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Executive summary

The Marine Chemistry Working Group [MCWG] (Co-Chairs Robin Law, UK, and Jacek Tronczynski, France) met at ICES Headquarters from 27–31 March 2006, along with WGBEC, WGMS and WGSAEM. Some issues of joint interest were discussed in subgroups comprising members of two or more working groups. The key outcomes from the terms of reference are described below.

Provide advice on whether the existing systems for monitoring dioxins in fish and shellfish for the purposes of safeguarding human health could be used to monitor trends in concentrations and/or spatial extent of dioxins in the marine environment

The group reviewed and discussed the extensive amount of data from surveys on dioxin and dioxin like PCB in fish, shellfish and fish products for the purposes of safeguarding human health available from UK, Sweden, Norway, Ireland and France. The timing of the surveys and the choice of products, species, tissues and sources are *ad-hoc* rather than regular and logically reflect the local/regional food market for each survey. In many reports no individual measurements but only ranges of concentration or TEQ values are given. In only some cases is it possible to trace back the fish/product samples to their exact origin at sea, and the samples are often collected from the consumer market (fishmongers and/or supermarkets). In addition, only edible tissues are analysed rather than those in which concentrations are likely to be highest (e.g. liver). The lack of information and control of key sample variables in these food-monitoring programmes and their *ad-hoc* nature make the data unsuitable for defining temporal and spatial trends. Retrospective monitoring of selected archived material from monitoring programmes can very well be used for temporal trend analysis as was shown by a paper from France.

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

Following the proposal made in 8.4 of the report of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (STGQAC) and following discussions between two of the group Co-Chairs, MCWG supports the suggestion that in future STGQAC are welcome to operate within MCWG.

MCWG also welcomed the proposal from STGQAC to elaborate technical notes on monitoring of brominated flame retardants (BFR) and organotins collaboratively. However, MCWG recommended a focus on monitoring in biota and sediment as proposed by OSPAR. Concerning organotin compounds, the existing OSPAR guideline on monitoring organotin compounds in sediment has to be taken into account and emphasis should be put on analysis in sediments and biota.

Assess the adequacy of the existing analytical methods for short-chain chlorinated paraffins, dioxins, toxaphene, perfluorinated compounds, BDEs and other brominated flame retardants for marine environmental assessment and provide guidance on the most appropriate techniques

Short-Chain Chlorinated Paraffins: SCCPs present many analytical challenges and it is not clear how many marine laboratories have capabilities for SCCP analysis. In addition to the information given in 2005, MCWG have been informed of new developments in the analysis of these compounds using multi-dimensional gas chromatography.

Dioxins and Dioxin-like PCBs): GC-HRMS remains the method of choice for dioxin analysis and is the only accepted analytical method for food safety analysis. However, this technique is expensive and not widely available to marine monitoring laboratories. MCWG agreed that GC-LRMS/MS is a promising technique for the analysis of dioxins in marine environmental monitoring. Any technique, should be acceptable if it is fit for the purpose (for example monitoring higher levels of dioxins as found in fish from the Baltic, or tissues containing higher levels), and has demonstrated adequate QA (e.g. as shown through adequate performance in round robin testing). Nonetheless, GC-HRMS is the preferred method and is still required for food compliance testing.

Coplanar PCBs: Certain non-*ortho* and mono-*ortho* CBs exhibit 'dioxin-like' toxicity (12 WHO-CBs) and some of these can exert toxicity at low concentrations (e.g. CB 126 a non-*ortho* CB). The above conclusions on analysis of dioxins could be considered applicable to the coplanar CBs. While GC-LRMSMS (NCI) would be appropriate for analysis of mono-*ortho* PCBs, GC-HRMS would be preferred for non-*ortho* PCBs, although LRMS/MS offers potential if stringent clean-up of sample extracts is applied.

Toxaphene: Toxaphene continues to present analytical challenges. In addition to GC-HRMS, a GC-ion trap MS/MS technique for the determination of six congeners in biota has been the subject of a successful inter-laboratory calibration of toxaphene in Canada. Five laboratories participated using different techniques including GC-LRMS and GC-ECD and the interlaboratory agreement was good. Information on toxaphene concentrations (3 congeners) in fish from European waters has been published.

Perfluorinated Compounds: The first global intercomparison exercise for perfluorinated compounds was carried out under the PERFORCE 6th Framework project (http://www.science.uva.nl/perforce). This was open to laboratories outside of the project consortium and results indicated problems with the analysis of PFOS and PFOA, especially for fish muscle. MCWG concluded that analysis of perfluorinated compounds is currently not routine and there are some problems with analysis of these compounds judging from the results of a recent intercomparison exercise in biota. Nonetheless, there is significant interest in these compounds and considerable work in progress on developing analytical methodology. A further intercomparison exercise is being developed

Brominated Flame Retardants: PBDEs: There is substantial data for BDEs in the marine environment and several MS based techniques have been employed. GC with ECNIMS detection is widely used as it is cost effective. However, the analysis of deca-BDE remains a problem as BDE 209 is thermally unstable (degrading during injection in heated injectors and on-column) and contamination is easily introduced during the analysis, both from foam-based materials within the laboratory and due to contamination of laboratory glassware.

HBCD and TBBP-A: HBCD can be analysed by HPLC-MS or GCMS. HPLC-MS analysis enables separation of the three diastereoisomers and this approach is recommended by MCWG. TBBP-A can also be analysed using the same HPLC-MS method. HBCD is becoming more important as, in the UK at least, concentrations in porpoise blubber began rising steeply after 2001. Intercomparison exercises for HBCD are needed in biota and sediments – in the past the level of participation has been too low. QUASIMEME has an exercise planned for 2006.

Critically review the new information on the use of membrane systems for sampling, and on their incorporation within national monitoring programmes

An intercomparison exercise is required in order to validate the applicability of passive sampling in different locations, and such an initiative will need to come from within ICES. Accordingly, WGMS and MCWG worked together to develop outline proposals for a trial survey. Technical guidelines will be prepared intersessionally, with the exercise timed to take place for a period of six weeks during the autumn (October onwards).

1 Opening of the meeting

The Co-Chairs (Robin Law (UK) and Jacek Tronczynski (France)) opened the meeting at 10.00 am on Monday 27 March 2006. The participants then introduced themselves and their affiliations and described their specific interests within the field of marine chemistry. Later in the meeting, the new ICES General Secretary, Gerd Hubold, welcomed the participants and wished them well in their deliberations. The List of Participants is given in Annex 1, and the Final Agenda in Annex 2. The ToR is given as Annex 3. Recommendations are listed in Annex 4, and the Action List is appended as Annex 5.

2 Adoption of the agenda

The agenda was adopted with one addition made during the meeting (Agenda Item 8.16) following a contact by the Norwegian Government to the ICES Secretariat.

3 Report of the 93rd ICES Statutory Meeting

A number of members of MCWG participated in Theme Session S on oil spills. In order to be able to respond to an OSPAR request via ACME, members of MCWG prepared a paper for the Theme Session S entitled “Assessing the long-term impact of oil spills: an examination of recent incidents”. No other items of specific interest to MCWG were identified.

4 Reports on Related Activities

4.1 OSPARCOM and HELCOM

All official requests from OSPARCOM or HELCOM which arose prior to the agenda have been included.

4.2 Intergovernmental Oceanographic Commission

In the past MCWG have received a report of relevant activities within the IOC from the ICES Hydrographer. In the absence of this input, information was sought from the IOC website. No recent relevant activities were noted. As no members of MCWG have regular contacts with IOC, we requested advice from ICES after MCWG2005 regarding the mechanism for updating us on IOC activities in the future in order that we may comment on them and take account of them within our work. As no advice has been received, this standing agenda item should be removed from future agendas, and only reinstituted if specific requests can be made, with reference to appropriate documentation.

4.3 Laboratory Performance Study QUASIMEME

Peter Korytár gave an update on QUASIMEME activities. From 1 April 2005, QUASIMEME has transferred to the University of Wageningen under Wim Cofino. Workshops have been organised on organochlorine pesticides (Aberdeen), organotins (Roskilde) and shellfish toxins (Nantes), with 20–30 participants in each. New workshops are planned: 26–27 September 2006 on alkylphenols and ethoxylates (Berlin) and 23–24 April 2007 on BFRs (Amsterdam) alongside the BFR2007 Workshop.

One specific question was raised regarding the frequency of exercise rounds – could they be conducted once per year instead of twice? It was felt strongly that there should be two opportunities per year even if only one were taken up, in case a laboratory was unable to participate at a particular time for some reason. Otherwise, this could result in a two-year gap in participation. Also, many laboratories are now using ICP/MS for analysis of trace elements – could the number of elements included be increased?

All protocols and reports on exercises will be made available to participants via a SharePoint website, www.QUASIMEME.org, via a login and password.

4.4 Other activities

Peter Lepom gave a presentation concerning current chemical monitoring activity under the Water Framework Directive, one important aim of which is to establish a guidance document on surface water monitoring, whilst taking account of related activities under e.g. EMMA (European Marine Monitoring and Assessment). Within the plenary group there are members from all member states, plus other stakeholders. Drafting groups have been established for:

- Groundwater monitoring;
- Surface water monitoring;
- Common issues (QA/QC).

The most difficult chapter is the one on monitoring design, as this is related to local conditions. This covers:

- Surveillance monitoring;
- Operational monitoring;
- Investigative monitoring.

Alternative monitoring methods will also be included.

The focus of this group is exclusively on chemical monitoring of:

- Priority substances;
- Annex VIII (river-basin specific) compounds;
- Physico-chemical parameters;
- Co-factors needed for data interpretation.

No work is being undertaken currently on background concentrations for heavy metals.

The principal matrix for determining EQS compliance will be whole water, as this is the only matrix for which they have been set. For compliance with other objectives (e.g. the no deterioration principle) whole water, biota and sediment will be acceptable.

One problem is that the daughter EQS directive is not yet published and so some aspects are unclear. Will the “added risk” approach be followed, for example? How should we deal with “less than” values, in order to assess compliance in a legally-binding manner? How should results be assessed if the method performance criteria cannot be met (so that concentrations are below the lod but greater than the EQS)? How can we use data for biota and sediments to assess compliance with EQSs set for water? How can passive sampling techniques be used in relation to compliance monitoring, as they reflect only dissolved concentrations?

Quality assurance aspects will be deemed within a legally binding Commission decision. The likely approach is that:

- Any validated methods which meet certain performance criteria can be used, except for operationally defined parameters;
- QA/QC systems should accord with EN/ISO/IEC 17025. Accreditation is recommended, but not obligatory;
- Successful participation in laboratory proficiency schemes is required. (Although in discussion it was noted that these do not exist currently for all required

matrix/determinand combinations, and will need to be established by member states).

The intention is for the guidance document to be completed by autumn 2006.

5 Reports on projects and activities in Member Countries

No submissions were made.

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 Norbert Theobald

Perfluorinated organic acids in the marine environment.

New data on the occurrence of a range of perfluorinated acids in water, sediment and biota from the North Sea, Baltic Sea and Greenland Sea were presented (see Section 8.11).

Sensitive and specific analytical procedures have developed for the investigation of perfluorinated organic acids (PFC) in sea water, marine sediments and biota. Water samples were extracted by SPE, whilst sediment and biota samples were extracted with methanol. Analysis was conducted using HPLC-MS-MS (ESI, negative ion). 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. PFOS is accumulated in sediments and biota to a greater degree than the other compounds. The River Elbe was identified as a local input source to the German Bight. The results underline the importance of the PFCs as a new group of widespread contaminants.

7.2 Ralf Ebinghaus

Polyfluorinated compounds in ambient air

Ralf described recent research activities related to polyfluorinated compounds conducted at the Institute for Coastal Research of GKSS Research Centre Geesthacht.

Polyfluorinated organic compounds represent a diverse class of chemicals produced in large amounts since the 1950s. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been determined in remote marine and polar ecosystems although they are almost non-volatile and hardly water-soluble. Perfluorooctane sulfonamides and fluorotelomer alcohols (FTOHs) are possible precursors of PFOS and PFOA and are both neutral and volatile, therefore having the potential for long-range atmospheric transport (LRAT).

High-volume air sampling and determination by GC-CI-MS has been developed, including full method validation. Results include ambient air concentration data from metropolitan Hamburg and Waldhof, a rural location in Northern Germany.

Results

At both sampling locations, FTOH (approx. 50–100 pg /m^3) concentrations are generally higher than those of FOSAs and FOSEs (approx. 10–50 pg /m^3). In Hamburg, 8:2 FTOH is the predominant compound, while in Waldhof, both 6:2 FTOH and 8:2 FTOH are found in rather high concentrations. Generally, there is no significant concentration difference between Hamburg city centre and a rural monitoring site approx. 100 km away.

Future Work

The method will be applied to air samples taken during two cruises of *RV Polarstern* to the Northeast Atlantic and the European Arctic (ARK-XX/1 & 2) and during the Atlantic transfer from Bremerhaven, North Germany to Cape Town, South Africa (ANT-XXIII/1).

Supplementary Information

1) ***Analytes and internal standards.*** The analytes determined in this study were 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH, 6:2 Perfluorooctane acrylate (6:2 PFOAc), NMeFOSA, NEtFOSA, NMeFOSE, NEtFOSE and PFOSA. Five mass-labelled IS have been applied: 6:2 FTOH M+4, 8:2 FTOH M+4, 10:2 FTOH M+4, NMeFOSA M+3 and NEtFOSA M+5. The recovery IS (RIS) added prior to GC-MS analyses were 7:1 and 11:1 fluorinated alcohol.

2) ***Blanks.*** For most analytes, no blank problems were found. Solvent blanks were not detected at all, while column blanks could be detected for 10:2 FTOH and NEtFOSA (<LOQ). Only for 8:2 FTOH, a column blank could be determined: 2.6 ± 0.5 pg/µL.

3) ***Precision.*** Within-day (100 pg/µL) and between-day precision (200 pg/µL) ranged from 4.2% (4:2 FTOH) to 7.4% (10:2 FTOH) and 5.5% (NMeFOSE) to 9.7% (PFOSA), respectively.

4) ***Recoveries.*** Several recovery experiments at two concentration levels (100 and 400 pg/µL) showed IS-corrected solvent recoveries between 44% (PFOSA) and 164% (NMeFOSE). IS-corrected column recoveries ranged from 56% (4:2 FTOH) to 151% (NMeFOSA). Only for two analytes where mass-labelled analogues were not available (NMeFOSE, NEtFOSE), column recoveries were very high: 311-319%.

5) ***LODs and LOQs.*** LODs and LOQs (PCI) were estimated from standard analyses at low concentrations at a signal-to-noise-ratio (S/N) of 3:1 and 10:1, respectively. Typical LODs were 0.2 (NEtFOSA, NMeFOSA) to 1.1 pg (PFOSA) while LOQs were 0.6 (NEtFOSA) to 3.7 pg (PFOSA).

7.3 Peter Korytár

Recent advances in multi-dimensional gas chromatography

Peter presented work from his recently completed (2006) Ph.D. thesis at the Vrije Universiteit, Amsterdam “Comprehensive two-dimensional gas chromatography with selective detection for the trace analysis of organohalogenated contaminants”. Compounds determined were dioxins, furans and dioxin-like CBs; toxaphene; CBs; BDEs and other BFRs; and chlorinated alkanes. Detectors used for GCxGC detection were micro-ECD detectors, quadrupole MS and time-of-flight MS. For the analysis of dioxins, data for a herring oil sample using GCxGC were comparable to those obtained using GC-HRMS. Also, possibilities for interference between analytes were investigated. No possible interferences were seen for CBs, PBBs, BDEs, polychlorinated naphthalenes, polychlorinated diphenyl ethers or organochlorine pesticides. The only possible overlap observed was with polychlorinated dibenzothiophenes.

Related references

Beens, J., and Brinkman, U.A.Th. 2005. Comprehensive two-dimensional gas chromatography – a powerful and versatile technique. Analyst, 130: 123–127.

Korytár, P., Haglund, P., de Boer, J., and Brinkman, U.A.Th. (in press). Comprehensive two-dimensional gas chromatography in analysis of organohalogenated microcontaminants. *TrAC*.

Korytár, P., Leonards, P.E.G., de Boer, J., and Brinkman, U.A.Th. 2005. Group separation of organohalogenated compounds by means of comprehensive two-dimensional gas chromatography. J. Chromatogr. *A.*, 1086: 29–44.

8 Main Agenda

8.1 Update the database of concentrations of metals and organic contaminants in biota/species of relevance to the OSPAR CEMP and prepare a table of new/updated background concentrations and background assessment concentrations for potential use in OSPAR assessments

At MCWG 2005, the use of Cofino statistics for the derivation of background concentrations from data available to the meeting was explored. Although MCWG felt that this approach showed promise, this was not the subsequent view of OSPAR. New data from remote locations are therefore needed, and those organising national monitoring programmes should be encouraged to include within their programmes the most suitable sampling points within their areas. This will obviously take some time. In the interim, it was noted that there are data available for contaminants (metals, OCs and PAH) in mussels (*Mytilus edulis*) from the east coast of the US/Canada (Gulf of Maine, Bay of Fundy) and MCWG propose that these be investigated for suitability. These data are available from Peter Wells (Environment Canada) and were requested in advance of the meeting, but did not arrive at ICES in time to be considered during MCWG 2006. All members are encouraged to submit data which may be appropriate for the determination of background concentrations to Patrick Roose intersessionally by the end of August 2006. This task will be addressed within the work programme of MCWG 2007.

8.2 With WGBEC, contribute to the development of detailed OSPAR guidelines deriving from the ICES/OSPAR Workshop on Integrated Monitoring of Contaminants and their Effects in Coastal and Open-sea Areas (WKIMON) [OSPAR 2005/6]. Specifically, to critically review the lists of target PAHs and CBs proposed by WKIMON in relation to ability to interpret information from the available biological effects techniques

Following the proposal by WKIMON and in view of recent proposals at OSPAR SIME, MCWG considered which PAHs and PCBs should additionally be monitored in order to facilitate integrated chemical and biological effects monitoring. Clearly, the main criteria for this are presence in the marine environment and toxicological relevance, i.e. being acutely toxic to organisms or posing a serious risk through chronic exposure.

PAHs

The PAH compounds currently proposed for inclusion are present in the marine environment and are toxicologically relevant, with humans and other higher organisms being most at risk. Analysis using GC-MS is, furthermore, relatively straightforward.

The proposed PAHs do not comprise all toxicologically relevant PAHs. A list was presented at the meeting which includes some additional toxic PAH which are not currently monitored:

Table 8.2.1. Toxic PAH list.

Cyclopenta[cd]pyrene
methylchrysenes
Methyl-substituted benzo[*a*]pyrenes
PAH with six rings (formula $C_{24}H_{14}$) m/z 302 *
dibenzo[*a,l*]pyrene
naphtho[2,1-*a*]pyrene**
naphtho[1,2-*b*]fluoranthene
dibenzo[*b,k*]fluoranthene
dibenzo[*a,i*]pyrene**
dibenzo[*a,e*]pyrene**
naphtho[2,3-*a*]pyrene
naphtho[2,3-*e*]pyrene
naphtho[2,3-*k*]fluoranthene
naphtho[2,3-*b*]fluoranthene
dibenzo[*e,l*]pyrene
naphtho[1,2-*k*]fluoranthene

*** Human mutagens (Durant *et al*. 1998, Environ. Sci. Technol., 32), ** Highest toxicity i.e. mutagenic potency**

Also, nitro-PAHs and certain heterocyclic PAHs, e.g. dibenzothiophenes, are important mutagens and taint-inducing compounds, respectively. The dibenzothiophenes are commonly found in petrogenic sources, which is another advantage of measuring additional PAHs. Determining alkylated 2- and 3-ring PAH (naphthalenes and phenanthrenes) allows us to distinguish between pollution caused as a result of combustion related processes and of petrogenic origin.

MCWG further considered the PAHs listed in Table A1.1. (reproduced in Table 8.2.2) of the JAMP Guidelines for Monitoring Contaminants in Biota as candidates for inclusion in the monitoring programmes.

Table 8.2.2. Compounds of interest for environmental monitoring for which the guidelines apply.

COMPOUND	MW	COMPOUND	MW
Naphthalene	128	C_2-Phenanthrenes/Anthracenes	206
C_1-Naphthalenes	142	C_3-Phenanthrenes/Anthracenes	220
C_2-Naphthalenes	156	Fluoranthene	202
C_3-Naphthalenes	170	Pyrene	202
C_4-Naphthalenes	184	C_1-Fluoranthenes/Pyrenes	216
Acenaphthylene	152	C_2-Fluoranthenes/Pyrenes	230
Acenaphthene	154	Benz[*a*]anthracene	228
Biphenyl	154	Chrysene	228
Fluorene	166	2,3-Benzanthracene	228
C_1-Fluorenes	180	Benzo[*a*]fluoranthene	252
C_2-Fluorenes	194	Benzo[*b*]fluoranthene	252
C_3-Fluorenes	208	Benzo[*j*]fluoranthene	252
Dibenzothiophene	184	Benzo[*k*]fluoranthene	252
C_1-Dibenzothiophenes	198	Benzo[*e*]pyrene	252
C_2-Dibenzothiophenes	212	Benzo[*a*]pyrene	252
C_3-Dibenzothiophenes	226	Perylene	252
Phenanthrene	178	Indeno[1,2,3-*cd*]pyrene	276

COMPOUND	MW	COMPOUND	MW
Anthracene	178	Benzo[*ghi*]perylene	276
C_1-Phenanthrenes/Anthracenes	192	Dibenz[*a,h*]anthracene	278

MCWG proposes that alkyl (C_1-C_3) naphthalenes, alkyl (C_1-C_3) dibenzothiophenes, alkyl (C_1-C_3) phenanthrenes and anthracenes should be added to the list of PAH determined in annual monitoring programmes.

MCWG recommends that MCWG and WGBEC should review the analytical methodology and toxicity information relating to these compounds at their 2007 meetings.

PCBs

Concerning the need to add additional CB congeners to the list of ICES7$^{©MCWG}$ (CB28, CB52, CB101, CB118, CB138, CB153 & CB180), this is mainly related to the determination of the non-*ortho* and mono-*ortho* congeners, as they exhibit the highest dioxin-like toxicity and contribute to the TEQ (toxic equivalent concentration) by which it is expressed. Mono-*ortho* CBs can be determined within the routine schemes of PCB analysis and it is suggested that, as a minimum, a selection of these congeners (e.g., CB105, CB156, CB157) is added to the current suite of CBs. Other mono-*ortho* congeners may not be present in environmental samples (CB114, CB123, CB167 & CB189). However, determining the concentrations of the non-*ortho* CB congeners (CB77, 126 and 169), which exhibit the highest dioxin-like toxicity, is less straightforward and requires specialised fractionation procedures. Moreover, concentrations of these congeners in environmental samples tend to be very low, which generally requires very low detection limits and the use of GC-HRMS instruments or GC with low resolution MS/MS for analysis. However, the TEFs (toxic equivalent factors) for these congeners are relatively high, and so they may contribute significantly to the TEQ values. In considering this question, it is also important to realise that, in fish, most of the "dioxin" toxicity (expressed as TEQs) is often due to planar CBs and not the dioxins and furans themselves (up to 75%). However, in different locations and/or species, any of the dioxins and furans, non- or mono-*ortho* CB congeners could dominate the TEQ. Two recent studies in fish in Canada and Ireland have shown that dioxin toxicity could be mostly related to the non-*ortho* CB congeners. Clearly, both mono-*ortho* and non-*ortho* CBs should be monitored but, given the difficulties with the latter, another possibility was considered. Is it possible to calculate the ratios of mono-*ortho* and non-*ortho* CBs to the concentrations of the, routinely monitored, ICES7 CBs, and to use that to estimate the overall risk for the environment? This is a suggestion which was also made at the last SIME meeting in February 2006. Clearly, these ratios may be site specific and and may not be applicable across the whole OSPAR area. Nevertheless, using region specific ratios was considered to be a reasonable approach, although analysis remains the preferred option. There are indications that these ratios are relatively constant and can be calculated but this hasn't been sufficiently well evaluated to date. The idea was therefore posed that we should examine existing datasets and so evaluate the possibilities of this approach. This work would be handled intersessionally: Jacek Tronczynski, Evin McGovern, Michel Lebeuf and Gert Asmund will submit relevant data, with Patrick Roose acting as the lead contact. All other MCWG members are invited to contribute relevant data from their own studies.

The MCWG was informed of an upcoming EU project, ATHON, which begins later in 2006 and will investigate the toxicity of non-dioxin-like CBs. Studies concerning the determination of new TEF value for these compounds will also be undertaken, as the standards used to prepare test solutions in the original studies may have been contaminated by dioxin-like CBs.

http://ki.se/ki/jsp/polopoly.jsp?d=2758&a=8309&l=en

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 2006/1]

No draft guidelines were available at the meeting, and discussions with the chair of OSPAR MON (Ian Davies) and WGSAEM (Rob Fryer) confirmed that these documents had not yet been completed. Discussion was therefore deferred to MCWG 2007.

8.4 Provide advice on whether the existing systems for monitoring dioxins in fish and shellfish for the purposes of safeguarding human health could be used to monitor trends in concentrations and/or spatial extent of dioxins in the marine environment. The specific questions to be addressed [OSPAR 2006/5] are:

i) What food safety monitoring of dioxins and furans in fish and shellfish is being carried out in the OSPAR area;

ii) To what extent it is possible to trace fish and shellfish samples to the locations in which they were caught;

iii) To what extent do the data obtained support the determination of trends in concentrations and/or spatial extent of dioxins in the marine environment.

The group reviewed and discussed the extensive amount of data from surveys on dioxin and dioxin like PCB in fish, shellfish and fish products for the purposes of safeguarding human health available from the UK, Sweden, Norway, Ireland and France. The reports of these studies showed a wide diversity of products being analyzed. The timing of the surveys and the choice of products, species, tissues and sources are *ad-hoc* rather than regular (as for temporal trend monitoring programmes in the marine environment), and logically reflect the local/regional food market for each survey. In many reports no individual concentrations are given, but only ranges of concentration or TEQ values. Sometimes, the data produced are not published in any summary report but only reported to the EU and stored on their database (e.g. in the case of Norway). In only some cases is it possible to trace back the fish/product samples to their exact location of origin at sea and also the samples are often collected from the consumer market (i.e. collected from fish markets, fishmongers and/or supermarkets). The surveys for food safety are directed by the need to assess the intake of dioxins, furans and dioxin–like CBs by human consumers. There is, therefore, no need to control many factors (selection of species, number and size of individuals) and record information (exact origin, age, length, condition etc) that are considered crucial to monitoring programmes conducted for spatial and temporal trends. In addition, only edible tissues are analysed rather than those in which concentrations are likely to be highest (e.g. liver). The lack of information and control in these food-monitoring programmes and their *ad-hoc* nature make the data unsuitable for defining temporal and spatial trends. Retrospective monitoring of selected archived material from monitoring programmes can very well be used for temporal trend analysis as is shown by a recent study from France (Annex 6).

8.5 Review the results of one-off surveys for the following chemicals identified by OSPAR for priority action; 2,4,6-tri-*tert*-butylphenol; endosulphan; and short-chain chlorinated paraffins

No results were available for assessment at the meeting. During OSPAR SIME 2006, a letter was drafted inviting contracting parties to undertake one-off surveys for endosulphan, short-chain chlorinated paraffins and 2,4,6-tri-*tert*-butylphenol. These surveys have not taken place as yet. This topic will be reconsidered at MCWG 2007.

8.6 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 realised that STGQAC provides quite general guidance on a number of issues and would appreciate some more clear recommendations or at least, assessments of the appropriateness of the various options given.

Following the proposal made in 8.4 of the report of the ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (STGQAC) and following discussions between two of the group Co-Chairs, MCWG supports the suggestion that in future STGQAC are welcome to operate within MCWG, for the following reasons:

- STGQAC has declined in the total number of members (the 2006 meeting was attended by 4 persons only) and it is now finding it difficult to work independently
- Quality assurance issues are an integral part of both analysis and monitoring activities, hence, there seems to be a continuous demand to update existing guidance on QA/QC and to elaborate new guidance on relevant issues.
- Many of the issues that STGQAC is dealing with are closely linked to the work of MCWG, and so the suggested organisational change would facilitate cooperation between the members of both groups. Direct exchange of information and ideas would be of benefit for both sides and would probably improve the quality and acceptance of the documents produced and would certainly reduce the timescales.

MCWG welcomes the proposal from STGQAC to develop technical notes on monitoring of brominated flame retardants (BFR) and organotins in co-operation with this group. However, the group questioned whether water would be the appropriate matrix for analysis of BFRs and recommends a focus on monitoring in biota and sediment as proposed by OSPAR. Concerning organotin compounds, the existing OSPAR guideline on monitoring organotin compounds in sediment has to be taken into account and emphasis should put on analysis in sediments and biota.

AnnexB3

No comment

Annex B4

MCWG sees a need to revise the recommendation on how to determine the limit of quantification (LOQ) for chromatographic methods. Three options should be included:

- Measure concentrations in a very low level sample x times and calculate standard deviation
- Spike analyte-free sample and measure x times, then calculate standard deviation
- Dilute natural low level sample extract to achieve the required concentration. Then measure x times and calculate standard deviation

The proposed options are arranged according to their appropriateness.

Annex B5 Table 5.7

Laboratory reference materials/intercomparison samples for use in a precision and trueness check should be added to the table. Such samples seem appropriate for the purpose if the laboratory has demonstrated its competence in appropriate Laboratory Proficency Schemes.

Annex B12

MCWG recommends that ICP-MS should be included as an additional method for the analysis of mercury in biota, as current instruments are very capable in this respect.

8.7 Discuss and report on potential contributions for the ecosystem overview of the advisory reports describing the quantity and quality of marine habitat and/or the health of the marine ecosystem, and to consider and report on potential indicators of significant change in these ecosystem attributes

Nutrients and organically-bound nutrient species act as drivers for processes which can directly influence the uptake and distribution of contaminants in the environment and ecosystems generally. MCWG will address this topic during its 2007 meeting. Klaus Nagel agreed to lead on this topic, and other MCWG members are encouraged to contribute.

8.8 Present to the Working Group on the Statistical Aspects of Environmental Monitoring (WGSAEM) proposals for collaboration for joint discussion

Taken under Agenda Item 8.14 below.

8.9 Review and update sub-regional tables and where necessary include new and/or data (parameters) updated where relevant. The data tables will be subject to thematic assessment to be undertaken at a REGNS workshop

MCWG considered the ways in which contaminant data may feed into the REGNS regional (North Sea) and thematic assessments. There are, however, major differences between contaminant data and other datasets gathered by ICES. Firstly, the major influences on contaminant concentrations are changes in inputs and factors such as river flows, rather than ocean climate or oceanographic forcing. Inputs from the atmosphere may also become dominant for some contaminants and locations. Secondly, the highest concentrations of contaminants are generally encountered in coastal waters, and many studies are concentrated in these areas. For this reason, coverage in offshore areas is often limited, apart from eg. German studies on pesticides (eg. HCHs) in water. An exception to this is for nutrients in seawater, for which many data are available, although both the oceanographic and contaminant databases hold these data. The data spreadsheet provided by REGNS indicated that the ICES data for contaminants in sediment have been included in the assessment process, but not those for biota. In addition, fish disease data (and associated contaminant data on the same fish) and data for contaminants in marine mammals may provide suitable inputs to the REGNS process. The implementation of the ecosystem approach in integrated assessment is likely to involve modelling on a broad scale, and contaminant data can feed into this activity.

MCWG indicated that they were happy to work with REGNS on the following datasets held either by ICES or nationally:

Metals in biota	ICES
OCs in biota	ICES
PAH in biota	ICES
Contaminants in seawater	nationally
Trace elements in marine mammals	nationally

OCs & CBs in marine mammals	nationally
Butyltins in marine mammals	nationally
BDEs in marine mammals	nationally
HBCD in marine mammals	nationally
Novel contaminants	nationally

8.10 Review developments within the UNEP Global POPs Monitoring Network with particular emphasis on opportunities for collaboration with ICES

Apart from updating the list of laboratories capable of undertaking POPs analysis to satisfy the requirements of the Stockholm POPs Convention, no other developments were known of. This topic will be reconsidered at MCWG 2007.

http://www.pops.int/

8.11 Assess the adequacy of the existing analytical methods for short-chain chlorinated paraffins, dioxins, toxaphene, perfluorinated compounds, BDEs and other brominated flame retardants for marine environmental assessment and provide guidance on the most appropriate techniques

Short-Chain Chlorinated Paraffins: SCCPs present many analytical challenges and it is not clear how many marine laboratories have capabilities for SCCP analysis. In addition to the information given in 2005, MCWG have been informed of new developments in the analysis of these compounds using multi-dimensional gas chromatography (see Agenda Item 7.3). Peter Lepom informed the meeting of a German project that includes method development for analysis of SCCPs. This project will report during 2006 and the outcome will be reported to MCWG 2007.

MCWG Report 2005. Annex 8: Review note on short chain chlorinated paraffins. Prepared by Peter Lepom.

Dioxins and Dioxin-like PCBs): GC-HRMS remains the method of choice for dioxin analysis and is the only accepted analytical method for food safety analysis. However, this technique is expensive and not widely available to marine monitoring laboratories. An alternative method that also offers high mass resolution is GC-Time of Flight (ToF) MS although this is also a relatively expensive option at present. The EU funded DIFFERENCE project (www.dioxins.nl) is now complete and has reported on the use of alternative methods for dioxin analysis. GC with low resolution MS/MS, particularly ion trap instruments, has been used by some laboratories as a screening method, with GC-HRMS analysis triggered if higher levels are seen. The downsides of LRMS/MS, compared with HRMS, are low mass resolution, potential false negatives, lower precision and, especially, lower sensitivity. The DR-CALUX assay is also used for screening purposes. Presumably GC-triple quadrupole MS/MS could be employed in a similar manner to GC with low resolution MS/MS. GCxGC with electron capture detection was also evaluated within the DIFFERENCE project, but this technique is not routinely available within monitoring laboratories. Dioxins exert toxic effects at very low levels and therefore very high sensitivity is required for their analysis.

MCWG agreed that GC-LRMS/MS is a promising technique for the analysis of dioxins in marine environmental monitoring. Any technique, should be acceptable if it is fit for the purpose (for example monitoring higher levels of dioxins as found in fish from the Baltic, or tissues containing higher levels), and has demonstrated adequate QA (e.g. as shown through adequate performance in round robin testing). Nonetheless, GC-HRMS is the preferred method and is still required for food compliance testing.

Van Loco, J., Van Leeuwen, S. P. J., Roos, P., Carbonnelle, S., de Boer, J., Goeyens, L., and Beernaert, H. 2004. The international validation of bio- and chemical- analytical screening methods for dioxins and dioxin-like PCBs: the DIFFERENCE project rounds 1 and 2. Talanta, 63: 1169–1182.

http://www.dioxins.nl/Difference/home_diff/framesetdiff.html

will contain the final report when available.

Coplanar PCBs: Certain non-*ortho* and mono-*ortho* CBs exhibit ‘dioxin-like’ toxicity (12 WHO-CBs) and some of these can exert toxicity at low concentrations (e.g. CB 126 a non-*ortho* CB). The above conclusions on analysis of dioxins could be considered to apply in the case of the coplanar CBs. While GC-LRMSMS (NCI) would be appropriate for analysis of mono-*ortho* PCBs, GC-HRMS would be preferred for non-*ortho* PCBs, although LRMS/MS offers potential if stringent clean-up of sample extracts is applied.

Toxaphene: Toxaphene continues to present analytical challenges. Michel Lebeuf informed MCWG of a GC-ion trap MS/MS method for the determination of 6 congeners in biota samples. These 6 congeners are the most important in fish and marine mammals. In other matrices (e.g. sediments) the congener profiles can be more complicated and the levels lower, necessitating the use of GC-HRMS and, as for dioxins in food, this is the reference technique. The GC-ion trap MS/MS technique in biota has been the subject of a successful inter-laboratory calibration of toxaphene in Canada.

Information on toxaphene concentrations (3 congeners) in fish from European waters has been published. Five laboratories participated using different techniques including GC-LRMS and GC-ECD and the interlaboratory agreement was good.

Gouteux, B., Lebeuf, M., Trottier, S., Gagné, J-P. Analysis of six relevant toxaphene congeners in biological samples using ion trap MS/MS., 2002. Chemosphere 49, 183-191.

McHugh, B., McGovern, E., Nixon, E., Klungsøyr, J., Rimkus, G.G., Leonards, P.E., and deBoer, J. 2004. Baseline survey of concentrations of toxaphene congeners in fish from European waters. J. Environ. Monitor, 6(8): 665–672.

Perfluorinated Compounds: Norbert Theobald reported that his laboratory measures a range of perfluorinated compounds including PFOS/ PFOA in seawater, marine sediment and fish using HPLC-MS/MS. Ralf Ebinghaus also reported on available methods for perflorinated compounds in atmospheric samples and in biota. The latter were also analysed by HPLC-MS/MS. Analysis of atmospheric samples for volatile precursor compounds such as fluorotelemers employed GCMS (positive EI). Further information on the programmes of measurement was presented under agenda item 7.2. CEFAS also have an operational method and are determining PFOS/PFOA in porpoise liver, and RIVO has developed an HPLC-MS method for fish.

PFOS tends to bioaccumulate but associates with protein rather than lipid. The first global intercomparison exercise for perfluorinated compounds was carried out under the PERFORCE 6th Framework project (http://www.science.uva.nl/perforce). This was open to laboratories outside of the project consortium and results indicated problems with the analysis of PFOS and PFOA, especially for fish muscle. *Chemistry, fate and effects of fluorinated alkylated compounds* is a topic session planned for the SETAC annual meeting in May 2006.

MCWG concluded that analysis of perfluorinated compounds is currently not routine and there are some problems with analysis of these compounds judging from the results of a recent intercomparison exercise in biota. Nonetheless, there is significant interest in these compounds and considerable work in progress on developing analytical methodology. A further intercomparison exercise is being developed.

de Voogt, P., and Sáez, M. 2006. Analytical chemistry of perfluoroalkylated substances. Trends in Analytical Chemistry, 25: 326–342.

Martin, J.W., Kannan, K., Berger, U., de Voogt, P., Field, J., Franklin, J., Giesy, J.P., Harner, T., Muir, D.C.G., Scott, B., Kaiser, M., Järnberg, U., Jones, K.C., Mabury, S.A., Schroeder, H., Simcik, M., Sottani, C., van Bavel, B., Kärrman, A., Lindström, G., and van Leeuwen, S. 2004. Advancements in Perfluoroalkyl Research Hampered by Analytical Challenges. Environmental Science & Technology, 38: 248A–255A.

Brominated Flame Retardants:

PBDEs: There is substantial data for BDEs in the marine environment and several MS based techniques have been employed. GC with ECNIMS detection is widely used as it is cost effective. However, the analysis of deca-BDE remains a problem in many laboratories as BDE209 is thermally unstable (degrading during injection in heated injectors and on-column) and contamination is easily introduced during the analysis, both from foam-based materials within the laboratory and due to contamination of laboratory glassware. Very short columns (ca. 2m length) are often used and J&W DB-1 columns appear to cause the least decomposition even at 30m length. Michel Lebeuf reported on recent research in Canada that has indicated that BDE209 does not produce any lower molecular weight BDEs other than those congeners already present as impurities in the deca-mix formulation due to thermal breakdown during their analysis. There is also a need to better characterise the other congeners present in the deca BDE mix.

Covaci, A., Voorspoels, S., de Boer, J. 2003. Determination of brominated flame retardants, with emphasis on polkybrominated diphenyl ethers (PBDEs) in environmental and human sample – a review. Environmental International, 29: 735–756.

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

Lebeuf, M., Couillard, C.M., Légaré, B., and Trottier, S. (in press 2006). Effects of DeBDE and PCB-126 on hepatic concentrations of PBDEs and methoxy-PBDEs in Atlantic tomcod. Environmental Science and Technology.

HBCD and TBBP-A: HBCD can be analysed by HPLC-MS or GCMS. HPLC-MS analysis enables separation into the three diastereomers and this approach is recommended by MCWG. GCMS only enables determination of total HBCD, although this methodology is difficult to keep under control as the HBCD breaks down on the GC column and yields a broad peak. TBBP-A can also be analysed using the same HPLC-MS method. Derivatisation of TBBP-A prior to GC analysis has also been used for screening purposes. HBCD is becoming more important as, in the UK at least, concentrations in porpoise blubber began rising steeply after 2001. Intercomparison exercises for HBCD are needed in biota and sediments – in the past the level of participation has been too low. QUASIMEME has an exercise planned for 2006.

Law, R.J., Bersuder, P., Allchin, C., and Barry, J. 2006. Levels of the flame retardants Hexabromocyclododecane and Tetrabromobisphenol A in the blubber of harbour porpoises (*Phocoena phocoena*) stranded or bycaught in the U.K., with evidence for an increase in HBCD concentrations in recent years. Environ. Sci. Technol., 40: 2177–2183.

Law, R.J., Kohler, M., Heeb, N.V., Gerecke, A.S. Schmid, P., Voorspoels, S. Covaci, A., Becher, G., Janák, K., and Thomsen, C. 2005. Hexabromocyclododecane challenges scientists and regulators. Environ. Sci. Technol., 39 : 281A –287A.

8.12 Continue to report on new information on *tris*(4-chlorophenyl)methanol (TCPM) and *tris*(4-chlorophenyl)methane (TCPMe) in flatfish

No new data were reported on this agenda item during the meeting. However, during the past year flatfish samples from Belgium and Spain were provided to Michel Lebeuf by Marc Raemaekers and Teresa Nunes, respectively. These samples were analysed in Canada (Michel Lebeuf) and data for TCPM/TCPMe and DDTs were merged with data produced previously for flatfish from Canada, Germany, The Netherlands and UK. At the last MCWG meeting, Michel Lebeuf had volunteered to collate all the data made available to him by the MCWG members. During the meeting, Michael Haarich (Germany) provided additional data for inclusion and additional data have also been produced during the past year by Stefan van Leeuwen and Jacob de Boer (The Netherlands) and will be provided to Michel Lebeuf in the near future. In collaboration with the other members that have contributed to the project, Michel Lebeuf intends to write a peer-reviewed paper reporting the finding of this MCWG international collaborative project and MCWG members will be kept informed of the outcome.

8.13 Critically review the new information on the use of membrane systems for sampling, and on their incorporation within national monitoring programmes.

This topic has been on the agenda of both OSPAR SIME and MCWG for a number of years, and the methodology is considered to be very promising. SIME has called for a proposal for a one-off survey using passive sampling techniques across the convention area, and the results will be used to assess the utility of these methods. WGMS 2006 has also discussed this topic in relation to sediment monitoring. Initially, Belgium, the Netherlands, UK and Denmark have been asked to prepare the proposal, although other countries (especially those which participated in a workshop held in the Netherlands during 2005) may also be involved. The final report of that workshop is not yet available.

For the interpretation of the data obtained from such surveys and the calculation of equivalent concentrations in the water-phase, partition coefficients must be derived for each of the sampling materials used. These are seldom published, and publication of this information should be encouraged so as to assist others. Where passive samplers are being used as an alternative to mussels, data can be compared directly without back-calculation to equivalent concentrations in the water phase. Passive samplers can be used routinely for sampling trace metals using diffusive samplers (as outlined during earlier MCWG meetings) as well as for hydrophobic and polar organic contaminants.

The group was informed of an EU project – STAMPS

www.port.ac.uk/research/stamps/

which is aimed at the normalisation of passive sampling techniques for monitoring priority pollutants in freshwater. The STAMPS programme has established a general framework for harmonized use of passive samplers. An International Passive Sampling Workshop will be held within this programme in Bratislava, 3–6 May 2006. The possibility of a similar bid for EU funding for a corresponding marine programme arising from the group undertaking the OSPAR one-off survey was discussed.

It was noted that in some countries (the UK, Belgium, France, Germany and the Netherlands, for example) passive samplers could be placed on instrumented buoys which are already being deployed for extended periods to continuously determine oceanographic parameters, nutrient and chlorophyll concentrations, etc. The possibility of using sampling devices for polar compounds to measure algal toxin concentrations was also discussed.

Later, a joint meeting was held between members of both MCWG and WGMS to discuss their interests in passive samplers. The proposed OSPAR one-off survey will require the preparation of technical guidelines, in common with other studies, and WGMS are keen to begin producing these for application to sediment sampling. This should be complemented by the preparation of technical guidelines for water sampling (the WFD provides a strong driver for this – in terms of being able to generate a better estimate of average concentrations of contaminants in a water body than spot sampling at a frequency of 12x or 2x per annum). They will also indicate spatial variations in "pressure" from contaminant concentrations, and so the risk of harm posed to organisms.

An intercomparison exercise is required in order to validate the applicability of passive sampling in different locations, and such an initiative will need to come from within ICES. Accordingly, WGMS and MCWG agreed to develop outline proposals for discussion within this year's meeting. For intersessional work to further develop a trial survey, Foppe Smedes will act as the focal point with assistance from Patrick Roose, Ton van der Zande and Jacek Tronczynski for MCWG and Ian Davies and Celine Tixier for WGMS. The basic idea would be to deploy multiple passive samplers for water (in duplicate at least) at a number of locations across the ICES area (number and positions to be decided by the participating laboratories). After the period of deployment, one of the duplicate samples would be analysed by the local participating laboratory and the second sent for analysis to a central laboratory (and similarly split if additional sampling devices are used). In this way, both spatial variations and analytical variability between laboratories could be explored. A single source of material would be used to prepare the passive samplers and performance reference compounds spiked by a single laboratory prior to distribution. If possible, it would be advantageous to deploy mussels at the same locations for comparative purposes. The intersessional group agreed to a target for the development of technical guidelines of summer 2006, with the aim of conducting the deployments for a period of six weeks during the autumn (October onwards). The laboratories of MUMM, BSH and IFREMER agreed to take part in the exercise, and participation from other laboratories is possible where further expertise exists. NERI, FIMR, RIVO, IOW (Germany) and the Marine Institute (Ireland) would like to participate. CEFAS (UK) indicated that work on passive sampling was ongoing and that there is an interest in taking part, but also indicated that a source of funding would need to be identified nationally before any commitment could be made. Silicone rubber is a suitable material for general application to sampling a broad range of chemical compounds and seems appropriate to test at this stage, even if at a later date alternative materials may prove more applicable to specific compounds.

This suggested approach was further discussed within MCWG. The advisability of transplanting mussels from a single site to all sampling locations was questioned. Why not use mussels naturally present at those locations? Is there any merit in limiting the number of determinands within e.g. CBs or PAH? Probably not, as little cost would be saved and, in any case, a wide range of K_{ow} values would need to be covered in each case to account for differing behaviour of compounds with differing polarity. A range of sampling sites should be selected, including at least one site with very low SPM concentrations in order that dissolved concentrations can be determined in samples without filtration.

Another meeting between members of WGMS and MCWG was held to further elaborate this proposal. It was agreed that the proposal would include both water and sediment components (drafted by MCWG and WGMS members, respectively), and would aim to take advantage of natural mussel populations wherever possible so as to simplify the logistics. Also, the group members agreed that the proposal should include the purchase of a single batch of silicone rubber, both to ensure that the same material is used in all elements of the programme but also so that the same material can be used in future programmes. Funding will need to be secured and, in order to be able to seek this, a detailed proposal for the trial survey must be developed.

A target date of the end of April was agreed for this task. It was agreed that Patrick Roose would explore at OSPAR ASMO the possibility of a study being funded from OSPAR rather than by a consortium of Contracting Parties – however, this would need endorsement by the Heads of Delegation and so would be an extremely slow process, and likely to delay the study. Also, it is not a traditional funding mechanism within OSPAR. The study is too small for funding as a stand-alone EU research study, but it may be eligible as policy support for the Water Framework Directive, and this possibility should be explored. It was also discussed whether a link with QUASIMEME would enhance the proposal. Detailed technical guidelines also need to be developed for both water and sediment components, and the target date for preparation of these documents was agreed as the end of July. The WGMS report will contain a suggested structure for the technical guideline documents, and Foppe Smedes will prepare a “to do” list for the elements of the study and the preparation of documents, with a timetable for intersessional work.

If the trial survey proceeds satisfactorily, both MCWG and WGMS will consider the results at their meetings in 2007. Ideally, both groups should meet at the same location.

8.14 Provide expert knowledge and guidance to the ICES Data Centre on a continuous basis

Rob Fryer (WGSAEM Chair) presented a working document following up the 2005 OSPAR MON assessment “Is there persistent bias in historical data “developed within his WG so as to solicit input from MCWG. This stemmed from study of the tentative trends in concentration assigned by MON. The main question arising was “is the quality of data in the ICES database as good as it can be and, if not, what process can be set in place to improve this?” Back-extrapolating trends from data with good QA associated with it (and so of demonstrably good quality) and then looking for “pivot points” within the trend plots which show where changes in trend may have occurred but where the QA status also changed. This allows the identification of critical data, which may have had poor or missing QA, and which can then be further studied and (hopefully) further validated with the aid of the data originators. Back-extrapolated data which do not match the apparent trend do not invalidate the measured data.

A lively discussion ensued. It was the general feeling that, for old data, it would be very difficult to either revisit old analyses in search of additional validation information (no records of quantitative changes due to method changes) or to reanalyse historic samples (not archived for periods of 10–20 years in most laboratories). Around the pivot point, however, it may be possible to find enough information to extend the “good QA” assignment to some earlier datapoints. MON focus is really though on recent trends (ca. 10 years) and so the situation will ease as additional years of data with good QA are submitted for assessment.

Hans Mose Jensen gave a presentation to all four working groups on the developments within the DOME database. Most useful is the web access now available via the ICES website to the Data Screening Utility (DATSU) which allows data submitters to screen their own data for errors before they are submitted to ICES.

Marilynn Sorensen and Hans Mose Jensen joined the group and outlined a database issue with which assistance was required. Data have been submitted to both the environmental database (in 2.2 format) and the oceanographic database. For some parameters these data are duplicated, which causes a problem when both sets of data are migrated to the DOME database as they will be duplicated. Parameters which are essential for the interpretation of 2.2 formatted data (co-factors) will need to be stored in DOME and associated with the contaminant data. It was agreed that data for suspended solids, DOC and POC should not be disassociated from the sample information. Also, the original data files will be kept in the event that they need to be revisited for assessment purposes.

Contact points for the ICES data centre:

- Trace elements – Gert Asmund.
- Organic contaminants – Robin Law.
- Chemical oceanography – Klaus Nagel.

8.15 Report on new information regarding perfluorinated compounds (particularly PFOS & PFOA) in environmental samples

New data were presented via the presentations given by Norbert Theobald and Ralf Ebinghaus. In discussion, questions arose regarding the consequences from current regulations concerning the production and use of perfluorinated compounds (PFCs). In Norway, the use of perfluorooctane sulphonate (PFOS) in fire extinguishing foams on oil platforms was phased out in 2003. One of the main manufacturers of PFCs (the 3M Corporation) restricted the production of perfluorooctanoic acid (PFOA) on a voluntary basis. In Europe, PFOS is currently undergoing a risk assessment under the OSPAR Convention; it is currently considered as a persistent, bioaccumulative and toxic (PBT) compound.

Gert Asmund advised the group that the analysis of PFOS has been implemented within the Danish component of the AMAP programme. MCWG also noted that:

- Toxicity data for marine organisms are still not available;
- Log K_{OW} values for the PFC are not known as they exhibit surface active properties. However, PFOS is enriched in sediments and biota to a greater degree than the other related compounds, suggesting that it is more hydrophobic.

8.16 One additional agenda item arose during the meeting via the ICES Secretariat. This item arose from the Norwegian government as a result of the finding of a sunken submarine (U-864) off the Norwegian coast which had been sunk during the Second World War whilst transporting 60 tonnes of metallic mercury in steel bottles. MCWG was asked to consider:

- how quickly metallic mercury might dissolve in seawater?
- does it need to be transformed to an organic form before it is available for uptake by marine organisms?
- if so, what kind of environment is required for this transformation?
- what is the estimated rate of this transformation?

The solubility of mercury in pure water is approx. 60 $\mu g\ l^{-1}$ – the corresponding value for seawater is unlikely to be higher. Elemental mercury under oxic conditions forms an oxide layer which will inhibit contact with the water. Whilst both inorganic mercury and organic mercury can be bioaccumulated, the accumulation factor is ca. 100x higher for organic mercury. Transformation of inorganic (not directly metallic) mercury requires bacterial action – sulphate-reducing bacteria can accomplish this. Mercury is very dense, and if there are soft sediments in the area the mercury would sink into the sediment, and so may end up in an anoxic environment. Diver surveys have apparently indicated no major leaks to date. Fish and shellfish from the area have been collected and analysed, and some have yielded slightly elevated concentrations of mercury. Pooling of metallic mercury on or within the seabed would greatly reduce the surface area available for reactions to occur relative to the mass of mercury spilt. It is impossible to estimate the likely rate of transformation from metallic to inorganic to organic mercury, but it seems likely to be very slow.

Metallic mercury is used in several places around the world in small scale mining for the extraction of gold as an amalgam. Spills of metallic mercury in river systems are known to result in uptake in fish by a process probably involving transformation to methylmercury. It can thus be concluded that the uptake of metallic mercury by fish is a proven process, which should be taken into consideration in the case of the sunken submarine off Norway. How rapidly it will happen and for how long uptake will continue will be a function of the physical environment at the location of the sunken vessel.

9 Plenary discussion of draft report

This took place on 30 and 31 March.

10 Election of chair(s)

One of the Co-Chairs, Robin Law, is stepping down after completion of two three-year terms of office. He thanked the members of MCWG for all their help and support during this period. The other Co-Chair, Jacek Tronczynski, agreed to continue for at least one more year after which time he would have served for three years. The group appointed Evin McGovern to assist him as Co-Chair. Jacek thanked Robin for his work for MCWG on behalf of the group.

11 Recommendations and action list

These are given as Annexes 4 and 5.

12 Date and venue of next meeting

ICES has suggested that MCWG meet during the week of 5–9 March 2007. 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 a tentative invitation to hold its 2007 meeting in Hamburg. If confirmed, this will be made formally at the Annual Science Conference. If this is not possible, MCWG could meet at ICES Headquarters.

13 Closure of the meeting

The members of MCWG thanked the outgoing Co-Chair, Robin Law, for his long service within MCWG both as member and Chair. The Co-Chairs closed the meeting at 09:55 am on Friday 31 March.

Annex 1: MCWG list of participants

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Annex 2: Agenda, 28th meeting of MCWG

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 93rd ICES Statutory Meeting

4) Reports on related activities

4.1) OSPARCOM and HELCOM

Any official requests from OSPARCOM or HELCOM which arose prior to the production of the agenda have been included.

4.2) Intergovernmental Oceanographic Commission (IOC)

An update on relevant IOC programmes will be given.

4.3) Laboratory Performance Study QUASIMEME

Dr Wells has been asked to provide an update on recent studies.

4.4) Other Activities

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

5) Reports on projects and activities in Member Countries

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) Norbert Theobald

Perfluorinated organic acids in the North Sea.

7.2) Ralf Ebinghaus

Perfluorinated organic compounds (PFCs)

7.3) Peter Korytar

Recent advances in multi-dimensional gas chromatography

8) Main agenda

8.1) update the database of concentrations of metals and organic contaminants in biota/species of relevance to the OSPAR CEMP and prepare a table of new/updated background concentrations and background assessment concentrations for potential use in OSPAR assessments;

8.2) with WGBEC, contribute to the development of detailed OSPAR guidelines deriving from the ICES/OSPAR Workshop on Integrated Monitoring of Contaminants and their Effects in Coastal and Open-Sea Areas (WKIMON) [OSPAR 2005/6]. Specifically, to critically review the lists of target PAHs and CBs proposed by WKIMON in relation to ability to interpret information from the available biological effects techniques;

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 2006/1];

8.4) provide advice on whether the existing systems for monitoring dioxins in fish and shellfish for the purposes of safeguarding human health could be used to monitor trends in concentrations, and/or spatial extent, of dioxins in the marine environment. The specific questions to be addressed are [OSPAR 2006/5]:

i) what food safety monitoring of dioxins and furans in fish and shellfish is being carried out in the OSPAR area;

ii) to what extent is it possible to trace fish and shellfish samples to the locations in which they were caught;

Agenda (continued)

iii) to what extent do the data obtained support the determination of trends in concentrations, and/or spatial extent, of dioxins in the marine environment.

(Report from this ToR is required for the OSPAR ASMO meeting starting 12 April 2006)

8.5) 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);

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

8.7) discuss and report on potential contributions for the ecosystem overview of the advisory reports describing the quantity and quality of marine habitat and/or the health of the marine ecosystem, and to consider and report on potential indicators of significant change in these ecosystem attributes.

8.8) present to the Working Group on the Statistical Aspects of Environmental Monitoring (WGSAEM) proposals for collaboration for joint discussion;

8.9) review and update sub-regional data tables and where necessary include new data (parameters) and/or existing data (parameters) updated where relevant. The data tables will be subject to thematic assessment to be undertaken at a REGNS thematic assessment workshop.

8.10) review developments within the UNEP Global POPs Monitoring Network with particular emphasis on opportunities for collaboration with ICES;

8.11) assess the adequacy of the existing analytical methods for short-chain chlorinated paraffins, dioxins, toxaphene, perfluorinated compounds, PBDEs and other brominated flame retardants for marine environmental assessment and provide guidance on the most appropriate techniques;

8.12) continue to report on new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane(TCPMe) in flatfish;

8.13) critically review the new information on the use of membrane systems for sampling, and on their incorporation within national monitoring programmes;

8.14) provide expert knowledge and guidance to the ICES Data Centre on a continuous basis;

8.15) report on new information regarding perfluorinated compounds (PFOS/PFOA) in environmental samples.

8.16) an additional agenda item arose during the meeting via the ICES Secretariat. This item arose from the Norwegian government as a result of the finding of a sunken submarine (U-864) off the Norwegian coast which had been sunk during the Second World War whilst transporting 60 tonnes of metallic mercury in steel bottles. MCWG was asked to consider:

- how quickly metallic mercury might dissolve in seawater?
- does it need to be transformed to an organic form before it is available for uptake by marine organisms?
- if so, what kind of environment is required for this transformation?
- what is the estimated rate of this transformation?

MCWG will report to ACME before 6 April 2006 on item 8.4 and generally by 24 April 2006 for the attention of the Marine Habitat and Oceanography Committees and ACME.

Agenda (continued)

9) Plenary discussion of draft report
10) Any other business
11) Election OF Chair(s)
12) Possible incorporation of helcom stgqac
13) Recommendations and action list
14) Date and venue of the next meeting
15) Closure of the meeting

Meeting documents

8.1.4/1 Retrospective monitoring of the contamination of marine mussels from the French coasts by PCDD/Fs (1981-2004).
8.1.4/2 UK survey for dioxins and PCBs in eels, June 1997.
8.1.4/3 UK survey of dioxins and PCBs in farmed trout, 1998.
8.1.4/4 UK survey of dioxins and PCBs in UK and imported marine fish, 1999.
8.1.4/5 UK survey of dioxins and dioxin-like PCBs in food, 2003.
8.1.4/6 Information on the Swedish monitoring of dioxins and furans in fish and shellfish.
8.1.4/7 Interim report 1 – Study of dioxin levels in fatty fish from Sweden 2000-2001.
8.1.4/8 Interim report 2 – Study of dioxin levels in fatty fish from Sweden 2000-2001.
8.1.4/9 Interim report 3 – Study of dioxin levels in fatty fish from Sweden 2001-2002.
8.1.4/10 Interim report 4 – Study of dioxin levels in fatty fish from Sweden 2000-2003.
8.1.4/11 Interim report 5 – Study of dioxin levels in fatty fish from Sweden 2000-2005.
8.1.6/1 Report of ICES/HELCOM Steering Group on Quality Assurance of Chemical Measurements in the Baltic Sea (STGQAC) 2006.
8.1.6/2 Notes from HELCOM MONAS meeting November 2005
8.1.7/1 Clarification of terms of reference relating to REGNS and WGRED
8.1.7/2 Report of the Regional Ecosystem Group for the North Sea (REGNS) 2005
8.1.7/3 Report of the Working Group for Regional Ecosystem Description (WGRED) 2005
8.1.7/4 Report of the Working Group for Regional Ecosystem Description (WGRED) 2006.
8.1.9/1 REGNS overview assessment.
8.1.9/2 REGNS overview and thematic data.

Annex 3: MCWG Terms of Reference 2005

2005/2/MHC03 The **Working Group on Marine Chemistry** [MCWG] (Co-Chairs: R. Law, UK, and Jacek Tronczynski, France) will meet jointly with WGMS, WGBEC, and WGSAEM at ICES Headquarters, Copenhagen, Denmark, from 27–31 March 2006 to:

a) update the database of concentrations of metals and organic contaminants in biota/species of relevance to the OSPAR CEMP and prepare a table of new/updated background concentrations and background assessment concentrations for potential use in OSPAR assessments;

b) with WGBEC, contribute to the development of detailed OSPAR guidelines deriving from the ICES/OSPAR Workshop on Integrated Monitoring of Contaminants and their Effects in Coastal and Open-Sea Areas (WKIMON) [OSPAR 2005/6]. Specifically, to critically review the lists of target PAHs and CBs proposed by WKIMON in relation to ability to interpret information from the available biological effects techniques;

c) 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 2006/1];

d) provide advice on whether the existing systems for monitoring dioxins in fish and shellfish for the purposes of safeguarding human health could be used to monitor trends in concentrations, and/or spatial extent, of dioxins in the marine environment. The specific questions to be addressed are [OSPAR 2006/5]:

  i) what food safety monitoring of dioxins and furans in fish and shellfish is being carried out in the OSPAR area;

  ii) to what extent is it possible to trace fish and shellfish samples to the locations in which they were caught;

  iii) to what extent do the data obtained support the determination of trends in concentrations, and/or spatial extent, of dioxins in the marine environment.

(Report from this ToR is required for the OSPAR ASMO meeting starting 12 April 2006)

e) 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);

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

g) discuss and report on potential contributions for the ecosystem overview of the advisory reports describing the quantity and quality of marine habitat and/or the health of the marine ecosystem, and to consider and report on potential indicators of significant change in these ecosystem attributes.

h) present to the Working Group on the Statistical Aspects of Environmental Monitoring (WGSAEM) proposals for collaboration for joint discussion;

i) review and update sub-regional data tables and where necessary include new data (parameters) and/or existing data (parameters) updated where relevant. The data tables will be subject to thematic assessment to be undertaken at a REGNS thematic assessment workshop.

j) review developments within the UNEP Global POPs Monitoring Network with particular emphasis on opportunities for collaboration with ICES;

k) assess the adequacy of the existing analytical methods for short-chain chlorinated paraffins, dioxins, toxaphene, perfluorinted compounds, PBDEs and other brominated flame retardents for marine environmental assessment and provide guidance on the most appropriate techniques;

l) continue to report on new information on tris(4-chlorophenyl)methanol (TCPM) and tris(4-chlorophenyl)methane(TCPMe) in flatfish;

m) critically review the new information on the use of membrane systems for sampling, and on their incorporation within national monitoring programmes.

n) provide expert knowledge and guidance to the ICES Data Centre on a continuous basis.

MCWG will report by 24 April 2006 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.
Scientific Justification and relation to Action Plan:	Action Plan Goals Nos: 2.2.2: (tor c and k). 2.2.3: (tor f) 2.8: (tor a, b, d, g, h, i, j, k, l and m) 4.12: (tor e) a) The development of BCs and BACs, following the joint ICES/OSPAR Workshop held early in 2004, continues. The use of these tools in the OSPAR CEMP temporal assessment at MON 2004 proved effective. However, gaps have been identified and further refinement is required. In addtion, BCs and BACs have not yet been defined for all CEMP determinands. Such tools are required for the OSPAR JAMP [OSPAR 2006/4]. b) This is in response to an OSPAR request [OSPAR 2005/6]. c) This is in response to an OSPAR request [OSPAR 2006/1]. d) This is in response to an OSPAR request [OSPAR 2006/5] e) This is in response to an OSPAR request [OSPAR 2005/1] f) This is in response to a standing request from HELCOM g) This is in response to a request by ACME. ICES is moving towards providing scientific advice for the integrated management of all human activities that affect marine waters. Information on the quantity and quality of habitat and the health of marine ecosystems will be essential to the achievement of this goal.. h) This is in response to a request from ICES. This task will support long-term planning for WGSAEM. i) This is response to a request from the REGNS group. j) The development of the UNEP monitoring programme is relevant to other collaborative international monitoring programmes, and a watching brief will be maintained h) This is in response to a standing request from HELCOM. k) The presence of persistent organic pollutant in the aquatic environment is of continuing concern. Both the distribution and effects of such compounds is relevant to on-going and future assessments of the state of the aquatic environment. The compounds listed are present on various lists (e.g. WFD, OSPAR) of compounds for priority action and are compounds for which marine targets are being set. l) This project was initiated several years ago among MCWG members on the basis of concerns regarding these contaminants in the marine environment. m) These systems are being reviewed for application to monitoring of contaminants in the marine environment. n) This is in direct response to a request from the ICES Data Centre. 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.
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, and WGSAEM.
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

RECOMMENDATION	ACTION
1. That additional mono-*ortho* CB congeners (CB105, CB156 & CB157 as a minimum) should be included within marine monitoring programes	ACME / OSPAR
2. Include a suite of alkylated PAHs (naphthalenes; dibenzothiophenes and phenanthrenes/anthracenes) within marine monitoring programmes	ACME / OSPAR
3. MCWG recommends that ICP-MS should be included as an additional method for the analysis of mercury in biota.	ICES / HELCOM STGQAC
4. MCWG recommends that dioxin data gathered for food safety purposes are not suitable for the investigation of environmental levels and trends due to the way in which the surveys are conducted.	ACME / OSPAR

Annex 5: Action List

- Ralf Ebinghaus to report on current studies concerning perfluorinated compounds to MCWG 2007
- Evin McGovern, Michel Lebeuf, Gert Asmund and Jacek Tronczynski agreed to submit data from their own studies relating to the determination of possible concentration ratios between non-*ortho* CBs and total CBs to Patrick Roose, and Patrick to report their findings to MCWG2007. Other members with suitable data are also encouraged to submit them to Patrick.
- MCWG Chairs will inform HELCOM STGQAC Co-Chairs that MCWG welcomed their proposal to operate within MCWG.
- Klaus Nagel agreed to inform MCWG 2007 regarding nutrients and organically-bound nutrient species in the marine environment as potential drivers for processes which can directly influence the uptake and distribution of contaminants in the environment and ecosystems generally. All MCWG members are encouraged to contribute and to communicate with Klaus Nagel intessessionally for preparing this presentation.
- Peter Lepom will inform MCWG 2007 of the outcome of report on German project that includes method development for analysis of SCCPs.
- Patrick Roose, Ton van der Zande and Jacek Tronczynski (MCWG) to assist Foppe Smedes in preparation of the program for the proposed trial survey of passive samplers. This includes the development of a proposal for the trial survey and the preparation of technical guidelines for the conduct of surveys using passive samplers.
- Patrick Roose to explore the possibility of the passive sampler trial survey being funded from OSPAR and to communicate outcome to the steering group.
- Peter Lepom to explore the possiblity of funding at EU level, as the operational development of passive sampler devices for monitoring may be eligible to policy support under the Water Framework Directive and to communicate outcome to the steering group.
- Patrick Roose, Ton van de Zande and Jacek Tronczynski to communicate the results of the passive sampler trial survey at MCWG 2007.
- Robin Law to transmit Canadian mussel watch data to Jacek Tronczynski when received, for consideration of their suitability for determining background concentrations.
- All members to submit data from their national monitoring programmes which might be suitable for use in the determination of background concentrations in biota to Patrick Roose, with a view to continuing this work at MCWG2007.
- Robin Law to circulate the draft executive summary of the MCWG 2006 report to all members for comment.
- MCWG members representing NERI, FIMR, RIVO, IOW, the Marine Institute and Cefas to explore the possibilities of participating within the proposed trial survey of passive samplers.
- Gert Asmund, Robin Law and Klaus Nagel to respond to intersessional requests from the ICES data centre.

Annex 6: Retrospective monitoring of the contamination of marine mussels from the French Coasts by PCDD/Fs (1981-2004)

EMV - POPs in Biota – Levels and Trends

Retrospective monitoring of the contamination of marine mussels from the French Coasts by PCDD/Fs (1981-2004)

Catherine MUNSCHY[1], Inger JOHANSSON[1], Nadège GUIOT[1], Karine HEAS-MOISAN[1], Jacek TRONCZYNSKI[1]

[1]Ifremer

1. Introduction

The contamination of marine mussels (*Mytilus edulis* or *Mytilus galloprovincialis*) by organohalogen compounds has been studied at different sites along the French coastlines. Archived mussel samples were collected over the past 23 years within the French national mussel watch network (RNO –Réseau National d'Observation). These samples were analysed for PCDD/Fs. The studied sites represent areas characterized by different environmental contamination levels receiving various inputs from human activities, over the English Channel, the Atlantic Ocean and the Mediterranean Sea.

The results presented here focus on the contamination levels and temporal trends of polychlorinated dibenzo-*p*-dioxins and polychlorinateddibenzofurans (PCDD/Fs) and are in line with a previous study which presented levels and temporal trends of PBDEs, PCBs and organochlorine pesticides in the same samples.[1,2]

2. Materials and methods

Sampling sites

The locations of the studied sites are shown in Figure 1. Villerville is located in the English Channel, and under the direct influence of the Seine river basin, which is a highly industrialized and urbanized zone, characterized by high levels of contamination by PCBs. On the Atlantic Coast, the studied site (PenBé) is located in the Bay of the Vilaine river, whereas the Mediterranean site is located in the Thau lagoon. The selected mussel samples were collected in the same way and at the same period each year (from late November to early December). This sampling scheme avoids possible differences of contaminant concentrations due to seasonal variations related to the reproduction and spawning periods.

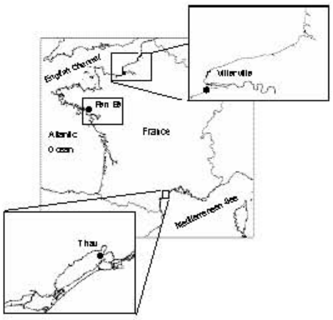

Figure 1: Location of the studied sampling stations

Mussel analysis

The analyses were conducted using approximately 5 grams (dry weight) of the archived samples. Detailed extraction and cleanup methods have been described elsewhere.[1,2,3] Analyses of PCDD/Fs were performed by High

Resolution Gas Chromatography - High Resolution Mass Spectrometry with an AutoSpec Ultima (Waters) operated in Electronic Impact ionisation mode at a resolution of 10000 in the Selected Ion Monitoring mode, and equipped with a Hewlett-Packard (Palo Alto, CA, USA) 6890 GC and a Combi-Pal autosampler (ATAS). Two columns were used: a DB-5MS (J&W Scientific, CA) capillary column (60 m x 0.25 mm i.d., 0.25 µm film thickness), and an RTX-Dioxin2 (Restek Corp.) capillary column (40 m x 0.18 mm x 0.18 µm film thickness) used as a confirmation column. Seventeen congeners of PCDD/Fs were quantified by isotopic dilution method based on the US EPA 1613 method. Recoveries of individual labelled congeners were between 76% +/-15% and 94% +/- 12% for each compound (mean value +/- rsd, n= 33). Quality Assurance / Quality Control procedures (blank determinations covering the whole analytical procedure, analysis of replicates and certified materials) were included within every batch of six to eight samples. The laboratory also routinely participates in the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) intercomparison exercises.

Results and Discussion

The concentrations of PCDDs and PCDFs determined in the mussels collected in the English Channel (Villerville), Atlantic Ocean (Pen Bé) and Mediterranean Sea (Thau) are presented in Table 1. The highest concentrations are found in the samples collected at Villerville, presumably due to the influence of the Seine river. High levels of contamination of mussels by PCBs and PBDEs have also been reported in this area[1,2] which receives higher inputs from human activities through the Seine river. The mussels collected at Pen Bé and Thau both show the same levels of contamination, which are 3 to 8 times lower than those determined in the mussels from Villerville.

When expressed as 2,3,7,8-TCDD equivalents (TEQs) using the WHO-TEFs for humans/mammals[4], the levels are in the 0.43-2.01 pg TEQ.g^{-1} wet weight (w.w.) range for the samples from the Atlantic and Mediterranean Coasts. The results obtained for the mussels collected at Villerville are in the 3.46-5.84 pg TEQ.g^{-1}w.w. range, thus exceeding the recommended limit set by the European Community for sea products intended for human consumption.[5] The TEQ values calculated for planar PCBs (IUPAC nos. 77, 126 and 169) in the same samples from Villerville are in the 6.34-18.55 pg TEQ.g^{-1}w.w. range, whereas the contribution of mono-ortho congeners (IUPAC nos.123, 118, 105, 167, 156, 189) is between 3.87 pg TEQ.g^{-1}w.w. and 10.61 pg TEQ.g^{-1}w.w. Compared with the results previously reported in the literature[6], the PCDD/F contamination levels determined in the mussels collected at Villerville are higher throughout the whole studied period.

	Villerville (n=12) (English Channel)		Pen Bé (n=6) (Atlantic Coast)		Thau (n=8) (Mediterranean Sea)	
	Min	Max	Min	Max	Min	Max
PCDFs pg.g^{-1} dry weight (d.w.)	72.06	129.51	16.50	46.66	13.90	49.65
PCDDs pg.g^{-1} d.w.	23.26	173.51	17.46	39.13	7.66	42.76
PCDFs pg.g^{-1} wet weight (w.w.)	18.97	32.43	3.63	10.26	2.92	11.32
PCDDs pg.g^{-1} w.w.	6.75	41.64	2.49	9.64	1.61	9.41
PCDFs pg WHO-TEQ.g^{-1} w.w	3.02	5.07	0.55	1.67	0.42	1.73
PCDDs pg WHO-TEQ.g^{-1} w.w.	0.30	1.01	0.15	0.37	0.01	0.17

Table 1: Concentrations of PCDFs (Sum of 10 congeners) and PCDDs (Sum of 7 congeners) expressed in pg.g^{-1} on a d.w. or w.w. basis, and in WHO-TEQ.g^{-1}w.w. in mussel samples collected at selected sites of the French Coasts, 1981-2004.

The temporal trends of the levels of PCDD/Fs determined in the archived samples over the 1981-2004 period are shown in Figure 2. The results show a general decrease in the contamination over the past 23 years at all sites. At Villerville, the levels determined in 1999, and to a lesser extent in 2001, show a significant increase, followed by a drop to the lowest concentrations in 2004. The same relative increase has been reported previously for PCBs and PBDEs, in relation to significant flooding of the River Seine during these years.[1,2]

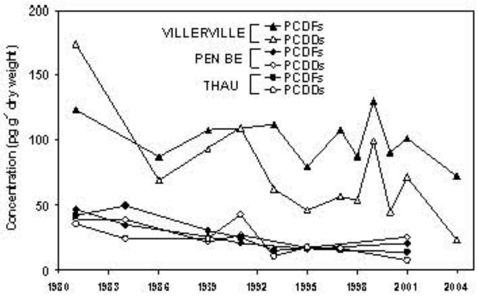

Figure 2: PCDD/F concentrations (pg.g^{-1} d.w.) in mussels from different sites over the years 1981-2004.

The contamination patterns in mussel samples are dominated by 2,3,7,8-TCDF and OCDD, these two compounds representing more than 60% of the sum of the seventeen 2,3,7,8-PCDD/F congeners (Figure 3). Moreover, the tetra-chlorinated furans' profile is characterized by a complex mixture of different congeners. This pattern is different from the one observed previously in dab in the Seine estuary[3], and from the PCDD/F profiles reported in the literature for different marine species[7]. However, this profile seems to be typical for mussels and is similar to observations already reported for mussels from other marine areas.[6] The patterns are similar for all samples among the different sites, suggesting that no distinct source could be identified on a local scale. Combustion and metallurgic processes are important sources of the dominant congeners identified in mussels.[8,9,10] However, the contamination of mussels is also related to assimilation preferences and metabolism.

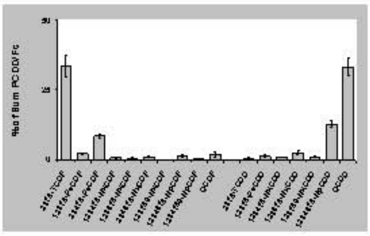

Figure 3: Normalized distribution pattern of PCDD/F congeners in mussel samples from Pen Bé (mean values, expressed as a percentage of the sum of 17 PCDD/F congeners, n=6). Error bars are for standard deviations.

This study provides new information with respect to contaminant levels and temporal trends of PCDD/Fs in the French coastal marine environment. A general decrease in levels of PCDD/Fs was observed at all studied sites, with still high levels remaining in the Seine Bay.

3. Acknowledgements

Funding for this work is from the French « Ministère de l'Ecologie et du Développement Durable » also supporting the RNO (Réseau National d'Observation) from which samples were available. I. Johansson received a grant from Ifremer for her post-doctoral studies.

4. References

1. Johansson I., Moisan K., Guiot N., Truquet I., Munschy C., and Tronczynski J., (2004) *Organohalogen Compounds* 66: 1844-1852.

2. Johansson I., Moisan K., Guiot N., Truquet I., Munschy C., and Tronczynski J., (2005) *Chemosphere*, accepted.

3. Munschy C., Moisan K., and Tronczynski J., (2004) *Organohalogen Compounds* 66: 1672-1680.

4. van Leeuwen F.W.R., Feeley M., Schrenk D., Larsen J.C., Farland W., Younes M., (2000) *Chemosphere* 40: 1095-1101.

5. 2002/201/CE, (2002) Journal officieldescommunautéseuropéennes, C(2002) 836.

6. Abad E., Pérez F., Llerena J.J., Caixach J., Rivera J., (2003) *Environ. Sci. Technol.* 37: 22, 5090-5096.

7. Knutsen J., Bjerkeng B., Naes K., Schlabach M., (2003) *Chemosphere* 52: 745-760.

8. Hellou J. and Payne J.F., (1993) *Mar. Environ. Res.* 36: 117-128.

9. Fernandez M.P., Ikonomou M.G., Courtenay S.C., and Wirgin I.I., (2004) *Environ. Sci. Technol.* 38: 976-983

10.Umlauf G., Christoph E.H., and Bidoglio G., (2004) *Organohalogen Compounds* 66: 1333-1339.

Annex 7: Draft resolutions 2006

2MHC03 The **Working Group on Marine Chemistry** [MCWG] (Co-Chairs: Jaceck Tronczynski, France and Evin McGovern; Ireland) will meet during the week of 5–9 March 2007. MCWG has received a tentative invitation to hold its 2007 meeting in Hamburg. [to be confirmed at the Annual Science Conference]. If this is not possible, MCWG could meet at ICES Headquarters.

a) update the database of concentrations of metals and organic contaminants in biota/species of relevance to the OSPAR CEMP and prepare a table of new/updated background concentrations and background assessment concentrations for potential use in OSPAR assessments;

b) 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 2006/1];

c) 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);

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

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

f) 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;

g) review intersessional activities undertaken within the REGNS process of regional and thematic assessment and the outcome of the 2006 theme session at the Annual Science Conference;

h) 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;

i) 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.

j) report on new information regarding perfluorinated compounds in environmental samples;

k) with WGBEC, review the analytical methodology and toxicity information relating to certain alkylated PAH compounds proposed for inclusion in monitoring programmes;

l) provide expert knowledge and guidance to the ICES Data Centre on a continuing basis.

MCWG will report by 30 April 2007 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:** 2.2.2: (tor a,b and g). 2.8: (tor a, c, e, f, h, i, j,) 4.12: (tor d) 6.1: (tor k) a) The development of BCs and BACs continues. Gaps have been identified and further refinement is required in the better determination of BCs. In fact, BCs and BACs have not yet been defined for all CEMP determinands. 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 OSPAR request [OSPAR 200x/x] d) This will be in response to an ICES request e) This project is initaited by MCWG to reinforce its nutrient activities f) This project is initaited by MCWG to reinoforce its nutrient activities and to create a better link between contaminants dynamics and ecosystems drivers; g) This will be in repsonse to the REGNS 2006 conference; h) This project was initiated several years ago among MCWG members on the basis of concerns regarding these contaminants in the marine environment; i) These passive sampler devices will be reviewed for application to monitoring of contaminants in the marine environment; j) This project was initiated among MCWG members on the basis of concerns regarding these contaminants in the marine environment; k) This is initiated by MCWG. l) This is in direct response to a request by the ICES Data Centre;
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, and WGSAEM.
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.