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4–8 March 2013

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Executive Summary

The Marine Chemistry Working Group [MCWG] (Chair: Katrin Vorkamp, Denmark) met at ICES offices in Copenhagen, Denmark from 4 – 8 March 2013. The meeting was attended by 21 participants representing ten different countries.

MCWG worked in a combination of plenary work, subgroups and specific task groups. The **chemical oceanography subgroup (COSG)** continued their work at this meeting and consisted of six MCWG members. Further ad-hoc subgroups were formed to deal with **chlorophyll analyses**, **perfluoroalkyl substances (PFAS)** and **passive sampling**, respectively. Since the 2012 meeting, two manuscripts had been submitted for publication, i.e. a **TIMES manuscript on PCB analyses** and a **CRR on ocean acidification**.

MCWG had not received any requests from OSPAR at this meeting. MCWG responded to several recommendations and requests received from other working groups, i.e. on passive sampling (WKPSPD), ocean acidification (SGOA) and marine litter (WGBEC).

Regarding **passive sampling**, MCWG developed preliminary Background Concentrations and Background Assessment Concentrations for freely dissolved concentrations of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and some chlorinated pesticides. MCWG worked on a guideline for the application of passive sampling techniques in sediments and decided to develop another guideline on the determination of relevant partition coefficients. The work on these guidelines will continue intersessionally, in collaboration with WGMS. Furthermore, the development of a proficiency testing scheme was planned together with a QUASIMEME representative. MCWG also provided comments on the results and conclusions of WKPSPD.

Regarding **ocean acidification**, SGOA had worked on data streams and reporting formats for carbonate parameters and MCWG/COSG continued this work, in collaboration with the ICES Data Centre. With a view of establishing a proficiency testing scheme for carbonate parameters, MCWG has planned a workshop on quality and comparability of sampling and analysis of Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC) in collaboration with QUASIMEME.

Regarding **marine litter**, MCWG had invited Jakob Strand (WGBEC) to give an introductory presentation. The environmental impacts of exchange processes between marine litter and contaminants were discussed, but more data will be needed for a better understanding of this problem. Together with the ICES Data Centre, MCWG discussed adjustments to the ICES database to accommodate data on marine litter and associated contaminants, possibly to be followed up in an ICES workshop.

The subgroup on **chlorophyll** discussed possibilities and limitations of different instrumental techniques and their comparability. A workshop on chlorophyll analyses and related QA/QC has been planned together with QUASIMEME.

The **PFAS** subgroup primarily dealt with the question of exchanges of PFAS between the ocean and atmosphere. The subgroup decided to combine MCWG's work on this topic of the last four years in one publication.

MCWG had invited **Prof. Katherine Richardson** of the University of Copenhagen for a plenary presentation on "Plankton biodiversity influences carbon and nitrogen cycling – and vice versa!!" Further **projects of relevance to MCWG** were presented by

MCWG members, including i) the Norwegian MAREANO programme, ii) the UK monitoring of polybrominated diphenyl ethers (PBDEs) and other organohalogen compounds, iii) the German monitoring of PBDEs in the North Sea and the Baltic Sea and iv) a case study from the Netherlands on effects of persistent organic pollutants (POPs) on eel.

Steven Tito of the **QUASIMEME project office** visited MCWG to present and discuss new developments at QUASIMEME. MCWG suggested extending parameter lists for trace elements and PAHs. In addition, development exercises and workshops on new techniques and parameters were planned, i.e. on passive sampling, carbonate parameters and chlorophyll analysis.

Following up on initial work at MCWG 2012, MCWG reviewed the literature on using **seabird eggs** as a monitoring matrix for organic contaminants and trace elements, including experiences from the Trilateral Monitoring and Assessment Program (TMAP) in the Wadden Sea, the Arctic Monitoring and Assessment Program (AMAP) and national monitoring programmes (e.g. Sweden). The decision about a concluding report was postponed to 2014 as more information, in particular on seabird biology, will be needed.

MCWG was informed about developments under the **Water Framework Directive (WFD)** in terms of a proposal for a directive amending the WFD and related environmental quality standards (EQS). MCWG highlighted its expertise with regard to contaminant monitoring, including the development of guidelines, which could tie into groups outside of ICES and OSPAR.

MCWG was also informed about activities under the **Marine Strategy Framework Directive (MSFD)**, including a workshop at the Joint Research Centre, an OSPAR compilation of national targets and indicators under Descriptor 8 and the European project PERSEUS. MCWG highlighted its marine expertise which could contribute to current activities in MSFD-related groups at the European level.

With a view to a concurrent meeting in 2014, MCWG suggested topics for **joint sessions** to WGBEC and WGMS, including marine litter, passive sampling and ocean acidification. MCWG also continues to be interested in activities in WGEEL, SGONS and SGOA.

1 Opening of the meeting

The Marine Chemistry Working Group (MCWG) (Chair Katrin Vorkamp, Denmark) met at ICES in Copenhagen, Denmark, from 4 – 8 March 2013. The chair opened the meeting on 4 March 2013 at 10 a.m. and welcomed the participants to the 35th meeting of MCWG.

The participants introduced themselves and their affiliations and described their specific interests within the field of marine chemistry. Katrin Vorkamp conveyed regards and messages from MCWG members who were not able to attend MCWG 2013.

The chemical oceanography subgroup (COSG) continued from the last two meetings, consisting of Carlos Borges, David Pearce, Evin McGovern, Mikael Krysell, Pamela Walsham and Sue Hartman. Three further informal subgroups were formed during the meeting to deal with chlorophyll analyses (agenda item 5.h see section 5.8), perfluorinated alkylated substances (agenda item 5.j, see section 5.10) and passive sampling (agenda item 5.k, see section 5.12), respectively.

The meeting was attended by 21 participants from 10 countries. The list of participants is given in Annex 1.

2 Adoption of the agenda

The draft agenda was discussed in connection with the action list of MCWG 2012. The agenda was adopted as shown in Annex 2.

Report of MCWG-related ICES activities since MCWG 2012

Katrin Vorkamp presented a summary of the main work at MCWG 2012, to refresh participants' memory and to provide links to the tasks at MCWG 2013. Since MCWG 2012, two manuscripts have been submitted to ICES by members of MCWG, both are currently in press:

Hydes, D.J., McGovern, E., Walsham, P., Borges, A.V., Borges, C., Greenwood, N., Hartman, S.E., Kivimae, C., Nagel, K., Olafsdottir, S., Pearce, D., Sahlsten, E., Rodriguez, C., Webster, L. In press. Chemical aspects of ocean acidification monitoring in the ICES marine area. ICES Cooperative Research Report.

Webster, L., Roose, P., Bersuder, P., Vorkamp, K., Kotterman, M., Haarich, M. In press. Determination of polychlorinated biphenyls (PCBs) in sediment and biota. ICES Techniques in Marine Environmental Sciences.

3 Report of MCWG-related ICES activities since MCWG 2012

3.1 Internal ICES business

Katrin Vorkamp presented the implementation plan accepted at ICES for the **multi-annual management** of SCICOM working groups (WGs). The main changes include the following points:

- WGs are appointed for 3 years and can request renewal.
- Study groups disappear.
- Terms of Reference are approved for the 3-year-period, with room for ad hoc requests.
- The WG chair serves for the same 3-year-period.
- WG members are nominated for the same 3-year-period.
- Reduced reports after year 1 and 2, full report after year 3.
- Self-evaluation of WGs (basis for SCICOM decision on renewal), with focus on outcomes.

Existing WGs move to multi-annual ToRs when they request this change or at the end of the term of the current chair.

These proposed changes and their consequences for MCWG had been discussed previously (see MCWG 2012) and MCWG's comments had been conveyed to ICES on two occasions. MCWG members confirmed their concern about potential interruptions of continuation. The commitment of WG members for a 3-year-period was regarded as unrealistic, given frequent structural changes at the home institutes and budget reductions. The transition to the multi-annual ToRs will take place for MCWG with the term of a new chair.

Katrin Vorkamp further informed MCWG about **SCICOM's comments on MCWG's draft ToRs** for the current meeting. SCICOM has considered MCWG's draft ToRs "too generic, with too much use of the word "reporting" and too few concrete outputs (review articles, CRRs, databases)". These comments had led to some changes in the ToRs, which Katrin Vorkamp explained to the MCWG members. In general, MCWG members were in favour of concrete outputs and emphasized that the group had published seven out of the last nine TIMES papers. Another TIMES article and a Cooperative Research Report (CRR) are in press, further publications are in preparation (see section 5.13 and Annex 3).

Katrin Vorkamp briefly informed about the **SSGHIE** Webex meeting in August 2012 which focused on aquaculture.

Following their draft resolution at MCWG 2012, MCWG proposed the **theme session "Physical-chemical aspects of ocean acidification in the ICES area" for the ICES Annual Science Conference (ASC)** at Reykjavik (Iceland) from 23-27 September 2013. The conveners will be David Hydes (UK), Alberto Borges (Belgium) and Jan Olafson (Iceland). Katrin Vorkamp highlighted the excellent collaboration with COSG on this proposal. Besides naming the conveners, the proposal required a description of the theme session and information about the scientific fields to be reached as well as linkages to the ICES Science Plan, the ICES Science Steering Groups and ACOM. The proposed theme session has been approved by ICES. Abstracts can be submitted via the ICES homepage. The deadline for abstract submission is 19 April 2013.

Action: ***Evin McGovern to inform the AMAP Secretariat about this theme session at ASC 2013.***

The **ICES homepage** has a new design and should include information about each working group. Evin McGovern, Patrick Roose and Gert Asmund volunteered to draft some text about MCWG, its history, current task and broad range of expertise, for the webpage. The draft was discussed in plenary (see section 6) and approved by all members at MCWG 2013. The text will be available at

http://www.ices.dk/community/groups/Pages/MCWG.aspx

Action: ***Katrin Vorkamp to forward the final version of the MCWG description – for the ICES webpage - to the ICES Secretariat.***

A set of **OSPAR requests** had originally been given to MCWG 2013, but had later been postponed. These requests include the updates of the following guidelines:

- Contaminants in biota: Determination of metals (technical annex 2)
- Contaminants in sediment: Determination of butyltins in sediments (technical annex 4)
- Contaminants in sediment: Determination of metals (technical annex 6)

As usual, the update of sediment guidelines should proceed in collaboration with the Working Group on Marine Sediments (WGMS). The requests might become part of the work programme of MCWG 2014.

3.2 Advice Drafting Group on Monitoring 2012

Katrin Vorkamp participated in the meeting of the Advice Drafting Group on Monitoring (ADGMON) in May 2012. The agenda included the following OSPAR requests:

- Development of a JAMP guideline on monitoring of contaminants in seawater
- Revision of JAMP guidelines on nutrients and dissolved oxygen
- Spatial design of a regional monitoring programme for contaminants in sediment

The draft guideline for the **monitoring of contaminants in seawater** had been a 2-year-project for MCWG. In 2011, MCWG had presented an initial draft to ADGMON and received internal advice for the finalization of the draft guideline. ADGMON 2012 based its work on the final draft guideline submitted by MCWG 2012 and comments of two independent reviewers.

Katrin Vorkamp presented the reviewer comments to MCWG. These comments are also available at an annex of the MCWG 2012 report. Taking into account the review comments, ADGMON 2012 finalized the guideline and forwarded it to OSPAR as a piece of ICES advice. ICES advised OSPAR to include the document into the JAMP guidelines.

The guidelines on **monitoring of nutrients and dissolved oxygen** had originally been revised by MCWG 2009. However, ICES advised OSPAR at the time to await developments at the EU level within the Marine Strategy Framework (MSFD) which might be relevant for these guidelines. In the meantime, some OSPAR contracting parties provided comments on these guidelines. At MCWG 2011, these comments, potential impacts by MSFD and other relevant information were gathered and reviewed. The revision of the guidelines was completed at MCWG 2012.

In the same way as for the seawater guideline, ADGMON 2012 based its work on the revised guidelines provided by MCWG 2012 and reviewer comments. Katrin Vorkamp presented the reviewer comments to MCWG, which are also included as an annex to the MCWG 2012 report. ADGMON 2012 finalized the revision and forwarded the revised guidelines to OSPAR as ICES advice.

The **spatial design of a regional monitoring programme** had been an OSPAR request to WGMS. WGMS had addressed this in a two-year-project and received internal advice by ADGMON 2011. WGMS had highlighted the significance of some parameters affecting comparability, for example sediment grain size. These parameters were further discussed at ADGMON 2012, as well as the question if passive sampling could overcome some of these issues. In order to follow up on this line of thinking, a workshop on passive sampling was suggested (see section 3.5).

Katrin Vorkamp had also been invited to the Advice Drafting Group on Lysosomal Activity (ADGLYSAC), but was unable to attend. ADGLYSAC also dealt with the OSPAR request to review environmental assessment criteria (see MCWG 2012).

3.3 Annual Science Conference 2012

No members of MCWG attended the Annual Science Conference (ASC) which had been held in Bergen (Norway) in September 2012.

As mentioned above (see item 3.1), MCWG has arranged a theme session on ocean acidification at ASC 2013. MCWG members are encouraged to submit abstracts and present their research in this theme session.

3.4 OSPAR/ICES Study Group on Ocean Acidification (SGOA)

Evin McGovern, co-chair of SGOA, presented the ToRs of SGOA, the outcomes of the first meeting of SGOA (11-14 December 2012) and thoughts on the role of MCWG in SGOA's work. The report of the first SGOA meeting is available at

http://www.ices.dk/community/groups/Pages/SGOA.aspx

SGOA is a joint OSPAR/ICES study group with a three-year-lifespan during which certain products should be developed for OSPAR. SGOA's ToRs are to:

a) Collate chemical data and information on ocean acidification in the OSPAR Maritime Area;

b) Seek information from relevant international initiatives on Ocean acidification; as listed in OSPAR MIME 11/3/3 (e.g. EU, Arctic Council);

c) Finalize guidelines for measuring carbonate system;

d) Collect and exchange information on biological effects on plankton, and macrozoobenthos;

e) Consider the strategy that would be required for an assessment framework appropriate for long-term assessment of the intensity/severity of the effects of ocean acidification, including any assessment criteria required;

f) Inform the development of biological effects indicators for ocean acidification, including the identification of suitable species and key areas;

g) Elaborate reporting requirements to ICES (taking account of the information in Table at OSPAR MIME 2011 SR Annex 6);

h) Report a first assessment of all available data in the OSPAR maritime area.

Regarding ToR a), SGOA noted that several countries monitored parameters related to OA, but these activities were not necessarily coordinated. Furthermore, few monitoring activities covered potential impacts of OA, suggesting that the developing of effect indicators (ToR f) might become challenging. The SGOA 2012 report summarised information on OA data and programmes provided by SGOA members. In addition, the CRR produced by members of MCWG includes information on ongoing OA research and monitoring activities in the ICES area (Hydes et al., in press).

Regarding ToR b), Evin McGovern highlighted the global OA observation network which had its first meeting in 2012 and is going to meet again in Scotland in July 2013. SGOA suggested OSPAR become a key regional component in this network. More information about the OA network, its goals and strategies is given in the SGOA report.

Regarding ToR c), MCWG 2012 had provided initial drafts of these guidelines, for further work by SGOA. The guidelines were finalised at SGOA 2012.

An underlying issue of most of the ToRs is the question of data reporting. The data obtained as part of the OSPAR monitoring are stored in the ICES database from which they can be extracted by OSPAR or other users for e.g. assessment purposes. Consequently, the ICES database should also accommodate OA monitoring data from the OSPAR area. In the current situation, data are stored in different databases of which The Carbon Dioxide Information Analysis Centre (CDIAC) database is a central database for international carbon chemistry data. SGOA had initial discussions on data reporting to the ICES database which should be moved forward by MCWG (see section 5.5.1).

Further areas of collaboration between SGOA and MCWG could be

- updates of protocols and methods for OA monitoring,
- QA/QC requirements (see section 5.1), including methods of sample conservation,
- completing overviews and lists of OA monitoring activities.

Evin McGovern highlighted that the CRR prepared by MCWG (Hydes et al., in press) had been a key starting point for SGOA.

The next SGOA meeting will be held at ICES in Copenhagen, from 7-11 October 2013. Evin McGovern mentioned that SGOA would benefit from the participation of experts in biogeochemical modeling.

References:

Hydes, D.J., McGovern, E., Walsham, P., Borges, A.V., Borges, C., Greenwood, N., Hartman, S.E., Kivimae, C., Nagel, K., Olafsdottir, S., Pearce, D., Sahlsten, E., Rodriguez, C., Webster, L. In press. Chemical aspects of ocean acidification monitoring in the ICES marine area. ICES Cooperative Research Report.

3.5 ICES Workshop on Passive Sampling and Passive Dosing (WKPSPD)

Kees Booij, co-chair of WKPSPD, presented the ToRs of WKPSPD and the main topics and conclusions of the workshop (29-31 January 2013). The WKPSPD report is not yet available.

The ToRs of the workshop were as follows:

a) Report to ICES on current experience of the use of Passive Sampling in the (marine) environment and Passive Sampling and Passive Dosing in the laboratory

b) Report to ICES on the practical application of Passive Sampling (PS) and Passive Dosing (PD) in compliance monitoring and assessments (WFD, MSFD and Regional Seas Conventions). Relevant issues encompass:

   i) Evaluate current knowledge for its practical applicability;

   ii) Investigate ways to link 1) passive sampling measurements to concentrations in biota (chemical monitoring) and 2) potential environmental effects (biological effects monitoring);

   iii) Investigate how a monitoring system based on PS/PD could be conceived;

c) Consider the legal aspects of monitoring with PS/PD e.g. compliance checking, uncertainties and the reliability in court;

d) Describe research needs and challenges in relation to Passive Sampling and Passive Dosing in marine assessment based on a), b) and c).

The workshop was structured along the following sessions:

1) Compliance monitoring

2) Passive sampling of marine and transitional waters

3) Passive sampling of sediment

4) Linking passive sampling to concentrations in biota

5) Passive sampling/dosing and toxicity testing

Each session consisted of several presentations and subsequent discussions. The workshop members agreed that the focus of the workshop should be on non-polar compounds for which passive sampling (PS) techniques are most mature. These compounds include polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and hexachlorobutadiene (HCBD). Established PS techniques might also be suitable for dicofol, heptachlor/heptachlor epoxide and dioxins, while uncertainty of sampling rates makes PS within compliance monitoring less suitable for e.g. perfluorooctane sulfonate (PFOS) and polar contaminants. There was a lack of available expertise regarding PS of metals.

The compliance monitoring focussed on potential applications of PS in the context of the EU Water Framework Directive (WFD) and OSPAR monitoring programmes. Environmental Quality Standards (EQS) in EU WFD have been defined for total water – in contrast to freely dissolved concentrations C_{free} - , but might originally have been derived from toxicological information involving C_{free}. For data comparison purposes, monitoring guidelines and QA/QC measures should be in place, including proficiency testing schemes. These requirements were further addressed by MCWG at this meeting, see sections 5.1. and 5.12.

Several presentations showed successful PS applications in marine/transitional water and in sediments, including low detection limits and better links to toxicity, in particular compared with “total sediment” concentrations. In these examples, equilibrium between the passive sampler and the sediment pore water could be reached within a reasonable time frame, while PS in water included kinetic and equilibrium sampling. In all cases, accurate partition coefficients are crucial.

Similarly, PS offers a direct toxicity link to organisms, avoiding issues of normalisation to lipids and inter-species variability. However, contaminant monitoring in the organisms will still be necessary to assess biomagnification and essentially food safety. PS has also directly been applied in lipids, which requires lipid-polymer partition coefficients, but results in all biota concentrations on the same scale. Passive dosing (PD) offers the possibility of testing mixture effects of non-polar compounds at equilibrium. For compounds that have not reached equilibrium in PS or PD, toxicity will likely be underestimated. Observed effects might also have other reasons than non-polar contaminants, e.g. sulphur toxicity.

WKPSPD concluded that PS could replace monitoring of non-polar contaminants in water, sediment and potentially biota. Several recommendations were formulated by WKPSPD for further work, among these the development of guidelines for determination of partition coefficients (see section 5.12.2), guidelines for PS in sediments (see section 5.12.3), intercalibrations and eventually proficiency testing schemes (see section 5.1). The development of assessment criteria based on C_{free} was recommended to WGBEC. Finally, WKPSPD recommended to OSPAR to include PS of water and sediment to the pre-Coordinated Environmental Monitoring Programme (CEMP).

The results and conclusions of WKPSPD were discussed by MCWG and some MCWG members disagreed with some of WKPSPD's conclusions. This discussion is summarised in section 5.12.

4 Plenary presentations

Katherine Richardson, professor at the Center for Macroecology, Evolution and Climate at the University of Copenhagen, gave the following plenary presentation:

Plankton biodiversity influences carbon and nitrogen cycling – and vice versa!!

For too long, it has been assumed that because they are easily observed and on the "front line" when it comes to receiving the sun's energy that it is the species and magnitude of phytoplankton activity in the surface layer of the ocean that control the magnitude of the carbon and nitrogen flux in the water column but this picture is changing. Drawing on examples from both offshore and coastal waters, this seminar will focus on surprises that can occur in carbon flux when we look below the surface and emphasize the importance of biodiversity for carbon fluxes. Take home messages include the following: 1) plankton can and do control their own positions in the water column and the vertical stratification of species in the water column can be so fine that it cannot be sampled using standard techniques, 2) We do not (yet) have good estimates for photosynthesis in the ocean and, indeed, much of the particulate carbon entering the food web at the "primary" level is probably not generated by photosynthesis 3)the vertical distribution of primary production can change in response to eutrophication 4)changes in the vertical distribution of primary production can mean changes in biodiversity and carbon flux 5)Changing ocean conditions are changing biodiversity – and thereby global C and N cycling and 6) it is not necessarily the most dominant species of phytoplankton on surface waters that contribute most to vertical carbon flux.

5 Main agenda

5.1 Report on developments with regard to quality assurance of marine chemistry, in particular with respect to QUASIMEME

Steven Tito (QUASIMEME) gave an update on recent developments within QUASIMEME, which is now part of WEPAL. QUASIMEME values the exchange of ideas with MCWG and other customers. The following news was presented:

- A new web portal facilitates the submission of data.
- The introduction of a new sample management system is expected to reduce sample dispatch errors.
- Some PT schemes had to be discontinued due to lack of participants, amongst these the exercise on perfluorinated alkylated substances (PFAS) in biota.
- A revised reporting scheme now includes all submitted data for participating laboratories.
- The report layout is revised. QUASIMEME wishes to reduce the number of graphical presentations of the data as some plots carry identical information.

MCWG suggested that participants submit data on optional parameters, beyond the standard parameters of the exercise, for example additional trace elements. This would give participants the option to compare their data with those of others and give QUASIMEME the opportunity to include these parameters for a full statistical analysis when a sufficient number of laboratories submit data. If only few results are reported, at least a mean and range should be given by QUASIMEME, so the reporting laboratories have some possibility of comparing data. MCWG felt that even if only 3-4 laboratories report these additional parameters, it would be a great help to evaluate data quality. Extended parameter list could also stimulate laboratories to provide data on a wider set of parameters.

A tentative list of additional trace elements is given in Annex 4. Steven Tito commented that QUASIMEME is willing to consider this option.

It was discussed that PAHs might be other candidates for which optional data could be submitted. However, it was noted that the parameter lists for PAHs in biota and sediment were recently extended. For PAH in seawater, the current list is shorter than for PAHs in biota and sediment.

Recommendation: ***For QUASIMEME to consider the optional submission of additional parameters, in particular trace elements, in the relevant QUASIMEME exercises.***

The reduction of graphs in the report was further discussed. Steven Tito identified the Kilt plots and the ranked overview plots as those most likely to be taken out. MCWG commented that this would not cause major difficulties.

MCWG suggested that the interest in the various PT schemes could be sounded out by QUASIMEME via a web based declaration of intent, before the questionnaire is sent out. This would allow QUASIMEME to more closely monitor the needs of their customers, also with respect to discontinued PT schemes. Steven Tito will take this suggestion on board.

MCWG expressed its concern that samples sent out by QUASIMEME were not always fit for purpose, because concentrations were outside the range of values that are encountered in typical marine samples. After some discussion, MCWG and Steven Tito agreed that general information on fish species could be disclosed, but that concentration ranges should not be given. It was also noted that the customer satisfaction rules requires that extreme concentrations (either high or low) are to be avoided. Steven Tito confirmed that QUASIMEME is in the position to identify extreme concentrations from an initial analysis of key determinands during homogeneity testing. However, extreme values for some individual analytes cannot always be avoided.

Regarding the test materials, some MCWG members would prefer exercises on hydrophobic compounds (PCBs, PAHs, BFRs) that always include mussels. In general, MCWG felt that the focus on marine test materials should be kept although some freshwater materials might be acceptable, provided that they are flagged as untypical. As mentioned above, species names would be a useful piece of information.

MCWG expressed its concern about QUASIMEME allowing laboratories to use an identifiable lab code. This might lead to undesirable side effects, such as the misinterpretation that anonymous labs were not confident in their results, the misuse of the PTS report by the local management, and the possibility of tracing the last anonymous labs on the list. MCWG strongly favours the use of anonymous lab codes only.

MCWG noted that PFOS is still missing in the list of PFAS determinands.

MCWG 2012 had recommended to QUASIMEME to include PFAS in their schemes for biota, sediment and seawater. However, Steven Tito informed MCWG that PFAS in biota had been discontinued because of too few participants. The exercise might be re-launched in cooperation with IVM Amsterdam.

Besides already established PT schemes, MCWG is particularly interested in two new potential PT schemes on:

- Carbonate parameters (see MCWG 2012)
- Passive sampling of non-polar compounds

In addition, Patrick Roose informed MCWG about tentative plans of a QUASIMEME workshop on the determination of chlorophyll and nutrients. This was supported by MCWG and further discussed in conjunction with agenda item 5.h, see section 5.8.

Carbonate parameters

Following up on initial discussions at MCWG 2012, MCWG emphasized the need for a PT scheme for ocean acidification because carbonate parameters are now in the OSPAR pre-CEMP. This scheme could start with a **workshop on quality and comparability of sampling and analysis of Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC).**

Historically carbonate chemistry analysis has been driven by research and as such has been undertaken by a limited number of expert groups. OSPAR has identified the carbonate chemistry parameters of TA and DIC as parameters in the pre-CEMP due to increasing concerns over ocean acidification. Therefore, TA and DIC samples will be collected and analysed by a wider range of monitoring agencies with varying levels of expertise in this area.

MCWG felt that a workshop covering TA/DIC and related parameters would be valuable to establish a consistent approach to sampling, sample pre-treatment, analysis and calculation of data. MGWG recommend that the workshop to address these is-

sues should be organised under the QUASIMEME banner. QUASIMEME would be willing to support such a workshop and NOC may be willing to host the workshop.

MCWG felt it would be valuable to invite Prof. Andrew Dickson (USA) as a leading expert in the field and as the Dickson et al. (2007) guidelines provide the basis for most measurements. Timing of such a workshop would depend on availability of key people but may be appropriate following reporting of the international inter-calibration exercise currently being undertaken and led by Prof. Dickson's laboratory. Attendance by relevant experts in the field of TA/DIC sampling would be necessary but given increase in interest in this field, new users would also benefit from participation.

Topics to be considered for the workshop are:

Sampling:

- Compare methods in use and define best practice for sampling and pre-treatment for TA/DIC and related parameters such as pH
    - Preservation, storage, filtration

Analysis:

- Best practice for analysing TA/DIC
    - Quality Control practices: Differences in instrumentation, instrument checks (blanks, precision analysis, sub-samples), use and availability of reference materials, alkalinity in low salinity waters
    - Calculations of TA/DIC
    - Laboratory environment
- Quality assurance schemes
- Calculation of carbonate system

Action: ***Sue Hartman to look into possibility of hosting a workshop on quality and comparability of sampling and analysis of Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC) at NOC.***

Action: ***Sue Hartman and Pam Walsham to contact Andrew Dickson, Eric Achterberg, Ute Schuster and Richard Bellerby about potential participation in a workshop on quality and comparability of sampling and analysis of Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC).***

Recommendation: ***For QUASIMEME to facilitate the organization of a workshop on quality and comparability of sampling and analysis of Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC), probably to be held at the National Oceanography Centre in Southampton, UK, and to contact Andrew Dickson's group regarding potential collaboration.***

Passive sampling

MCWG also sees the need for a PT scheme on passive sampling of non-polar contaminants, in order to include this method in monitoring programmes. This scheme could be developed via several steps:

MCWG proposes as a first step that laboratories report concentrations of non-polar contaminants (e.g. PAH, PCBs, PBDEs, which are on the OSPAR CEMP list) in an exposed and an unexposed silicone passive sampler as well as in a standard solution.

Results for the unexposed sampler can also be used by MCWG to derive better estimates of Background Assessment Concentrations, see section 5.12.1.

In addition, a check on the participants' ability to calculate aqueous concentrations (C_w) is needed, because calculation errors can be a major source of error. This would be a purely mathematical exercise in which participants are supplied with the exact concentrations of target analytes and performance reference compounds (PRCs).

Further, this first step should include an inventory of internal standards that are used by the participants, as these compounds consequently cannot be used as PRCs in the next step of the PT scheme development.

In a second step, laboratories should be asked to report concentrations of target analytes and PRCs in exposed silicone samplers, and report the concentrations in the sampler as well as the derived C_w. A possible third step could be that participants send in their own samplers (silicone based or other, exposed at the same location), and report the C_w. MCWG recognises that this third step may not be feasible in the end. Nine members of MCWG expressed interest in participating in such a PT scheme. MCWG offers assistance to QUASIMEME in the development and sample preparation, and will contact Steven Crum to further discuss the options.

Recommendation: ***For QUASIMEME to organise an interlaboratory exercise on passive sampling which includes a) the analysis of hydrophobic compounds in a passive sampler provided by QUASIMEME, b) the analysis of a standard solution with the same target analytes, c) a calculation exercise to derive water concentrations from passive sampling results.***

Action: ***Kees Booij to contact the QUASIMEME project office with regard to the design of the passive sampling exercise.***

Action: ***Katrin Vorkamp to provide MCWG 2013 report to QUASIMEME.***

Following WKPSPD, Katrin Vorkamp had contacted Ulrich Borchers who chairs the network of PT schemes with relation to the Water Framework Directive (WFD-PTS). Ulrich Borchers replied that he was not aware of network participants working with passive sampling, but he would be happy to make further enquiries. He regarded the issue of financing a new exercise as critical – with few participants, the participation fee would become too high to cover all costs, and he was not hopeful about external financial support. However, Ulrich Borchers was interested in MCWG's activities in this field and encouraged further communication.

5.2 Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD)

MCWG has expertise with regard to contaminants in the marine environment, which could be beneficial for groups working in the same area in relation to WFD and MSFD. For example, MCWG was informed that the development of guidelines was suggested for biota monitoring under WFD and the application of biota Environmental Quality Standards (EQS). MCWG noted its experience in this area and also the OSPAR and HELCOM guidelines already in place. Current processes under MSFD at EU level seem to be driven by WFD experiences and the marine expertise might be underrepresented. Also in this context, MCWG could contribute with the relevant expertise, covering eutrophication (Descriptor 5), ocean acidification (Descriptor 7) and in particular, contaminants (Descriptors 8 and 9).

Recommendation: ***For ICES ACOM to highlight at EU level MCWG's expertise with regard to contaminants, a central item in WFD and MSFD (Descriptors 8 and 9), and eutrophication (MSFD, Descriptor 5).***

5.2.1 Discuss developments in Water Framework Directive monitoring programmes

Evin McGovern provided an overview of the current situation with regards to the Proposal for a Directive amending the WFD and EQS.

Negiotiations with respect to this directive which will amend certain EQS and add additional EQS are advanced, with the following items still under discussion:

a) the links between the Water Framework Directive and other legislation,

b) the specific mention of 3 pharmaceutical substances on the priority substance list,

c) the deadlines for implementation and achievement of the new EQS for reaching the objectives of the Water Framework Directive and

d) the number of substances in the watch list and the possibility to make use of existing monitoring data.

As there are a number of new biota EQS proposed, there is a proposal to develop guidelines for biota monitoring and application of biota EQS. As mentioned above, OSPAR and HELCOM guidelines are in place and should be taken into account in developing practical guidelines.

During the discussion it was remarked that ICES has no direct influence on this process. The most adequate way to assure input is for MCWG members to approach their national representatives in the various WFD fora and working groups and provide them with the feedback from MCWG. Any information contained in the report on this matter is then useful. MCWG members from Belgium, Ireland and France reported doing this in their countries with success.

There was a general discussion if recommendations from this group concerning activities outside ICES reach the targeted forum. Apparently, recommendations mainly apply within the ICES system, and they are forwarded to OSPAR and HELCOM. ICES should have a procedure to advertise or promote the full range of scientific advice regarding WFD from its working groups to the European Commission.

Action: ***MCWG members to contact their national representative in WG E to draw attention to existing guidelines and MCWG expertise.***

5.2.2 Prepare a status report on activities under the Marine Strategy Framework Directive in member states

Jacek Tronczynski presented a new European project, PERSEUS ("Policy-oriented marine Environmental Research in the Southern EUropean Seas"), funded under the FP7 Theme "Oceans of Tomorrow". There are ten work packages in this project, work package 5 involves the review and analysis of the approaches used for MSFD environmental status assessment. This work is led by D. Fernandez Gonzalez (JRC/Ispra e-mail: daniel.gonzalez@jrc.ec.europa.eu) and involves three levels of analysis: 1) coverage of MSFD Descriptors, 2) strategic approach to MSFD Descriptors and 3) assessment strategy at criteria and indicator level. Highlights were that there was a predominance of international methodological frameworks. However, different methodologies were used and it was recognised that there is a need for harmonisa-

tion. In contrast to WFD, EU member states define with their own targets and indicators for MSFD.

OSPAR has compiled a table of targets and indicators for contracting parties (CPs) (MIME document 2012, Ireland and Denmark are missing from this table). In addition a list of common indicators was proposed for Descriptor 8. For Descriptor 8 the level of ambition proposed by individual CPs varied greatly from the minimal to the highly ambitious. However, most have a similar approach, using WFD monitoring and comparison to EQSs and OSPAR CEMP monitoring and comparison to Background Assessment Concentrations (BACs)/Environmental Assessment Concentrations (EACs). Most CPs saw no need to monitor WFD contaminants in offshore waters as they are unlikely to be a problem because they are often below EQS in coastal waters. Monitoring programmes need to be in place by 2014. It is unlikely that countries will have additional resources for MSFD work, therefore, a realistic and practical approach can be expected, which might not lead to any major changes to existing monitoring programmes. However, some CPs (e.g. Belgium and Ireland) are considering to monitor contaminants in sea bird eggs in addition to CEMP monitoring.

An MSFD workshop organised by the Joint Research Centre (JRC) took place in Ispra in 2012. This workshop covered the MSFD descriptors relevant to eutrophication and contaminants - Descriptors 5 (eutrophication), 8 (contaminants and effects) and 9 (contaminants in food). Gaps and issues were identified for each descriptor. However, presentations were mainly focussed on WFD, and many experts did not have a marine background. From an EU side the MSFD is apparently seen as an extension of the WFD and the process seems to be pushed in that direction. The marine community appears to have very little influence on the process so far. The open and deep seas are currently much less covered by monitoring than the coastal areas. Therefore, there is a need to cover these areas in a representative and efficient way. One way of dealing with this is for joint efforts by Member States/Regional Sea Conventions in multi annual cruises. Furthermore harmonised strategies should be derived: e.g. master stations, distributed spatial spread, transect sampling. The workshop also identified a need for a future review of EQS setting and monitoring guidance with an input from experts from the marine field. This falls within the remit of WFD WG E (see section 5.2.1).

MCWG highlighted that the marine expertise provided to the various MSFD/GES groups needs to be more visible. Marine aspects for contaminants are not well represented in European groups (including WG E), which are currently dominated by the WFD. ICES could play a role to improve this, see also section 5.2.1.

<u>Action:</u> Katrin Vorkamp and Jacek Tronczynski to take contact to JRC (Georg Hanke) about MCWG's expertise on MSFD descriptors 5, 7, 8 and 9.

5.3 Present projects of relevance to MCWG activities.

The following presentations were given under this agenda point:

- Stepan Boitsov: PAHs, PBDEs and heavy metals in the northern area of the Norwegian shelf – an update of the MAREANO programme
- Philippe Bersuder: Time trend of PBDEs and other organohalogens in the UK marine environment
- Michael Haarich: Trends of PBDEs in the North Sea and in the Baltic Sea
- Michiel Kotterman: All starts with proper monitoring: A case study on toxicological and ecological effects of POPs on eels

Abstracts of the first three presentations are given below.

In the discussion following Stepan Boitsov's presentation, the elevated PAH levels in the Svalbard area were noted, which primarily have natural causes, as local coal deposits are spread out due to bedrock erosion. MCWG also noted the decreasing Pb concentrtions in modern sediments at some locations, which may be due to the reduction in the use of leaded gasoline. It was further remarked that some alkylated PAHs were also formed in combustion processes and therefore contribute to the profile of petrogenic PAH if included there, but hardly any correlation between pyrogenic and petrogenic PAH was apparent in the given examples, presumably due to low levels. Stepan Boitsov informed that results of Ba also were available.

Regarding the PBDE results presented by Philippe Bersuder and Michael Haarich, it was discussed if the analysis of PBDE-209 and PBDE-47 for sediment and PBDE-47 and PBDE-100 for biota would be sufficient for monitoring purposes. It was concluded that more PBDE congeners should be monitored because (1) PBDE patterns may change with time and (2) several other PBDEs may occur at high concentrations: PBDE-154 is one of the major PBDEs at several locations in the UK, PBDE-153 is important to take into account because of its long half-life in organisms, PBDE-49 has been detected at relatively high concentrations at several locations. It was also stated that PBDE-209 may possibly degrade to lower brominated PBDEs.

Stepan Boitsov: Contaminants in sediments from the Norwegian continental shelf

An update on the Norwegian MAREANO programme of detailed seabed mapping was given with regard to organic and inorganic contaminants in sediments from northern parts of the Norwegian continental shelf (south-western Barents Sea and eastern Norwegian Sea). The MAREANO programme was started in 2006 with the purpose of, in its geochemical part, providing reliable reference levels of contamination in sediments, investigating the possible sources and elucidating any trends in contaminant levels. The institutions generating the data are the Institute of Marine Research (IMR) and the Geological Survey of Norway (NGU).

The sampling locations were chosen based on multibeam maps of the seabed provided by the Norwegian Mapping Authority Hydrographic Service and on subsequent video observations of the seabed, identifying the locations with fine-grained sediments with an approximate density of 1 sampling station per 2000 km^2. Up to 6 sediment cores of up to approximately 50 cm length have been gathered by means of multicorer or boxcorer, sliced onboard into 1 cm thick samples which were then kept frozen until the analysis. At present, results of the geochemical analyses are available from 92 locations. The analyses carried out at IMR included total hydrocarbon contents (THC) in all the surface samples; PAH (48 single compounds, parent and alkylated 2-6 ring) in every second cm of one core from each location; PBDE (28

congeners) in surface samples from 76 locations; and Cs-137 in sediment cores from 11 locations. NGU analysed heavy metals and other elements in every second cm of the cores from a selection of locations; total organic carbon contents (TOC) and grain size in every second cm of one core from 42 locations and surface samples from the remainder of the locations. Pb-210 radiodating of the cores from 23 locations was purchased from the Danish Hydrological Institute (DHI).

The levels of THC in the MAREANO area were found to be mostly low, below 50 mg/kg dry weight, with the lowest levels found in the open sea and somewhat higher levels in the fjord and coastal areas. The variation in the levels correlates well with TOC levels, with most fine-grained sediments also found in the fjord and coastal areas. The distribution of total PAH has a different pattern, with the levels slightly higher at several locations west of Lofoten Islands (less than 3000 μg/kg dry weight for the sum of 48 components) than in the coastal areas or the majority of open-sea locations (less than 1000 μg/kg dry weight). These levels are significantly lower than what was previously found in sediments from the Svalbard area (Boitsov et al., 2009a). Thus, there are no signs of significant PAH contamination in the MAREANO area. However, the study of sediment cores revealed increasing levels of PAH (normalized to TOC) in recent sediment layers at the majority of locations, the increase starting mostly around the start of the 20th century as dated by Pb-210. The increase is observed primarily for pyrogenic PAHs while the levels of petrogenic PAHs are low at most locations. The increase in combustion-related PAH in industrial times may be attributed to human influence. The levels of petrogenic PAHs, found to increase in the deepest layers of a few sediment cores from locations close to known oil deposits and/or pockmark fields, may be due to natural causes (Boitsov et al., 2009b). A study of hopanes in deep sediments from the same area confirmed this suggestion (Boitsov et al., 2011). Levels of perylene are low throughout the cores and are only found to increase in deepest sediments from locations with low sedimentation rates, due to natural diagenetic processes.

PBDE in surface sediments were low, mostly around 1-5 μg/kg dry weight or less for the sum of 28 congeners and not exceeding 20 μg/kg dry weight at any locations. The dominating congener was PBDE-209. Cs-137 measurements are only available for a few cores but have revealed a characteristic peak below the surface at a number of locations, typically around 30 Bq/kg dry weight. This is attributed to the fallout from nuclear tests carried out at Novaya Zemlya in the 1950s (see for example Heldal et al., 2002). This roughly confirms the Pb-210 dating, according to which the increase is due to the middle of 1960s. Inorganic contaminants are found at background levels at most locations, with somewhat increased concentrations found in surface samples for Pb (up to 35 mg/kg dry weight); Ni (up to 41,5 mg/kg dry weight); while Hg has low absolute levels (below 0,07 mg/kg dry weight) but exhibits an increase as compared to deeper sediments in sediment cores from a number of locations. This increase, same as Pb, may be due to human activities. The levels of certain other elements, such as As, were found in much higher concentrations near Svalbard than in the MAREANO area, which may be due to natural reasons (Jensen et al., 2009).

The results are updated annually on the website of the MAREANO programme, www.mareano.no, in terms of reports from each institute and in an aggregated form as maps, and have partly been published in the open literature. Future plans include mapping areas further south and north-east of the currently mapped area; completing the analyses of radioactive elements in the cores; and including new groups of contaminants as PCB and chlorinated pesticides.

References

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Heldal, H.E., Varskog, P., Føyn, L. 2002. Distribution of selected anthropogenic radionuclides (137Cs, 238Pu, 239, 240Pu and 341Am) in marine sediments with emphasis on the Spitsbergen-Bear Island area. Science of Total Environment 293, 233–245.

Philippe Bersuder: Time trend of PBDEs and other organohalogens in the UK marine environment

Philippe Bersuder reported on spatial and temporal trends of the polybrominated diphenyl ethers (PBDEs) flame retardants in surface sediments and dab (*Limanda limanda*) livers collected as part of the UK Clean Seas Environment Monitoring Programme (UK CSEMP) and in harbour porpoises (*Phocoena phocoena*) monitored through the UK Cetacean Strandings Investigation Programme (UK CSIP). With regards to PBDEs levels in surface sediments, congeners were detected in thirteen out of the fourteen stations monitored in England and Wales in 2010, with total congener concentrations ranging from 0.06 to 16 μg/kg (dry weight), the highest level being found in Liverpool Bay. PBDE-209 was systematically the dominant congener making up 75-100% of the 12 congeners measured. The PBDE congeners pattern reflected the penta-PBDE technical mixture which was banned in the EU in 2004, while PBDE-183, indicative of the octa-PBDE technical mixture, was only detected at one station. For dab livers, PBDEs were detected in all 18 stations monitored in 2010 ranging from 0.6 to 19 μg/kg wet weight (ww), PBDE-47 being usually the most abundant congener present followed by PBDE-100. Over the period 2003-2010, a significant decline in PBDE congeners in dab liver was observed in over half the locations monitored (no increase observed). It was noted that, under the Water Framework Directive (WFD), the Environment Quality Standard (EQS) for PBDEs in biota is proposed to be 0.0085 μg/kg ww for the sum of 6 congeners, and that based on this dataset (with the caveat of being fish liver), concentrations would be seventy one to two thousand times higher than the new proposed EQS concentration, therefore not achieving Good Environmental Status.

A total of nine PBDE congeners were monitored in the blubber of four hundred and fifteen individual harbour porpoises stranded around the UK between 1992 and 2008. PBDEs ranged from not detected in a fifteen year old male from Eastern England sampled in 1998 to 15.7 mg/kg lipid weight in a juvenile female porpoise from the Shetland Islands sampled in 1993. Median concentrations of the PBDEs peaked around 1998, and decreased by approximately two-thirds since. This decline was not confounded by a range of other factors such as geographical area, season, nutritional status, stranded/bycaught and age class. The decline since 1998 indicates that it is

likely that the replacement in the market of the penta-mix PBDE technical product occurred before its European Union ban in 2004.

The data presented indicates that PBDE levels are generally declining in selected marine biota samples from the UK, although these compounds are likely to be an issue with regards to exceeding its proposed EQS under the WFD. It was also emphasised that there is an on-going requirement for assessment tools for PBDEs in biota and sediment.

Michael Haarich: Trends of PBDEs in the North Sea and in the Baltic Sea

Following the presentation of trends of PBDEs in the UK marine environment Michael Haarich added results of PBDEs in dab (liver) from two areas in the eastern North Sea (Danfield close to oil and gas offshore installations and German Bight close to island of Helgoland) and from the Bay of Kiel (Kieler Bucht) in the western Baltic Sea.

For the North Sea stations data were available for 4 years (2005-2008) and therefore too short for trend determination. Concentrations of PBDE-47 ranged from 1.5-5 μg/kg ww, resp. 2.6-8.4 μg/kg ww for sum of 9 PBDEs (28, 47, 66, 199, 99, 85, 154, 153 and 183) at Danfield station and 1.2-1.5 μg/kg ww resp. 2.2-2.7 μg/kg in the German Bight. Particularly Danfield showed a high between-year variability and a tendency to increasing concentrations, on average twice as high as in the German Bight at Helgoland, where no tendency was indicated. Concentrations were in a range comparable with those presented for UK North Sea stations (ranging from about 1.6-8.9 μg/kg ww for the sum of 11 PBDEs). For dab from the Bay of Kiel concentrations were much lower than in the North Sea and ranged for PBDE-47 between 0.8-1.8 μg/kg ww, resp. 1.5-2.8 μg/kg ww for sum of 9 PBDEs, showing a decreasing trend for the period from 2002-2011, particularly until 2008.

5.4 Review and report on the role of marine litter as a potential source of contaminants.

Katrin Vorkamp had invited Jakob Strand, senior scientist at Aarhus University, Denmark, and member of WGBEC, to give an introductory presentation on the issue of marine litter, in particular its association with organic contaminants. Marine litter is one of the MSFD Descriptors (Descriptor 10) and includes macroscopic and microscopic pieces, the latter often defined as < 5 mm. Macroplastics have been counted and classified as part of OSPAR beach surveys. The detection and characterisation of microplastics often occurs under the microscope describing shape, structure and colour. Fourier Transform Infrared spectra are typically used for the determination of the polymer material. Along with the global plastic production, the amount of microplastics in marine waters and sediment has increased significantly.

For marine species, the uptake of macro- and microplastics can be life-threatening. OSPAR has defined an EcoQO of 0.1 g macroplastics in the stomachs of seabirds, however, examples were shown that clearly exceeded this value. Besides plastic uptake, animals can also become entangled in plastic debris, for example from fishing gear. Plastics in the ocean can act as a passive sampler and thus a vector for contaminants. On the other hand, plastics can also release chemicals, for examples plasticizers or flame retardants.

In addition to Jakob Strand's presentation, Katrin Vorkamp presented two documents previously discussed at WGBEC 2012: (1) A review by Deltares and the Institute for Environmental Studies at the VU Amsterdam (Leslie et al., 2011) and (2) a

report on technical recommendations for the implementation of MSFD requirements, by the MSFD GES Technical Subgroup on Marine Litter (JRC, 2012).

MCWG discussed the role of marine litter for contaminant exposure of marine organisms. As described above, contaminants can be released into the environment from the plastic material. However, it was unclear if this process caused significant contaminant exposure to marine organisms. Some preliminary data were presented suggesting little impact from this process, but these initial findings require confirmation.

Furthermore, it was discussed to what extent plastic-associated contaminants would be absorbed by the organism after plastic uptake. Some studies suggest that the uptake of plastics can be a significant source of contaminant exposure, however, insufficient information was available at the meeting to draw firm conclusions. This will be followed up at MCWG 2014 (see Annex 3), including topics proposed for joint sessions with WGBEC and WGMS (see also 5.6).

Several MCWG members are involved in current or forthcoming projects on marine litter (and associated contaminants), including projects in Belgium, Germany, Norway and the UK. MCWG members are encouraged to bring information from these and other projects to MCWG 2014.

WGBEC had recommended work on the ICES database to accommodate future monitoring data on microplastics (and associated contaminants). This was addressed under agenda item 5.5.2.

References:

JRC (2011). Marine litter – technical recommendations for the implementation of MSFD requirements. MSFD GES Technical Subgroup on Marine Litter. JRC Scientific and Technical Reports EUR 25009 EN, European Commission, Joint Research Centre, Institute for Environment and Sustainability. ISBN (pdf) 978-92-79-21802-6.

Leslie, H.A., van der Meulen, M.D., Kleizzen, F.M., Vethaak, A.D. (2011) Microplastic litter in the Dutch marine environment. Deltares Report 1203772-000.

Action: ***Michiel Kotterman and co-workers to prepare a literature review of marine litter and associated contaminants.***

5.5 ICES Data Centre: Provide expert knowledge and guidance to the ICES Data Centre, as may be requested.

5.5.1 Questions on data streams and reporting formats originally posed to SGOA 2012 and transferred to MCWG 2013 for further discussion (SGOA recommendation).

A presentation was made to the group by Hans Jensen on data at the ICES Data Centre. This presentation followed on from a presentation which was given to SGOA in December 2012 (see section 3.4). Hans Jensen described the two possible routes for data entry of carbonate chemistry data into ICES, namely through the Oceanographic database or the Environmental Seawater Database.

Data entry through the Oceanographic database is in a free format, containing limited method information, although the BODC (P011)/SeaDataNet method codes can be used. Quality Control is automated with additional visual profiling and regional review. In comparison data enters the Environmental database using the ICES environmental reporting format 3.2 (ERF 3.2) and contains detailed method and quality assurance information. Quality control is automated using DATSU. The Environmen-

tal database is primarily geared to discrete samples and will not be suitable for continuous monitoring data such as from pCO_2 systems.

OSPAR prefer that data, for assessments, is entered in the ERF 3.2 format.

Following discussions it was agreed that neither MCWG nor SGOA will recommend a specific route for data entry to ensure all OA data is captured. However, for an integrated monitoring approach to data assessment, including both chemical and biological data, everything should be in the same system in so far as practicable.

At the SGOA 2012 meeting it was highlighted that the OA carbonate chemistry community considered the Carbon Dioxide Information Analysis Centre (CDIAC) database as a the main receptacle for international carbon system data, although there are gaps in the data that is contained within it. Detailed requirements for reporting chemical oceanography data are elaborated in the GoShip manual and are reproduced in Annex 4 of the OA CRR prepared by MCWG (Hydes et al., in press). Further developments in standardising oceanographic reporting formats are anticipated within the context of establishing of the Global Ocean Acidification – Observation Network (GOA-ON). Evin McGovern has been in contact with Hernan Garcia (Co-chair of IODE Group of Experts on Biological and Chemical Data Management and Exchange Practices GE-BICH) and noted some interest in a session/workshop on standardisation of OA metadata reporting at the second meeting of GOA-ON in July 2013. It would seem premature for MCWG to further define oceanographic formats for data reporting in advance of these discussions. MCWG recommends that ICES Data Centre should be involved in global activities relating to defining reporting formats for ocean acidification data.

MCWG focused on defining the ERF 3.2 reporting codes for OA monitoring. The chemical oceanography sub-group reviewed and expanded the MIME 2011 Annex 6 (Supporting tables for OSPAR development of Ocean Acidification monitoring and assessment), to meet the requirements for the discrete carbonate chemistry parameter, i.e. reporting of pH, Dissolved Inorganic Carbon and Total Alkalinity in ERF 3.2. In conjunction with Marilynn Sørensen of the ICES Data Centre, the ICES Data Centre request form was prepared for submission of carbonate chemistry parameters to the ICES Environmental Seawater Database. This specifies the data checks required for submission of OA monitoring data. These documents are appended to this report (Annexes 5 and 6).

References:

Hydes, D.J., McGovern, E., Walsham, P., Borges, A.V., Borges, C., Greenwood, N., Hartman, S.E., Kivimae, C., Nagel, K., Olafsdottir, S., Pearce, D., Sahlsten, E., Rodriguez, C., Webster, L. In press. Chemical aspects of ocean acidification monitoring in the ICES marine area. ICES Cooperative Research Report.

Recommendation: ***For the ICES Data Centre to be involved in global activities relating to defining reporting formats for ocean acidification data.***

Action: ***Ireland (Evin McGovern) and UK (Pam Walsham, Sue Hartman, David Pearce) to test reporting system by reporting carbonate system data to ICES database in ERF 3.2.***

5.5.2 The ICES Data Centre together with WGBEC, WGMS and MCWG should prepare the entrance of litter and microplastic and associated contaminants data in the Environmental Data Base, to prepare for likely future requirements for assessment across the ICES region and reporting under MSFD Descriptor 10 (WGBEC recommendation)

MCWG were requested by WGBEC to progress future requirements for Descriptor 10 assessments. Marilynn Sorensen (ICES Data Centre) updated the group on progress in adding marine litter data and contaminant data for marine litter to the ICES database. Adding marine litter data to ICES data will require major changes to the ICES database and cannot be done easily or quickly.

However, once marine litter monitoring is accommodated, addition of contaminant data in litter should be relatively straightforward and could be added through the ICES environmental database. For this to be possible an additional marine litter matrix will be required to allow contaminant data to be added for litter, as we currently do for sediment and biota.

Regarding the adjustments in the database, it will have to be clear exactly what litter type the contaminants are being measured in. ICES have been looking into this issue for a couple of years but will only be able to progress this when the categories have been standardised. This category standardisation is being done at an EU level and is well underway. Therefore, ICES now feel they are in a position to begin developing the reporting formats. To this end, a workshop is planned during 2013 to develop the reporting formats required for database submission.

Marilynn Sørensen inquired whether MCWG supports the inclusion of contaminant monitoring data for marine litter. The feelings of MCWG on this issue are mixed as the role of marine litter as a source or vector of contaminants is not well established. However, further discussions on contaminants in marine litter, by the group is required. Although currently there is very little contaminant data for marine litter, what data there is shows concentrations are low and may be not of concern. At this stage, it is not clear if there is a real need for contaminants data for litter (See section 5.4). Furthermore contaminants data is not required for Descriptor 10 assessments, although data is required on the amount and type of litter.

5.6 Prepare joint meeting with WGMS and WGBEC and report on activities in other expert groups on the interface to MCWG (e.g. WGEel, SGONS, SGOA).

Joint meeting with WGMS and WGBEC

At its 2012 meeting, MCWG suggested a joint meeting with WGMS and WGBEC to discuss matters of common interest. This suggestion was well received by the two other groups, and a joint meeting at ICES offices in Copenhagen was envisioned for 2014. In response to MCWG's suggestion, WGBEC 2012 made the following recommendation to MCWG and WGMS:

"That MCWG, WGMS and WGBEC hold a concurrent meeting in 2014 with a full day joint plenary to address common areas of interest:

a) To define the role of passive sampling in integrated monitoring and assessment (sampling strategy, assessment criteria, deployment alongside bioindicator species) and use of toxicity tests on passive sampler extracts in monitoring programmes.

b) Microplastics"

MCWG agreed with these topics as areas of common interest and would be interested in addressing them together with WGMS and WGBEC in joint sessions, as recommended by WGBEC. Substantial progress has been made on topic a) in the meantime, through WKPSPD, further work at this meeting (see section 5.12) and presumably at the forthcoming meetings of WGMS and WGBEC. More specific questions might have to replace the current topic a) in 2014 (see below).

MCWG suggests the following items for joint sessions with WGMS and WGBEC, as also indicated in the draft terms of references (see Annex 3):

- Present projects of relevance to MCWG, WGMS and WGBEC, in a joint session (Draft ToR c).
- Marine litter and its role as a potential source of contaminants: Combine information on plastics in sediment, on plastic/contaminant interactions and on their effects in biota for a comprehensive problem description and assessment, in a joint session with WGMS and WGBEC (Draft ToR d iii)
- Ocean acidification: Report on pH measurements in sediments, in a joint session with WGMS and WGBEC (Draft ToR g v)
- Passive sampling: Review and discuss information on effects of freely dissolved concentrations, with a view of developing environmental assessment criteria, in a joint session with WGMS and WGBEC (Draft ToR k ii).
- Passive sampling: Review and discuss information on mixture toxicity derived from passive dosing, in a joint session with WGMS and WGBEC (Draft ToR k iii).

Furthermore, MCWG continues to collaborate with WGMS on publications about organic contaminants in sediments. A TIMES manuscript on analytical methods of PCBs submitted shortly after MCWG 2012 is currently in press and a new TIMES manuscript on passive sampling in sediments is in preparation (see Section 5.12). In addition, a TIMES manuscript on the determination of passive sampler-water partitioning coefficients has been suggested as a collaboration project with WGMS (see Section 5.12).

Action: ***Katrin Vorkamp to convey the draft ToRs for joint sessions to the chairs of WGMS and WGBEC, for discussions at their 2013 meetings.***

Recommendation: ***WGMS, WGBEC and MCWG to hold a concurrent meeting in spring 2014 and to address in joint sessions the ToRs drafted by MCWG 2013 and forwarded to WGMS and WGBEC for potential comments and additions.***

WGEEL – Working Group Eel

Michiel Kotterman is a member of the joint EIFAAC/ICES WGEEL, but did not attend the 2012 meeting of WGEEL. Michiel Kotterman informed MCWG that with regard to contaminants in eel, a relatively large and growing data amount is available. On the other hand, little is known about links to toxicology and in particular, the stock declines generally observed in the last 20-30 years.

It was noted that the WGEEL's 2012 ToRs included the item "In conjunction with WGBEC and MCWG, review and develop approaches to quantifying the effects of eel quality on stock dynamics and integrating these into stock assessments." MCWG had not been aware of potentially expected contributions to this ToR, but will be happy to contribute where possible.

SGONS – Study group on nutrient standards

David Hydes did not attend MCWG 2013, but informed MCWG about SGONS activities by correspondence:

The ICES and IOC supported the SGONS, which worked formally from 2008 to 2010. The group's members have continued their work since then. These activities have been partly funded by grants to Michio Aoyama at the Geochemical Research Department, Meteorological Research Institute, Japan. Work has covered: (1) promoting the use of certified reference materials (CRM) for nutrient analyses in seawater, (2) conducting inter-comparison exercises, (3) looking at improvements that can be made in analytical methods.

Three activities took place in 2012. Two reports will be published in 2013. The first will be on the inter-comparison study to which data were reported in April 2012. Globally about 80 laboratories took part in the study. RMs produced by the KANSO Company in Japan were used. Nitrate, silicate, phosphate were the minimum parameters on which participants were asked to report. In addition many laboratories reported values for nitrite and ammonia, a sub set of laboratories reported values for organic nitrogen and organic phosphorous. The second report will be from a workshop held at NIOZ in the Netherlands, December 2012, which worked on optimizing the determination of phosphate when using segment flow analyzers.

In February 2012 a meeting was held to begin discussions of how a unified system could be developed for a global system for standardizing how the CRMs would be used and how the data would be recorded and archived. That meeting agreed to seek support from SCOR-IAPSO to set up a working group that would develop the required consistent approaches. The approach to SCOR was not successful in 2012. The proposal is being re-written in 2013. This proposal will make a clearer case that the work is at this stage about how to use of RMs and CRMs from whatever source and not tied to the KANSO materials. It aims to demonstrate that what is required is best practice in methodologies for measurements and their calibration with respect to RMs and CRMs and the subsequent reporting of the data in a way that is fully traceable. It will state clearly that the work is required for supporting long term comparability of measurements in both deep ocean and coastal waters.

MCWG has previously identified gaps in the availability of appropriate CRMs so it supports this initiative to improve QA of nutrient measurements, in particular, recognizing the importance of the availability and use of suitable CRMs. Results from various proficiency testing schemes demonstrate that the major issues are related to laboratory biases caused by calibration problems and method discrepancies and CRMs are designed to address these issues.

SGOA – Study group on ocean acidification

See section 3.4.

5.7 Ocean acidification (OA)

MCWG suggested a workshop on quality and comparability of sampling and analysis of Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC). This could be arranged in cooperation with QUASIMEME, see Section 5.1.

5.7.1 Present and discuss new chemical oceanographic data relating to ocean acidification.

The CRR prepared by MCWG members on the basis of the 2010 OSPAR request on monitoring of ocean acidification was continuously extended and updated to include a complete list of OA-related activities in the ICES area. The CRR manuscript was submitted to ICES in December 2012, has undergone external review and is currently in press (see Section 3).

Jacek Tronczynski provided additional information from France, based on a document on OA prepared in context with MSFD. As far as other MCWG members could judge, OA was not considered in MSFD in their countries.

Katrin Vorkamp informed that assessment report on Arctic OA of the Arctic Monitoring and Assessment Programme (AMAP) was in press. Arctic OA processes and their effects on the marine environment and societies of the Arctic are of high priority for AMAP and the Arctic Council.

5.7.2 Report on activities in the OSPAR/ICES study group on Ocean Acidification and provide comments and input as may be requested.

See Section 3.4 and Section 5.5.1.

5.7.3 Review progress on interconnectivity of databases with respect to carbonate system data.

See Section 5.5.1.

5.8 Review aspects of chlorophyll analysis and related QA/QC.

This point was on the agenda as a result of the presentation on Chlorophyll at the MCWG meeting last year. The current discussion mainly focussed on the analytical techniques, in particular HPLC versus spectrophotometric/fluorimetric methods, current developments and the need for a workshop on this topic.

In the discussion on the analytical techniques and principles, it was pointed out that HPLC is the only way to distinguish between different pigments, mainly Chlorophyll a and b if fluorescence detection is used. Some group members still considered that LC is more suitable for research work, not necessarily for daily monitoring of chlorophyll concentrations. HPLC is also a suitable method to identify species, as different species have different pigment patterns. This, however, requires an LC-MS, as the fluorescence detector is mainly suitable for Chlorophyll a and b. It was also noted that LCs are harder to run at sea than spectrophotometers/fluorimeters due to their size and sensitivity to environmental conditions, and a change in technique might thus lead to extended storage of samples, if the analyses have to be done in the land-based laboratory rather than on-board.

Concerns were also raised on the possibility of disrupting time series if a change of method from spectrophotomer/fluorimeter to HPLC is made, as LC results have frequently given lower results for some sample types, almost certainly because of specificity problems with the spectrophotometric techniques, though no exact explanation for the discrepancies could currently be given. In QUASIMEME it has likewise been found that the LC techniques sometimes are identified as outliers because the results, under some circumstances, become much lower than for the conventional techniques. Patrick Roose, on the other hand, informed the group that his institute has already changed the technique, from spectrophotometry to HPLC, without any major problems, though the results in general tend to become a bit lower with the LC technique.

Filter extracts have been stored under liquid nitrogen for at least 6 months without problems. He also reported that he is about to scrutinize all QUASIMEME proficiency testing data to look for potential method differences, and in such case under what circumstances these might appear.

The second main topic discussed was the need for a workshop, to be held under the QUASIMEME umbrella, to discuss various aspects of Chlorophyll determination. Patrick Roose is willing to host such a workshop, later this spring, in Oostende (Belgium), covering determinations of both Chlorophyll and nutrients. It was decided to form a new subgroup of MCWG to discuss these matters in more detail. The subgroup consisted of Patrick Roose, Philippe Bersuder, David Pearce, Pam Walsham, Sue Hartman and Mikael Krysell.

The conclusion of the discussion was that at the 2014 MCWG meeting MCWG should be prepared to give method advice based mainly on the QUASIMEME workshop, but also on the upcoming method difference study based on the QUASIMEME database of proficiency testing results. It will be interesting to see if the OSPAR JAMP guidelines are in line with outcomes of the QUASIMEME workshop, however, they were revised recently (not by MCWG).

The subgroup further discussed questions for the QUASIMEME workshop which will have two main topics: Chlorophyll and nutrients. It will concentrate on analytical issues, not scientific interpretation of the data, and should be as hands-on as possible. A few seminars will be given, followed by discussions in smaller groups on specific topics (with brief presentations to trigger the discussion). The expected length of the workshop is 3 days, and the expected timing is late May (in Oostende).

Suggested discussion session topics for **Chlorophyll** were:

- -QA/QC issues (reference materials, standards, calculations, validation etc.)
- Extraction
- Filtration and storage of filters
- HPLC versus Spectrophotometer/Fluorimeter
- HPLC techniques (separation columns, gradietns, detectors etc.)
- Calibration of sensors (probes, Ferry boxes etc.)

Suggested discussion session topics for **Nutrients** were:

- Methods and analytical principles – latest developments
- In-situ systems (calibration, QA/QC, drift etc.)
- Organic nutrients
- Reference materials (RM, SRM, CRM)
- Sampling issues (filtration or not, how to filter, preservation etc.)

A short list of potential speakers was discussed, and the conclusion was that each sub-group member should quickly contact potential speakers, in particular from their own institutes, and forward any information on names and topics to Patrick Roose and/or QUASIMEME as soon as possible.

<u>Recommendation:</u> A workshop on Chlorophyll and nutrients, held in Oostende, Belgium in spring 2013 under the auspices of QUASIMEME.

Action: ***Patrick Roose, Philippe Bersuder, Pam Walsham, Sue Hartman, David Pearce and Mikael Krysell to contact potential keynote speakers and discussion group chairs for the QUASIMEME workshop on Chlorophyll and nutrients.***

5.9 Emerging contaminants

5.9.1 Report on new information regarding emerging contaminants in the marine environment.

Katrin Vorkamp informed MCWG about a recent Danish screening study on compounds proposed as priority substances of the WFD. These compounds included the pesticides aclonifen, bifenox, cypermethrin, heptachlor/heptachlor epoxide, the biocides cybutryn and terbutryn and the brominated flame retardant hexabromocyclododecan (HBCD). The study was based on freshwater and seawater samples collected in October 2012, i.e. outside the period of typical pesticide and biocide application. Heptachlor/heptachlor epoxide and HBCD were additionally analysed in fish samples. While aclonifen, bifenox and cypermethrin were below detection limits, the remaining compounds were frequently detected. No concentrations exceeded environmental quality standards proposed as maximum allowable concentrations, but some results were higher than proposed annual averages.

5.10 Discuss the role of atmospheric transport and deposition for the assessment of inputs of PFOS and other PFCs to the marine environment and prepare concluding report.

Lutz Ahrens presented new results were about the atmospheric transport and fate of per- and polyfluoroalkyl substances (PFASs). Katrin Vorkamp presented results of the atmospheric monitoring conducted by NILU (Norway) on PFAS. With regard to a concluding report, some MCWG members agreed on preparing a manuscript for a peer-reviewed scientific journal.

Lutz Ahrens: The role of atmospheric transport of per- and polyfluoroalkyl substances (PFASs)

For conducting measurements in air, passive air samplers are ideal due their simplicity and low cost, especially for the purpose of generating spatially resolved data. When shorter time resolution is required and for the determination of gas-particle partitioning, high-volume active air samples are typically used. However, sampling artifacts associated with conventional high-volume active air sampler were reported for perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkanesulfonic acids (PFSAs). Gas-phase compounds were shown to accumulate on the glass fiber filter (GFF) by adsorbing to particulate matter already collected on the GFF, resulting in an overestimation of the particle-phase concentration ("blow-on" artifact). The comparison of denuder and high-volume active air sampler measurements demonstrated a considerable overestimation of the particle-phase fraction for PFCAs and PFSAs for results based on the high-volume active air sampler (Ahrens et al., 2011a; Ahrens et al., 2012).

Wastewater treatment plants (WWTPs) are potential emission sources for PFASs. The emissions of PFASs to air was investigated at a WWTP and two landfill sites in Ontario, Canada, in summer 2009 using sorbent-impregnated polyurethane foam (SIP) disk passive air samplers (Ahrens et al., 2011b). Generally, the target analytes showed elevated concentrations at the WWTP compared to the reference sites. For example, ΣPFAS concentrations in air were 3–15 times higher within the WWTP (2300–24000 pg/m3) compared to the reference sites (600–1600 pg/m3). Variations in the com-

pound pattern were observed within the WWTP sites. For instance, highest air concentrations of PFASs were at the aeration tanks compared to the other tanks (i.e. primary and secondary clarifier) and likely associated with increased volatilization during the aeration process. Yearly emissions estimated using a simplified dispersion model were 2.6 kg/year for ΣPFASs. These results highlight the important role of WWTPs as emission sources of emerging pollutants to the atmosphere.

The widespread global distribution of PFASs and their occurrence in biota and humans is believed to arrive through various mechanisms including oceanic transport, air transport and association with aerosols. Once they have entered the aquatic environment, PFASs can sorb to particles/sediment and accumulate in aquatic biota. The short-chain PFASs are potentially more water soluble whereas long-chain PFASs seems to bind more strongly to particles and accumulate in the marine food chain (Ahrens et al., 2009a; Ahrens et al., 2009b; Ahrens et al., 2011c). The perfluorocarbon chain length and functional group were identified as the dominating parameters that had an influence on the partitioning behaviour of the PFCs in the marine environment.

References:

Ahrens, L., Shoeib, M., Harner, T., Lane, D.A., Guo, R., Reiner, E.J. 2011a. Comparison of annular diffusion denuder and high volume air samplers for measuring per– and polyfluoroalkyl substances in the atmosphere. Anal. Chem. 83, 9622–9628.

Ahrens, L., Harner, T., Shoeib, M., Lane, D.A., Murphy, J.G. 2012. Improved characterization of gas-particle partitioning for per- and polyfluoroalkyl substances in the atmosphere using annular diffusion denuder samplers. Environ. Sci. Technol. 46, 7199–7206.

Ahrens, L., Shoeib, M., Harner, T., Lee, S.C., Guo, R., Reiner, E.J. 2011b. Wastewater treatment plant and landfills as sources of polyfluoroalkyl compounds to the atmosphere. Environ. Sci. Technol. 45, 8098–8105.

Ahrens, L., Barber, J.L., Xie, Z., Ebinghaus, R. 2009a. Longitudinal and latitudinal distribution of perfluoroalkyl compounds in the surface water of the Atlantic Ocean. Environ. Sci. Technol. 43, 3122–3127.

Ahrens, L., Yamashita, N., Yeung, L.W.Y., Taniyasu, S., Horii, Y., Lam, P.K.S., Ebinghaus, R. 2009b. Partitioning behaviour of per- and polyfluoroalkyl compounds between pore water and sediment in two sediment cores from Tokyo Bay, Japan. Environ. Sci. Technol. 43, 6969–6975.

Ahrens, L., Herzke, D., Huber, S., Bustnes, J.O., Bangjord, G., Ebinghaus, R. 2011c. Temporal trends and pattern of polyfluoroalkyl compounds in tawny owl *(Strix aluco)* eggs from Norway, 1986–2009. Environ. Sci. Technol. 45, 8090–8097.

Katrin Vorkamp presented an overview of the results of several **NILU reports** on airborne PFASs in filter samples from three monitoring stations in Norway (NILU, 2010; NILU, 2011a; NILU, 2011b; NILU, 2012). The filter samples were collected on weekly basis since 2008 and analysed for perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkanesulfonic acids (PFSAs), perfluorooctane sulfonamide (PFOSA) and 6:2 fluorotelomer sulfonate (6:2 FTS). Gas-phase samples were not analysed. The detection limits seemed to show a certain variability between the different stations and years. The reasons for these varying detection limits were not known to MCWG, but some MCWG members reported on blank issues with PFAS analyses at low levels.

References:

Norsk Institutt for Luftforskning (NILU), 2010. Overvåking av langtransportert forurenset luft og nedbør. Rapportnr. 1074/2010.

Norsk Institutt for Luftforskning (NILU), 2011a. Overvåking av langtransportert forurenset luft og nedbør. Rapportnr. 1099/2011.

Norsk Institutt for Luftforskning (NILU), 2011b. Tilførselsprogrammet 2010. Atmosfærisk tilførsel – Overvåking på Andøya. Rapportnr. 1098/2011.

Norsk Institutt for Luftforskning (NILU), 2012. Overvåking av langtransportert forurenset luft og nedbør. Atmosfæriske tilførsler, 2011. Rapportnr. 1126/2012.

The topic of atmospheric transport and deposition of PFASs has been discussed on the basis of literature reviews at the MCWG meetings since 2010. In 2010, advice was provided to OSPAR on this question. Following the literature review in 2011, the initial piece of advice to OSPAR was confirmed. As MCWG considered the question of atmosphere-water exchange scientifically interesting and relevant for the long-range transport of PFAS, further information was collected and discussed in 2012 and 2013.

On the basis of this material, an MCWG subgroup consisting of Katrin Vorkamp, Norbert Theobald, Zhiyong Xie, Stepan Boitsov and Lutz Ahrens agreed on writing a critical review for a peer-reviewed journal on the role of atmospheric transport of PFASs. The MCWG member Ralf Ebinghaus had previously contributed to this topic and will be invited to contribute to the manuscript.

The preliminary title of the manuscript is: "Atmosphere-water exchange of PFASs in the marine environment – a critical review on the current state of knowledge". The critical review will cover the following topics: (i) The occurrence of PFASs in the marine atmosphere and water, (ii) air-water exchange of PFASs, (iii) transport processes in the marine environment, (iv) implications for monitoring strategies, and (v) recommendations and future perspectives.

***Action:** Katrin Vorkamp to contact Ralf Ebinghaus and invite him to co-author manuscript on the atmosphere-water exchange of PFASs in the marine environment.*

***Action:** Katrin Vorkamp, Norbert Theobald, Zhiyong Xie, Stepan Boitsov and Lutz Ahrens to prepare a manuscript on the atmosphere-water exchange of PFASs in the marine environment, for presentation at MCWG 2014.*

5.11 Update information on using seabird eggs as a monitoring matrix for trace metals and persistent organic pollutants and discuss potential for concluding report.

Katrin Vorkamp, Michael Haarich and Gert Asmund presented a summary on new monitoring data on metals and organic contaminants in the seabird eggs. This is in addition to what was presented at the MCWG 2012 meeting (see report of MCWG 2012).

In the introduction it was reminded that seabird eggs had been included in the OSPAR JAMP guideline for monitoring of biota since 1998. Furthermore, OSPAR ecological quality objectives (EcoQOs) were developed for mercury and organochlorine contaminants in seabird eggs.

Contaminants are monitored in seabird eggs in several monitoring programs including the Swedish Environmental Monitoring in Marine Biota (Baltic Sea and Kattegat), the Trilateral Monitoring and Assessment Program (TMAP) in the Wadden Sea

(Denmark, Germany, The Netherlands), and the Arctic Monitoring and Assessment Program (AMAP) (Canada, Greenland/Denmark, Norway and others).

Recent publications on contaminant monitoring in seabird eggs include an article on the levels of Hg and organochlorines in eggs of oystercatchers *(Haematopus ostralegus)*, Common and Arctic tern *(Sterna hirundo* and *paradisaea)* at several locations of the North Sea (Dittmann et al., 2012). These levels were compared to OSPAR EcoQOs. This study also gives information on the spatial patterns of egg contamination in the North Sea, for instance, higher concentrations of ΣDDT and ΣHCH were determined in eggs from the western North Sea and the Elbe estuary and higher levels were found for Hg, ΣPCB and HCB in the southern stations. No definite decreasing time trends were found for contaminants in seabird eggs, showing strong variations between species and determinands. For certain contaminants increasing trends were detected (for instance Hg, HCB and ΣHCH in the terns). Assessment in relation to EcoQO shows that in the oystercatcher Hg, ΣPCB and ΣDDT exceeded evaluation criteria in the North Sea, while HCB and ΣHCH were below EcoQO at most sites.

In a recent study from the Swedish west coast, results were reported for a number of organic contaminants, such as PBDEs, polybrominated biphenyls (PBBs), PCBs, DDTs and PFAS, in samples of herring (*Clupea harengus*) and in eggs samples of common eider (*Somateria mollissima*) and eggs and livers of herring gull (*Larus argentatus*) (Carlson et al., 2011). The comparison with fish results showed considerably lower concentrations in herring than in eggs for the chlorinated and fluorinated compounds while PBDEs were higher in herring than in eggs of common eider, but lower than in gull eggs. PBDE-209 was detected in eggs and liver of the herring gulls, as well as very low levels of PBBs. A comparison with levels in the Norwegian Arctic generally showed higher levels for the Arctic seabirds.

An interesting study of rockhopper penguins (*Eudyptes chrysocome*) and imperial shags (*Phalacrocorax atriceps*) from the Falkland Islands showed no significant variation in pollutants levels (PCB, organochlorine pesticides OCP and PBDEs) with the egg laying sequence (van der Steen et al., 2011). These findings underpin that seabird eggs are an appropriate matrix for pollutant monitoring. The levels of organohalogenated contaminants (PCBs and OCPs) in eggs of imperial shags were significantly higher than in eggs of rockhopper penguins.

Nordlöf et al. (2012) reported on a comparison of organohalogen compounds in a white-tailed sea eagle egg (*Haliaeetus albicilla*) laid in 1941 with eggs from 1996 to 2001. This study clearly showed the absence of certain contaminants (DDE and PBDE) in a white-tailed sea eagle egg laid in 1941. Low levels of higher chlorinated PCBs and of HCB were detected in the old egg sample and a very strong increase was shown of PCBs, DDE and PBDE concentrations in white-tailed sea eagle eggs since 1941 to 1996-2001. It is also shown that concentrations of PCDD/Fs were in the same order of magnitude in old and recent samples of white-tailed sea eagle eggs.

Day et al. (2012) studied mercury stable isotopes in seabird eggs of Alaskan murre (Uria spp.). Elevated mercury concentrations were determined in eggs from the coastal embayment of Norton Sound relative to insular colonies in the northern Bering Sea-Bering Strait region. Stable isotopes of Hg, carbon, and nitrogen were measured to investigate the source of this enrichment. It was shown that Hg stable isotopes in murre eggs effectively differentiated terrestrial/geogenic Hg sources from oceanic reservoirs.

Furthermore, a rather controversial critical review on standardization of egg collection from aquatic birds for biomonitoring was presented (Klein et al., 2012). The

presentation showed a somewhat inconsistent review of bird eggs as a matrix for biomonitoring. Several statements (such as "one of the most critical problems with this method is the extreme biological variability in bird eggs") are not supported by examination of the published data or by appropriate scientific literature exploration. This review is of uncertain value, may be biased and partly incorrect in some aspects concerning the use of bird eggs for environmental pollution monitoring and studies.

Following up on the presentation by Katrin Vorkamp at MCWG 2012, Gert Asmund presented the monitoring of organic pollutants in black guillemot eggs *(Cepphus grylle)* from remote sites of the central east coast of Greenland, which is part of the Danish/Greenland monitoring under AMAP. The trends (1999 – 2010) were presented for PCB, HCB, DDT, HCH, trans-nonachlor and toxaphene. No significant trend was observed for any of the organochlorine compounds, with the exception of a significantly increasing trend of HCB and a significantly decreasing trend of toxaphene. A relatively low variability between individuals was highlighted and related to few biological co-factors which may influence pollutants levels in seabird eggs, however, the variability between individuals was not constant between years.

It is also noted that seabird eggs are currently used in many countries for pollutant monitoring (see above) allowing widespread comparison.

In concluding remarks and discussion MCWG recommended that the material presented at this meeting and at MCWG 2012 should be noted by OSPAR. MCWG's reports provide relevant information on seabird eggs as a monitoring matrix for trace metals and persistent organic pollutants. Bird eggs have been proven to be a favorable matrix in various long-term monitoring programs in several countries. The existence of EcoQOs allows assessments.

It was also emphasized that some countries considered pollutant monitoring in seabird eggs in their MSFD monitoring schemes.

MCWG felt that more information was needed on seabird biology, life cycles, and relations between pollution levels and effects. The question whether or not migratory species might also be good indicators of local pollutant contamination was not finally resolved – on the one hand, concentrations in eggs might reflect pollutant uptake by the female foraging close to the colony in the few days prior to egg laying, on the other hand, the main contaminant exposure might take place outside the breeding area. This might also differ between species. MCWG felt that more biological expertise would be needed for adequate discussions of these questions. Additional information (e.g. source diet apportionment studies, contaminants signatures (e.g. Pb and Hg table isotopes), biological signatures (stable isotopes 13C, 15N)) might be helpful in these discussions.

MCWG has defined draft terms of references for follow up discussions at MCWG 2014. The question whether or not the discussion on seabird eggs as a monitoring matrix for organic contaminants and trace elements could lead to a concluding report will also be discussed at MCWG 2014.

References:

Carlsson, P., Herzke, D., Wedborg, M., Gabrielsen, G.W. 2011. Environmental pollutants in the Swedish marine ecosystem, with special emphasis on polybrominated diphenyl ethers (PBDEs). Chemosphere 82, 1286-1292.

Day, R.D., Roseneau, D.G., Berail, S., Hobson, K.A., Donard, O.F.X., Vander Pol, S.S., Pugh, R.S., Moors, A.J., Long, S.E., Becker, P.R. 2012. Mercury stable isotopes in seabird eggs re-

flect a gradient from terrestrial geogenic to oceanic mercury reservoirs. Environ. Sci. Technol. 46, 5327-5335.

Dittmann, T., Becker, P.H., Bakker, J., Bignert, A., Nyberg, E., Pereira, M.G., Pijanowska, U., Shore, R.F., Stienen, E., Toft, G.O., Marencic, H. 2012. Large-scale spatial pollution patterns around the North Sea indicated by coastal bird eggs within an EcoQO progamme. Environ. Sci. Pollut. Res. 19, 4060-4072.

Klein, R., Bartel-Steinbach, M., Koschorreck, J., Paulus, M., Tarricone, K., Teubner, D., Wagner, G., Weimann, T., Veith, M. 2012. Standardization of egg collection from aquatic birds for biomonitoring – a critical review. Environ. Sci. Technol. 46, 5273-5284.

Nordlöf, U., Helander, B., Eriksson, U., Zebühr, Y., Asplund, L. 2012. Comparison of organohalogen compounds in a white-tailed sea eagle egg laid in 1941 with five eggs from 1996 to 2001.

van den Steen, E., Poisbleau, M., Demongin, L., Covaci, A., Dirtu, A.C., Pinxten, R., van Noordwiik, H.I., Quillfeldt, P., Fens, M. 2011. Organohalogenated contaminants in eggs of rockhopper penguins *(Eudyptes chrysocome)* and imperial shags *(Phalacrocorax atriceps)* from the Falkland Islands. Sci. Total Environ. 409, 2838-2844.

Recommendation: ***MCWG recommends that OSPAR notes the material on contaminant monitoring in seabird eggs compiled by MCWG 2012 and MCWG 2013.***

5.12 Review new information on passive sampling of contaminants in the marine environment, including discussions and results from WKPSPD, and respond to potential requests from WKPSPD.

The WKPSPD report was not yet available by the time of the MCWG meeting, but Kees Booij, one of the co-chairs of WKPSPD, presented the main topics and conclusions of WKPSPD to MCWG (see Section 3.5).

MCWG appreciated the work done by WKPSPD and supported the wider use of passive samplers. During the meeting, MCWG worked on the development of background concentrations and background assessment concentrations (see Section 5.12.1) and on guidelines for passive sampling in sediments (see Section 5.12.2). MCWG members also expressed their interest in participating in an interlaboratory comparison using passive samplers and discussed the practical arrangements of this study (see Section 5.1).

However, some MCWG members did not agree with WKPSPD's conclusion (see Section 3.5) that passive sampling is mature enough to replace compliance monitoring of total water (in the context of the EU WFD), and sediments (in OSPAR CEMP). Some MCWG members also expressed concern that the capabilities of passive sampling may be overrated by WKPSPD.

It was also mentioned that based on the presentation of WKPSPD, logistic aspects of passive sampling deployment and use as a monitoring tool in the environment had not been discussed at WKPSPD.

MCWG discussed that there was need for frameworks for further interpretation and evaluation of passive sampling data. MCWG suggests addressing toxicity-related questions together with WGBEC in a joint meeting at MCWG 2014 (see Section 5.6 and Annex 3).

Develop Background Assessment Concentrations (BACs) for PAHs, PCBs, etc that are expressed as freely dissolved concentrations (C_{free}). Participants of WKPSPD are willing to provide suitable data.

Background concentrations (BCs) are required for use in OSPAR's CEMP assessment of temporal trends. The OSPAR strategy for hazardous substances (OSPAR, 2010) sets an "ultimate aim of achieving concentrations in the marine environment near background values for naturally occurring substances and close to zero for man-made synthetic substances".

Background concentrations of anthropogenic compounds also occurring naturally in the marine environments have previously been proposed for biota and sediments. Due to recent developments of passive sampling devices it is now possible to envision that this concept is extended to BCs for freely dissolved concentrations (C_{free}).

However, MCWG underlines that as for biota and sediments:

- There is a difficulty with the concept of a unique natural background concentration for individual contaminants in the water phase for the entire OSPAR convention area, due to the differences across the convention area (for example due to geochemical differences, oceanographic factors such as upwelling, and different transport pathways).
- There is no sound methodology to determine natural background (pre-industrial) concentrations for these contaminants in the water phase.

Approaches to date have largely focused on using contaminant data that are collected from "remote"/ "pristine" areas within the convention area to determine background concentrations. The group recalled that MCWG 2007 had considered some basic criteria for identifying a remote/pristine area (i.e. likely to have relatively low anthropogenic inputs). Specifically, such areas should:

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

A difficulty with this approach is that even remote areas are not pristine as they are affected by anthropogenic contamination due to long range transport, i.e. the second criteria is difficult to meet. This was further illustrated by the occurrence of appreciable concentrations of man-made substances in remote areas, for example in biota from Greenland and in deep seawater in the Irminger Sea.

A more practical difficulty has been the paucity of suitable data from such remote areas. An MCWG subgroup compiled data of PAHs and PCBs in the water phase during the meeting (see below). Some data had been provided by members of WKP-SPD.

It was noted that BC=0 for all non-polar contaminants on the present OSPAR list of hazardous compounds, except for PAHs, for which natural sources may exist. The group recognised that Background Assessment Concentrations (BACs) should be based on a statistical analysis of interlaboratory variability in results obtained from proficiency testing schemes, and that provisional estimates could be used in this case until such data become available.

Besides the approach of deriving BCs from data of remote locations, a subgroup at MCWG 2013 discussed some other approaches for further exploration. Provisional estimates of BC and BAC can thus be derived using the following three methods:

1) Evaluate C_w data from remote areas that are determined by passive sampling or high volume filtration/extraction methods.

2) Convert current BC/BAC values for sediments to those for water by applying a generic sediment to organic carbon water partition coefficient, such as the Karickhoff relationship (K_{oc}=0.63K_{ow}). For non-planar compounds this relationship is acceptable, but for PAHs the apparent partition coefficients are about 10 times higher (Lohmann et al., 2005; Witt et al., 2009; Smedes et al., 2013). This approach yields

PAHs : $$BC_{water} \cong \frac{BC_{sed}}{10\ f_{oc} 0.63 K_{ow}}$$

other non-polar compounds : $$BC_{water} \cong \frac{BC_{sed}}{f_{oc} 0.63 K_{ow}}$$

3) Evaluate concentrations in pre-industrial times in dated sediment cores, and calculate the corresponding C_w using the method outlined under 2. above.

The following datasets were considered for the three approaches (Annex 7):

- Schulz-Bull et al. (1998) report C_w values for open ocean sites NW and SE of Iceland, determined by high volume filtration/extraction in the water column at 0.3 - 2 km depth below surface. The lowest values were selected.
- NIOZ (The Netherlands) exposed passive sampling devices (PSDs) in the Irminger Sea and the Canary Basin, near the sea floor and the surface (0.1-5 km depth). The Canary Basin is outside the OSPAR area, but still in the Atlantic Ocean. The lowest values were selected (Canary basin, 5 km depth).
- NIVA (Norway) exposed semi-permeable membrane devices (SPMDs) at remote Norwegian sites (near Kristiansand, Tromsø/Narvik, Svalbard, Jan Mayer). The lowest values were selected (Jan Mayen).
- IFREMER (France) measured concentrations of dissolved PAHs by high volume filtration/extraction in the open ocean (Gulf of Biscay). The lowest observed values were selected.
- Marine Scotland exposed PSDs in a number of coastal sites in the UK and Ireland, including several remote lochs. The lowest observed values were selected.
- BSH (Germany) measured concentrations of dissolved organic contaminants by high volume (100 L) filtration/extraction in the central North Sea and the Baltic Sea. The lowest observed values were selected.
- OSPAR BC and BAC values for sediments (OSPAR MIME 12/2/Info.1-E, December 2012). An organic carbon fraction of 0.025 was used to calculate BC and BAC values for C_w.
- IFREMER (France) analysed a dated sediment core from the Eastern Mediterranean (Azoury et al., subm.). Concentrations observed for pre-industrial times (<1850) were converted to C_w values, adopting a reported organic carbon fraction of 0.0088, and applying the generic conversion described above.

BC values estimated from the current BCs for sediments (approach no. 2) were relatively high and were not considered to be realistic values for uncontaminated areas. BC values estimated from high volume filtration extraction measurements, pre-industrial sediment deposits, and PSD exposures in remote areas showed a fair de-

gree of correspondence, particularly for the 4-6 ring PAHs. These values could well be used as a realistic estimate for the true PAH background concentrations.

The 25% percentiles of the values from all data sources were selected (Table 1, Annex 7). For the calculation of these percentiles, the reported values below limits of determination (LOD) were replaced by half of the reported LOD. For organochlorine compounds, the BC was set to 0.

To arrive at BAC values, the uncertainty in the analytical results must be taken into account. These consist of a bias that originates from contamination during sampler preparation, transport and analytical procedures, and a precision by which these lowest observed amounts in the samplers can be quantified. The group chose not to consider the contribution of analytical precision to the uncertainty in the analytical results, because sample contamination (the bias) was considered to dominate the uncertainty in the analytical results. This can be adjusted as more data become available on accuracy and precision.

With regard to the bias, an expert judgment was made for the LODs expressed as ng per sampler that could be found in a typical laboratory (Annex 7). These LODs were converted to C_w values as follows: From passive sampler theory, the equivalent water volume (V_{eff}) extracted during the exposure is given by

$$V_{eff} = K_{sw} m_s \left[1 - \exp\left(- \frac{R_s \, t}{K_{sw} m} \right) \right]$$

where K_{sw} is the sampler-water partition coefficient, m is the sampler mass, R_s is the sampling rate, and t is time. The LOD for C_w (ng/L) can be obtained by dividing the maximum amount in the sampler that originates from sample contamination (ng) by V_{eff} (L). For this estimation, K_{sw} values were taken from Smedes et al. (2009). A sampling rate of 10 L/d, a sampler mass of 0.01 kg and an exposure time of 40 d were used.

Table 1 summarises the current estimates of BCs and BACs for PAHs and various organochlorine compounds. The data used for these calculations are shown in Annex 7. MCWG would like to make the following comments in connection with Table 1:

- The concentrations presented for the use as BCs for the water phase are concentrations that MCWG considers as "low concentrations". However, they are not proposed as natural background concentrations.
- The concentrations are proposed to assist OSPAR in deriving assessment criteria for passive sampling applications in (pre-)CEMP assessments and should not be used for other purposes.

The results of the estimated uncertainty are listed in Annex 7, column "95% CI, pg/L". The values for the compounds with low K_{ow} values (e.g. naphthalene, HCHs) are relatively high because the effectively extracted water volume for these compounds is rather low (~11 liter for naphthalene, and 25 liter for HCHs) compared with more hydrophobic compounds (e.g. 400 liter for PCB 153 for a 40 day exposure with a sampling rate of 10 liter/day). BAC values were obtained by adding the 95% CI to the BC.

Table 1: Summary of preliminary Background Concentrations (BC) and Background Assessment Concentrations (BAC) for freely dissolved concentrations of non-polar contaminants in water. See text for comments. More details are given in Annex 7.

Compound	BC (pg/L)	BAC (pg/L)
Naphthalene	160	5760
Phenanthrene	43	286
Anthracene	6	73
Dibenzothiophene	21	78
Fluoranthene	16	55
Pyrene	9	46
Benz(a)anthracene	2	10
Chrysene/Triphenylene	4	13
Benzo(b)fluoranthene + Benzo(j)fluoranthene	4	11
Benzo(k)fluoranthene	5	13
Benzo(e)pyrene	3	10
Benzo(a)pyrene	2	10
Indeno(1,2,3-cd)pyrene	1	9
Dibenz[a,h]anthracene	0.2	8
Benzo(ghi)perylene	1	9
PCB-28	0	1
PCB-52	0	1
PCB-101	0	1
PCB-118	0	1
PCB-138	0	1
PCB-153	0	1
PCB-180	0	1
γ-HCH	0	40
α-HCH	0	40
p,p'-DDE	0	1
HCB	0	1
Dieldrin	0	2

MCWG proposed an intercalibration exercise on passive sampling of non-polar compounds, organised by QUASIMEME (see section 5.1). This exercise could include unexposed sampler which might be used by MCWG to derive better estimates of Background (Assessment) Concentrations.

References:

Azoury, S., Tronczyński, J., Chiffoleau, J.F., Cossa, D., Nakhlé, K., Schmidt, S., Khalaf, G. 2013. Historical records of Hg, Pb and PAH depositions in a dated sediment core from the Eastern Mediterranean. Submitted to Environ. Sci. Technol.

Lohmann, R., Macfarlane, J.K., Gschwend, P.M. 2005. Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York, Harbor sediments. Environ. Sci. Technol. 39, 141-148.

OSPAR. 2010. Hazardous Substances. The North-East Atlantic Environment Strategy. OSPAR Agreement 2010-03. www.ospar.org

Schulz-Bull, D.E., Petrick, G., Bruhn, R., Duinker, J.C. 1998. Chlorobiphenyls (PCB) and PAHs in water masses of the northern North Atlantic. Mar. Chem 61, 101–114.

Smedes, F., Geertsma, R.W., van der Zande, T., Kooij, K. 2009. Polymer-water partition coefficients of hydrophobic compounds for passive sampling: Application of cosolvent models for validation. Environ. Sci. Technol. 43, 7047–7054.

Smedes, F., van Vliet, L.A., Booij, K. 2013. Multi-ratio equilibrium passive sampling method to estimate accessible and pore water concentrations of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in sediment. Environ. Sci. Technol. 47, 510-517.

Witt, G., Liehr, G.A., Borck, D., Mayer, P. 2009. Matrix solid-phase microextraction for measuring freely dissolved concentrations and chemical activities of PAHs in sediment cores from the western Baltic Sea. Chemosphere 74, 522-529.

Recommendation: ***MCWG recommends that OSPAR note preliminary Background Concentrations and Background Assessment Concentrations derived for polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds, including polychlorinated biphenyls (PCBs) in water, with a view to applications of passive sampling techniques.***

Action: ***MCWG to evaluate if results from QUASIMEME passive sampling exercise allow better estimates of Background (Assessment) Concentrations.***

5.12.1 Produce a TIMES guideline document (in collaboration with WGMS) detailing how to determine sampler-water partition coefficients and sampler-sampler partition coefficients, including expressions of uncertainty.

MCWG agreed that this was an important document to be produced for further work towards routine applications of passive sampling. It was agreed that Kees Booij would take the lead and contact potential co-authors among the international experts. From MCWG, Patrick Roose and Lynda Webster would like to contribute to this manuscript. Further co-authors might be found in WGMS.

Action: ***Kees Booij to contact potential co-authors on TIMES manuscript on the determination of sampler-water and sampler-sampler partition coefficients.***

5.12.2 Update and finalise (in collaboration with WGMS) an earlier drafted document on passive sampling of sediments, for future publication as an ICES TIMES paper.

A draft on passive sampling in sediments had previously been prepared by Foppe Smedes. This draft was welcomed by MCWG as a valuable contribution to passive sampling in sediments. MCWG feels that it is important to detail the procedures for determining pore water concentrations of hydrophobic chemicals for laboratories that have little experience in making such measurements. The group outlined some suggestions for further development of this guideline, which will be forwarded to Foppe Smedes as the main author. From MCWG, Lynda Webster, Patrick Roose and Katrin Vorkamp would like to contribute to the further work on these guidelines.

Action: ***Katrin Vorkamp to forward MCWG comments on draft document on passive sampling in sediments to Foppe Smedes.***

5.13 Follow up on discussions of publications on

5.13.1 The development and review of environmental assessment criteria

Following critical discussions about environmental assessment criteria at MCWG 2012, some MCWG members considered a publication on the possibilities and limitations of the EAC development, including a critical data analysis, preferably in collaboration with WGBEC. This idea still seemed relevant, but MCWG members had doubts about sufficient time and resources to take this forward. Patrick Roose informed MCWG that OSPAR had prepared the report "Environmental Assessment Criteria (EACs) for hazardous substances in the marine environment: OSPAR contribution to addressing the challenge of assessing chemical quality across all marine waters" (MIME 12/2/Info.1-E).

5.13.2 Passive sampling in a monitoring context, including results from WKPSPD

This publication was considered by MCWG 2012, but has been replaced by the TIMES guidelines currently in preparation (see sections 5.12.2 and 5.12.3).

6 Plenary discussion of the draft report

Sections of the draft report, the recommendations and actions (see section 8) and the draft terms of references for MCWG 2014 (see Annex 3) were discussed in plenary on Friday 8 March 2013. The final draft version of the report was circulated by e-mail after the meeting, for approval by MCWG.

7 Any other business

MCWG supported extending the term of the current chair, Katrin Vorkamp, for another year.

Katrin Vorkamp asked MCWG members to copy her in on all MCWG-related correspondence, as this will facilitate the preparations of the next meeting.

8 Recommendations and Action List

MCWG's recommendations and actions are listed below, in their order of appearance in the text.

8.1 Recommendations

Recommendation	Adressed to	Section
1. MCWG recommends the possibility of optional submission of additional parameters, e.g. trace elements and polycyclic aromatic hydrocarbons (PAHs), in the relevant QUASIMEME exercises.	QUASIMEME	5.1
2. MCWG recommends that QUASIMEME facilitates a workshop on quality and comparability of sampling and analysis of Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC), probably to be held at the National Oceanography Centre in Southampton, UK, and that QUASIMEME contacts Andrew Dickson's group regarding potential collaboration.	QUASIMEME	5.1
3. MCWG recommends an interlaboratory exercise on passive sampling which includes a) the analysis of hydrophobic compounds in a passive sampler provided by QUASIMEME, b) the analysis of a standard solution with the same target analytes, c) a calculation exercise to derive water concentrations from passive sampling results.	QUASIMEME	5.1
4. Highlight at EU level MCWG's expertise with contaminants, a central item in the Water Framework Directive (WFD) and the Marine Strategy Framework Directive (MSFD), Descriptors 8 and 9, and eutrophication (MSFD, Descriptor 5).	ICES ACOM	5.2
5. MCWG recommends that the ICES Data Centre should be involved in global activities relating to defining reporting formats for ocean acidification data.	ICES Data Centre	5.5
6. MCWG recommends a concurrent meeting in spring 2014, to address in joint sessions the ToRs drafted by MCWG 2013 and forwarded to WGMS and WGBEC for potential comments and additions	WGMS, WGBEC	5.6

7. MCWG recommends a workshop on Chlorophyll and nutrients, held in Oostende, Belgium in spring 2013 under the auspices of QUASIMEME.	QUASIMEME	5.8
8. MCWG recommends that OSPAR note the material on contaminant monitoring in seabird eggs compiled by MCWG 2012 and MCWG 2013.	OSPAR	5.11
9. MCWG recommends that OSPAR note preliminary Background Concentrations and Background Assessment Concentrations derived for polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds, including polychlorinated biphenyls (PCBs) in water, with a view to applications of passive sampling techniques.	OSPAR	5.12

8.2 Actions

Action	Who	Section
Contact AMAP Secretariat and inform about theme session on ocean acidification at ASC 2013.	Evin McGovern	3.1
Send text on MCWG for ICES website to ICES Secretariat.	Katrin Vorkamp	3.1
Look into possibility of hosting a workshop on quality and comparability of sampling and analysis of Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC) at NOC.	Sue Hartman	5.1
Contact Andrew Dickson, Eric Achterberg, Ute Schuster and Richard Ballerby about participitation in QUASIMEME workshop on ocean acidification.	Sue Hartman, Pam Walsham	5.1
Contact the QUASIMEME project office with regard to the design of the passive sampling exercise.	Kees Booij	5.1
Provide MCWG 2013 report to QUASIMEME.	Katrin Vorkamp	5.1

Contact national representatives in Working Group E (at EU level) to draw attention to existing guidelines on contaminant monitoring and MCWG expertise.	All	5.2
Take contact to JRC (Georg Hanke) about MCWG's expertise on MSFD descriptors 5, 7, 8 and 9.	Jacek Tronczynski, Katrin Vorkamp	5.2
Prepare literature review of marine litter and associated contaminants.	Michiel Kotterman and co-workers	5.4
Test reporting system by reporting carbonate system data to ICES database in ERF 3.2.	Evin McGovern, Sue Hartman, Pam Walsham, David Pearce	5.5
Convey draft ToRs for joint sessions to the chairs of WGMS and WGBEC, for discussion at their 2013 meetings	Katrin Vorkamp	5.6
Contact potential keynote speakers and discussion group chairs for the QUASIMEME workshop on Chlorophyll and nutrients.	Patrick Roose, Philippe Bersuder, Pam Walsham, Sue Hartman, David Pearce, Mikael Krysell	5.8
Contact Ralf Ebinghaus and invite him to co-author a manuscript on atmosphere-water exchange of perfluorinated alkylated substances (PFAS).	Katrin Vorkamp	5.10
Prepare manuscript on atmosphere-water exchange of perfluorinated alkylated substances (PFAS)	Lutz Ahrens, Norbert Theobald, Zhiyong Xie, Ralf Ebinghaus, Katrin Vorkamp	5.10
Evaluate if results from QUASIMEME passive sampling exercise allow better estimates of Background (Assessment) Concentrations.	All	5.12
Contact potential co-authors on TIMES manuscript on the determination of sampler-water and sampler-sampler partition coefficients.	Kees Booij	5.12
Forward MCWG comments on draft document on passive sampling in sediments to Foppe Smedes.	Katrin Vorkamp	5.12

Present software for estimation of measurement uncertainty.	Mikael Krysell	For MCWG 2014
Provide information on marine litter (and associated contaminants).	All	For MCWG 2014
Present results of contaminants in sediment cores from the Eastern Mediterranean Sea.	Jacek Tronczynski	For MCWG 2014
Present results on contaminants in lower trophic levels of the food chain.	Jacek Tronczynski	For MCWG 2014
Provide information on sample conservation for carbonate parameters.	Sue Hartman	For MCWG 2014
Present data on ocean acidification.	Pam Walsham, Sue Hartman, Mikael Krysell, David Pearce	For MCWG 2014

9 Date and venue of the next meeting

The next meeting will take place at ICES offices in Copenhagen in March 2014, concurrently with meetings of WGBEC and WGMS. The precise date is yet to be confirmed.

10 Closure of the meeting

The meeting was closed on Friday, 8 March 2013, at 1 p.m.

Annex 1: List of participants

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Annex 2: Agenda

ICES Marine Chemistry Working Group - 35th meeting

ICES, Copenhagen, Denmark

4th – 8th March 2013

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 FROM ICES ACTIVITIES

i) Internal ICES business
ii) 2012 Advice Drafting Group
iii) 2012 Annual Science Conference
iv) OSPAR/ICES Study Group on Ocean Acidification (SGOA)
v) ICES Workshop on Passive Sampling and Passive Dosing (WKPSPD)

4 PLENARY PRESENTATIONS

4.a Katherine Richardson (University of Copenhagen): Plankton biodiversity influences carbon and nitrogen cycling – and vice versa.

5 MAIN AGENDA

General

5.a Report on developments with regard to quality assurance of marine chemistry, in particular with respect to QUASIMEME.
Presentation by Steven Tito (QUASIMEME)

i) Ask QUASIMEME and/or the association of Water Framework Directive Proficiency Testing schemes to develop an exercise for passive sampling (PS) that would be suitable for practitioners of water or sediment PS (i.e. the ability of participants to determine hydrophobic compounds in PS polymer/s). Participants of WKPSPD would be willing to advise on how to conduct such as exercise.

5.b Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD):

i) Discuss developments in Water Framework Directive monitoring programmes

ii) Prepare a status report on activities under the Marine Strategy Framework Directive in member states

5.c Present projects of relevance to MCWG activities.

Stepan Boitsov: PAHs, PBDEs and heavy metals in the northern area of the Norwegian shelf – an update of the MAREANO programme.

Philippe Bersuder: Time trend of PBDEs and other organohalogens in the UK marine environment.

Michiel Kotterman: All starts with proper monitoring: A case study on toxicological and ecological effects of POPs on eels.

Michael Haarich: Trends of PBDEs in the North Sea and in the Baltic Sea

5.d Review and report on the role of marine litter as a potential source of contaminants.
Presentation by Jakob Strand (Aarhus University)

5.e ICES Data Centre: Provide expert knowledge and guidance to the ICES Data Centre, as may be requested.

i) Questions on data streams and reporting formats originally posed to SGOA 2012 and transferred to MCWG 2013 for further discussion (SGOA recommendation).

ii) The ICES Data Centre together with WGBEC, WGMS and MCWG should prepare the entrance of litter and microplastic and associated contaminants data in the Environmental Data Base, to prepare for likely future requirements for assessment across the ICES region and reporting under MSFD Descriptor 10 (WGBEC recommendation).

5.f Prepare joint meeting with WGMS and WGBEC and report on activities in other expert groups on the interface to MCWG (e.g. WGEel, SGONS, SGOA).

Chemical Oceanography

5.g Ocean acidification:

i) Present and discuss new chemical oceanographic data relating to ocean acidification;

ii) Report on activities in the OSPAR/ICES study group on Ocean Acidification and provide comments and input as may be requested;

iii) Review progress on interconnectivity of databases with respect to carbonate system data;

5.h Review aspects of chlorophyll analysis and related QA/QC.

Contaminants

5.i Emerging contaminants:

i) Report on new information regarding emerging contaminants in the marine environment

Katrin Vorkamp: A screening study on compounds proposed as priority substances of the Water Framework Directive

5.j Discuss the role of atmospheric transport and deposition for the assessment of inputs of PFOS and other PFCs to the marine environment and prepare concluding report

Lutz Ahrens: The role of atmospheric transport of PFOS and other PFASs

5.k Update information on using seabird eggs as a monitoring matrix for trace metals and persistent organic pollutants and discuss potential for concluding report.

5.l Review new information on passive sampling of contaminants in the marine environment, including discussions and results from WKPSPD, and respond to potential requests from WKPSPD.

i) Develop Background Assessment Concentrations (BACs) for PAHs, PCBs, etc that are expressed as freely dissolved concentrations (C_{free}). Participants of WKPSPD are willing to provide suitable data.

ii) Produce a TIMES guideline document (in collaboration with WGMS) detailing how to determine sampler-water partition coefficients and sampler-sampler partition coefficients, including expressions of uncertainty.

iii) Update and finalise (in collaboration with WGMS) an earlier drafted document on passive sampling of sediments, for future publication as an ICES TIMES paper.

5.m Follow up on discussions of publications on e.g:

i) The development and review of environmental assessment criteria

ii) Passive sampling in a monitoring context, including results from WKPSPD.

6 PLENARY DISCUSSION OF DRAFT REPORT

7 ANY OTHER BUSINESS

8 RECOMMENDATIONS AND ACTION LIST

9 DATE AND VENUE OF THE NEXT MEETING

CLOSURE OF THE MEETING

Annex 3 MCWG draft terms of reference for the next meeting (MCWG 2014)

The **Marine Chemistry Working Group** (MCWG), chaired by Katrin Vorkamp, Denmark, will meet in Copenhagen, Denmark, 3-7 March 2014 to work on the following terms of references:

1) Quality assurance of marine chemistry
   i) Report and discuss new developments in QUASIMEME.
   ii) Provide information on other proficiency testing schemes with relevance to MCWG.
   iii) Demonstrate new software developed by the Finnish Environmental Institute for estimations of measurement uncertainty.
2) Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD)
   i) Review and discuss developments of WFD, in particular regarding new priority (hazardous) substances and associated EQS values.
   ii) Review and discuss developments in MSFD, in particular regarding the monitoring of descriptors 5, 7, 8 and 9.
3) Present projects of relevance to MCWG activities.
   i) Present projects of relevance to MCWG, WGMS and WGBEC, in a joint session.
4) Marine litter and its role as a potential source of contaminants.
   i) Report on new information on marine litter and its role as a potential source of contaminants.
   ii) Review the literature with regard to the role of marine litter as a potential source of contaminants.
   iii) Combine information on plastics in sediment, on plastic/contaminant interactions and on their effects in biota for a comprehensive problem description and assessment, in a joint session with WGMS and WGBEC.
5) ICES Data Centre: Provide expert knowledge and guidance to the ICES Data Centre, as may be requested.
   i) Report on workshop for the development of reporting formats for marine litter and associated contaminants.
6) Report on activities in other expert groups on the interface to MCWG (e.g. WGMS, WGBEC, WGEEL, SGONS).
7) Ocean acidification
   i) Report from the OSPAR/ICES Study Group on Ocean Acidification and provide comments and input as follows:
      – Review and discuss developments of analytical methods
      – Update QA/QC requirements
      - Assist SGOA in elaborating reporting requirements
   ii) Present and discuss new chemical oceanographic data relating to ocean acidification.

iii) Report on QUASIMEME workshop on ocean acidification and discuss implications for ocean acidification monitoring.
iv) Report from theme session on ocean acidification at the ICES Annual Science Conference 2013.
v) Report on pH measurements in sediments, in a joint session with WGMS and WGBEC.

8) Chlorophyll and nutrients
ii) Report from QUASIMEME workshop on chlorophyll and nutrient analysis.
iii) Review if OSPAR guidelines for chlorophyll determination are in line with outcomes of the QUASIMEME workshop on chlorophyll analysis and provide advice on most appropriate methodology.
iv) Discuss comparability of methods for ammonia analysis.

9) Report on new information on emerging contaminants in the marine environment.

10) Seabird eggs as a monitoring matrix for organic contaminants and trace elements
i) Review literature that has become available since MCWG 2013 on the monitoring of organic contaminants and trace elements in seabird eggs.
ii) Review if OSPAR guidelines on seabird eggs as a monitoring matrix present the current state of knowledge.
iii) Collect biological information on seabird egg production to elucidate the transfer of contaminants from birds to eggs.
iv) Report and comment on OSPAR and HELCOM activities with regard to seabird eggs as a monitoring matrix.
v) Discuss potential of concluding report on seabird eggs as a monitoring matrix for organic contaminants and trace elements.

11) Passive sampling
i) Report on QUASIMEME exercise on passive sampling.
ii) Review and discuss information on effects of freely dissolved concentrations, with a view of developing environmental assessment criteria, in a joint session with WGMS and WGBEC.
iii) Review and discuss information on mixture toxicity derived from passive dosing, in a joint session with WGMS and WGBEC.
iv) Report and comment on OSPAR and HELCOM activities with regard to passive sampling.

12) Publications
i) Present final draft manuscript on atmosphere-water exchange of PFAS in the marine environment.
ii) Review final draft TIMES manuscript on passive sampling in sediments.
iii) Review draft TIMES manuscript on determinations of sampler-water partitioning coefficients.

iv) Discuss potential of a TIMES publication on chlorophyll measurements.

MCWG will report by 15 April 2014 to the attention of SCICOM and ACOM.

Supporting Information

Priority	This group maintains an overview of key issues in relation to marine chemistry, both with regard to chemical oceanography and contaminants. The activities are considered to have a high priority.MCWG provides input across the field of marine chemistry, which underpins the advice given by ICES, and also supports the work of national and international collaborative monitoring programmes, e.g. within OSPAR.
Scientific justification	MCWG has a particular interest in quality assurance and maintains strong links with QUASIMEME with a view to supporting quality assurance activities in this field. MCWG has initiated several new activitites in QUASIMEME. This work was inititated by MCWG and will be of interest to EU/OSPAR/HELCOM. It will also tie into internal ICES initiatives, e.g. MSFDSG, and provide information exchange between EU member states. MCWG members are interested in receiving reports on relevant projects and activitites from other members. This is a new focus area within marine chemistry (MSFD descriptor 10) and an area of common interest for MCWG, WGMS and WGBEC. This is in direct respons to possible requests by the ICES Data Centre. Collaboration between expert groups, as highlighted by SSGHIE. These items will support the OSPAR/ICES study group on Ocean Acidification. This item was identified by MCWG 2012 as a relevant area for more in-depth discussions, and will be of interest to OSPAR. This was initiated by MCWG members on the basis of concerns regarding emerging contaminants in the marine environment and is an ongoing area of interest to the group. This was initiated by MCWG 2011 as an item of general interest to the group and will probably be of interest to OSPAR. This continues work by WKPSPD and MCWG 2012 and will be of interest to OSPAR. Specific parts of MCWG's work might be of interest to a larger scientific community, i.e. relevant for publication beyond the annual report.
Resource requirements	The research programmes which provide the main input to this group are already underway, and resources are already committed. The additional resource required to undertake additional activities in the framework of this group is negligible.
Participants	The Group is normally attended by some 20–25 members and guests.
Secretariat facilities	None.
Financial	No financial implications.
Linkages to advisory committees	ACOM
Linkages to other committees or groups	SCICOM/SSGHIEWGMS, WGBEC OSPAR/ICES study group on Ocean Acidification ICES Data Centre

Linkages to other organizations	The work of this group is closely aligned with EU Working Groups under the Water Framework Directive (e.g. Working Group E). Specific agenda points will be directly relevant for QUASIMEME. The group provides the basis for some advice to OSPAR.

Annex 4: Parameters proposed for optional submission to QUASIMEME

This annex relates to section 5.1 of the main report.

MCWG mentioned that some laboratories might want to add more parameters than currently included in the exercises, for example additional trace elements in the two QUASIMEME exercises "Trace elements in biota" and "trace elements in sediments"

The elements already included in the test schemes give a good representation of the most analysed elements in environmental studies. Some laboratories, however, might have an extended list of analytes, for example as part of environmental background studies which try to cover as many elements as can be measured by ICP-MS after nitric acid (and HF for sediments) dissolution. The following list is typical of a background study and includes elements that all were above detection limits in a recent Danish study:

Li, Be, Na, Mg, Al, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, Sn, Sb, Te, Cs, Ba, La, Ce, Nd, Ta, W, Pt, Au, Hg, Tl, Pb, Bi, Th, U.

Annex 5: Data reporting requirements (ocean acidification) – part 1

Recommended data and meta data Field Codes (ICES ERF 3.2 http://www.ices.dk/env/repfor/ERF3.2.doc) for reporting OSPAR ocean acidification monitoring data to ICES.

ICES Field Codes	Definition	Mandatory Field
RLABO	Reporting laboratory	Y
CNTRY	IOC Country Codes	Y
MYEAR	Monitoring year	Y
OWNER	Owner of data	
PRDAT	Public release date	
Sampling Information		
SHIPC	SeaDataNet Ship and Platform Codes	Y
CRUIS	Cruise identifier	Y
STNNO	Station number	Y
LATIT	Latitude	Y
LONGI	Longitude	Y
POSYS	Positioning System Codes	
SDATE	Sample date	Y
STIME	Sample time	Y
WADEP	Water depth (sounding in m)	
DEPHU	Sampling depth (upper)	R
DEPHL	Sampling depth (lower) (i.e. for flow rated sample)	R
SLABO	Sampling lab	R
SMTYP	Sampler type	R
Station Information		
STATN	Station name	Y (OSPAR)
MPROG	Monitoring programmes & activities (e.g. JAMP)	Y (OSPAR)
WLTYP	Water and land station types (e.g. WFD water bodies)	
MSTAT	Type of monitoring station (e.g. WFD baseline station)	
PURPM	Purpose of Monitoring (e.g. trend)	Y (OSPAR)

Sample / Measurement Information		
SMPNO	Sample number	Y
SUBNO	Subsample	
NOAGG	Number of aggregated samples	
FINFL	Factors potentially influencing guideline compliance and interpretation of data	
MATRX	Matrix code (WT or SPM)	Y
PARAM	Parameters Codes	Y
MUNIT	Measurement unit	Y
BASIS	Basis of determination	
VFLAG	Data Validity Codes	R
QFLAG	Qualifier flag (i.e. "<")	
VALUE	Value	Y
PERCR	Percentage recovery (%)	

SIGND	Significant digits	
UNCRT	Uncertainty value	R
METCU	Method of calculating uncertainty	R
Method and Quality Control Information		
ALABO	Analysis lab	Y
METDC	Method documentation	
REFSK	Reference source or key	R
METST	Method of storage	R
METFP	Methods of Chemical Fixation/Preservation of Samples	R
METPT	Method of pretreatment	
METCX	Method of chemical extraction	
METPS	Method of purification/separation	
METOA	Method of analysis/assay type	Y
SREFW	Source of reference sea water	
FORML	Formulas used in calculations	
DETLI	Detection limit	
LMQNT	Limit of quantification	
PRFLG	Pressure Flag (if depths are by pressure, "Y")	
ACCRD	Accredited laboratory	
ACORG	Accrediting organization	
CONCH	Reference material type used as control chart basis	R
CRMCO	Reference material codes	R

Annex 6: Data reporting requirements (ocean acidification) – part 2

The table in this Annex is based on Annex 6 of the OSPAR MIME 2011 report. Changes to the original table in the OSPAR MIME document are marked ***in italics and bold.***

ICES Codes: Reporting format codes used to report Ocean acidification data (METCX and METOA needed for some methods to ensure traceability to method used for analysis)
ICES ERF format will only accept discrete sample information.

		PARAM	METCX	METOA	***MUNIT***
	Total dissolved inorganic carbon	DIC*			
(A)	Acidification / vacuum extraction / manometric determination		VXA*	MAN*	***µmol kg-1***
(B)	Acidification / gas stripping / coulometric determination		GSA*	COU*	***µmol kg-1***
(C)	Acidification / gas stripping / infrared detection		GSA*	SPEC-IR	***µmol kg-1***
(D)	Closed-cell acidimetric titration			TIT-CCA*	***µmol kg-1***
(E)	Auto-analyser colorimetric			COL	***µmol kg-1***
	Total alkalinity	***ALKY***			
(F)	Closed-cell acidimetric titration			TIT-CCA*	***µmol kg-1***
(G)	Open-cell acidimetric titration			TIT-OCA*	***µmol kg-1***
(H)	***Titrimetric, Gran Plot***			TIT-***GRAN***	***µmol kg-1***
(I)	***Other titration systems***			***TIT***	***µmol kg-1***
	pH	PH			
(J)	Electrometric determination with standard TRIS buffer.			PH	***Codes required suggested – SC-PHT, SC-PHF, SC- PHSWS, SC-PHNBS***
(K)	Spectrophotometric determination using I. m-cresol purple			SPEC-MCP*	***Codes required suggested – SC-PHT, SC-PHF, SC-PHSWS, SC-PHNBS***
(L)	***Ion selective field effect transistor***			***Code required – suggested ISFET***	***Codes required suggested – SC-PHT, SC-PHF, SC-PHSWS, SC-PHNBS***
	xCO2 / pCO2 µatm#	PCO2*			
(M)	Direct - equilibrator infrared determination of xCO2			SPEC-IR	
(N)	Indirect - membrane colorimetric determination of xCO2		MEM*	COL	
(O)	Direct - membrane infrared determination of xCO2		MEM*	SPEC-IR	

At least two carbonate parameters must be submitted for Ocean Acidification (OA) assessment. (Dataset accepted but Error on submission)

These are the mandatory supporting parameters for reporting (Dataset accepted without these parameters but Warning on submission)

1) ***Salinity***
2) ***Temperature***
3) ***Pressure***
4) ***Phosphate, Silicate***

These are the recommended parameters which should be reported

1) ***Dissolved Oxygen***
2) ***TOxN***

*: New code added to ICES Reference Code list of PARAM, METCX or METOA during MIME 2011

#: μatm has also been added to the Code list of UNIT

Annex 7: Preliminary Background Concentrations (BC) and Background Assessment Concentrations (BAC) for freely dissolved concentrations of non-polar contaminants in water

locations					North Atlantic off Iceland	Canary Basin	Norwegian coast and islands	East Med.	Gulf.Biscay	Scottish Lochs	Centr. North Sea			
source	OSPAR	OSPAR	MCWG	MCWG	Schulz-Bull	NIOZ	NIVA	IFREMER	IFREMER	Marine Scotland	BSH			
method	sediment	sediment	calc	calc	HiVol	PSD	PSD	sediment core	HiVol	PSD	HiVol			
details	BC	BAC	LOD	LOD	lowest value	lowest value	lowest value	pre 1850	lowest value	lowest value	lowest value	BC quartile	95% CI	BAC
unit	pg/L	pg/L	ng	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L	pg/L
Naph	13000	21000	60	5600		<5000			188	1072	81	160	5600	5760
Phen	2900	5400	30	244	<5	<100	61	565	162	698	35	43	244	286
Anth	540	900	10	67	7	11	30	133	4	18	<3	6	67	73
DBT	160	-	5	56		<30				40		21	56	78
Flua	750	1500	10	39	5	18	210	124	142	241	14	16	39	55
Pyr	540	990	10	37	5	13	56	162	30	22	<7	9	37	46
BaA	69	120	3	8	11	7	11	14	3	1	<1	2	8	10
Chr/Triph	95	170	3	8	5	4	30	19	22	21	<1	4	8	13
BbF				8		1	30	30	12	11	<2	4	8	11
BkF				8			13	6	4	11		5	8	13
BeP				8		1	20	22	10	<7	<5	3	8	10
BaP	86	170	3	8		1	<10	5	2	<7	<4	2	8	10

IP	99	200	3	8		0.2	<10	4	2	2	<2	1	8	9
dBahA				8		0.2	<10	0	2		<4	0.2	8	8
BghiPer	89	160	3	8		4	<10	3	2	0.4	<2	1	8	9
PCB28	7	-	0.5	1.3	<0.002	0.6				1.1	<0.1	0	1	1
PCB52	5	-	0.5	1.3	<0.002	0.4				1.1	<0.2	0	1	1
PCB101	1	-	0.5	1.3	0.003	0.7				1.2		0	1	1
PCB118	1	-	0.5	1.3	<0.002	0.1				0.1		0	1	1
PCB138	0	-	0.5	1.3	0.004	0.3				0.1	0.4	0	1	1
PCB153	0	-	0.5	1.3	<0.002	0.1				1.2	0.3	0	1	1
PCB180	0	-	0.5	1.3	<0.002	0.1				0.0		0	1	1
γ-HCH	495	-	1.0	40							7.2	0	40	40
α-HCH	0	-	1.0	40							13.4	0	40	40
p,p'-DDE	4	-	0.5	1.3		0.6					<0,1	0	1	1
HCB	11	-	0.5	1.5		0.3					0.5	0	1	1
Dieldrin	10	-	0.5	1.5							<1,0	0	2	2