.1 Date and venue of next meeting

ICES has suggested that MCWG meet during the week of 10 March 2008. The timetable for OSPAR meetings is not known as yet, but MCWG and the OSPAR SIME meeting should not take place at the same time as there is considerable overlap in membership. MCWG has received an invitation from FIMR to hold its 2008 meeting in Helsinki with provisional dates of 10–14 March.

12 Closure of the meeting

Evin McGovern thanked Michael Haarich and BSH for hosting MCWG 2007 and for providing such excellent facilities and a convivial atmosphere. The meeting was closed at 12:45.

Annex 1: List of participants

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Annex 2: Agenda

ICES Marine Chemistry Working Group: 29th meeting, BFAFi, Hamburg, Germany, 19–23 March 2007

1. OPENING OF THE MEETING

The meeting will begin at 10.00 am on the first day, and 09.00 am thereafter.

2. ADOPTION OF THE AGENDA

3. REPORT OF THE 94th 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

An update on the QUASIMEME scheme will be given.

4.4 Other Activities

All members who wish to make a presentation under this item should prepare a note for MCWG.

4.4.1 New ICES science and advisory structures

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.

5.1 Ralf Ebinghaus

Current GKSS-research on per- and polyfluorinated compounds in the coastal and marine environment

5.2 Harri Kankaapaa

Cyanobacterial phycotoxins in the Baltic Sea

Recent trends in organochlorine contamination in the area.

6. REQUESTS FROM ACE, ACME AND REGULATORY AGENCIES

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

7. PLENARY PRESENTATIONS

7.1 Ashok Deshpande
Use of PCB fingerprints for the identification of subpopulations of young-of-the-year bluefish in the New York Bight.

7.2 Katrin Vorkamp
Levels of perfluorinated compounds and toxaphene in biota from Greenland.

7.3 Gerhard Dahlman
Source identification of Oil Spills by GCMS techniques

8. MAIN AGENDA

8.1 to revisit the current accepted and proposed background concentrations for biota and to evaluate the methodology that was used to derive them with the aim of:

(i). developing proposals for deriving BCs in biota, with priority given to metals in fish and shellfish, bearing in mind that a pragmatic approach has to be identified that will be applicable for the wider OSPAR area;

(ii). identify those parts of the OSPAR maritime area for which the proposed BCs in biota may not be applicable so that this can be taken into account during the assessments, and;

(iii). for the parts of the OSPAR maritime area identified, determine how assessments of whether concentrations are of at or near background should be prepared;

d) **8.2 develop background concentrations for the following alkylated PAHs in sediments and biota:**
(i) C1-, C2- and C3-naphthalenes;
(ii) C1-, C2- and C3-phenanthrenes, and;
(iii) C1-, C2- and C3-dibenzothiophenes, as well as the parent compound dibenzothiophene;

8.3 examine any proposals developed by OSPAR for guidelines on the frequency and spatial coverage of monitoring for nutrients and eutrophication parameters and provide draft advice on the statistical validity of the guidelines and make proposals for their improvement;

8.4 review the results of one-off surveys for the following chemicals identified by OSPAR for Priority Action: 2,4,6 tri-tert butylphenol (exploratory one-off survey to establish whether the substance is actually found in sediments in the OSPAR area), endosulphan, (exploratory one-off survey and a hot-spots survey to establish whether the substance is actually found, and to define "hot-spots" of the substance, in sediments of the OSPAR area), and short chained chlorinated paraffins (baseline survey to establish baseline in sediments in the OSPAR area against which to measure progress on the substance towards the goals of the OSPAR Hazardous Substances Strategy);

8.5 report on any new annexes on Quality Assurance from the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea;

8.6 review and discuss the *in situ* semi-continuous nutrients measurements and the progress and pitfalls of the use of these methods of data acquisition;

8.7 review available information regarding the role of nutrients and organically-bound nutrient species as potential drivers for processes which can influence

the uptake and distribution of contaminants in the environment and ecosystems;

8.8 report on peer-reviewed paper reporting the finding of MCWG international collaborative project on new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane(TCPMe) in flatfish;

8.9 review (in collaboration with WGMS) the draft guidelines for the preparation, use and analysis of passive samplers;

8.10 critically review and report the results and findings from joint MCWG / WGMS trial-survey of passive samplers, and review any new information on the use of membrane systems for sampling, and on their incorporation within national monitoring programmes;

8.11 report on new information regarding perfluorinated compounds in environmental samples;

8.12 together with WGMS, to carry out the following development work with regard to the JAMP Guidelines for monitoring Contaminants in Sediments (OSPAR agreement 2002-16) and JAMP Guidelines for monitoring Contaminants in Biota (OSPAR agreement 1992-2) to ensure that monitoring guidance is in place to support a revised Co-ordinated Environmental Monitoring Programme;

1) develop draft technical annexes on monitoring of polybrominated diphenyl ethers and hexabromocyclododecane in sediments and biota following the structure of the existing technical annexes. SIME 2007 will be invited to clarify the congeners and compartments that are relevant for the development of monitoring guidance for brominated flame retardants.

4) together with WGBEC and MCWG, review the existing technical annexes on PAHs to see whether they are adequate for monitoring of target alkylated PAHs and, as appropriate, prepare advice on any revisions that are necessary.

5) to develop a draft technical annex on monitoring of TBT and its breakdown products in biota;

8.13 report on the developments in Water Framework Directive monitoring programmes for physico-chemical parameters (priority substances, other pollutants, nutrient status) in transitional and coastal waters. This will focus on providing information on the specific parameters being measured, the approach to monitoring hazardous substances (e.g. matrices, frequency, etc.), classification tools, and the extent of surveillance and operational programmes;

8.14 provide expert knowledge and guidance to the ICES Data Centre as requested.

8.15 report on relevant new annexes on Quality Assurance from the ICES/OSPAR/HELCOM Steering Group on Quality Assurance of Biological Measurements (STGQAB);

8.16 report information on the relationship between co-planar PCBs and marker PCBs and consider the implications for monitoring programme. (This item was added to agenda at the start of the meeting by consensus)

8.17 MCWG will report by 2 April 2007 for the attention of the Marine Habitat and Oceanography Committees and ACME.

9. PLENARY DISCUSSION OF DRAFT REPORT

10. ANY OTHER BUSINESS

10.1 Election of Chair(s)

10.2 Working Arrangements with STGQAC

11. RECOMMENDATIONS AND ACTION LIST

12. DATE AND VENUE OF THE NEXT MEETING

13. CLOSURE OF THE MEETING

Annex 3: MCWG Terms of Reference for the next meeting

The **Marine Chemistry Working Group** [MCWG] (Chair: E. McGovern, Ireland) will meet in Helsinki, Finland from 10–14 March 2008 (provisional) to:

a) Review intersessional progress in deriving background concentrations for metals, parent and alkylated PAH

b) review the results of one-off surveys for the following chemicals identified by OSPAR for Priority Action: 2,4,6 tri-tert butylphenol (exploratory one-off survey to establish whether the substance is actually found in sediments in the OSPAR area), endosulphan, (exploratory one-off survey and a hot-spots survey to establish whether the substance is actually found, and to define "hot-spots" of the substance, in sediments of the OSPAR area), and short chained chlorinated paraffins (baseline survey to establish baseline in sediments in the OSPAR area against which to measure progress on the substance towards the goals of the OSPAR Hazardous Substances Strategy);

c) report on any new annexes on Quality Assurance from the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea;

d) review and discuss use of *in situ* semi-continuous nutrients measurements and the progress and pitfalls of the use of these methods of data acquisition;

e) review available information regarding the role of nutrients and organically-bound nutrient species as potential drivers for processes which can influence the uptake and distribution of contaminants in the environment and ecosystems;

f) report on peer-reviewed paper reporting the finding of MCWG international collaborative project on new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane(TCPMe) in flatfish;

g) review (in collaboration with WGMS) the draft guidelines for the preparation, use and analysis of passive samplers in seawater;

h) critically review and report the results and findings from joint MCWG / WGMS trial-survey of passive samplers, and review any new information on the use of membrane systems for sampling, and on their incorporation within monitoring programmes;

i) report on new information regarding perfluorinated compounds in the marine environment;

j) together with WGMS and based on intersessional work, finalise Technical Annexes for alkyl PAH in sediment and organotins in biota for inclusion in the JAMP Guidelines for monitoring Contaminants in Sediments (OSPAR agreement 2002-16) and JAMP Guidelines for monitoring Contaminants in Biota (OSPAR agreement 1992-2) ;

k) report on the developments in Water Framework Directive monitoring programmes for physico-chemical parameters (priority substances, other pollutants, nutrient status) in transitional and coastal waters and update tables outlining national activities.

l) provide expert knowledge and guidance to the ICES Data Centre as requested.

m) report information on the relationship between co-planar PCBs and marker PCBs and the consider the implications for monitoring programme.

n) Review information on integrated chemical and biological effects monitoring and assessment including information on effect directed chemical analysis

o) Consider new information on brominated flame retardants in the marine environment and specifically review new information on the environmental fate of DecaBDE.

p) Report on study on sediment surface/water interface partitioning of hydrophobic organic contaminants

q) Report on available information on pharmaceuticals as an emerging group of contaminants in the marine environment

r) Report on a study on PCB fingerprinting in migrating fish

MCWG will report by [to be decided]April 2008 for the attention of the Marine Habitat and Oceanography Committees and ACME.

Supporting Information

Priority:	This Group maintains an overview of key issues in relation to marine chemistry, both with regard to chemical oceanography and contaminants. These activities are considered to have a high priority. MCWG provides input across the field of marine chemistry which underpins the advice given by ACME, and also supports the work of national and international collaborative monitoring programmes, e.g., within OSPAR.
Scientific Justification and relation to Action Plan:	**Action Plan Goals Nos:** a) The development of BCs and BACs continues and further work has been identified. Such tools are required for the OSPAR JAMP [OSPAR 200x/y]. b) This will be in response to an OSPAR request [OSPAR 200x/x] c) This will be in response to an ICES request d) This project is initiated by MCWG to reinforce its nutrient activities e) This project is initiated by MCWG to reinoforce its nutrient activities and to create a better link between contaminants dynamics and ecosystems drivers; f) This project was initiated several years ago among MCWG members on the basis of concerns regarding these contaminants in the marine environment; g & h) These passive sampler devices will be reviewed for application to monitoring of contaminants in the marine environment; i) This was initiated among MCWG members on the basis of concerns regarding these contaminants in the marine environment j) This will be in response to an OSPAR request. k)this work was initiated by MCWG and will be of interest to OSPAR/EC/HELCOM l) This is in direct response to a request by the ICES Data Centre; m) This is initiated by MCWG members and will be of interest to OSPAR n) This is initiated by MCWG members and will be of interest to OSPAR o, p,q,r) These activities are initiated by MCWG
Resource Requirements:	The resource required to undertake activities within the framework of this group is negligible.
Participants:	The Group is normally attended by some 20–35 members.
Secretariat Facilities:	None.
Financial:	No financial implications.
Linkages to Advisory Committees:	There is a close and direct linkage with ACME.
Linkages To other Committees or Groups:	There is a close working relationship with WGMS, WGBEC, WGSAEM and STGQAC.
Linkages to other Organisations:	The work of this group is closely aligned with work being undertaken within the EU Chemical Monitoring Group on the requirements and implementation of the Water Framework Directive. This group provides the basis for some advice to OSPAR.
Secretariat Marginal Cost Share:	40% OSPAR, 60 % ICES.

Annex 4: Recommendations

NO	RECOMMENDATION	ACTION
1	Quasimeme to take note of comments of MCWG as highlighted in MCWG report section 4.3	QUASIMEME Project Office
2	MCWG are unclear as to the future for working groups in the new ICES structure but strongly recommends that this group should continue its role as a permanent working group of ICES. ICES should consider how best to strengthen chemical oceanography.	ICES Marine Habitats & Oceanography Committees
3	OSPAR to consider the reservations of MCWG in relation to the current approach for derivation of BCs (MCWG 2007 report 8.1 & 8.2) and to consider the approach of estimating pre-industrial concentrations in biota using enrichment factors determined from sediment cores to verify the OSPAR approach.	OSPAR MON WG
4	ICES to publish the final report of the Passive Sampling Trial Survey.	ICES
5	MCWG recommends that OSPAR adopt the technical annex on monitoring PBDEs in biota and the technical annex on monitoring HBCD in biota and incorporate them into the JAMP guidelines for monitoring of contaminants in biota.	OSPAR SIME/ASMO
6	OSPAR to take note of advice of MCWG concerning monitoring of co-planar PCBs in the marine environment as given in section 8.16 of the MCWG 2007 report.	OSPAR SIME

Annex 5: MCWG Action List

ACTION	
Report to MCWG 2008 on theme sessions I and J at ICES ASC 2007	Evin McGovern, Patrick Roose, Koen Parmentier, Victoria Besada
Provide further advice to QUASIMEME to assist them progress the issues raised by MCWG 2007 (4.3).	MCWG members on QUASIMEME SAG and advisory board
Consider appropriate theme sessions for ASC 2008/9 on chemical oceanography field	MCWG Members
Members to forward relevant data (PAH, Alkyl PAH and metals) from remote areas on metals in mussel and fish and PAH in mussel (OSPAR recommended species/tissues) to Patrick Roose.	MCWG members, Patrick Roose
Investigate whether sediment core data for metals/PAH/alkyl PAH and local biota data is available and to submit such data to EMcG/JT/PR. Other MCWG members are also encouraged to submit relevant data. Subject to appropriate data being available EMcG/JT/PR to estimate BCs for biota based on the approach suggested at MCWG and report to MCWG 2008. Initial values for MON 2007 to trial.	Norbert Theobald, Katrin Vorkamp, Jacek Tronczynski, Evin McGovern, Patrick Roose
Report on activities in relation to *in situ* monitoring of nutrients in home countries.	Evin McGovern, Patrick Roose, Ton van der Zande
Present the outcome of the MCWG international collaborative study of TCPM/TCPMe flatfish and the results of a time trend study of TCPM/TCPMe in blubber of beluga whales from the SLE, Canada at MCWG 2008.	Michel Lebeuf
Report temporal trends of TCPM/Me in fish collected from the North Sea/German Bight and also from the Baltic Sea, if sufficient data available, at MCWG 2008.	Michael Haarich
In cooperation with the PSTS coordination group to prepare draft guidelines for the preparation, use and analyes of passive samplers for seawater	Kees Booij, Ton van der Zande, Jacek Tonczynski
Investigate potential avenues for supporting joint activities in the field of passive samping (e.g. FP7)	Kees Booij and members of the PSTS coordination group
Report on use of passive samplers in studying deep sea contaminant concentrations	Kees Booij
Prepare technical annex for the analyses of C-PAHs, SPAH and C-SPAH in biota and sediments by the end of the year.	Lynda Webster, Ton van der Zande, Norbert Theobald and Jacek Tronczynski with WGMS subgroup
Patrick Roose to approach Els Monteyne (MUMM) to enquire whether she would be prepared to take a lead in preparing a technical annex for TBT in biota intersessionally with contributions from Ton van der Zande, Katrin Vorkamp, Phillipe Bersuder and Michael Haarich or colleagues. Draft Technical Annex to be submitted to MCWG 2008.	Patrick Roose, Ton van der Zande, Katrin Vorkamp, Phillipe Bersuder and Michael Haarich or colleagues they identify.
MCWG members to provide updated information on national WFD monitoring programmes for transitional and coastal waters at MCWG 2008	All MCWG members

ACTION	
MCWG members to present any further relevant information on the relationship between indicator PCBs and coplanar PCBs at MCWG 2008	All MCWG members
Report to MCWG 2008 on Belgian project on integrated chemical and biological effects monitoring and assessment	Patrick Roose
Report to MCWG 2008 on ModelKey project – effect directed chemical analysis	Harri Kankaanpää
Report to MCWG 2008 on new information on brominated flame retardants in the Marine Environment including information on the environmental fate of DecaBDE.	Micehl Lebeuf, Peter Lepom
Report on study on sediment surface/water interface partitioning of hydrophobic organic contaminants	Jacek Tronczynski
Report on studies on pharmaceuticals as an emerging group of contaminants in the marine environment	Norbert Theobald
Report on a study on PCB fingerprinting in migrating fish	Katrin Vorkamp

Annex 6: Estimation of Background Concentration in Mussels using Sediment Core Data – Example Calculation

During MCWG 2007 one proposal for estimating pre-industrial or Background Concentrations (BC) of PAH and metals in biota was to calculate enrichment factors in sediments from pre-industrial times to the present using sediment core data. The enrichment factors are calculated by dividing present day ambient concentrations of specific substance in the surface sediments in a specific area by background pre-industrial concentrations of this substance in the dated sediment core layer of pre-industrial times. These enrichment factors may be used to estimate background concentrations in biota (e.g. mussels) by dividing the current concentrations in biota (e.g. mussels) by the calculated enrichment factor for a given parameter. This needs to be done on an area-by-area basis by using present day mussels and surface sediment data from each area and only selected background concentrations from representative dated sediment cores. The estimates of background concentrations in biota assume that sediment and mussels reflect ambient concentrations and make assumptions that bioavailability and partitioning into these compartments has not substantially altered. The errors from such assumptions are probably low in regards to uncertainty of estimating background concentrations of contaminants from the present day data in biota.

$$\text{BC in biota} \cong C_{\text{biota-parameter}}/EF_{\text{parameter}} = C_{\text{biota-parameter}}/(C_{\text{sed current}}/ C_{\text{sed pre-ind}})$$

Example

In this example the present day concentrations of PAHs in mussels, in the surface sediments and in the dated sediment core, all from same area in Vilaine bay (Biscay Bay, Atlantic, OSPAR zone IV), were used to estimate background concentrations in mussels. The BCs were calculated for unsubstituted PAHs (Table A6.1) and alkyl substituted PAHs (Table A6.2). In this example the enrichment factor was calculated for summed concentrations of both groups of PAHs.

Table A6.1.

Determined concentrations in µg kg^{-1} of wet weight tissue for selected unsubstituted polycyclic aromatic hydrocarbons (PAHs) in marine mollusc tissue (mussel *Mytilus edulis*); station Pen Bé mean of five determination of the samples collected in November/ December 1999 (pre T/V Erika oil-spill) and one determination in November 2005. **Recalculated background concentrations** of same PAH compounds in mussels, based on the background (pre-industrial)/surface concentrations ratio in the dated sediment core from the same geographical area. For illustrative purposes in this case, an indicative enrichment ratio of 30 was used, (for summed concentrations of parent PAH), although in practice individual enrichment factors for each compound would be preferred.

STATION					
Taxon	Mytilus edulis	Present day		BC recalculated	
Parent PAHs		1999	2005	1999	2005
		µg/kg w.w.	µg/kg w.w.	µg/kg w.w.	µg/kg w.w.
Naphthalene		0,28		0,01	
Phenanthrene		1,52	1,88	0,05	0,06
Anthracene			0,18		0,01
Fluoranthene		4,32	6,62	0,14	0,22
Pyrene		3,60	7,82	0,12	0,26
Benz(a) Anthracene		0,82	1,86	0,03	0,06
Chrysene/triphenylene		2,61	4,08	0,09	0,14
Benzo(e)pyrene		2,23	4,21	0,07	0,14
Benzo(a)pyrene		0,21	0,88	0,01	0,03
Indeno(1,2,3, cd)pyrene		0,52	0,77	0,02	0,03
Dibenz(ah)anthracene			0,21		0,01
Benzo(ghi)perylene		0,75	1,25	0,03	0,04

Table A6.2.

Determined concentrations in µg kg^{-1} of wet weight tissue for selected alkyl substituted polycyclic aromatic hydrocarbons (C-PAHs) in marine molluscs tissue (mussel *Mytilus edulis*); station Pen Bé November 2005.

Recalculated background concentrations of same PAH compounds in mussels, based on the background/surface concentrations ratio in the dated sediment core from the same geographical area. Sulfur heterocycle compounds were below detection limit in the deep pre-industrial layer of the dated sediment core.

ALKYLATED PAHS	PRESENT DAY 2005	RECALCULATED BC[1]
	µg/kg w.w.	µg/kg w.w.
C1-N	0,30	0,02
C2-N	0,23	0,01
C3-N	0,37	0,02
C1-P	6,66	0,37
C2-P	15,19	0,84
C3-P	19,21	1,07

1. An indicative enrichment factor of 18 is based on summed concentrations of alkylated PAH.

Annex 7: Protocol for the passive sampler trial survey

Protocol for Participants

Passive Sampling ICES Trial Survey for hydrophobic organic contaminants in Water and Sediment, Including laboratory intercalibration.

Foppe Smedes, Céline Tixier and Ian Davies (ICES/WGMS) and Patrick Roose, Ton van der Zande and Jacek Tronczynski (ICES/MCWG)

1 Short overview

For the Passive Sampling Trial Survey participants deploy samplers in water preferably in association with mussels. A Passive sampler is silicon rubber (PDMS) sheet spiked with Performance Reference Compounds (PRC). One sampler consists in 6 sheets. Deployment is carried out in duplicate and one sampler is analysed by the participating laboratory and one by a reference laboratory. Samplers are spiked with Performance Reference Compounds (PRC) that will be partially released to the environment. To compare the residual concentration of PRC with the initial amount of PRC, the participants will also analyse a sampler that has not been exposed (to determine PRC initial amount).

A similar exercise is done with sediment but the exposure period will take place in the lab. Wet sediment (preferably fine grained) is shaken with in a bottle coated internally with a thin layer of PDMS (silicone rubber). Where possible participants do parallel uptake bioassays with sediment living organisms. Sediment is shaken in duplicate and one bottle is sent to the reference laboratory. For comparing the amounts PRCs before and after exposure a reference bottle is analysed for PRCs without exposure to sediment.

Therefore, the objectives of the trial are to:

- extend the geographical range of the validation of the use of passive samplers in water;
- transfer knowledge of the methods more widely within the ICES community;
- to gain experience in the use of passive samplers;
- estimate the contribution of the analytical component to total variability;
- to gain further information towards the validation of passive samplers in sediment.

The exercise is learning for participants as well as coordinators; Make notes of your experiences during the survey, any suggestions that can help to improve or simplify the procedures.

Unless agreed differently with individuals a standard set of materials as described in here will be supplied to all participants for each station sampled. Note that the silicon sheets and the coated bottles should be stored in the freezer until exposure.

2 Passive Sampling in Water

2.1 Sampler Frame

The sampler frame is made of stainless steel and this frame has a fixing eye that allows the frame to turn around and give flexibility. You can use a shackle or rope through this eye to fix the sampler frame to what ever you have available to hang the sampler frame on. Secure a shackle with a pin, cable strap or stainless steel wire. Knots in ropes can be secured with cable straps and tape. At RIKZ we expose samplers at 1.5 to 2 meters below surface. In exceptional

cases, for example if the total water depth is less than 3 meters it is suggested to hang the sampler frame at half depth. In tidal areas the shallowest depth, i.e. low tide, should be considered for this rule of thumb.

2.2 Deployment

Each participant will receive 3 jars alufoil lined lid with 6 sheets each. Note that for this exercise, one" passive sampler" consists in 6 sheets. Until exposure the jars are stored in a freezer.

Two sets of non-sharp tweezers are required for mounting the sheets and a clean working place to sort the sheets on: either in stainless steel, a place covered with pre-baked (450°C) aluminium foil or a large glass Petri. Sampler sheets may stick these surfaces. Sticking is less when the surfaces are wetted with Milli-Q or local water. Make sure the material you use is clean. Sheets are mounted just before exposure and removed from the sampler directly after recovery. Two sheet holders are already mounted in the frame. A video can be downloaded here (20 MB) to give an impression of how that works.

(You can change the position to create space for a mussel cage). A cable strap is keeping the fixing rod in place. Cut the cable strap and pull out the fixing rod. Take the sheets from the jar with the number that corresponds to the sampler holder number. If sheets cannot be taken from the bottle one by one because they stick together, take them all out on the Petri dish or wire mesh and separate them using tweezers. Then mount the sheets on the holder with the short side upwards. Feed the fixing wire through the holes on the stem and fix it tight with the cable strap. Mount the sheets on all positions and deploy the samplers for 6 weeks or more. The following parameters are to be recorded and reported in the excel data sheet:

- Date and time of deployment;
- Salinity in o/oo;
- Water and air temperature;
- Some measure of SPM; SPM content by filtration or Secci disk.

If your conditions during deployment do not allow you to mount the sheets onboard, you can unfix the sheet holder from the frame and mount sheets in the lab. Directly place them in a stainless steel container or if not available, wrap them in prebaked aluminium foil and transport them in a cool clean container to the deployment station where they are fixed in the sampler frame. The time between mounting and exposure should be as short as possible. Make record of the process

2.3 Recovery after deployment

During recovery the same parameters are recorded as at the time of deployment. Depending on the season and place of deployment the recovered sampler can be clean or totally overgrown with whatever organisms. It is suggested to document the recovered situation by taking picture of the recovered sheets. Sheets that are almost clean are first wiped with a soaking wet tissue and subsequently patted dry with tissue and transferred to the alufoil-lined lid jar in which they were delivered. If fouling organisms grow on the sheet they should be scraped of as completely as possible. Further residues can be removed using a very wet scourer. A nylon type (as use in kitchen) without sponge and rinsed with washed with methanol is appropriate. Work on a wet glass surface and for rinsing you can use local water. When that is not available use Milli-Q, but try to limit the amount of water as much as possible. Only use gloves if local water is that contaminated that contact needs to be avoided, otherwise properly washed and rinsed hands contaminate less than gloves doD:\CIEM2007\PSTS_Table\8.9 Protocol PSTS.htm - _ftn1. The cleaning should be done in the shortest time possible, e.g. less than 5 minutes.

Losses are linearly related to the time of the process. It is not necessary to aim for a sheet as clean as new. Document the situation using a camera. Finally the recovered samplers are place back in the storage jar and stored in the dark, and as soon as possible are transferred to a freezer, until analysis or dispatch to the reference laboratory.

Although the weight of the 6 sheets in one sampler is known within certain limits the exact weight must be determined **after extraction**. The dry weight of the 6 sheets is considered as the sampler or reference mass (m).

3 Passive sampling experiments in Sediment

A draft guideline for sediment equilibrium sampling is available on the web although the information below contains some specific additional suggestions.

3.1 Material

The standard material delivered is 3 one-liter bottles for each sampling station. The bottles have alufoil lined caps and the inside wall is coated with about 300 mg PDMS spiked with PRC. Please store them in the dark and in a freezer until use. Each bottle is engraved with a number. The exact weight of your bottles (without cap) and the coating weight will be listed on the web. Please weigh the bottles (1 mg accuracy) upon arrival (it is advisable to clean the outside before weighing). Do not stick any labels on the bottle as this will affect the weight.

3.2 Exposure

Sediment samples are taken according OSPAR guidelines. At least 3 kg is collected in a container and homogenised as good as possible. The container is preferably glass or stainless steel. If you use any plastic, make sure the residence time is as short as possible. For homogenisation water may be added now to support the mixing process. Sub samples are taken for dry weight determinations. A larger sub sample is taken to determine the total concentration of the target compounds in the sediment, as well as the total Organic Carbon content. Two bottles are filled with the sediment up to 50 to 60% and the amount recorded by weighing the bottle with sediment. Fill the bottles using a wide opening stainless steel or glass funnel.

If the sediment is not well fluidized sufficient water to obtain that situation should be added. Ideally this water should be from location, otherwise milli-Q water can be used, Record the weight again. Then purge the bottle with N2 to remove oxygen as much as possible and close the bottle. The bottle is ready to be shaken (100 rpm) for at least 20 days in the dark at a temperature 20°C. If no climate room is available, find a place with a temperature as close as possible to 20°C. Alternatives to shaking are to roll the bottle (30 RPM), or tumble (30 rpm) but a lower degree of equilibrium will be obtained.

3.3 Recovery

After the equilibration period the bottles are emptied and vigorously shaken with portions of 50–100 ml milli-Q water to remove all sediment. This should be done in the shortest possible time and using the smallest amount of water. Usually 3 times 30 s is sufficient. Then let the bottle drain upside down on a tissue and/or swing the bottle to remove all water as much as possible. Close the bottle and store in freezer until analysis or dispatch to the reference laboratory. After extraction the bottle is dried and weight of the bottle determined. With the empty weight for the bottle number obtained from the web the weight of the film can be calculated. Comparison with the original weight will show possible wearing during shaking.

4 Analyses of, Bottles and Sheets

4.1 Extraction

Extraction and cleanup possibilities are described more extensively in the "Draft guidelines for equilibrium passive sampling of sediments". Many variations are thinkable, some are summarised below: It is important to have the sheets or bottles as dry as possible before extraction. Recovery Standards can be added to the extraction solvent before extraction starts.

Bottles

Before bottles are extracted make sure to swing out the water as much as possible. The bottle can be extracted twice with 50 ml methanol or methanol+acetonitril (1+3 v/v) for 4 hours. After addition of the solvent first acclimatise the bottle to allow the solvent to saturate the vapour phase. Only then close the bottle completely. It is even advisable to warm the bottle slightly under warm water so only pressure reduction can occur in the bottle during the further processes (weighing before and after is a good QC measure). When shaking (horizontal) make sure the solvent is wetting the whole film surface. Otherwise turn the bottle through 180 degrees half way the extraction. An alternative to shaking and safer approach to possible leakage is to roll the bottle for extraction for the same time. A procedural blank is done equally without film in a clean one liter bottle.

Sheets

The simplest and safest way to extract the 6 **sheets** is putting them loosely in a soxhlet and extract with methanol for 8 hours. (Alternatively methanol+acetonitril (1+3 v/v) can be used). If all sheets do not fit in at once extractions can be done in portions by replacing the extracted sheets after 8 hours and continue with the next portion using the same portion of solvent. A procedural blank is done in the same way, but without sheets.

Another method to extract **sheets** is cold extraction procedure. Take a 300 or 500 ml Erlenmeyer flask with glass stopper and transfer sheets to it. Add 150 ml methanol and shake gently overnight. Pour out the methanol and repeat the extraction with fresh solvent for another 8 hours. The combined extract is your sample to analyse. It is suggested that completeness of extraction is confirmed by taking all sheets from the different samplings together and extract them once more analysing the extract separately (the most critical compounds here are the higher PCBs). A procedural blank is done in the same way, but without sheets.

(1) Extraction with other solvents is also possible but causes in often considerable swelling (up to 200%) of the sheets and, although not likely after the extensive pre-extraction, the co-extraction of small amounts of oligomers cannot be excluded.

Optional cleanup

Optional is a cleanup with C18 Bounded Silica. This ensures that no oligomers will be present in the extract. For this to be done the extract has to be made into methanol or acetonitrile. Concentrate the extract obtained above to <2 ml. Pre-rinse a column containing 300-500mg C18 bounded silica with 6-10 ml methanol/acetonitrile. Transfer the extract to the column and elute with 6-10ml methanol/acetonitrile. Coronene is the last eluting compound.

Acetonitrile boils at 85°C. Addition of 20% methanol will decrease the boiling point to 64°C. Acetonitrile also forms an azeotrope with water, and so extracts are always dry after boiling down to concentrate.

4.2 Solvent transfers

(1) Azeotropic solvent transfer of methanol/acetonitrile to hexane can be done by concentrating the extract obtained as above to 2 ml and then adding 10 ml hexane for each ml of methanol/acetonitrile. With boiling stones boil the (two phase) mixture down to <2 ml on a water bath. If two phases are still present, repeat the procedure. If the two phases remain it is probably not methanol but water. Add 20 ml hexane and after vortexing 1 minute remove the water with a Pasteur pipette. Evaporate again (Note, this isotropic phase transfer does not work in nitrogen blow down systems). For rota-vapour systems, do not apply vacuum, as the azeotrope will change in an unknown way.

(2) Less efficient is to concentrate the methanol to <50 ml, transfer the extract to a separation funnel with 100 ml hexane or DCM and dilute by addition of mili-Q water until the aqueous phase has less than 20% methanol. Then extract the aqueous phase and repeat this with a second portion of Hexane or DCM. A mixture that has a density of more than 1 g/ml is also suitable. If the organic layer is on the top, the emulsion can be broken, after removal of the separated water phase, by dropping some methanol on it. Evaporation will end in a hexane extract.

4.3 Cleanup

Cleanup of the extract can be carried out according to the laboratory methods used routinely in participant labs. The extracts above are suitable to use in any cleanup you will have available for water, sediment or biota. For sediment extracts from the coated bottles should be treated for sulphur removal.

4.4 Quantification

The target compounds will be quantified as you normally perform analyses of sediments or biota. For determination of the PRCs the qualitative standard delivered can be used for finding the retention times and to set a response factor.

> The qualitative standard is dissolved in a small disc of silicon rubber. The PRC s and its amounts will be listed on the web from 25 September, as well retention information. The standard can be dissolved by addition of at least 1 ml of solvent of your choice.

Note that the true concentration of PRCs is not relevant but the ratio between the amount after and before exposure, i.e. sample and reference. Therefore the qualitative standard supplied would be sufficient for calibration. The reference sheet and bottle can also function as a storage blank for non-PRC compounds. This blank should not be subtracted from the sample. Only the procedural blank, i.e. solvent passing through the procedure, is generally subtracted from the sample (and reference) result. However, for this exercise we ask you not to apply blank correction and to report Sample, Reference and Procedural blank data without correction.

4.5 Reporting

The reporting is done on a self-containing spreadsheet that is named according to the matrix and station code. Each field shows the required help information when selected. Where applicable a dropdown menu allows selection of the relevant code. All info on deployment

and recovery can be collected on the form. The amounts of target compounds determined on the sheets are reported in ng absolute. Likewise PRC data are reported in amount although peak area/height after correction IS will also apply.

5 Parallel work

5.1 Mussels

Mussels from the sampling location are best depurated for 24 hours using local water. Native mussels or mussels deployed during the water sampling are processed according to the procedures routinely used in your laboratory. Average shelve length should be recorded as well as the average body weight. (The mussels used for the RIKZ mussel watch are selected on a shelve length of ± 50 mm.).

In case additional information on procedures is required an example can be supplied.

Data are reported on a dry weight basis in the same spreadsheet as the water sampling data.

5.2 Sediment assays

Participants are invited to apply uptake bioassays with the sampled sediments using sediment living organisms. Since this will be different among the participants data can be reported in a free format.

5.3 Other contributions

Participants that measure compounds in additional to the target compounds can create more lines in the report sheet. Other additional work such as applying different sampling techniques can be reported in free format if it does not fit in the standard format.

6 Calculation

6.1 Sediment

Calculation of the free dissolved concentration (C_W) in an equilibrated system is done by:

$$C_W = \frac{N_R - Bl_R}{m_R \cdot K_{RW}} \quad (1)$$

In which N_R is the amount (ng) of compound measured in the extract of the sheet/bottle; Bl_R the procedural (solvent) blank (ng); m_R the mass of passive sampling material (kg) after exposure and K_{RW} the material-water partition coefficient (l/kg). The obtained result is in ng/l but it is often more conveniently to express the results on pg/l.

The K_{RW} values are already measured for this material. Presently they are verified by a repeating the measurements. The will be available mid November.

For process QA and further information check the draft guidelines.

6.2 Water

The procedure below is a rule of thumb procedure. More extensive and statistically based procedures are given in literature.

6.2.1 Step 1

Prior to calculating the sampling rate first the PRC data are screened. If the PRC-amount measured is less than 10 times the DL the PRC is rejected. If the amount is more than half the amount of the reference the PRC is also rejected. The remaining compounds are used to determine a sampling rate: R_S.

6.2.2 Step 2

The sampling rate can be calculated from the release of the PRCs that were spiked on the sampler before exposure. The release of compounds from the passive sampler (PS) follows:

$$N^t = N^0 . e^{-k_e . t} \qquad (2)$$

Where N^0 is the mass of PRC measured in reference samplers that were not deployed, N^t is the mass of PRC remaining in the PS after deployment, k_e (d^{-1}) is the first order dissipation constant that rules the release process, and t the sampling time (d). After rewriting k_e is calculated from:

$$k_e = -\frac{\ln\left(N^t / N^0\right)}{t} \qquad (3)$$

From eq. 3, the mass of the sampler (m) (kg) and the K_{SW} [1[ii]] (kg/l) the sampling rate R_S (l/d) is calculated through:

$$R_S = k_e \; m \; K_{SW} = -\frac{\ln\left(N^t / N^0\right)}{t} m K_{SW} \qquad (4)$$

The R_S values are calculated for all the PRCs that pass the criteria in step 1. From the obtained R_S values the median is used for further calculation of aqueous phase concentrations.

6.2.3 Step 3

For estimation of the freely dissolved concentration (C_W) in the water phase the full uptake model that is valid for equilibrium and non-equilibrium situations is applied. The uptake is described by the following equation that includes the sampling rate (R_S) estimate for that specific station and sampling period in the previous step:

$$N^t = N^\infty \left(1 - e^{-\frac{R_S \, t}{m \; K_{SW}}} \right) \qquad (5)$$

Here N^t is the amount of compound (ng) in the sampler after deployment for time t (days). The final amount taken up in the equilibrium situation (N^∞) equal the equilibrium concentration C_S^∞ times the mass of the sampler (m) in kg. C_S^∞ is related to C_W by the partition coefficient K_{SW} (l/kg)and consequently:

$$N^{\infty} = m\ C_S^{\infty} = m\ C_W\ K_{SW} \qquad \text{that gives} \qquad C_W = \frac{N^{\infty}}{K_{SW}\ m} \tag{6}$$

From eq. 5 and 6 the concentration in the water (C_W) in ng/l, is given by:

$$C_W = \frac{N^t}{m\ K_{SW}} \frac{1}{1 - e^{-\frac{R_S.t}{m\ .K_{SW}}}} \tag{7}$$

In equilibrium the first term is dominating and far from equilibrium the second.

6.2.4 Step 4

Report for each sample station a list of the R_S values, the median R_S in l/d, and C_W values in pg/l you have calculated for the target compounds. Any format you like as long as the name abbreviations of the compounds as displayed on the web are used.

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It was suggested that cotton gloves may be useful for manipulation of sheets. This is for convenience but will not likely contribute to prevention of contamination.

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For the PRCs new in use the KSW values are still to be determined. Likewise a new batch of silicone rubber is applied for this survey and KSW values need confirmation. Available in November.

Annex 8: Review of the progress with the passive sampler trial (PSTS)

Note: Copy of this Annex is also included in the 2007 Report of WGMS

Presented by the PSTS Coordinating Group, WGMS/MCWG March 2007

1 Execution of the plan for the project

The joint session of WGMS and MCWG in 2006 developed the initial plan for the ICES Trial Survey and Intercalibration on Passive Sampling (PSTS). They also developed a timetable for the exercise. This is attached as Table A8.1, together with an additional column indicating the outturn dates for each step in the process. The exercise has been carried out and data are available for discussion at WGMS and MCWG in March 2007.

To summarise, the preparatory work to gain commitment from participants, prepare a protocol for the trial, prepare materials for deployment in the field, and distribute them to the laboratories closely followed the projected timetable. The final distribution of materials to participating laboratories was made on 29 September; only four days later than planned.

Deployment of samplers in the field was planned to begin in early October, but was delayed in some laboratories and was the last deployment occurred around 10 November. This delay was inevitably reflected in later aspects of the project, i.e. the sending of samples to the central laboratory for analysis, analyses in-house and by the central laboratory, and the reporting of data to the coordinator. Final samples for analysis were not received by the coordinator until March 2007 (target December 2006–January 2007). The coordinating laboratory will complete all outstanding analyses by the end of April. This date has also been agreed by the Steering Group as a deadline for the submission of in-house analytical data to the coordinator.

In total, 13 laboratories participated in PSTS, and sampling was undertaken at 31 locations for water and 25 locations for sediment.

Table A8.1. ICES Trial Survey and Intercalibration Passive Sampling, 2006-2007.

INITIATIVE FROM WGMS AND MCWG			
PLANNING and OUTTURN TIMETABLE			
Activity	**Who**	**Planned Completion date**	**Actual Completion date**
Draft protocol for the experiment	Coordinating Group	May 2006	May
Get firm commitments from participants.	Coordinating Group and participants.	September	September
Determine degree of replication *	Coordinating Group	July	July
Confirm participants and locations	Participants / Coordinating Group	July	September
Draft Guidelines SEDIMENT	Coordinating Group	End of July	September
Purchase sampler sheets	RIKZ	June–August	June–August
Prepare and spike sampler sheets	RIKZ	August–September	August–September
Purchase of bottles	RIKZ	June–August	June–August
Prepare, spike bottles	RIKZ	August–September	August–September
Distribute bottles	RIKZ	September (25th)	September (29th)
Build frames to support samplers	RIKZ	July – mid September	July – mid September
Purchase mussels or use local animals	Participants	October	October
Distribute sample frames	RIKZ	September (25th)	September (29th)
Distribute sampler sheets	RIKZ	September (25th)	September (29th)
Deploy mussels, samplers and sediment	Participants	Early October.	5 October - 10 November
Record supporting data (CTD-data)	Participants	Simultaneous with the sampling	Simultaneous with the sampling
Recover mussels and samplers	Participants	Late November/early December	November - December
Shake sediment	Participants	October–November	?
Send sediment sampler bottles to central lab	Participants	December 06 - January 07	December 06 - March 07
Send sampler sheets to central lab	Participants	December 06 - January 07	December 06 - March 07
Analyses of samplers at central lab	RIKZ	Mid-January - February 07	December 06 - April 07
Complete analyses at local labs	Participants	Mid-January - February 07	January 07 - April 07
Send data to central lab	Participants	Early February	February 07 - April 07
Collate data	Foppe Smedes	End of February	March 07 - May 07
Review data	All	At WGs next year	March 07 and through to ASC 07

2 Issues arising in analysis of samples

2.1 Technical analytical problems associated with use of PRCs and other sources of problems.

Several laboratories had reported difficulties during the analysis of passive samplers. In most cases, these were rather detailed points and varied between laboratories. The summary given here is a combination of comment from FRS (UK) and IFREMER (France). Information is being requested from other participants so that a wider view can be taken of the issues and that solutions can be developed that meet the needs of as many laboratories as possible.

2.1.1 Difficulties related to sampling:

- Filling of the coated bottle with the sediments slurry:
- Low dynamics of exchanges (Weak bottle shaking, weak water mass dynamics)
- Difficulties in estimating the sampling rate due to low water mass dynamics at the exposure site.

2.1.2 Difficulties encountered in the laboratory

2.1.2.1 Selection of Performance Reference Compounds (PRCs).

- Not all PRCs could be accurately determined with routinely used calibration standards. An accurate determination of PRC was not aimed because calculations of water concentrations are based on the relative loss of PRC. A reproducible determination of the PRCs was achieved in the silicone rubber before and after exposition with an modified adequate method.
- For the PCB PRCs we have to use an external calibration to quantify them as they are not part of the UKAS accredited method of the lab (we have identified the retention times and will be running such as soon as possible).

2.1.2.2 Extraction method:

- The main problem came from the use of a relatively large volume of MeOH for the cold extraction. All the analytical steps on the extract are routinely carried out in non-polar solvent. Therefore the exchange from the MeOH to non-polar solvent was necessary and required also a relatively large volume of intermediate solvent.

2.1.2.3 Interferences in analyses related to PRCs.

- Interferences of peaks (poor separation): Some of the PRCs are being used as internal standards (like d8-naphthalene), which makes quantification of the PRC d8 naphthalene difficult. FRS does not use some of the PRCs (D12-phenanthrene, D12-perylene, D12-coronene, and all the CB PRCs), therefore, for the deuterated phenanthrene and Perylene, the calibration of their non-deuterated analogues were used to quantify them. The GC programme was not set up to look at coronene and therefore no result was presented. PCB 50 co-eluted with PCB 31 while PCB 104 co-eluted with a recovery standard (PCB 35).
- Interference PRC with standards (recovery, calibration, injection)
- Interference PRC with other contaminants:
- Only CB78 PRC could not be determined because of coelution on both analytical columns. The coelution problem for two other CB50 and CB204 PRC was overcome by the analysis on two analytical columns

2.1.2.4 General

- The most obvious issue is the differences in analytical procedure for extraction, clean-up, and quantification. We split the extracts into two (PAHs and PCBs) and the PAHs were cleaned up using the HPLC (silica column), while the PCBs are to be cleaned up with Alumina column. The PAHs were analysed by GC MS and the PCBs using GC ECD.

2.2 Evidence of gross contamination of samplers

Gross contamination of samplers is most likely to arise through mis-handling of sheets used for water sampling, or contamination of films on sediment sampling bottles during preparation or distribution.

Some sheets and bottles were spiked with Performance Reference Compounds and distributed to participants. These were not used for field exposures or sediment extractions, but were returned to the central laboratory for analyses. These analyses showed no evidence of gross contamination and therefore gross contamination during preparation or transport of rubbers is considered unlikely.

It is possible that contamination could occur during field deployment and recovery of PS material. To attempt to limit the probability of this occurring, the exercise protocol contained detailed advice on how to handle the PS materials.

There is no evidence in the analytical data from the central laboratory to suggest that the samplers became grossly contaminated during the transport and handling necessary for their use in the field. The correlations observed between the results for water samplers and for those in sediment at the same sites indicate that gross contamination could not have frequently occurred. In a few cases, the concentrations of some PRCs in the water samplers appeared higher than might be expected from the data for other PRCs in the same sampler. This mainly occurred in samplers deployed at heavily contaminated sites. It is possible that in such circumstances the concentrations of contaminants in the environment and consequently absorbed by the PS were sufficiently high to interfere with the measurements of the residual concentrations of some PRCs in the samplers.

2.3 Are the values for the partition coefficients satisfactory?

Accurate values for partition coefficients of contaminants between PS materials and water are necessary for the calculation of concentrations of contaminants in both water and pore water. Values for some partition coefficients are available in the grey literature. The central laboratory has put considerable effort into the determination of partition coefficients for a range of PS materials, including the material used in the water sampling sheets and that used in the sediment sampling films. The values obtained from direct partitioning between water and passive sampling material are consistent with those obtained by extrapolation of coefficients obtained from a series of water/methanol mixtures and are considered to be reliable to within <0.05 log units.

The difference between the sets of partition coefficients for the two different PS materials used in sheets and in films is small (<0.1 log units), and calculations by the central laboratory have been based upon the mean of the two sets of data. These means were distributed to the participating laboratories for use in their own calculations.

2.4 Discussion of model of sampling rates

It is necessary to estimate sampling rates of PS in water in order to calculate the concentrations of contaminants in the water phase. PRCs (PAHs and CBs) are added to sampler prior to exposure, and the dissipation rates of the PRCs are used to estimate the sampling rate. The protocol for the PSTS instructed participants that they should only use PRCs for which the retained amounts were greater than 10x the detection limit, and less than 50% of the initial amount added to the sheets. Sampling rates should be calculated for each PRC that met these criteria, and then the median value used as the best estimate of the sampling rate.

In practice, this caused some participants some difficulties. For example,

a) Some PRCs interfered with other compounds in the analyses, for example with analytes, internal standards or recovery standards

b) Some PRCs were not covered by the normal instrument method used

c) PAHs and CBs could be analysed separately, thereby reducing the number of PRCs available for the estimation of sampling rate

d) In some cases, only a small number of PRCs met the acceptability criteria listed above

e) In some heavily contaminated areas, there is greater possibility of interfering compounds being present which co-elute with the PRCs, and this can be difficult to recognise.

f) Estimates of sampling rates derived from different compounds could be rather different, for example as a result of e) above.

In recognition of these sources of uncertainty, an alternative improved method of handling the PRC data has been applied by the central laboratory to their own data (and will be applied to the raw data provided by participating laboratories).

The loss of PRCs is modelled as a function of a set sampling rate. By using Excel solver, the sampling rate is optimised to minimise the sum of the squares of the differences between the observed and modelled values. Deviations from the fitted model are normalised to an estimate of the measurement error in the observed values.

The modelling uses data for all PRCs for which the remaining amount is between 1% and 90% of the original amount added to the sampler. Outliers arising from processes such as those described in a) – f) above can be easily recognised and assessed for their effect on the modelled sampling rate.

2.5 What physical problems and difficulties have we seen?

In general, few practical problems were encountered during the exercise. Problems with potential differences in the interpretation of the protocol were largely eliminated by the text being reviewed by more than one person. However, a very few misunderstandings still occurred and the protocol for any future exercise will take these into account.

Only one instance of loss of water samplers was reported. This occurred in the Seine estuary after a storm, despite being attached a 2 tonne flotation buoy. The buoy was recovered from a beach, but the samplers were lost.

Some damage occurred to sampling films in 4 (20%) of the sediment sampling bottles. Loss of film can be detected visually and by the routine weighing the bottles at the end of the process. This procedure can be confounded if the glass of the bottle is chipped, as weighing cannot distinguish between loss of film and loss of glass.

Damage/loss of PS films is normally associated with extraction of sandy sediments, which act as an abrasive over the extraction period. This can be greatly reduced by avoiding the use of sandy sediments. There may also be some potential for improving the adherence of the PS film to the glass surface of the sampling bottle, or for different methods to detect abrasion of films.

2.6 Influence of biofouling

Some participants experience very heavy growth of fouling organisms on both the frames and sampler sheets deployed in the water. Fouling was particularly heavy at the two stations in Brisbane, Australia and at one station close to Vigo, Spain.

It is likely that this has had only limited impact on the data. Firstly, it is unlikely that the fouling will have significantly reduced the transport of contaminants to the sampler. The rate of transport is the product of the solubility of the material and its diffusion coefficient in the material being considered. The solubility of contaminants will be greater in the fouling organisms than in water by a factor equal to the bioaccumulation factor, and the diffusion coefficient is unlikely to be reduced to the same extent. Therefore, the rate of transport is unlikely to be greatly reduced by the presence of fouling organisms. In addition, the PRCs added to the samplers act as a control for the rate of sampling and should reflect any changes in the sampling rate induced by the presence of the fouling communities (Booij, 2005).

2.7 Influence of low sampling rates on detectable residues and hence on confidence of concentrations in water.

One important advantage of passive samplers is that they continue to sample water over long periods of time, and thereby both integrate over time and also accumulate contaminants from relatively large volumes of water. For example, sampling rates in the current experiment for deployments of sets of 6 sheets were typically 5–40 litres per day, giving a total volume sampled over a deployment for 40 days of 200–1600 litres. These very large volumes allow the estimation of rather low concentrations of dissolved contaminant in the pg/l range, using commonly-available instrumentation for detection of the analytes.

The effective sampling rate strongly increases linearly with the surface area of the sheets deployed and the flow rate of water past the sampler (which controls the thickness of the diffusive boundary layer around the sampler). Clearly, if the effective sampling rate, and hence the total volume sampled is reduced, for example by deployment of a smaller number of sheets, the lowest detectable concentrations will increase by an equivalent factor.

Similarly, deployment of samplers in areas where water movements are not strong also reduces the volume sampled. For example, Loch Etive is a very sheltered fjordic inlet in the west of Scotland and the effective rate of sampling at this point was 3.6 litres per day. This problem can be very significant in quiescent waters, such as in lakes, but is normally less important in estuaries and the open sea where tidal and other currents ensure that water flows past the samplers.

A potential significant improvement in the capability of passive samplers in water would be a system to keep the sampler sheet in motion (e.g. spinning) for several weeks of deployment. However, the energy required for this is significant and systems have yet to be developed.

3 General comments on results obtained up to March 2007

The objectives of the PSTS project were:

a) to extend the geographical range of the validation of the use of passive samplers in water;
b) to transfer knowledge of the methods more widely within the ICES community;
c) to gain experience in the use of passive samplers;
d) to estimate the contribution of the analytical component to total variability;
e) to gain further information towards the validation of passive samplers in sediment.

Even at this early stage in the collation and interpretation of the results from the project, it is clear that objectives b) and c) have been met. Thirteen laboratories have participated in the trial. In addition, passive samplers have been used in new areas such as Faroe, Ireland, Spain and Portugal that are distant from the original uses of silicone rubber samplers in the Netherlands.

Some other objectives cannot yet be addressed until the data set is more complete. For example, the low numbers of data on mussels and worms have delayed consideration of the relations between residues in organisms and concentrations detected by passive samplers. These matters will be addressed as the data become available.

However, the datasets for samplers analysed by the central laboratory, while not complete, is at a stage where some preliminary observations can be made as to whether the data are reasonable in terms of our understanding of inputs of contaminants and of environmental processes affecting their behaviour.

The following bulleted points are preliminary observations on the distribution maps of concentrations of contaminants (PAHs, CBs, HCB) in water and in sediment pore waters.

3.1 Water

PAH

- For all PAHs, the concentrations in Norwegian samples are very much higher than all other locations. This may reflect the source from aqueous discharges, particularly of heavier compounds, from aluminium smelters.
- There is a tendency for concentrations in far west stations (Scotland, Ireland, Faroe) to be as high as those in areas of the SE North Sea where concentrations might be expected to be higher. This could reflect high concentrations of SPM in the North Sea adsorbing PAHs and reducing the free concentrations, whereas atmospheric inputs in the west occur into water with low SPM and therefore higher concentrations may remain in solution.
- In the outer parts of the Scheldt, concentrations of lighter PAHs increase seawards, This could also be a result of dominating atmospheric input. Alternatively degradation of organic matter cause PAHs to desorb from the solids. This is not to be likely the main reason as this increase seawards is not present for heavier compounds.

CBs

- CB concentrations at sampling stations in Norway and western locations (e.g.Scotland, Ireland, Faroe) are all low. There are no large local inputs, and no significant atmospheric inputs, in these areas.
- The high concentrations in the inner Scheldt decrease seawards. This could reflect dilution of river water by open sea water and lack of desorption of CBs from suspended solids.
- Concentrations of more chlorinated CBs are relatively dominating in Vigo, Spain.

HCB

One very high concentration of HCB was found in the Elbe. Apart from that, there is a tendency for higher concentrations in western parts of the survey area, particularly in Faroe. This may reflect atmospheric transport and deposition in areas of low SPM.

3.2 Sediment pore water

PAH

- Concentrations are generally high at stations in Norway. The pattern is more pronounced for heavier compounds (e.g. Indeno(1,2,3-cd)pyrene, Benzo(ghI)perylene, Benzo(a)pyrene, Benz(a)anthracene), possibly reflecting sources of heavy PAHs from aluminium smelters.
- There is a tendency for higher concentrations of lighter compounds (e.g. Acenaphtene, Fluorene) in areas likely to receive petrogenic inputs, such as Aberdeen harbour and Scheldt (Antwerp).
- In the Scheldt area, concentrations generally decrease in a westerly direction out of the estuary and away from river inputs

CBs

- There are high concentrations in the Seine and Scheldt estuaries, where it is known that inputs occur.
- Concentrations in Norway and Scotland are low, and these areas are likely to be remote from inputs.
- The relative concentrations in Vigo, Spain increase with increasing degree of chlorination (44, 101, 153, 187,).

HCB

- HCB is prominent in 1 out of 2 samples from the Kiel area, and low in Western Scotland and Portugal.

4 Further work on PSTS and other perspectives for the future

As discussed earlier, the full set of data for PSTS is not yet available. The target is to complete all analyses and for them to be submitted to the central laboratory by the end of April. Once this has been completed it will be possible to address outstanding aspects of the objectives, including:

- Intercomparisons between laboratories;
- Validation of the water sampling through combination of analyses of mussels and PS in water;
- Validation of the pore water (sediment) sampling through combination of analyses of worms and PS in sediment;
- More complete sets of field data and more detailed interpretation of the field data;
- Comparisons of water and pore water analyses from the same location.

Opportunities will be sought to communicate the results more widely. Firstly, Theme Session J at the ICES ASC07 is concerned with the application of passive samplers and it is hoped that several papers will be presented in PSTS. Publication in the open literature will also be an objective.

Already it is possible to see some themes emerging from the practical experience gained through PSTS. Firstly, the selection of PRCs is very important. They must cover the necessary range of K_{OW} values, be compatible with routine analytical procedures for target contaminants (such as CBs and PAHs), not degrade during the exposure period, and not be found in the environment. Individual laboratories have additional factors to consider, such as avoidance of interference with internal standards or recovery standards. Analytical comments of this type will be collated and reviewed when all data have been received.

One of the difficulties encountered is the low rate of sampling (as low as 3 litres per day) at some sampling points where water movements are weak. Weak currents result in a relatively thick diffusive boundary layer around the PS, and reduce the rate of transfer of contaminants to the PS. If it was possible to artificially maintain the sampler in motion (e.g. spin a disk of rubber) this could reduce the problem. However, so far the energy requirements for this have not been solved.

Silicone rubber PS are not particularly suitable for more polar compounds. Other materials may be more suitable, but in many cases it may be simpler to analyse the water directly as the compounds will partition more strongly into the water phase than, say, CBs or PAHs.

It is now necessary to seek other opportunities for the application and development of passive sampling. Some national projects are emerging that use passive samplers, and this is to be encouraged. In addition, the proposed NSHealth/ICON project might be a vehicle for quite widespread deployment of passive samplers over the OSPAR area.

OSPAR has so far paid relatively little attention to water sampling in its monitoring and assessment activities. Poor detection limits in relation to environmental concentrations, high inter-sample variability of water samples, and the inability of water analyses to reflect the pollution hazard presented by contaminants in water were significant considerations in OSPAR decisions to concentrate contaminants monitoring on sediment and biota as being at the time a more effective approach to monitoring the consequences of control measures. Passive sampling holds out the prospects that these difficulties may now be less significant and it may be that the previous decisions could be reviewed in the light of OSPAR long term objectives for contaminants in the marine environment.

Normalisation of contaminant concentrations in sediments has been used to reduce the influence of gross changes in sediment composition between samples and sites, in the hope that polluted sediments might be more clearly recognized. The application of passive sampling of sediments directly addresses the potential biological impact of contaminated sediments and therefore opens new opportunities in the assessment of sediment quality.

Other possible areas of application include the EU Water Framework Directive and the emerging Marine Strategy Directive.

Annex 9: Technical Annex : Polybrominated diphenyl ethers (PBDEs) in biota

Technical Annex : PBDEs in biota

1. Introduction

This annex provides advice on polybrominated diphenyl ether (PBDE) analysis for biota. The analysis of PBDEs in biota generally involves extraction with organic solvents, clean-up (removal of lipid) and gas chromatographic separation with mass-spectrometric detection. All stages of the procedure are susceptible to insufficient recovery and/or contamination. Where possible, quality control procedures are recommended in order to check the method's performance. These guidelines are intended to encourage and assist analytical chemists to reconsider their methods and to improve their procedures and/or the associated quality control measures where necessary.

Polybrominated diphenyl ethers (PBDEs) constitute a group of additive flame retardants that are predominately found in electrical equipment, textiles and furniture. PBDEs are used as additives to polymers and resins and are thought to be more easily released to the environment compared to reactive flame retardants. PBDEs consist of two phenyl rings, connected by an ether bridge, each ring containing up to 5 bromine atoms. There are a possible 209 PBDE congeners depending on the position and number of bromines, with molecular weights ranging from 249 to 960 daltons. Congeners are named according to the International Union of Pure and Applied Chemistry (IUAPAC) numbering format developed for chlorobiphenyl (CB) congeners. However, PBDE technical mixtures used as flame retardants contain only a limited number of these congeners (~20). Commercial PBDE mixtures are classified according to the degree of bromination. The penta mix contains mainly tetra- to hexa-BDEs, the octa mix mainly hexa- to octa-BDEs and the deca mix containing mainly deca-BDE. Penta-BDE is primarily used in furniture and upholstery, octa-BDE in plastics, and deca-PBDEs in textiles and polymers. In the EU, a restriction on the use of the penta and octa technical mixture was put in place on 15 August 2004, restricting the use of the penta and the octa technical mixtures to a limit of 0.1% by mass for all articles placed in the market according to the European Directive 2003/11/EC[1], 24th amendment of 76/769/EEC.

PBDEs can be released to the environment during their production, while manufacturing other products, and during disposal of products containing these chemicals. In addition, PBDEs may continue to leak out of treated material and constitute a diffuse source of these compounds to the environment. Atmospheric transportation is a major pathway for PBDEs into the marine environment. Other possible pathways include direct discharge from point sources such as storm waters and waste water. PBDEs have been found to concentrate in the Arctic and bioaccumulate in native animals and humans.

Due to the similarity in structure between PBDEs and CBs, PBDEs are expected to persist in the marine environment and exhibit similar toxic properties. PBDEs have high (Log $K_{ow} > 4$) octanol water partition coefficients ranging from 4.3 for di-BDE to 10.33 for deca-BDE (Table A9.1). PBDEs are readily taken up by marine animals both across gill surfaces and from their diet, and may bioaccumulate.

2. Appropriate Species for Analysis of PBDEs

Guidance on the selection of appropriate species for contaminant monitoring is given in the JAMP guidelines. Other species such as sole, hake and oysters may also be appropriate. Existing data indicates that PBDE concentrations for shellfish are very low and, therefore, detecting long term trends may be difficult using these species. High trophic level organisms and lipid rich tissue will

accumulate higher levels of PBDEs and, therefore, may be more suitable for temporal trend monitoring.

3. Transportation

Fish samples should be kept cool or frozen (−20°C or lower) as soon as possible after collection. Live mussels should be transported in closed containers at temperatures between 5°C and 10°C, but preferably below 10°C. For live animals it is important that the transport time is short and controlled (e.g. maximum of 24 hours). Frozen fish samples should be transported in closed metal or glass (cleaned and pre-baked) containers at temperatures below −20°C.

4. Pre-treatment and Storage

4.1 Contamination

Sample contamination may occur during sampling, sample handling, pre-treatment and analysis, due to the environment, the containers or packing materials used, the instruments used during sample preparation, and from the solvents and reagents used during the analytical procedures. Controlled conditions are therefore required for all procedures, including the dissection of fish organs on-board ship. It is important that the likely sources of contamination are identified and steps taken to preclude sample handling in areas where contamination can occur. A ship is a working vessel and there can always be procedures occurring as a result of the day-to-day operations (deck cleaning, automatic overboard bilge discharges, etc.) which could affect the sampling process. One way of minimising the risk is to conduct dissection in a clean area, such as within a laminar-flow hood away from the deck areas of the vessel.

4.2 Shellfish

4.2.1 Depuration

Depending upon the situation, it may be desirable to depurate shellfish so as to void the gut contents and any associated contaminants before freezing or sample preparation. This is usually applied close to point sources, where the gut contents may contain significant quantities of PBDEs associated with food and sediment particles which are not truly assimilated into the tissues of the mussels. Depuration should be undertaken in controlled conditions and in filtered water taken from the sampling site; depuration over a period of 24 hours is usually sufficient. The aquarium should be aerated.

4.2.2 Dissection and storage

Mussels should be shucked live and opened with minimal tissue damage by detaching the adductor muscles from the interior of at least one valve. The soft tissues should be removed and homogenised as soon as possible, and frozen in glass jars (pre-baked at 450^{o}C) or aluminium tins at -20°C until analysis. When samples are processed, both at sea and onshore, the dissection must be undertaken by trained personnel on a clean bench wearing clean gloves and using clean stainless steel knives and scalpels. Stainless steel tweezers are recommended for holding tissues during dissection. After each sample has been prepared, all tools and equipment (such as homogenisers) should be cleaned by wiping down with tissue and solvent washed. Knives should only be sharpened using steel to prevent contamination of the blade from the oils used to lubricate sharpening blocks.

4.3 Fish

4.3.1 Dissection and storage

Ungutted fish should be wrapped separately in suitable material (e.g. solvent washed aluminium foil) and stored at < -20°C. If plastic bags or boxes are used, then they should be used as outer containers

only, and should not come into contact with tissues. Organ samples (e.g. liver) should be stored in solvent washed containers made of glass, stainless steel or aluminium, or should be wrapped in solvent washed aluminium foil. In the latter case, care should be taken that the capacity of the freezer is not exceeded. Cold air should be able to circulate between the samples in order that the minimum freezing time can be attained (maximum 12 hours). The individual samples should be clearly and indelibly labelled and stored together in a suitable container at a temperature of -20°C ± 5°C until analysis. If the samples are to be transported during this period (e.g. from the ship to the laboratory), then arrangements must be made which ensure that the samples do not thaw out during transport.

When samples are processed, both at sea and onshore, the dissection must be undertaken by trained personnel on a bench previously washed with detergent (e.g. Decon 90) wearing clean gloves and using solvent washed stainless steel knives and scalpels. Stainless steel tweezers are recommended for holding tissues during dissection. After each sample has been prepared, all tools and equipment (such as homogenisers) should be cleaned by wiping with tissue and rinsing with solvent.

4.3.2 Sub-sampling

When sampling fish muscle, care should be taken to avoid including any epidermis or subcutaneous fatty tissue in the sample. Samples should be taken underneath the red muscle layer. In order to ensure uniformity, the right side dorso-lateral muscle should be sampled. If possible, the entire right side dorsal lateral fillet should be homogenised and sub-samples taken for replicate PBDE determinations. If, however, the amount of material to be homogenised is too large, a specific portion of the dorsal musculature should be chosen. It is recommended that the portion of the muscle lying directly under the first dorsal fin is used in this case.

When dissecting the liver, care should be taken to avoid contamination from the other organs. If bile samples are to be taken then they should be collected first. If the whole liver is not to be homogenised, a specific portion should be chosen in order to ensure comparability.

When pooling of tissues (e.g. liver or muscle) is necessary, an equivalent quantity of tissue should be taken from each fish, e.g., 10% from each whole fillet.

5 Analysis

5.1 Precautionary Measures

Special precautions are required in the laboratory when analysing PBDEs due to their sensitivity to UV light. PBDEs are prone to photolytic degradation; if exposed to UV light debromination can occur, especially for BDE209 (Covaci *et al.,* 2003; de Boer and Wells, 2006). Therefore, incoming light to the laboratory should be minimised by placing UV filters on the windows and over fluorescent lightings, or by not using any artificial lighting within the laboratory. It is recommended that all calibration and spiking standards are prepared and stored in amber glassware.

The use of plastics, in the laboratory as well as during sampling, should be avoided as they can contain PBDEs. BDE209 can adsorb to dust particles and can be a source of contamination in the laboratory. Therefore, it is recommended that an ioniser be placed in the laboratory and the laboratory kept as dust free as possible. Heating of glassware in an oven (e.g. at 450°C overnight) can also be useful for removing PBDE contamination. In addition all glassware should be covered with aluminium foil to keep out any dust.

5.2 Solvent Purity and Blanks

BDE209 can stick to glassware (or any other chemically active sites). This can result in contamination of glassware. For work at low concentrations, the use of high-purity solvents is essential, particularly when large solvent volumes are being used for column clean-up. All batches of

solvents should be checked for purity by concentration of an aliquot of solvent by at least the same volume factor as used in the overall analytical procedure. Batches which show significant contamination, so as to interfere with analysis, should be rejected. All glassware should be solvent-rinsed immediately prior to use as it will collect contamination from the laboratory atmosphere during storage. Pre-cleaning of all reagents (alumina, silica, sodium sulphate, hydromatrix etc) is essential.

5.3 Preparation of materials

Solvents, reagents and adsorptive materials must be 'free' of PBDEs and other interfering compounds. If not, then they must be purified using appropriate methods. Reagents and absorptive materials should be purified by solvent extraction and/or by heating in a muffle oven as appropriate. Glass fibre materials (e.g. Soxhlet thimbles and filter papers used in pressurised liquid extraction (PLE)) should be cleaned by solvent extraction or pre-baked at 450^{o}C overnight. It should be borne in mind that clean materials can be re-contaminated by exposure to laboratory air, particularly in urban locations, and so the method of storage after cleaning is of critical importance. Ideally, materials should be prepared immediately before use, but if they are to be stored, then the conditions should be considered critically. All containers which come into contact with the sample should be made of glass or aluminium, and should be pre-cleaned before use. Appropriate cleaning methods would include washing with detergents, rinsing with water of known quality, and finally solvent rinsing immediately before use.

5.4 Lipid determination

The determination of the lipid content of tissues can be of use in characterising the samples. This will enable reporting concentrations on a wet weight or lipid weight basis. The lipid content should be determined on a separate subsample of the tissue homogenate, as some of the extraction techniques used routinely for PBDE determination (e.g., PLE with fat retainers, alkaline saponification) destroy or remove lipid materials. The total lipid content of fish or shellfish should be determined using the method of Bligh and Dyer (1959) as modified by Hanson and Olley (1963) or an equivalent method such as Smedes (1999). Extractable lipid may be used, particularly if the sample size is small and lipid content is high. It has been shown that if the lipid content is high (>5%) then this will be comparable to the total lipid.

5.5 Dry weight Determination

The dry weight of samples should be determined gravimetrically so that concentrations can also be expressed on a dry weight basis.

5.6 Extraction and clean-up

The similarity in structure of the PBDEs to CBs means that techniques used for the analysis of CBs may also be applied to the analysis of PBDEs (de Boer *et al.*, 2001). PBDEs are lipophilic and so are concentrated in the lipids of an organism. A range of extraction methods have been used for the extraction of PBDEs from biota. These include the more traditional methods such as Soxhlet and the newer automated methods such as pressurised liquid extraction (PLE). Supercritical fluid extraction (SFE) has also been applied to PBDE extractions, although reproducibility was poor compared to Soxhlet (Covaci *et al.,* 2003). However, most laboratories are still using the traditional Soxhlet extraction. For soxhlets, hexane/acetone mixtures or toluene (particularly for BDE209) have been shown to give the best recoveries for the extraction of PBDEs combined with an extraction time of between 6 and 24 h. Hexane/acetone mixtures or toluene are also used with PLE (if no fat retainers used) with an extraction time of ~ 10 min per sample. PLE or soxhlet are therefore the preferred methods with PLE having the advantage of using less solvent, being fully automated and taking less time than Soxhlet.

Tissue extracts will always contain many compounds other than PBDEs, and a suitable clean up is necessary to remove those compounds which may interfere with the subsequent analysis. Different techniques may be used, either singly or in combination, and the choice will be influenced by the selectivity and sensitivity of the final measurement technique and also by the extraction method employed. PBDEs are stable under acid conditions; therefore treatment with sulphuric acid or acid impregnated silica columns may be used in the clean-up. If Soxhlet extraction is used, then there is a much greater quantity of residual lipid to be removed before the analytical determination can be made than in the case of alkaline digestion. An additional clean-up stage may therefore be necessary. The most commonly used clean-up methods involve the use of alumina or silica adsorption chromatography, but gel permeation chromatography (GPC) is also employed. When using GPC the elution of PBDEs should be carefully checked particularly for BDE209. Destructive methods for lipid removal such as saponification have also been investigated; however this method can result in the degradation of the higher brominated PBDEs and, therefore is not recommended. When applying gel permeation chromatography (GPC), two serial columns are often used for improved lipid separation. Solvent mixtures such as dichloromethane/hexane or cyclohexane/ethyl acetate can be used as eluents for GPC. However, a second clean-up step is often required to separate the PBDEs from other orgnaohalogenated compounds. When silica columns are used, the PBDEs will elute in the second, more polar, fraction (along with the organochlorine pesticides). However, this will be dependent on the solvents used and the adsorbents and the degree of deactivation.

One advantage of using PLE extraction is that it is possible to combine the clean up with the extraction, especially where mass spectrometry will be used as the detection method. Methods have been developed by Lund University for online clean-up and fractionation of dioxins, furans and PCBs with PLE for food, feed and environmental samples (Sporring *et al.,* 2003). The first method utilises a fat retainer for the on-line clean-up of fat. Silica impregnated with sulphuric acid, alumina and florisil have all been used as fat retainers. A non-polar extraction solvent such as hexane should be used if fat retainers are used during PLE. This method can also be applied to the extraction of PBDEs. However, problems have been highlighted with BDE209 which can be lost during PLE extraction through adsorption on to the extraction system tubing. However, with careful optimisation it is possible to use PLE for BDE209. Losses of BDE209 may be accounted for by using labeled BDE209 as an internal standard.

5.7 Pre-concentration

Turbo-vap sample concentrators can be used to reduce solvent volume. This is a rapid technique, but needs to be carefully optimised and monitored to prevent both losses (both of volatiles and solvent aerosols) and cross-contamination. The use of rotary-film evaporators is more time consuming but more controllable However, evaporation of solvents using this technique should be performed at low temperature (water bath temperature of $\leq 30°C$) and under controlled pressure conditions, in order to prevent losses of the more volatile PBDEs. For the same reasons, evaporation to dryness should be avoided at all costs. Syncore systems are also more controllable but as rapid as Turbo-vaps and have the advantage of automatically rinsing down the sides of the vial (if the flushback module fitted) while concentrating. Again water-bath temperatures should be minimised to prevent losses. When reducing the sample to the required final volume, solvents can be removed by a stream of clean nitrogen gas. Suitable solvents for injection into the gas chromatograph (GC) include hexane, heptane, toluene and *iso*-octane.

5.8 Selection of PBDEs to be determined

PBDE technical mixtures used as flame retardants contain only a limited number of the possible 209 congeners (~20). The penta mix contains mainly tetra- to hexa-BDEs, the octa mix mainly hexa- to octa-BDEs and the deca mix containing mainly deca-BDE. Nine BDE congeners have been detected in the penta mix, the major ones being BDE47 (37%) and BDE99 (35%). The octa mix contains

hexa- to octa-brominated congeners, with the main congener being BDE183, a hepta-brominated congener. The deca mix contains 98% decaBDE (BDE209).

PBDE congeners currently analysed vary considerably, however the congeners found in environmental samples are relatively consistent. Most laboratories analyse for the penta-mix compounds, tetra- to hexa-BDEs. In addition, these congeners are thought to be the most toxic and likely to bioaccumulate. In biota the dominant congeners are normally BDE47, 99, 100, 153 and 154. BDE 209 is less frequently measured, due to the analytical difficulties. It is rarely found in biota, but can degrade to lower brominated BDEs. Law *et al*. (2006) proposed a minimum congener set for use when determining BDEs to cover all three technical mixtures and what is commonly found in biota and sediment. This list consisted of BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183 and BDE209. This list is consistent with the congeners required by the QUASIMEME Scheme for biota and are routinely measured by the majority of laboratories. However, it is apparent that other congeners are found in marine samples (e.g. BDE 66 and 85) and so should also be analysed.

Standards are available for all these congeners. Table A9.1 lists the PBDEs most commonly monitored

Table A9.1 Congeners commonly monitored in environmental samples along with their degree of bromination, chemical name and the octanol water partition coefficient (Log K_{OW}), where available (Braekevelt *et al.*).

PBDE CONGENER	NUMBER OF BR	NAME	LOG K_{OW}
BDE17	3	2,2',4-tribromodiphenyl ether	5.74
BDE28*	3	2, 4,4'-tribromodiphenyl ether	5.94
BDE75	4	2, 4,4', 6-tetrabromodiphenyl ether	
BDE49	4	2, 3,4, 5'-tetrabromodiphenyl ether	
BDE71	4	2, 3', 4', 6-tetrabromodiphenyl ether	
BDE47*	4	2, 2',4, 4'-tetrabromodiphenyl ether	6.81
BDE66	4	2, 3',4, 4'-tetrabromodiphenyl ether	
BDE77	4	3, 3',4, 4'-tetrabromodiphenyl ether	
BDE100*	5	2, 2',4, 4', 6-pentabromodiphenyl ether	7.24
BDE119	5	2, 3',4, 4', 6-pentabromodiphenyl ether	
BDE99*	5	2, 2',4, 4', 5-pentabromodiphenyl ether	7.32
BDE85	5	2, 2',3, 4, 4'-pentabromodiphenyl ether	7.37
BDE154*	6	2, 2',4, 4', 5, 6'-hexabromodiphenyl ether	7.82
BDE153*	6	2, 2',4, 4', 5, 5'-hexabromodiphenyl ether	7.90
BDE138	6	2, 2',3, 4, 4', 5'-hexabromodiphenyl ether	
BDE190	7	2,3,3',4,4',5,6-heptabromodiphenyl ether	
BDE183*	7	2,2',3,4,4',5',6-heptabromodipheny l ether	8.27
BDE209*	10	Decabromodiphenyl ether	10.33

*** Congeners proposed by Law *et al.* as a minimum congener set for use when determining BDEs; they are also included in the QUASIMEME scheme**

5.9 Instrumental determination of PBDEs

Splitless, pulsed-splitless, programmed temperature vaporiser (PTV) and on-column injectors have been used for the determination of PBDEs, all of which are capable of yielding good results. Automatic sample injection should be used wherever possible to improve the reproducibility of injection and the precision of the overall method. For PBDE analysis, the cleanliness of the liner is very important if adsorption effects and discrimination are to be avoided, and the analytical column should not contain active sites to which PBDEs, particularly BDE209, can be adsorbed. Helium is

the preferred carrier gas, and only capillary columns should be used. Mainly non-polar columns are used, e.g. HT-8, DB1701 and STX-500 (DB1 is usually used for BDE209) Korytar *et al*. (2005) provide comprehensive information on various capillary columns used for PBDE analysis. Baseline separation should be achievable for all BDEs listed in Table A9.1. However, BDE31 may coelute with BDE28. Because of the wide boiling range of the PBDEs to be determined and the surface-active properties of the higher PBDEs, the preferred column length is 25–50 m, with an internal diameter of 0.1 mm to 0.3 mm. Film thicknesses around 0.2 μm are generally used.

BDE209 can be measured in the same run but will give a smaller and broader peak compared to other PBDEs. Detection limits will be approximately 10 fold higher for BDE209. Since the retention time is long, the determination of BDE209 is often done separately using thinner films (0.1 μm) and/or a shorter column, both of which have been found to improve the detection of BDE209.

5.9.1 Detection Methods

Either gas chromatography- mass spectrometry (GC-MS) or GC- MS-MS (ion trap or triple quadropole) should be used. GC-ECD is rarely used due to the limited linear range, and lack of selectivity. If GC-ECD is used then the clean-up will need to separate out all other organohalgenated compounds which may give co-elution problems. Both high and low resolution GC-MS can be used in conjunction with either electron ionisation (EI) or electron capture negative ionisation (ECNI). Although gas chromatography-high resolution mass spectrometry with electron impact ionisation (GC-HRMS) is the best method to unambiguously identify and quantify PBDEs in environmental samples, the expense and limited availability means that most laboratories use low resolution GC-MS normally in ECNI mode. Lower brominated PBDEs (mono- and di-BDEs) show better sensitivity in EI mode. However, the higher brominated PBDEs (> 3 bromines) give better sensitivity using the ECNI mode; limits of detection for these congeners are approximately 10 fold lower in ECNI compared to EI. ECNI shows improved sensitivity compared to positive impact chemical ionisation (PCI). Therefore, GC-ECNI-MS is used most frequently for the analysis of PBDEs in environmental samples. Either ammonia or methane may be used as the reagent gas when using chemical ionisation.

5.9.2 GC-MS

The base ions detected using NCI are the bromine ions (*m/z* = 79/81) for the tri- to hepta-BDEs. BDE congeners show the typical ^{79}Br (50.5%) and ^{81}Br (49.5%) isotope distribution pattern. One of the drawbacks of the CI mode is that isotopically labelled standards (^{13}C) cannot be used as internal standards for quantification purposes when only the bromide ions are monitored. However, mono fluorinated BDEs may be used as internal standards. Alternatively using GC-ECNI-MS a recovery standard can be added prior to extraction. CB198 and other halogenated compounds not present in environmental samples can be used as recovery standards. Larger fragment ions, necessary for confirmation, are only found for BDE209. These are formed by the cleavage of the ether bond to give the pentabromo phenoxy ion (*m/z* = 484/486). In general an internal standard method should be used for the quantification of PBDEs.

One advantage of using EI is that ^{13}C labelled internal standards may be used. The major ions formed in EI mode are the molecular ions which can be used for identification and quantification purposes. Other fragment ions are also formed in EI mode which can be used as confirmatory ions.

5.9.3 Possible pitfalls and solutions

Degradation of PBDEs, particularly BDE209, can occur on the GC. The presence of a hump or rising baseline before BDE209 is an indication of degradation during injection, whereas the presence of lower brominated BDE (nona-, octa- and eventually other lower brominated BDEs) indicates possible degradation during extraction and clean-up. To minimise this, the GC liners and injection syringe should be changed regularly. Silanising both the syringe and liner may help. When using on-column injection, the choice of retention gap can also have an effect on the degradation of BDE209 during analysis. Deactivated fused silica retention gaps are often used. The QUASIMEME (Quality

Assurance of Information for Marine Environmental Monitoring) external quality assurance scheme has also highlighted the difficulties with the analysis of BDE209 with CV% for this congener ranging from 40–256%. As a result, many laboratories do not analyse for BDE209.

6. Calibration and Quantification

6.1 Standards

Standard solutions of known purity should be used for the preparation of calibration standards. If the quality of the standard materials is not guaranteed by the producer or supplier (as for certified reference materials), then it should be checked by GC-MS analysis. In addition, certified standard solutions are available from QUASIMEME and other suppliers for cross-checking. Calibration standards should be stored in the dark because some PBDEs are photosensitive, and ideally solutions to be stored should be sealed in amber, glass ampoules. Otherwise, they can be stored in a refrigerator in stoppered measuring cylinders or flasks that are gas tight to avoid evaporation of the solvent during storage.

Ideally, internal standards should fall within the range of the compounds to be determined, and should not include compounds which may be present in the samples. A range of ^{13}C-labelled PBDEs are available for use as internal standards in PBDE analysis using GC-EIMS. However, when using GC-ECNI-MS these are of little value as, for the majority of congeners, only the bromine ions can be monitored. For BDE209 a high molecular weight fragment is formed during GC-ECNI-MS and, therefore, ^{13}C labelled BDE209 should be used. When GC-ECNIMS is used mono fluorinated BDEs may be used as internal standards or a recovery standard added to each sample prior to extraction and the recovery calculated as a check on the method.

6.2 Calibration

Multilevel calibration with at least five calibration levels is preferred to adequately define the calibration curve. In general, GC-MS calibration is linear over a considerable concentration range but exhibits non-linear behaviour when the mass of a compound injected is low due to adsorption. The use of a syringe standard is recommended, for example BDE190. Quantification should be conducted in the linear region of the calibration curve, or the non-linear region must be well characterised during the calibration procedure. Internal standardisation should be used for the quantification of PBDEs.

7. Analytical Quality Control

Planners of monitoring programmes must decide on the accuracy, precision, repeatability, and limits of detection and determination which they consider acceptable. Achievable limits of determination for each individual component are as follows:

- for GC-ECNI-MS measurements: 0.05 μg kg^{-1} wet weight for tri- to hepta-BDEs and 0.50 μg kg^{-1} wet weight for BDE209;
- for GC-EIMS: 0.5 μg kg^{-1} wet weight.
- for high resolution GC-MS: 0.02 ng kg^{-1} wet weight for tri- to hepta-BDEs and 0.5 ng kg^{-1} wet weight for BDE209.

A procedural blank should be measured with each batch of samples, and should be prepared simultaneously using the same chemical reagents and solvents as for the samples. Its purpose is to indicate sample contamination by interfering compounds, which will result in errors in quantification. Recoveries should be checked for all samples. Recoveries should be between 70 and 120% if not samples should be repeated. The procedural blank is also very important in the calculation of limits of detection and limits of quantification for the analytical method. In addition, a

laboratory reference material (LRM) or certified reference material (CRM) should be analysed within each sample batch. The LRM must be homogeneous and well-characterised for the determinands of interest within the analytical laboratory. Ideally the LRM or CRM should be of the same matrix type (e.g., liver, muscle, mussel tissue) as the samples, and the determinand concentrations should be in the same range as those in the samples. The data produced for the LRM or CRM in successive sample batches should be used to prepare control charts. It is also useful to analyse the LRM or CRM in duplicate from time to time to check within-batch analytical variability. The analysis of an LRM is primarily intended as a check that the analytical method is under control and yields acceptable precision. A CRM may be analysed periodically in order to check the method bias. CRMs certified for PBDEs are available (Wise et al.). At regular intervals, the laboratory should participate in an intercomparison or proficiency exercise in which samples are circulated without knowledge of the determinand concentrations, in order to provide an independent check on performance.

8. Data Reporting

The calculation of results and the reporting of data can represent major sources of error. Control procedures should be established in order to ensure that data are correct and to obviate transcription errors. Data stored on databases should be checked and validated, and checks are also necessary when data are transferred between databases. If possible data should be reported in accordance with the latest ICES reporting formats.

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Annex 10: Technical Annex : Hexabromocyclododecane (HBCD) in biota

Technical Annex : Hexabromocyclododecane (HBCD) in biota

1. Introduction

This annex provides advice on hexabromocyclododecane (HBCD) analysis for biota. The analysis of HBCD in biota generally involves extraction with organic solvents, clean-up (removal of lipid) and either gas chromatographic separation with mass-spectrometric (MS) detection or liquid chromatography with MS detection. All stages of the procedure are susceptible to insufficient recovery and/or contamination. Where possible, quality control procedures are recommended in order to check the method's performance. These guidelines are intended to encourage and assist analytical chemists to reconsider their methods and to improve their procedures and/or the associated quality control measures where necessary.

HBCD is produced by the bromination of cycldodec-1,5,9-triene and has been used since the late 1970s. HBCD is an additive flame retardant that is predominately used in foams and expanded polystyrene and in textile back coatings. HBCD can be released to the environment during its production and while manufacturing other products, and during disposal of products containing this chemical. In addition, HBCD may continue to leak out of treated material and constitute a diffuse source of this compound to the environment. Atmospheric transportation is thought to be a major pathway for HBCD into the marine environment; in addition, point sources may exist. HBCD has been found in remote areas of Sweden and Finland and in the Arctic.

Theoretically, there are sixteen possible stereoisomers of HBCD; 6 enantiomeric pairs and 4 meso forms. However, in technical HBCD mixtures mainly three of the 6 enatiomeric pairs are found, namely α-, β- and γ-HBCD, with the dominant isomer being γ-HBCD (Law *et al.*, 2005). In sediment the γ- isomer also dominates but in biota the major isomer is α-HBCD. β-HBCD is always a minor component. HBCD has a high octanol water partition coefficient (Log K_{ow} = 5.8) and, the potential to bioaccumulate.

2. Appropriate Species for Analysis of HBCD

Guidance on the selection of appropriate species for contaminant monitoring is given in the JAMP guidelines. Other species such as sole, hake and oysters may also be appropriate. Existing data indicates that HBCD concentrations for shellfish are very low and, therefore, detecting long term trends may be difficult using these species. High trophic level organisms and lipid rich tissue will accumulate higher levels of HBCD and, therefore, may be more suitable for temporal trend monitoring.

3. Transportation

Fish samples should be kept cool or frozen (at a temperature of -20°C or lower) as soon as possible after collection. Live mussels should be transported in closed containers at temperatures between 5°C and 10°C. For live animals it is important that the transport time is short and controlled (e.g. maximum of 24 hours). Frozen fish samples should be transported in closed metal or glass (cleaned and pre-baked) containers at temperatures below -20°C.

4. Pre-treatment and Storage

4.1 Contamination

Sample contamination may occur during sampling, sample handling, pre-treatment and analysis, due to the environment, the containers or packing materials used, the instruments used during sample preparation, and from the equipment, solvents and reagents used during the analytical procedures. Controlled conditions are therefore required for all procedures, including the dissection of fish on-board ship. It is important that the likely sources of contamination are identified and steps taken to preclude sample handling in areas where contamination can occur. A ship is a working vessel and there can always be procedures occurring as a result of the day-to-day operations (deck cleaning, automatic overboard bilge discharges, etc.) which could affect the sampling process. One way of minimising the risk is to conduct dissection in a clean area, such as within a laminar-flow hood, away from the deck areas of the vessel.

4.2 Shellfish

4.2.1 Depuration

Depending upon the situation, it may be desirable to depurate shellfish so as to void the gut contents and any associated contaminants before freezing or sample preparation. This is usually applied close to point sources, where the gut contents may contain significant quantities of HBCD associated with food and sediment particles which are not truly assimilated into the tissues of the mussels. Depuration should be undertaken in controlled conditions and in filtered water taken from the sampling site; depuration over a period of 24 hours is usually sufficient. The aquarium should be aerated and temperature controlled?

4.2.2 Dissection and storage

Mussels should be shucked live and opened with minimal tissue damage by detaching the adductor muscles from the interior of at least one valve. The soft tissues should be removed and homogenised as soon as possible, and frozen in solvent washed glass jars (pre-baked at 450^{o}C) or aluminium tins at −20°C until analysis.

When samples are processed, both at sea and onshore, the dissection must be undertaken by trained personnel on a clean bench wearing clean gloves and using clean stainless steel knives and scalpels. Stainless steel tweezers are recommended for holding tissues during dissection. After each sample has been prepared, all tools and equipment (such as homogenisers) should be cleaned by wiping down with tissue and solvent washed. Knives should only be sharpened using steel to prevent contamination of the blade from the oils used to lubricate sharpening blocks.

4.3 Fish

4.3.1 Dissection and storage

Ungutted fish should be wrapped separately in suitable material (e.g. aluminium foil) and frozen. If plastic bags or boxes are used, then they should be used as outer containers only, and should not come into contact with tissues. Organ samples (e.g. livers) should be stored in solvent washed containers, made of glass, stainless steel or aluminium, or should be wrapped in pre-cleaned aluminium foil. Cold air should be able to circulate between the samples in order that the minimum freezing time can be attained (maximum 12 hours). The individual samples should be clearly and indelibly labelled and stored together in a suitable container at a temperature of -20°C until analysis. If the samples are to be transported during this period (e.g. from the ship to the laboratory), then arrangements must be made which ensure that the samples do not thaw out during transport.

When samples are processed, both at sea and onshore, the dissection must be undertaken by trained personnel on a bench previously washed with detergent (e.g. Decon 90) wearing clean gloves and

using solvent washed stainless steel knives and scalpels. Stainless steel tweezers are recommended for holding tissues during dissection. After each sample has been prepared, all tools and equipment (such as homogenisers) should be cleaned by wiping with tissue and rinsing with solvent.

4.3.2 Sub-sampling

When sampling fish muscle, care should be taken to avoid including any epidermis or subcutaneous fatty tissue in the sample. Samples should be taken underneath the red muscle layer. In order to ensure uniformity, the right side dorso-lateral muscle should be sampled. If possible, the entire right side dorsal lateral fillet should be homogenised and sub-samples taken for replicate HBCD determinations. If, however, the amount of material to be homogenised is too large, a specific portion of the dorsal musculature should be chosen. It is recommended that the portion of the muscle lying directly under the first dorsal fin is used in this case.

When dissecting the liver, care should be taken to avoid contamination from the other organs. If bile samples are to be taken then they should be collected first. If the whole liver is not to be homogenised, a specific portion should be chosen in order to ensure comparability. When pooling of tissues is necessary, an equivalent quantity of tissue should be taken from each fish, e.g. 10 % from each whole fillet.

5 Analysis

5.1 Solvent Purity and Blanks

For work at low concentrations, the use of high-purity solvents is essential and particularly when large solvent volumes are being used for extraction and column clean-up. All batches of solvents should be checked for purity by concentration of an aliquot of solvent by at least the same volume factor as used in the overall analytical procedure. Batches which show significant contamination, which will interfere with analysis, should be rejected. All glassware should be solvent-rinsed immediately prior to use as it will collect contamination from the laboratory atmosphere during storage. Heating of glassware in an oven (e.g. at 450°C for 24 hours) can also be useful in removing contamination. Pre-cleaning of all reagents (alumina, silica, sodium sulphate, hydromatrix etc) is essential.

5.2 Preparation of materials

Solvents, reagents and adsorptive materials must be free of HBCD and other interfering compounds. If not, then they must be purified using appropriate methods. Reagents and absorptive materials should be purified by solvent extraction and/or by heating in a muffle oven as appropriate. Glass fibre materials (e.g. Soxhlet thimbles and filter papers used in pressurised extraction (PLE)) should be cleaned by solvent extraction and/or pre-baked at 450^{o}C overnight. It should be borne in mind that clean materials can be re-contaminated by exposure to laboratory air, particularly in urban locations, and so storage after cleaning is of critical importance. Ideally, materials should be prepared immediately before use, but if they are to be stored, then the conditions should be considered critically. All containers which come into contact with the sample should be made of glass or aluminium, and should be pre-cleaned before use. Appropriate cleaning methods would include washing with detergents, rinsing with water and finally solvent rinsing immediately before use.

5.3 Lipid determination

The determination of the lipid content of tissues can be of use in characterising the samples. This will enable reporting concentrations on a wet weight or lipid weight basis. The lipid content should be determined on a separate subsample of the tissue homogenate, as some of the extraction techniques used routinely for HBCD determination (e.g. PLE with fat retainers) destroy or remove lipid materials. The total lipid should be determined using the method of Bligh and Dyer (1959) as

modified by Hanson and Olley (1963) or an equivalent method such as Smedes (1999). Extractable lipid may be used, particularly if the sample size is small and lipid content is high. It has been shown that if the lipid content is high (>5%) then this will be comparable to the total lipid. Gravimetric determination of the dry matter content of the sample is recommended.

5.4 Extraction and clean-up

HBCD is lipophilic and, therefore, can concentrate in the lipids of an organism. HBCD can be extracted using extraction techniques used for other lipophilic, non-polar compounds such as CBs and PBDEs (Morris *et al.*, 2006). A range of extraction methods have been used for the extraction of HBCD from biota. These include the more traditional methods such as Soxhlet or Ultra Turrax homogenisation and newer automated methods such as pressurised liquid extraction (PLE). However, most laboratories are still using the traditional Soxhlet extraction. For Soxhlets, hexane/acetone mixtures are commonly used combined with an extraction time of between 6 and 24 hrs. Hexane/acetone mixtures are also used with PLE (if no fat retainers are used) with an extraction time of ~ 10 min per sample. PLE or Soxhlet are therefore the preferred methods with PLE having the advantage of using less solvent, being fully automated and taking less time than Soxhlet.

Tissue extracts will always contain many compounds other than HBCD, and a suitable clean up is necessary to remove those compounds which may interfere with the subsequent analysis. Different techniques may be used, either singly or in combination, and the choice will be influenced by the selectivity and sensitivity of the final measurement technique and also by the extraction method employed. If Soxhlet extraction is used, then there is a much greater quantity of residual lipid to be removed before the analytical determination can be made. The most commonly used clean-up methods involve the use of alumina or silica adsorption chromatography, but gel permeation chromatography (GPC) can also be employed. For GPC, two serial columns are often used for improved lipid separation. Solvent mixtures such as dichloromethane/hexane or cyclohexane/ethyl acetate can be used as eluents for GPC. Depending on the detection method being used and the lipid content of the sample it may be necessary to use a second clean-up step to separate HBCD from other interfering compounds. HBCD is stable under acid conditions; therefore treatment with sulphuric acid or acid impregnated silica columns may be used in the clean-up.

One advantage of using PLE extraction is that it is possible to combine the clean up with the extraction, especially where mass spectrometry is being used as the detection method. Methods have been developed by Lund University for online clean-up and fractionation of dioxins, furans and PCBs with PLE for food, feed and environmental samples (Sporring *et al.* 2003). The first method utilises a fat retainer for the on-line clean-up of fat. Silica impregnated with sulphuric acid, alumina and florisil have all been used as fat retainers. A non-polar extraction solvent such as hexane should be used if fat retainers are used during PLE. This method can also be applied to the extraction of HBCD. However, if tetrabromobisphenol A (TBBP-A) is also to be extracted, this method is not possible due to retention on the fat retainer.

5.5 Pre-concentration

Turbo-vap sample concentrators can be used to reduce solvent volume. The use of rotary-film evaporators is more time consuming but more controllable. Buchi Syncore systems are also more controllable and are as rapid as Turbo-vaps and have the advantage of automatically rinsing down the sides of the vial (if flushback module fitted) while concentrating. In contrast to PBDEs and CBs where the evaporation steps have to be carefully optimised to avoid losses of the lower brominated/chlorinated compounds, loss of HBCD during concentrations is not an issue. When reducing the sample to a final volume, solvents can be removed by a stream of clean nitrogen gas. Suitable solvents for injection into the gas chromatograph (GC) include pentane, hexane, heptane and *iso*-octane. For analysis by LC-MS samples are normally taken to dryness and reconstituted in methanol.

5.6 Instrumental determination of HBCD

Analysis of HBCD is less straightforward than the analyses of PBDEs and a different approach is normally required. HBCD can be determined by gas chromatography- mass spectrometry (GC-MS), but the analysis can be problematic. The uncertainty is greater than for PBDEs analysed using the same method (Covaci *et al.*, 2003). In addition, the three main HBCD diastereoisomers found in technical mixtures cannot be separated by GC and a total concentration only can be determined. A liquid chromatography (LC) method is required to separate the three diastereoisomers, with separation of enantiomers being possible with a chiral HPLC column.

5.6.1 GC-MS

Few publications analyse HBCD along with the PBDEs by GC-MS, although it has been done using both GC- electron capture negative ionisation (ECNI) and high resolution GC-MS. GC-electron capture detection (ECD) is rarely used due to the limited linear range, and lack of selectivity. If GC-ECD is used then the clean-up will need to separate out all other organohalgenated compounds which may give co-elution problems. Splitless, pulsed-splitless, programmed temperature vaporiser (PTV) and on-column injectors have been used for the determination of HBCD. Automatic sample injection should be used wherever possible to improve the reproducibility of injection and the precision of the overall method. Mainly non-polar columns are used, for example HT-8, DB-5, STX-500. Both high and low resolution GC-MS can be used in conjunction with either electron ionisation (EI) or ECNI. Most laboratories using GC for HBCD use low resolution GC-MS normally in ECNI mode. ECNI shows improved sensitivity compared to EI or positive impact chemical ionisation (PCI). When GC-ECNI-MS is used, the bromine ion is monitored. One of the drawbacks of the CI mode is that isotopically labelled standards (^{13}C) cannot be used as internal standards for quantification purposes when only the bromine ions are monitored. Larger fragment ions, required for structural confirmation are not formed in ECNI mode. Either ammonia or methane may be used as the reagent gas when using chemical ionisation.

HBCD isomers interconvert at temperatures >160^{o}C, therefore the three HBCD diastereoisomers cannot be separated and a broad hump is obtained in the GC chromatogram. In addition, the three diastereoisomers will have different response factors and, therefore, the concentration of HBCD cannot be determined accurately by GC-MS (Wells and de Boer, 2006). Furthermore HBCD degrades at 240^{o}C, therefore, there may be significant losses of HBCD during GC analysis. Cold on-column injection, short GC columns and thin stationary films can minimise the degradation of HBCD. When analysing for HBCD by GC-MS the liner should be changed after each batch of samples to keep it as clean as possible. Co-elution of HBCD with certain PBDEs can also be a problem.

5.6.2 LC-MS

A reverse phase column should be used for analysis of HBCD by LC-MS. The three diastereoisomers found in the technical mixture should separate easily using a column such as a C_{18} and either methanol/water or acetonitrile/water, normally with ammonium acetate (10 mM), as the mobile phase. Typically the flow rate will be around 250 µl min^{-1} and a gradient programme will be required. HPLC with chiral columns such as permethylated β-cyclodextrin columns can also be used to separate the enantiomers of the α, β, γ-HBCD diastereoisomers. Either electrospray or atmospheric pressure chemical ionisation (APCI) can be used. However, electrospray is more sensitive and is therefore recommended. Clean-up of the samples before analysis is important to avoid matrix effects and ion suppression. The deprotonated molecular ion (*m/z* = 640.7) should be the major ion, fragment ions may also be identified to be used as qualifier ions. LC-MS has been reported to have poorer detection limits compared to GC-MS, with the sensitivity being approximately 10 times less than that of the GC-NCIMS method. Using LC-MS and with an injection volume of ~15 µl, it should be possible to detect around 0.5 ng on column (Morris *et al.*, 2004). LC-MS-MS can usually overcome the problem of higher detection limits.

6. Calibration and Quantification

6.1 Standards

HBCD standard solutions for each of the three major stereoisomers (α-, β- and γ-HBCD) of known purity should be used for the preparation of calibration standards. If the quality of the standard materials is not guaranteed by the producer or supplier (as for certified reference materials), then it should be checked by GC-MS analysis. In addition, certified standard solutions are available from QUASIMEME and other suppliers for cross-checking. Calibration standards should be stored in sealed amber glass ampoules. Otherwise, they can be stored in a refrigerator in stoppered measuring cylinders or flasks that are gas tight to avoid evaporation of the solvent during storage.

Ideally, internal standards should fall within the range of the compounds to be determined, and should not include compounds which may be present in the samples. Deuterated and ^{13}C-labelled HBCD standards are available for the three major diastereoisomers for use as internal standards in HBCD analysis using GC-EIMS or LC-MS. However, deuterated standards are less expensive and are therefore the preferred option. As HBCD is prone to ion suppression it is recommended that a labelled standard should be used for each isomer being analysed by LC-MS. When using GC-ECNI-MS these are of little value as only the bromine ions can be monitored. When GC-ECNI-MS is used for the analysis a recovery standard should be added to each sample prior to extraction and the recovery calculated as a check on the method.

6.2 Calibration

Multilevel calibration with at least five calibration levels is preferred to adequately define the calibration curve. In general, GC-MS calibration is linear over a considerable concentration range but exhibits non-linear behaviour when the mass of a compound injected is low due to adsorption. Quantification should be conducted in the linear region of the calibration curve, or the non-linear region must be well characterised during the calibration procedure. External standardisation is used for HBCD with GC-ECNI-MS as the bromine ions only are monitored. An internal standard method may be used when GC-EIMS or LC-MS is used.

7. Analytical Quality Control

Planners of monitoring programmes must decide on the accuracy, precision, repeatability, and limits of detection and determination which they consider acceptable. Achievable limits of determination for each individual component are as follows:

- for GC-ECNI-MS: 0.05 μg kg^{-1} wet weight;
- for LC-MS: 0.5 μg kg^{-1} wet weight;
- for LC-MS/MS: 0.05μg kg^{-1} wet weight.

A procedural blank should be measured with each batch of samples, and should be prepared simultaneously using the same chemical reagents and solvents as for the samples. Its purpose is to indicate sample contamination by interfering compounds, which will result in errors in quantification. The procedural blank is also very important in the calculation of limits of detection and limits of quantification for the analytical method. For GC-EIMS or LC-MS analysis, labelled standards can be added after or prior to extraction, whilst those from which the absolute recovery will be assessed are added prior to GC-MS injection. This ensures that the calculated HBCD concentrations are corrected for the recovery obtained in each case. For GC-ECNI-MS, recovery of HBCD should be checked and reported. In the case of GC-ECNI-MS a recovery standard such as CB198 should be added prior to extraction and the recovery calculated for each sample, by reference to an external standard.

In addition, a laboratory reference material (LRM) or certified reference material (CRM) should be analysed within each sample batch if available. The LRM must be homogeneous and well-characterised for the determinands of interest within the analytical laboratory. Ideally the LRM or CRM should be of the same matrix type (e.g., liver, muscle, mussel tissue) as the samples, and the determinand concentrations should be in the same range as those in the samples. The data produced for the LRM or CRM in successive sample batches should be used to prepare control charts. It is also useful to analyse the LRM or CRM in duplicate from time to time to check within-batch analytical variability. The analysis of an LRM is primarily intended as a check that the analytical method is under control and yields acceptable precision. A CRM may be analysed periodically in order to check the method bias. The availability of biota CRMs certified for HBCD is very limited. At regular intervals, the laboratory should participate in an intercomparison or proficiency exercise in which samples are circulated without knowledge of the determinand concentrations, in order to provide an independent check on performance.

8. Data Reporting

The calculation of results and the reporting of data can represent major sources of error. Control procedures should be established in order to ensure that data are correct and to obviate transcription errors. Data stored on databases should be checked and validated, and checks are also necessary when data are transferred between databases. If possible data should be reported in accordance with the latest ICES reporting formats.

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Annex 11: Overview of some national WFD monitoring activities for hazardous substances and physico-chemical parameters in transitional, coastal and territorial waters

Report on the developments in Water Framework Directive monitoring programmes for physico-chemical parameters (priority substances, other pollutants, nutrient status) in transitional and coastal waters. This will focus on providing information on the specific parameters being measured, the approach to monitoring hazardous substances (e.g. matrices, frequency, etc.), classification tools, and the extent of surveillance and operational programmes.

COUNTRY/REGION	DENMARK (KATRIN VORKAMP)		
No. of Surveillance monitoring sites	**Sediment: 35. Blue mussels: 53. Fish: 4**		
No of operational monitoring sites			
	Parameter	*Matrix*	*Frequency*
Parameter 1	PCB and OC pesticides	Sediment	Once in 6 years.
Parameter 2	PBDE	Sediment	
Parameter 3	PAH	Sediment	
Parameter 4	Alkyl-PAH	Sediment	
Parameter 5	TBT	Sediment	
Parameter 6	Hexachlorbutadien	Sediment	
Parameter 7	Metals	Sediment	
Parameter 8	PCB and OC pesticides	Blue mussels	3x in 6 years
Parameter 9	PBDE	Blue mussels	
Parameter 10	PAH	Blue mussels	
Parameter 11	Alkyl-PAH	Blue mussels	
Parameter 12	TBT	Blue mussels	
Parameter 13	Metals	Blue mussels	
Parameter 14	PCB and OC pesticides	Fish	Yearly
Parameter 15	Metals	Fish	
Physico-chemical parameters			
Parameter 1	Nutrients, oxygen	water	
Classification tools			

COUNTRY/REGION	GERMANY (ONLY BSH , NO NATIONAL PROGRAMME; NORBERT THEOBALD)		
No. of Surveillance monitoring sites	5–13 transitional locations (German Bight), 9 (Western Baltic Sea); 6 sed. Stations (GB)		
No of operational monitoring sites			
	Parameter	***Matrix***	***Frequency***
Parameter 1	PBDE (8)	sed	(s)*
Parameter 2	PAH (16)	Water; sed	2–3; 1
Parameter 3	Naphthalene	Water; sed	2–3; 1
Parameter 4	SCCP(total)	Sed	(s)*
Parameter 5	PCP	Water	1
Parameter 6	Nonylphenol, Octylphenol, DEHP	Water	(s)*
Parameter 7	Trichlorobenzenes (3)	Water	1
Parameter 8	Drins (3), DDTs(3), HCB, HCBD, Pentachlorbenzene	Water; sed.	1
Parameter 9	HCH's (4), Trifluralin	Water; sed.	2–3; 1
Parameter 10	Endosulfan (2) &, Chlorpyrifos	Water; sed.	1
Parameter 11	Atrazine, Simazine, Alachlor, Chlorfenvinfos, Isoproturon, Diuron	water	2–3
Parameter 12	TBT, DBT, MBT, TeBT, TPhT	water	1
	Cd,Cu,Hg,Ni,Pb	Water; sed.	3–4; 1
Physico-chemical parameters	Temp, PH, Salinity, O2, SPM,	water	4
Parameter 1	Total-P, Total-N	water	4
Classification tools			

(s)* : survey every second to 5th year

COUNTRY/REGION	SPAIN (CARMEN RODRIGUEZ)		
No. of Surveillance monitoring sites	17 coastal stations (9 areas)		
No of operational monitoring sites			
	Parameter	**Matrix**	**Frequency**
Physico-chemical parameters			
	Temperature, Salinity, dissolved O_2, fluorescence	water	12/year
	nitrate-nitrite, phosphate, silica, ammonia, Chlor a	water	12/year
Note	Stations are under the framework of a Monitoring Programme managed by the Central Government and not directly related to WFD (http://www.seriestemporales-ieo.net). As the responsabilities for transitional and coastal waters are transferred, many other monitoring programmes are being carried out by the regional administrations in 10 different coastal regions.		

COUNTRY/REGION	FINLAND (HARRI KANKAANPÄÄ)		
No. of Surveillance monitoring sites	10 in rivers (planned, not operational) + seven coastal regions (fish)		
No of operational monitoring sites	none		
Hazardous Substances	***Parameter***	***Matrix***	***Frequency***
Parameter 1	trace metals	river water	not decided
Parameter 2	alkylphenols,	river water	not decided
Parameter 3	pesticides/insecticides (ca. 100 different compounds	river water	not decided
Parameter 4	PAHs	river water	not decided
Parameter 5	phtalates	river water	not decided
Parameter 6	PBDEs	fish	biannual
	TBT, TPT (+ break-down products)	fish	biannual
Parameter 7	PAHs	sediment	not decided
Parameter 8	phtalates	sediment	not decided
Parameter 9	PBDEs	sediment	not decided
Parameter 10	TBT, TPT (+ break-down products)	sediment	not decided
Physico-chemical parameters	to be decided		
Parameter 1			
Classification tools	to be decided		
Notes	**In Finland the WPD involves the Finnish Environment Institute (FEI) and local environment centres, not the Finnish Insitute of Marine Research (FIMR). The FIMR will be focussing to comply with the requirements of the EU Marine Environment Directive. How this directive will affect monitoring of the marine environment is still unknown.** **The list of priority substances (organic compounds) of the WPD has been taken into account at FEI which will not begin monitoring of priority substances in 2007 yet. Instead, the FEI will carry out a one-year pilot survey in 10 rivers.**		

COUNTRY/REGION	FRANCE		
No. of Surveillance monitoring sites	66 coastal, 43 transitional (without La Réunion, West Indies and French Guyana)		
No of operational monitoring sites	not yet determined		
	Parameter	**Matrix**	**Frequency**
priority substances (list of 41 contaminants)		water and sediment and biota (1)	water : monthly (1 year/6) sediment and biota : once/6 years
OSPAR list	metals, HAP, organoCl	sediment and biota (2)	annual
specific contaminants (dir 76/464) = 113 substances	hydrophilic substances	water (3)	quarterly, 1/6 years
	hydrophobic substances	sediment and biota (3)	once a year, 1/6 years
Physico-chemical parameters			
interpretative parameters	temperature, salinity and turbidity		as the main parameter they are associated to (chemical or biological parameters)
oxygen	DO		every year, once / month, from june to september
nutrients	N-NH3, NO3+NO2, PO4, SIOH		evrey 3 years, monthly from november to february
Classification tools	a grid (5 classes) for dissolved oxygen, none for other physico-chemical parameters		

(1) for bioaccumulative contaminants, analysis in sediment or biota sample are done only on 25% of monitoring sites
(2) for OSPAR monitoring (french atlantic coasts), only 50% of surveillance monitoring sites will be sampled
(3) monitoring in 25% of surveillance monitoring sites

COUNTRY/REGION	IRELAND* (EVIN MCGOVERN)		
No. of Surveillance monitoring sites	12 coastal, 23 transitional		
No of operational monitoring sites	13 transitional		
Hazardous Substances	**Parameter**	**Matrix**	**Frequency**
Parameter 1	PBDEs	Water/biota/sediment	Water 12 pa once per cycle Sediment/biota –annual
Parameter 2	Alkyl phenols	Water	12 pa once per cycle
Parameter 3	Phthalates	Water	12 pa once per cycle
Parameter 4	PAH	Water/Sediment/biota	Water 12 pa once per cycle Sediment/biota –annual
Parameter 5	Organotins	Sediment	Annual
Parameter 6	Metals	Water/Sed/biota	Water 12 pa once per cycle Sediment/biota –annual
Parameter 7	Mercury	Water/Sed/biota	Water 12 pa once per cycle Sediment/biota –annual
Parameter 8	PCBs	Sed/biota	Annual
Parameter 10	Pesticides[#]	-	
Physico-chemical parameters			
Parameter 1	Dissolved nutrients (TOxN, Nitrite, Silicate, Ammonia, ortho-Phosphate)		At least quarterly.
	Total N & P		At least quarterly.
	DO, Salinity, temperature, fluorescence, turbidity/SPM		At least quarterly.
Classification tools	For physico-chemical parameters a project is underway to define numerical classification tools, e.g standards. For nutrients in transitional waters these will be salinity related		

*** The information presented represents current discussions but the details for TCW monitoring for priority substances have yet to be finalised**

 # Pesticides will not be given a high priority in TCW monitoring. This will be subject to ongoing review on the basis of findings from an extensive riverine monitoring network..

COUNTRY/REGION	NETHERLANDS (TON VAN DE SANDE)		
No. of Surveillance monitoring sites	17 estuarine and coastal locations (3 catchment area's)		
No of operational monitoring sites			
Hazardous Substances	**Parameter**	**Matrix**	**Frequency**
Parameter 1	PBDE (8)	water	12
Parameter 2	PAH (16)	water	12
Parameter 3	Benzene, Naphthalene, VCA(12)	water	12
Parameter 4	SCCP(total)	water	12
Parameter 5	PCP	water	12
Parameter 6	Nonylphenol, Octylphenol, DEHP	water	12
Parameter 7	Trichlorobenzenes (3)	water	12
Parameter 8	Drins (5), DDTs(6), Heptachlors(3) HCB, HCBD, Pentachlorbenzene	water	12
Parameter 9	HCH's (4), Endosulfan (2) & Trifluralin, Chlorpyrifos	water	12
Parameter 10	Atrazine, Simazine, Alachlor, Chlorfenvinfos, Isoproturon, Diuron	water	12
Parameter 11	TBT, TFT	water	12
Parameter 12	Cd,Cu,Hg,Ni,Pb	water	12
Physico-chemical parameters			
Parameter 1	Temp, PH, Salin, O2, SM, POC, DOC	water	12
Parameter 2	Total-P, Total-N	water	12
Classification tools			

COUNTRY/REGION	PORTUGAL (ANA CARDOSO)		
No. of Surveillance monitoring sites	All transitional and coastal areas (number?)		
No of operational monitoring sites			
Hazardous Substances	**Parameter**	**Matrix**	**Frequency**
Parameter 1	Benzo(a)pyrene, benzo(b)phluoranthene, benzo(k)phluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)perylene, fluoranthene	water	3x/year
Parameter 2	gHCH, HCB, HCBD, Drins (3), DDTs(6), alachlor, atrazin, simazin, ensossulphan (I/II), chlorphenvinfos, metolachlor, bentazon, 3,4-dichloroanilin, dimetoato, molinato, terbutylazin, propanil, trifluralin, antracen,	water	3x/year
Parameter 3	TBTs	water	3x/year
Parameter 4	Benzene, trichlorobenzene, perchloroethilene, 1,2-dichloroethane, naphthalene, noniphenol, octilphenol, pentachlorophenol, trichloromethan, dichloromethan, trichloroethilene, pentabromodiphenyl ether, chloroalcans C10-13	water	3x/year
Parameter 5	PCBs	water	3x/year
Parameter 6	Cd dissolved/total, Hg dissolved/total, Pb dissolved/total, Ni dissolved/total, Cu, Zn, Cr	water	3x/year
Physico-chemical parameters			
Parameter 1	Granulometric composition (sediments), Temp, pH, transparency/turbidity, Salin, O2, SM, CBO5, CQO, NO3, NO2, NH4, N/Ptotal, PO4, SiO2, Clo a	Water	3x/year
Classification tools			