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SCICOM STEERING GROUP ON HUMAN INTERACTIONS ON ECOSYSTEMS

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## Report of the Marine Chemistry Working Group (MCWG)

28 February–4 March 2011

Gothenburg, Sweden



ICES

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

H. C. Andersens Boulevard 44–46  
DK-1553 Copenhagen V  
Denmark  
Telephone (+45) 33 38 67 00  
Telefax (+45) 33 93 42 15  
[www.ices.dk](http://www.ices.dk)  
[info@ices.dk](mailto:info@ices.dk)

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## Executive summary

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The Marine Chemistry Working Group (MCWG), chaired by Katrin Vorkamp, Denmark, met at the Swedish Hydrological and Meteorological Institute in Gothenburg, Sweden, 28 February–4 March 2011. The meeting was attended by 26 participants representing 12 different countries. MCWG worked in a combination of plenary work, subgroups and specific task groups. Following an efficient approach to chemical oceanography in 2010, the **chemical oceanography subgroup (COSG)** continued in 2011, consisting of 10 MCWG members.

MCWG 2011 addressed two **OSPAR requests** on i) developing the general text of a guideline on monitoring of contaminants in seawater ("**seawater guideline**") and ii) updating the JAMP Eutrophication Monitoring Guideline ("**nutrient guideline**"). An MCWG subgroup had prepared an initial draft of the seawater guideline prior to MCWG 2011 which was reviewed and extended at the meeting, assisted by Anders Grimvall of the former ICES Working Group on Statistical Aspects of Environmental Monitoring (WGSAEM). The guideline will be completed by MCWG 2012. COSG discussed review comments which MCWG had received on the nutrient guideline and suggested other relevant information to be included in the update, to take place at MCWG 2012.

New developments were presented and discussed for the **Water Framework Directive (WFD)** and the **Marine Strategy Framework Directive (MSFD)**. Those included the revision of priority pollutants and related Environmental Quality Standards (EQS) under WFD, which MCWG commented on. Furthermore, suitable statistical methods of compliance checking were discussed. As several MCWG members are actively involved in initial assessments and other MSFD-related work, information on initial assessments in member countries will be compiled at MCWG 2012.

Marilynn Sørensen of the **ICES Data Centre** visited MCWG 2011 to i) discuss changes in the database to accommodate data obtained by **passive sampling** and ii) present and discuss ICES's involvement in the European Marine Observation and Data Network (**EMODNET**). Assistance from MCWG was requested, in terms of an EMODNET subgroup to work intersessionally.

COSG compiled a list of **certified reference materials** currently available for **nutrients in seawater** and proposed additions. Following up on an OSPAR request on ocean acidification monitoring methodology at MCWG 2010, COSG also reviewed recent developments in **pH measurements**, both in terms of methodology and results from the OSPAR area, as well as related quality assurance issues. Several countries have initiated pH monitoring in seawater, and MCWG members will bring relevant information to MCWG 2012. The document produced at MCWG 2010 on ocean acidification has been revised in view of publication as an **ICES Cooperative Research Report**. MCWG has also suggested a **theme session** on ocean acidification for the Annual Science Conference 2012.

Based on previous MCWG technical annexes, **ICES TIMES manuscripts** were reviewed and completed on i) the determination of dioxins/furans and dioxin-like PCBs in biota and sediments and ii) passive sampling based on silicone rubbers. A third manuscript on PCB analysis of biota and sediment has been drafted and will be completed at MCWG 2012.

New information on **emerging contaminants** was presented in three presentations on i) alternative brominated flame retardants, ii) organophosphorous flame retardants in

the UK and iii) retrospective monitoring of perfluorinated compounds (PFC) in Germany. Following an OSPAR request at MCWG 2010, a literature review was provided on the role of **atmospheric transport of PFC** for inputs into the marine environment, confirming MCWG's conclusion in 2010.

Further **contaminant-related presentations** covered i) results from a passive sampling project in the UK and ii) toxicological and ecological effects of persistent organic pollutants (POPs). MCWG has links to a number of other expert groups, and being interested in **scientific exchange and collaboration**, MCWG received reports from the Working Group on Eel (WGEel), the Working Group on Marine Sediments (WGMS), the Working Group on Biological Effects of Contaminants (WGBEC), the IOC/ICES Study Group on Nutrients in Seawater (SGONS) and the ICES/OSPAR Study Group on Integrated Monitoring of Contaminants (SGIMC).

Lars Förlin of the University of Gothenburg had been invited for a plenary presentation on "Integrated fish monitoring in coastal areas". **Integrated chemical and biological effects monitoring** was also addressed in two presentations by MCWG members on i) the Belgium INRAM project and ii) a Belgium case study on TBT in shrimp. As a standing agenda point, quality assurance was discussed, in particular with regard to **QUASIMEME**. MCWG continues to receive updates by QUASIMEME and to provide feedback and information exchange with QUASIMEME.

## **1 Opening of the meeting**

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The Marine Chemistry Working Group (MCWG), chaired by Katrin Vorkamp, Denmark, met at the Swedish Meteorological and Hydrological Institute (SMHI) in Gothenburg, Sweden, 28 February–4 March 2011. Elisabeth Sahlsten and Bertil Håkansson, the Coordinator for Oceanography and Marine Environment at SMHI, welcomed the participants and wished MCWG a successful meeting.

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 2011. The chemical oceanography subgroup (COSG) continued from MCWG 2010, consisting of Carlos Borges, Carmen Rodriguez, David Hydes, David Pearce, Elisabeth Sahlsten, Evin McGovern, Klaus Nagel, Naomi Greenwood, Pam Walsham and Solveig Olafsdottir.

## **2 Adoption of the agenda**

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The agenda was adopted as presented in Annex 2.

## **3 Report from the 98<sup>th</sup> ICES Statutory Meeting**

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### **3.1 Advice Drafting Group on Monitoring 2010**

Katrin Vorkamp attended the 2010 meeting of the Advice Drafting Group on Monitoring (ADG MON) and presented its work to MCWG, including the comments by the Review Group 2010 (see MCWG 2010 report, Annex 11).

MCWG 2010 had worked on three OSPAR requests, i.e. advice on monitoring methodologies for ocean acidification, the question of atmospheric monitoring of per-fluorinated compounds (PFC) and a guideline for analysis of polychlorinated dibenzo-p-dioxin and polychlorinated furans in sediment. The report by MCWG 2010 was thus the main source for ADG MON's work on these three pieces of advice, complemented by reports by the Working Group on Zooplankton Ecology (WGZE), the Working Group on Deepwater Ecology (WGDEC) and the Review Group.

With regard to atmospheric monitoring of PFC, the conclusion of MCWG 2010 (and ADG MON 2010) was that further research into partitioning and transport processes would be necessary to advise on the role of atmospheric transport and deposition for PFC input into the marine environment. Evin McGovern informed that Norway as one of the OSPAR contracting parties had included PFCs in an atmospheric monitoring programme.

With regard to ocean acidification monitoring, ADG MON 2010 suggested an ICES/OSPAR workshop to further develop ocean acidification monitoring. MCWG discussed that this work should probably be extended to HELCOM.

### **3.2 Annual Science Conference 2010**

During the ICES Annual Science Conference (ASC) 2010 at Nantes, France, Katrin Vorkamp attended meetings of the SCICOM Steering Group on Human Interactions on Ecosystems (SSGHIE) and the Advisory Committee (ACOM).

The SSGHIE agenda included, among other items, a presentation of the ICES Expert Group (EG) reports and a discussion on collaboration between EGs. Katrin Vorkamp

showed the report presentation to the group and conveyed the feedback by the ICES secretariat and the chair of SSGHIE. MCWG was considered a hard-working and productive group, especially with regard to OSPAR requests, with a wide range of tasks and topics.

During the discussion of collaboration between EGs, the chair of the Working Group for Biological Effects of Contaminants (WGBEC) called for more involvement of MCWG in ICES/OSPAR work on integrated monitoring of contaminants, e.g. the ICES/OSPAR Study Group on Integrated Monitoring of Contaminants (SGIMC). This wish was discussed at MCWG who agreed that WGBEC, SGIMC and MCWG had common goals in terms of contributing to the state of the environment. Prior to MCWG 2011, Katrin Vorkamp had contacted the chairs of WGBEC and SGIMC to exchange ideas about collaboration (see agenda item 5.7) and she will also attend the SGIMC 2011 meeting for one day.

At the ACOM meeting at ASC 2010, the approach to and timetable for the OSPAR request for a seawater guideline (see agenda item 5.1) was agreed upon.

### 3.3 Internal ICES business

In December 2010, the SCICOM chair informed EG chairs about SCICOM's work following the restructuring of the Science Programme. Information on strategic initiatives on Area-based Science and Management, Stock Assessment Methods, Biodiversity Advice and Science and Climate Change were conveyed to the group.

The next ICES ASC will be held in Gdansk, Poland, 19–23 September 2011. Deadline for abstract submission is 15 April 2011. Katrin Vorkamp reported briefly from the session "Monitoring biological effects and contaminants in the marine environment" at ASC 2010, which was of direct relevance to the work of MCWG. MCWG would be interested in regular sessions at ASC on MCWG-related work, for example contaminants, which would also provide a joint forum for MCWG, WGBEC and related EGs (see section 3.2), or chemical oceanography.

For ASC 2012, MCWG proposes a Theme Session on physico-chemical aspects of ocean acidification in the ICES area (see Annexes 4 and 5).

#### Recommendation

For ICES to note MCWG's proposal of a Theme Session for the Annual Science Conference 2012. Preliminary title "Physico-chemical aspects of ocean acidification in the ICES area".

## 4 Plenary presentations

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Elisabeth Sahlsten and Katrin Vorkamp had invited two guest speakers to present their work at the meeting.

### 4.1 Lars Förlin (University of Gothenborg): Integrated fish monitoring in coastal waters

An overview of fish monitoring work in Sweden was given and a few case studies were presented. It was reported that the health status of two sentinel fish species perch (*P. fluviatilis*) and the viviparous eelpout (*Z. viviparus*) have been regularly studied in environmental monitoring programmes in Swedish coastal site for many years. In reference (pristine) coastal sites with no or small local point sources of contaminants fish health has been assessed to study emerging impacts of pollutants or

other stressors. In these sites the perch and eelpout health studies together with analytical chemistry work to measure anthropogenic chemicals and fish ecology studies, form an integrated fish monitoring programme supported by the Swedish Environmental Protection Agency. The fish health work has been run yearly for more than 20 years, and the integrated work for 15 years.

Generally the fish health studies seem to indicate good statues in the reference sites but some fish health parameters (i.e. biomarkers) clearly indicate significant time trends of concern. For example in female perch from Baltic Sea coastal sites ca. 30% reduction of gonad size, and a more than five times increase of the activity of the detoxification enzyme EROD have been observed. The chemical work has not identified any causative agent (yet), but the working hypothesis is that these changes are caused by unknown or not yet analysed chemical(s). The presentation also included earlier work on the serious impact of pulp and paper mill effluents on the fish health, but also the successive fish health improvements after cleaning measures taken at the mills. In addition the work with large scale gene expression profiling in eelpout and the development of a cDNA microarray was presented. This global gene expression technique is applied and combined with traditional monitoring measurements in the BONUS+ project Balcofish including studies in coastal sites of Germany, Denmark and Sweden.

#### **4.2 Kristin Andreasson (SMHI): Monitoring of primary production in the Baltic Sea**

The presentation had to be cancelled due to illness.

### **5 Main agenda**

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#### **5.1 Development of a JAMP guideline for monitoring of contaminants in seawater**

As agreed upon with ACOM, MCWG was to produce a first draft at its 2011 meeting and is going to finalise this guideline by 2012.

A subgroup consisting of Gert Asmund, Jacek Tronczynski, Katrin Vorkamp, Koen Parmentier, Norbert Theobald, Ralf Ebinghaus and Zhiyong Xie had prepared a draft prior to the meeting and continued this work at MCWG 2011.

Katrin Vorkamp had contacted ICES with regard to assistance with statistical expertise and had been given contact details by former members of the ICES Working Group on Statistical Advice in Environmental Monitoring (WGSaEM). Anders Grimvall (University of Linköping, Sweden) and Bernard Iooss (EDF, France) kindly agreed to help with statistical questions. Anders Grimvall attended the MCWG 2011 meeting on Thursday afternoon.

The first draft as of MCWG 2011 is attached as Annex 6.

#### **5.2 Report of developments with regard to quality assurance of marine chemistry, in particular with respect to QUASIMEME**

In correspondence with QUASIMEME prior to the meeting, QUASIMEME notified MCWG that they considered a biannual visit to MCWG sufficient for information exchange and asked Patrick Roose to inform MCWG about recent developments.

Patrick Roose updated MCWG on the following points:

- QUASIMEME has joined forces with WEPAL, an accredited proficiency testing organisation. WEPAL was visited for yearly re-inspection February 8th, 2011 by the Dutch accreditation board, and the joint-venture with QUASIMEME was discussed. QUASIMEME will be visited within a few months, and it is expected that accreditation of QUASIMEME will be achieved soon.
- The Cofino statistics, explained to MCWG last year by Wim Cofino, will be published in the peer-reviewed literature and included in the accreditation of QUASIMEME.
- The new web-based system to submit data is now operational. This also allows easy access to the data by the participants.
- An SSCP development exercise is being organised, after a successful workshop in Oostende.
- A recurring problem is a limited number of participants for some exercises, even for compounds of the Water Framework Directive (WFD), which can result in no assignments of z-scores.
- The requested changes in the BFR exercises have been executed; sediment and biota rounds are now separated.

Michiel Kotterman who is a member of the QUASIMEME Scientific Advisory Group and collaborates with QUASIMEME on production of test materials put forward a question on behalf of QUASIMEME, regarding the preparation of suitable mussel materials for organic pollutants, more specifically, of spiking the mussel test material with organic contaminants. The reason for this is the following:

For mussels, as for all materials, there is a need for specimens with suitable concentration levels: High enough to obtain Z-scores, as many participants require this for their accreditation, but low enough to be representative of environmental concentrations.

It has been difficult for QUASIMEME to obtain mussels in sufficient quantities which are polluted with a variety of POPs at detectable levels. Harvesting and preparing these mussels has required great effort. An alternative might therefore be to use easily accessible, but low contaminated mussels which then are spiked with detectable amounts of the target analytes, including the following aspects:

- Concentrations will only be raised to levels to enable common environmental analysis.
- Environmental chemical profiles will be taken into account, but it is unlikely that natural profiles can be obtained.
- Homogeneity will be closely checked (as always for biota).
- Possible side effects in the analytical routine will be checked as well.

This would have some advantages (detectable concentrations, wide array of chemicals, lower price) and would only apply to organic contaminants in mussels, but QUASIMEME acknowledges that the customers might have some reservations.

In view of a protocol to be developed by QUASIMEME for the use of spiked mussels as test materials, MCWG is asked for their comments.

**MCWG's comments**

- Concern is expressed about homogeneity, chemical profiles, and matrix effects [Reply Michiel Kotterman: These parameters will be tested and will have to meet QUASIMEME's standards before a test material will be prepared].
- Although typical environmental chemical profiles are the target, it is quite certain that the profile in the spiked sample will deviate from that of non-spiked samples. The question remains whether or not this can be seen as a negative aspect, or as a test if the analytical procedure is capable of dealing with aberrant samples. The general opinion at MCWG was that a chemical profile close to that in environmental samples would be preferred.
- "Natural spiking" of mussels, i.e. mussels placed in polluted water and fed with polluted food had been discussed at MCWG 2010 and found acceptable. However, Michiel Kotterman explained that an intensive recirculation system would be required as one cannot discharge the polluted water easily and mussels require large quantities of water. This would likely be a very costly method.
- The suggestion is made of obtaining mussels from polluted areas in e.g. China. Though interesting, the chemical profile may be rather different from what is being monitored in Europe. Besides, it may prove to be both laborious and expensive to obtain mussels with a suitable level of contamination. Nonetheless, participants with connections to regions of higher pollution are invited to inform QUASIMEME about options.

It is concluded that a spiked mussel material could be used in one round, provided that no problems are indicated in QUASIMEME's tests. According to Michiel Kotterman, the materials will only be used beyond this test round if evaluations are positive, based on customers' feedback. MCWG emphasised that an evaluation should be formalised and should not be based on the absence of customer complaints.

Another question to MCWG was the use of whole fish, for example small flounder. It is expected that this would add to the range of contaminants and levels. The general opinion was neutral, with one MCWG member being against this. If the use of whole fish results in a suitable test material with levels not otherwise obtained, this will be introduced in QUASIMEME. Again, only after evaluation it will be decided if this whole fish material will be used more often. MCWG had the same comment as stated above, regarding customer satisfaction evaluations.

**Further remarks by MCWG**

- Due to the use of ICP-MS, some participants can easily report more elements than presently included in the scheme. According to Michiel Kotterman, adding additional elements should not be a problem for QUASIMEME. Of course it becomes more useful when a larger number of labs report these additional elements and z-scores can be calculated.
- It was noted that although the BFR scheme was changed (i.e. separation between biota and sediment) the protocol had not been updated.
- The name of fish species was not mentioned in some of the last rounds. This was checked with Steven Crum of QUASIMEME and it appears that this was intentional. As some samples are used twice in different rounds, as little information as possible is disclosed to the customers. The question

from QUASIMEME to MCWG is whether or not an indicative fat-content would be a suited alternative, and if so, within what margins?

The MCWG response was that ideally, test materials should not be re-used at all. MCWG accepts this change, but does not really approve. With regard to the practical procedures, the lipid content should be known prior to analysis, i.e. be included in the protocols. The information on what species is being analysed should be given at some point, e.g. in the report of each round.

- MCWG discussed whether other intercalibration exercises or proficiency testing schemes be discussed at the meetings. The conclusion was that this would always be worthwhile, but it should be checked how they are run. QUASIMEME is rather strict, low z-scores are not easy to obtain.
- In some trace metal exercises many labs have a 100% score. MCWG members wondered whether or not the bar could be raised so less labs would have a 100% score. However, this was not seen as a valid argument.
- MCWG wondered whether the number of analyses in 1 sample could be optimised, either by increasing the number of analytes in 1 sample (not easily achieved, might require spiking) or by identifying the samples so labs could use, if applicable, 1 jar instead of two for analyses of those compounds that use the same method.

This report will be sent to QUASIMEME, but MCWG members are encouraged also to contact QUASIMEME individually with specific questions or remarks.

#### **Recommendation**

For QUASIMEME to note MCWG's comments.

### **5.3 Water Framework Directive (WFD) and Marine Strategy Framework Directive (MSFD)**

#### **5.3.1 General overview of WFD and MSFD and their key parameters**

As an introduction to this field, Patrick Roose gave a general overview of these two directives and their main features, with focus on assessment criteria. In particular, a number of acronyms were defined, e.g. Good Environmental Status (GES) under MSFD being different from Good Ecological Status (GES) used under WFD in connection with Good Chemical Status (GCS). Other members added information on the time lines for MSFD implementation, e.g. assessment of current status, determination of Good Environmental Status and targets and indicators by July 2012.

#### **5.3.2 OSPAR updates: New OSPAR structure and OSPAR Quality Status Report (QSR) 2010**

Evin McGovern presented the post 2010 OSPAR structure (Annex 7) and changes of importance for MCWG. The new OSPAR structure reflects the outline of the Marine Strategy Framework Directive, with five committees dealing with specific GES descriptors. Above these committees, the Coordination Group (CoG) oversees the technical work.

The former Environmental Assessment and Monitoring Committee (ASMO) which usually dealt with MCWG advice does not exist anymore in the new structure. Organic contaminants and chemical oceanography issues will likely be addressed by the new Hazardous Substances and Eutrophication Committee (HASEC).

Patrick Roose presented the OSPAR Quality Status Report 2010. Summarising the results of the Joint Assessment and Monitoring Programme (JAMP) of the last 10 years, it provides assessments of the environmental quality status of the OSPAR region as well as trends in pressures and impacts. The report is structured along OSPAR's five thematic strategies for eutrophication, hazardous substances, radioactive substances, offshore oil and gas industry and biodiversity and ecosystems, with additional chapters on climate change, new tools in ecosystem approaches and regional summaries. The full report is available from OSPAR's website ([www.qrs2010.ospar.org](http://www.qrs2010.ospar.org)) which also offers interactive access to specific figures or sub-chapters.

### 5.3.3 Report on the developments in WFD monitoring programmes

Anja Duffek presented recent developments under the WFD with focus on Priority Substances. In 2001, a first list of 33 priority substances was adopted (Decision 2455/2001) and added to Directive 2000/60/EC as Annex X. In 2008, Environmental Quality Standards (EQSs) expressed as the maximum allowable concentration (MAC-EQS) and/or annual average concentration (AA-EQS) for 33 priority substances and 8 other pollutants were established (Directive 2008/105/EC).

The WFD Article 16 requires the Commission to review the list of priority substances periodically. Article 8 of the Directive 2008/105/EC requires the Commission to finalise its next review by January 2011, accompanying its conclusion, where appropriate, with proposals to identify new priority substances and to set EQSs for them in water, sediment and/or biota. The ongoing review process will probably be finished by June 2011.

The draft list of reviewed Priority Substances and their corresponding EQS values as well as the new identified Priority Substances with their proposed EQS values have been discussed (Annex 8). MCWG had the following comments:

- Some of the proposed EQS values seem to originate from food legislation, e.g. the EQS values for PAH and dioxins in fish. As PAH are readily metabolised in fish, it is generally accepted that PAH monitoring in fish does not provide useful information.
- Monitoring of dioxins and dioxin-like PCBs in fish is useful, but the proposed EQS should be re-evaluated with regard to environmentally meaningful levels.
- Dicofol is unstable in water and should not be monitored in this matrix.
- PCBs have been added to the list of priority hazardous substances, but have not been specified in terms of individual congeners. MCWG recommends monitoring of six indicator PCB congeners (CB-28, CB-52, CB-101, CB-138, CB-153 and CB-180) in addition to dioxin-like PCBs.
- It is unclear why no EQS is given for PCBs. Dioxin-like PCBs are included in the EQS values for dioxins (expressed as toxicity equivalent concentration, TEQ), which as a minimum should be specified.
- Heptachlor / Heptachlor epoxide are listed with only one EQS instead of two. MCWG also wondered about the scientific basis for this value.
- ΣDDT might be difficult to determine for technical reasons, i.e. low concentrations of o,p'-substituted compounds. Thus, results might be difficult to interpret. It might be more useful to set EQS values for the individual p,p'-substituted DDT and degradation compounds.

- Zinc is included on the list of new priority substances although Zinc is not considered as harmful at environmentally relevant concentrations.
- Given the low concentrations in water, EQS should be stated in ng/l instead of µg/l.

### **Recommendation**

For EU Working Group E on Chemical Aspects (Chair: Jorge Rodriguez Romero (DG Env D.1)) as well as OSPAR and HELCOM to note MCWG's comments with regard to revisions of priority substances, priority hazardous substances and related EQS values.

#### **5.3.4 Report on the developments under the Marine Strategy Framework Directive (MSFD)**

The Marine Strategy Framework descriptors relevant to contaminants are Descriptor 8 (Pollution effects of contaminants) and Descriptor 9 (Contaminants in fish and other seafood).

The aim of MSFD is to achieve Good Environmental status (GES) for the eleven descriptors in marine waters. To be able to assess progress towards achieving GES, targets must be set for all descriptors, including 8 and 9. These targets will be set by member states. However, there needs to be collaboration between member states, particularly where regions are shared. The process of setting targets is currently going forward and should be in place by June 2012.

Although both Descriptor 8 and 9 relate to contaminants, MCWG decided not to address Descriptor 9. For Descriptor 8, monitoring should be covered by OSPAR and HELCOM monitoring programmes, for CEMP determinants. To assess progress towards GES for Descriptor 8, the general approach will be to compare concentrations to relevant Environmental Assessment Criteria (EACs), where available. One of the targets for OSPAR is to achieve background concentrations for naturally occurring substances and close to zero for man-made substances. For the MSFD, the aim is that concentrations of contaminants in the marine environment should not cause harm, therefore the EAC is the appropriate target.

For the Water Framework Directive (WFD), concentrations of contaminants in water (except for mercury, hexachlorobenzene and hexachlorobutadiene, where EQSs are set for biota), are assessed against Environmental Quality Standards (EQS) with the aim of achieving Good Chemical Status. Good Ecological status (GES) is used under WFD as goal for the ecosystem of water bodies. There was concern that there may be a conflict between WFD and MSFD. There was some discussion on what would happen if a substance was above the EAC but below the EQS in the same sub-region and how this sub-region would be classified. However, this was considered unlikely as, for the most part, matrices were different (water for WFD, biota and sediment for MSFD), and the parameters measured in WFD water bodies and marine monitoring programmes had limited overlap at present.

For MCWG's next meeting in 2012, MCWG members are asked to bring information from their respective countries on current activities within MSFD, in particular with regard to the initial assessments.

### 5.3.5 Discuss suitable statistical methods of compliance checking of Environmental Quality Standards in WFD

Directive 2008/105/EC sets the Environmental Quality Standards for Priority Substances and the basic provisions for compliance checking. As laid down in the preamble (14) and Annex I, Part B, 2<sup>nd</sup> point of this Directive "...statistical methods, such as a percentile calculation... may be introduced ...to ensure an acceptable level of confidence and precision for determining compliance with the MAC-EQS."

The application of statistical methods for compliance checking of the MAC-EQS is a task within the subgroup "Chemical Monitoring and Emerging Pollutants" (CMEP) of the Working Group E on Chemical Aspects.

It is planned to split this task into two steps:

Step 1: Assessment of transposition of the Directive 2008/105/EC into national law using a questionnaire in order to describe the current practise and experience in checking compliance with the MAC-EQS, particularly with regard to the application of statistical methods.

Step 2: Comparing different approaches of compliance checking using real monitoring data.

As already discussed at MCWG 2010, the UK prepared a proposal based on the method described in ISO 5667-20. This proposal means that, depending on the number of measurements performed and the desired statistical confidence of failure, a certain number of monitoring results above the MAC-EQS can be accepted.

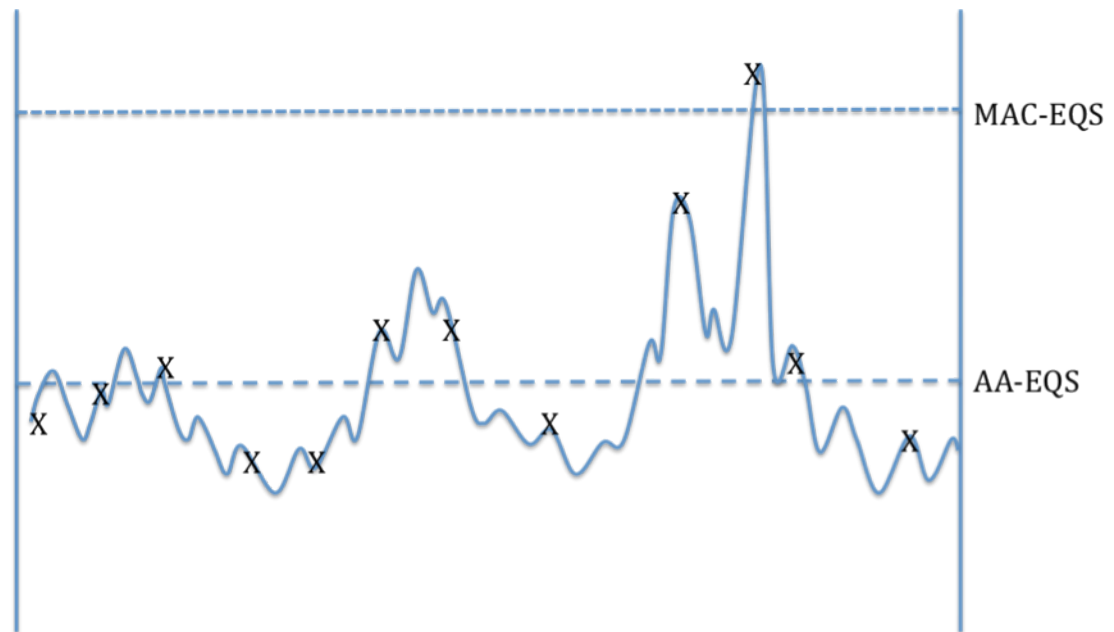
Anja Duffek informed that in Germany, checking compliance of measured values with MAC-EQS will be transposed into national law as follows in order to be protective against acute toxic effects exerted by exposure to short-term pollution peaks:

Compliance with the EQS expressed as MAC-EQS is achieved if each individual measurement result is less than or equal to the MAC-EQS. No statistical methods such as application of percentile calculations will be introduced for checking compliance of measurement results with MAC-EQS

A small MCWG subgroup consisting of Anja Duffek, Koen Parmentier and Patrick Roose discussed further how compliance checking of MAC-EQS could be done in a statistically sound way. The suggestion to work on real monitoring data as mentioned in MCWG's action list of 2010 was abandoned due to time constraints but the subgroup examined the EQS directive once again in relation to the UK proposal for compliance with the MAC-EQS (see MCWG 2010).

The MAC-EQS is meant to protect the environment against occasional high loads of a contaminant. However, using the 95-percentile of the entire dataset for a station does not correspond with the precautionary principle. Furthermore, datasets might not include more than the minimum of 12 monthly samples. Although the EQS directive states that statistical tools are allowed to handle outliers or extreme values, the subgroup does not consider the UK approach to be in line with the purpose of the MAC-EQS.

The question further remains if an error calculation is required around the AA-EQS or MAC-EQS for compliance checking. Nothing on this topic is mentioned in the EQS directive but it is also incorrect to state that it is not allowed. With regard to the AA-EQS, the advice that sampling events should be equally spread throughout the monitoring period remains. Monthly averages should be used to calculate the annual average.



The group benefited from the presence of Anders Grimvall, Professor in Statistics at the University of Linköping, Sweden (see agenda item 5.1). When faced with this problem he sketched the situation as follows: If one assumes a natural variability of a contaminant in the environment (Figure above), periodical sampling (crosses in the graph) will not allow reconstruction of the actual variation, but the average can be used, without error correction, to check compliance with the AA-EQS. Correction for e.g. measurement uncertainty does not appear necessary (unlike the MAC, see below), as the variation of the average, based on 12 individual measurements, will be smaller than for the maximum concentration. In the case above, the average varies around the AA-EQS and one has to accept it can be below or above from year to year.

For the maximum concentration, the situation is more complicated as the variation of the maximum as a single value will be much higher than that of the average. In this case, an estimate of this variation should be calculated and used for compliance checking against the MAC-EQS. Unfortunately, due to time restrictions, this could not be further worked out and will be re-addressed by MCWG at their next meeting.

## 5.4 MCWG members to report on projects of interest to MCWG

### 5.4.1 Michiel Kotterman: Toxicological and ecological effects of POPs

As part of this presentation, Michiel Kotterman informed MCWG about chemistry-related activities and interests of the Joint EIFAC/ICES Working Group on Eels (WGEel). Michiel Kotterman attended the WGEel 2010 meeting in Hamburg. In the subgroup "Quality", a database is created with contaminant data from all over Europe. For now, eel is divided into different categories depending on contaminant loads, parasites and other parameters like fat percentage. Although the effects of these parameters are not quantified, it is assumed that an eel with "high quality" (i.e. low contaminant levels, not infected with parasites and with a normal fat content) has a better chance of reaching the spawning grounds and to reproduce than an eel with "low quality". It should be noted that there is little information about the percentage of the European eel spawning stock that is of "low quality". For some geographic areas the level of information is high, i.e. data are available of the three quality parameters. However, more information on types and levels of contaminants

(organic and inorganic) in eels is required, and MCWG is asked to collate data where available (see also section 5.7).

Within the European research project PRO-EEL, artificial reproduction of eels is investigated. IMARES will investigate the pollutant levels (both organic and inorganic) in eels and eggs. These will be related to reproduction success; if not to glass eel stage then towards larvae, as larvae can be acquired successfully already. As part of PRO-EEL, the toxicity of contaminants towards eel reproduction is reviewed. As eel reproduction itself cannot be investigated, effects towards other species have been extrapolated. These extrapolations have failed so far to give threshold conditions that may affect reproductive capacity of eels.

The PhD research by Edwin Foekema (IMARES) with early life stage test (eggs and larvae) of sole (*Solea solea*) has shown in single compound exposure that dioxin-like activity of PCBs (TEQ) is the main toxicant of those tested. Brominated flame retardants and PFOS only had an effect on larval development and survival at high concentrations. Multi-contaminant exposure also suggests that TEQ is the main factor. Extracts of sole itself (from polluted area) have also been tested, but the results are not available yet.

Triggered by the eel and sole research, population effects were considered and discussed. It is well known that above a certain spawning stock size the recruitment success is not further increased (due to lack of food, space, predation pressure etc). A negatively affected reproduction (caused by contaminants) can therefore stay unnoticed if the spawning stocks (with non-impaired spawners) is large enough. In circumstances that spawning stocks decrease, the effect of contaminants may become apparent.

#### **5.4.2 Philippe Bersuder: Applicability of passive samplers for contaminant monitoring in the UK marine environment**

Philippe Bersuder reported on a project assessing the applicability of passive samplers for contaminant monitoring in the UK marine environment. Contaminant monitoring for priority pollutants is an integral part of the UK obligations under the Water Framework Directive (WFD) and OSPAR monitoring programmes. The Marine Strategy Framework Directive (MSFD) requires Good Environmental Status (GES) be maintained and descriptor 8 of GES states that the concentrations of contaminants are at levels not giving rise to pollution effects. It is therefore important to establish whether environmental concentrations of chemicals on existing EC and OSPAR chemical priority lists are of toxicological significance, and whether there are additional substances with potential to cause harm in the UK marine environment.

In order to perform this process, passive samplers (silicone rubber and POCIS) were deployed to provide information on the presence and freely dissolved concentrations of a wide range of potential target substances for monitoring programmes. The survey covered a wide range of locations (38 sites) around the UK, from industrial estuaries to relatively un-impacted offshore waters. Samplers were deployed for periods of 4–8 weeks during spring and summer 2009. Silicone rubber passive samplers were prepared, deployed, retrieved and analysed following guidelines developed by the ICES MCWG. Results were obtained for chlorobenzenes, chlorinated alkanes, dioxins and furans, PCBs, PAHs, pesticides/biocides, musk xylenes, SCCPs, brominated flame retardants, phthalates, alkylphenols, organotins and pharmaceuticals.

The presentation focused on the presence of brominated flame retardants (PBDEs, HBCD, and TBBPA) and the pharmaceutical clotrimazole. PBDEs were detected at all

sites assessed, ranging from 0.6 pg/L to 1007 pg/L (Thames), although results were deemed semi-quantitative as quantification could only be achieved by external calibration (due to an interference with internal standard). The method LOQs (0.0002–0.0078 ng/L) were well below the Annual Average-EQS for PBDEs (0.2 ng/L) set in the WFD. The PBDE congeners distribution was not typical of that found in marine compartments such as sediments and biota, but possibly as a result of false-positives (particularly for BDE 153) from interfering compounds. The mass spectra obtained by gas-chromatography-mass spectrometry (GC-MS) indicated the presence of brominated compounds, likely to be either PBDEs other than those targeted or 'novel' brominated contaminants.

In a smaller subsequent follow-up survey in early 2010, samplers (including DGT) were also deployed alongside mussels. The mussels are currently being analysed for priority substances as well as for effects such as stress on stress, DNA damage, neutral red and a number of biomarkers via qPCR and the full set of results will be presented at the MCWG 2012 meeting. The UK Department for Environment, Food and Rural Affairs (Defra) was acknowledged for funding this project, along with project collaborators (Cefas, Deltares, UK Environment Agency, Marine Scotland Science, Northern Ireland Environment Agency, Scottish Environment Protection Agency).

### **5.5 Provide expert knowledge and guidance to the ICES Data Centre as may be required**

Marilynn Sørensen of the ICES Data Centre visited MCWG and requested MCWG to make recommendations on:

- 1) restructuring the matrix codes for water, aiming to eliminate the matrices "seawater sample, after filtration" (AF) and "seawater sample, before filtration" (BF), because these matrices are method-based and cannot support newer methods such as the passive sampling technique. This causes difficulties in the data exchange with other marine databases.
- 2) how to accommodate data from passive sampling devices (PSDs) in the ICES database.

MCWG considered that:

- the information presently stored under the AF/BF matrix code can well be stored in the method pre-treatment section.
- information on future methods to probe the various speciations of metals and organic compounds in water will be more conveniently stored in the methods section than in the matrix section.
- passive sampling is essentially a sampler type (SMTYP) rather than a method of pre-treatment (METPT). However, SMTYP is presently less clearly visible than METPT information, so for the moment there is an advantage in also flagging passive sampling data in the METPT section.

MCWG therefore recommends that:

- the matrices AF and BF be replaced with the matrix "water";
- suspended particulate matter be retained as a matrix;
- mandatory fields for matrices "water" and suspended particulate matter "SPM" be:
  - sampler type (SMTYP)
  - method of pre-treatment (METPT)

- method of analysis (METOA)
- the mandatory requirement for reporting filtration should be unchanged;
- passive sampling be listed in the sections “sampler type” (SMTYP) and method of pre-treatment (METPT);
- the passive sampling technique should be specified under “sampler type” (SMTYP). The following samplers are currently used (additional samplers could be added in the future):
  - PS-DGT           Passive sampler - Diffusive Gradients in Thin Films (DGT)
  - PS-SPMD       Passive sampler - Semipermeable membrane device
  - PS-SR           Passive sampler - Silicone rubber
  - PS-LDPE       Passive sampler - Low-density polyethylene
  - PS-POCIS       Passive sampler - Polar organic chemical integrative sampler
- the mandatory fields for passive sampling be as follows:
  - sampler type (SMTYP = PS-\*)
  - method of pre-treatment is “not filtered- passive sampling technique” (METPT = NF-PST)
  - method of analysis (METOA)
- mandatory parameters for reporting passive sampling data are:
  - estimated water sampling rate.
  - duration of the exposure
  - exposed surface area
  - the estimated temperature range during the exposure
  - the estimated salinity range during the exposure
- filtration information under METPT should contain two levels, the first one being “filtration” or “none” and if “filtration” is selected, a selection of the various filter types (MCWG 2010) should come up.

Marilynn Sørensen asked about MCWG contact persons representing different scientific fields who can be contacted intersessionally in case of ad hoc queries. The following MCWG members would act as contact persons:

- Jacek Tronczynski: Organic contaminants
- Gert Asmund: Trace metals
- Anja Duffek: Database parameters

Depending on the nature and complexity of the query, these contact persons will include other experts or put the questions forward at the following MCWG meeting. It was also highlighted that opinions or advice given by the contact persons or other individual MCWG members would be that of the individual scientist and not of MCWG as a whole.

### **Recommendations**

ICES Data Centre to make the database changes as described.

## 5.6 Discuss the European Observation and Data Network (EMODNET) chemical portal, with input from the ICES Data Centre

Prior to the MCWG 2011 meeting, MCWG had contacted the ICES Data Centre to express interest in current developments, in particular EMODNET, and to invite somebody from the ICES Data Centre to MCWG 2011, for a presentation on the status and vision for EMODNET.

Marilynn Sørensen attended the MCWG 2011 meeting on Wednesday afternoon and had compiled several presentations on EMODNET, explaining the idea behind EMODNET, its structure and workplan, ICES's involvement in this project and specific aspects of QA/QC reporting. In summary, EMODNET was launched as an EU initiative in 2007, with the objective to provide access to all data collected as part of European marine monitoring and research activities. Although substantial funding had been granted for this type of data collection, the data have often not been accessible for a wider scientific community or the private sector, leading to suboptimal use of the data available. In the long run, it should also be possible to combine data from EMODNET with other information, e.g. from the data collection framework in fisheries.

Four pilot components have been created, including hydrographic data (Lot 1), marine geological data (Lot 2), chemical data (Lot 3) and biological data (Lot 4). The chemical pilot is run by a consortium of 25 partners, representing the SeaDataNet network of data centres (<http://www.seadatanet.org>), in terms of 5 Work Packages (Project management, Data collection and metadata compilation, QA/QC and products, Technical development and operation, Analysis and operation). Geographically, the work in this pilot phase is focussed on data sets from the North Sea and the Black Sea, with additional areas of the Mediterranean. Six groups of chemicals have been chosen, in coordination with the Marine Strategy Framework Directive (Synthetic compounds, heavy metals, radionuclides, fertilisers (and other N- and P-rich compounds), organic matter and hydrocarbons, including oil). The pilot project is expected to be finished by 2012. The website is:

<http://www.emodnet-chemistry.eu/portal/portal/emodnet/Overview>

As part of the work package on analysis and operation, a web-based questionnaire for the EMODNET data user had been developed, to obtain feedback from users. Marilyn Sørensen encouraged MCWG members to fill in this questionnaire (<http://www.emodnet-chemistry.eu/portal/portal/emodnet/Feedback>). MCWG started on the questionnaire, but felt that they needed more experience with the EMODNET chemical portal in order to answer the questions.

Marilynn Sørensen presented a range of QA/QC questions and issues that the ICES led work package had covered. The work built, among other input, on HELCOM COMBINE and OSPAR MIME procedures as well as on guidelines and decisions developed by MCWG. As a result, QA/QC basic guidelines have been produced, which are considered living documents and will be adjusted during the project. An open question at the moment, awaiting decisions by OSPAR and HELCOM, is the reporting of measurement uncertainty which MCWG suggested as mandatory information in QA/QC reporting (see MCWG 2010).

Marilynn Sørensen concluded her presentation with a list of potential tasks for MCWG, including short-term advice on guidelines, evaluations of the system's efficiency, suggestions of improvement and review of methods used for data assembly, as well as involvement in a future EMODNET assessment. As most of these tasks will

have to be addressed this year, i.e. prior to MCWG 2012, Marilyn suggested that an EMODNET subgroup was formed and met for a 2-days-workshop at ICES headquarters in June 2011. Travel expenses would be covered, but whether or not the work time would also be funded could not be clarified for the moment.

The following MCWG members expressed their interest in joining an EMODNET subgroup:

- David Hydes (main expertise: chemical oceanography, e.g. nutrients)
- Patrick Roose (main expertise: organic contaminants)
- Carlos Borges (main expertise: nutrients)

The chair of MCWG, Katrin Vorkamp (main expertise: organic contaminants), would like to follow the subgroup's work intersessionally and might also contribute more actively if circumstances allow this.

## **5.7 Describe MCWG interests and activities on the interface to other expert groups (e.g. WGMS, WGEel, WGBEC, SGIMC, SGONS)**

**Evaluate potential for collaboration with other EGs in relation to the ICES Science Plan and report on how such cooperation has been achieved in practical terms (e.g. joint meetings, back-to-back meetings, communication between EG chairs, having representatives from own EG attend other EG meetings).**

### **WGMS**

MCWG and WGMS have worked and continue to work closely together. Areas of cooperation in the past included the passive sampler study and collaboration on OSPAR Guidelines and Technical Annexes. Ongoing communication between the MCWG and WGMS will be facilitated through Patrick Roose, WGMS Co-chair and MCWG member. Patrick Roose requested that MCWG could assist WGMS by providing any deep core preindustrial dated sediment data for parent and alkylated PAH, dioxins, mercury, cadmium and lead.

### **WGEel**

WGEel has an interest in contaminants in eels (*Anguilla anguilla*). Given MCWG's expertise in contaminants in biota this is an area of mutual interest. Michiel Kotterman attended WGEel 2010 and gave a presentation to MCWG 2011 on current activities of that group with respect to contaminants in eels (see section 5.4.1). Contaminants such as PCBs have been proposed as a potential contributory factor in the marked decline of eel stocks. The difficulties in establishing such cause-effect links were discussed by MCWG. MCWG expressed an interest in working with WGEel and agreed to collate any additional data for contaminants in eel for WGEel 2011. Michiel Kotterman agreed to act as a link between MCWG and WGEel.

### **WGBEC and SGIMC**

MCWG suggests that SGIMC is the appropriate group to coordinate activities of various expert groups with an interest in integrated monitoring of contaminants. MCWG can provide key expertise by identifying relevant chemical parameters, providing data and developing guidance for chemical monitoring. MCWG considers passive sampling to be a key technique for integrated monitoring in so far as it provides information on the bioavailable fraction of contaminants and this is a key area in which MCWG and WGMS can contribute. Katrin Vorkamp presented the SGIMC

2010 report at the meeting (see section 5.12). She will participate for one day in SGIMC 2011 to facilitate collaboration and report back to MCWG 2012.

On request of WGBEC, MCWG 2011 reviewed a draft guideline on “Receptor H4IIE-Luciferase (DR-LUC) cell bioassay for screening of dioxins and/or dioxin-like compounds in environmental samples” and provided comments. Katrin Vorkamp will send MCWG’s comments to John Thain, co-chair of WGBEC.

## SGONS

COSG have identified several links with the IOC/ICES Study Group on Nutrient Standards (SGONS). Both groups have identified the need for CRMs to support nutrient monitoring in north Atlantic shelf seas and will collaborate to address this issue (see section 5.8). MCWG 2012 will review the JAMP nutrient guidelines with a view to ensuring consistency with the GO-SHIP manual (see section 5.11). David Hydes and Patrick Roose, as members of both EGs, will facilitate links.

### 5.8 Discuss the need and availability of certified reference materials for the analysis of nutrients in seawater.

Seawater nutrient standards are particularly useful with automated chemistry systems which measure nutrients colorimetrically. A table with certified reference materials is given in Annex 9.

During the discussions on the availability of certified reference materials (CRM) for nutrients in seawater, COSG considered the concentrations currently available from KANSO. COSG recognises an increasing demand for the use of CRMs in nutrients analysis as laboratories receive formal accreditation for the analysis of nutrients.

The laboratories represented at COSG predominantly sample seawater from the North Atlantic and European shelf seas. The concentrations of nutrients typically measured in these waters are significantly different from those currently offered by the KANSO CRMs. COSG suggests that two additional CRMs be produced with the approximate concentrations in the table below. COSG proposes to consult a wider network on whether these suggested concentrations are acceptable and of interest to a sufficiently large number of laboratories, so production of such CRMs would be commercially viable. An efficient way of gauging this interest would be to use the list of laboratories which participate in the nutrient exercises of QUASIMEME, if access could be gained to this list. Laboratories represented at COSG would be able to collect suitable water which can be provided to KANSO for production of these CRMs.

**Proposed nutrient concentrations for certified reference materials obtainable from surface winter sampling in the North Atlantic**

Parameter	Low level	High level
	Concentration ( $\mu\text{mol l}^{-1}$ )	
Nitrate	8	15
Nitrite	0.2	0.4
Phosphate	0.5	1.1
Silicate	3	12
Ammonium	~ 0.5	~ 0.5

## 5.9 Ocean acidification (OA)

### 5.9.1 Report on recent developments in methodology of pH measurements and required standardisation procedures

Essentially two methods are in use for pH, the electrometric determination with standards based on TRIS and AMP buffers and the spectrophotometric determination using *m*-cresol purple. This chapter summarises some features, challenges and limitations of these methods, further details and relevant references are given in Annex 10.

#### pH scales

It is important to remember to compare pH data on the same scale. For work on the carbonate system the “total scale” should be used for reporting pH data. In every case, the pH scale used must be reported, together with salinity, temperature and pressure, which will allow conversion between scales to be calculated if necessary.

#### Electrometric determination

For Ocean Acidification (OA) monitoring, pH may appear to be the ideal parameter to measure. However, knowing pH alone does not let you understand the carbonate system. Moreover, the direct measurement of sufficiently accurate pH values in the marine environment is extremely challenging. The following points have to be considered carefully to avoid (or minimise) analytical errors:

- Regular and correct calibration (availability and use of suitable buffers);
- Checks against certified reference materials;
- Choice of hydrogen electrode;
- Choice of reference electrode;
- Electronics and pH cell design;
- Design of analogue electronics, screening and earthing.

These points are discussed in detail in Annex 10. The discussion shows that there are several potential sources of errors in the electrometric determination of pH. The combination of these errors, especially for autonomous measurements, contributes to lower accuracies obtainable in the field than under controlled laboratory conditions. Such sources of error include:

- 1) Reference electrode selection and use (changes in liquid junction potential affecting measured cell voltage).
- 2) Seawater buffer pH uncertainties (absolute values and drift).
- 3) Hydrogen electrode selection and use (including Nernstian response checks).
- 4) Noise and voltage offsets brought about by poor earthing and/or electronics design.

To improve the accuracy of *in-situ* and other autonomous measurements of pH using electrometric techniques, development work is required for these issues. The following recommendations are made:

- 1) Electrodes are not currently recommended for autonomous use on moorings and ship flow through systems where data accuracy greater than about 0.02 pH is required.
- 2) Only with extreme care and training it is possible to obtain accuracies approaching 0.005 pH for field-collected seawater samples (salinity ca. 35)

that are subsequently analysed in the laboratory. An enhanced and more detailed version of SOP 6a (see Annex 10) would improve this situation, increasing the confidence in measurements made in non-reference laboratories.

- 3) There is a requirement for further sources and increased quantities of certified reference materials (TRIS and AMP), which will help improve confidence in electrode-based pH measurements.
- 4) Further developments are required before reliable, accurate autonomous measurements can be made. The aim should be to produce recommended, accredited electrodes and electronics/software systems to ensure inter-comparability between monitoring organisations.
- 5) Interlaboratory checks with reference seawater solutions of known pH would ensure reliability and accuracy of these measurements.

### **Spectrophotometric determination**

Several laboratories are working on the automation of the spectrophotometric method. Details are given in Annex 10.

### **Conclusion**

pH measurements of high accuracy, especially in the field, will continue to be difficult even with the availability of reference solutions. For example, the dyes used must be calibrated on an individual batch basis and calibration data extrapolated to true ionic medium composition, and uncertainties still exist with regard to what is achievable with electrometric measurements. Currently in the absence of gross error an accuracy of 0.01 might be achievable by both approaches.

### **5.9.2 Report on recent results of pH measurements in marine systems (especially in the OSPAR area)**

“Ocean Acidification” – decreasing pH – of ocean waters is an inescapable consequence of the rising concentration of carbon dioxide in the atmosphere. Orr *et al.* (2005) suggested an average decrease of 0.0015 to 0.002 pH units per year in the open ocean. Regional differences in this rate are likely to be large. Coastal and shelf regions because of their heterogeneity are likely to show the largest deviation from the projected average trend. This includes factors such as atmospheric deposition of nitrogen and sulphur oxides which induce additional acidification at the sea surface (Doney *et al.*, 2007; Duce *et al.*, 2008). Similarly conditions in shallow seas unlike ocean waters will be affected by interactions at the sea bed (Soetaert *et al.*, 2007), the effect of nutrient delivery by rivers (Borges and Gypens, 2010), and variable total alkalinity and DIC inputs from rivers (Gypens *et al.*, 2011). Observations are now beginning to be published that show that there are distinct regional patterns.

Evidence is available from time-series, basin-scale measurements and models that indicate that surface water pH varies substantially - seasonally, inter-annually and decadal. For acidification research, these observations are important because their magnitude sets a boundary for what might constitute damaging pH change. The periods of variations in pH need to be quantified if we are to be able to detect permanent changes. Similarly spatial variability needs to be quantified. For example, it is believed that the polar and sub-polar ecosystems are particularly at risk because they are presently the closest to undersaturation with respect to aragonite (Bellerby *et al.*, 2005).

A detailed review of recent results of pH measurements, divided into ocean waters, shelf seas and the North Sea, is given in Annex 11. The main findings in this review are summarised below.

### Summary points

- Orr *et al.* (2005) suggest a decrease of 0.0015 to 0.002 pH units per year in the open ocean.
- Areas vulnerable to higher rates of change need to be identified. Waters in OSPAR area I may be particularly vulnerable (Bellerby *et al.*, 2005).
- Santana-Casiano *et al.* (2007) report a decline in pH off the Canary Islands which is consistent with that predicted by Orr *et al.* (2005).
- Off Iceland distinct regional differences in the rate of change have been found (Olafsson *et al.*, 2009a; 2009b) above and below the mean predicted rate.
- Lower winter pH observed in surface waters of the Rockall Trough to the west of Ireland in 2010 compared with WOCE 1996 data may, at least in part, reflect different surface mixed layers for the two surveys. Also, the saturation state in summer in the Porcupine Sea Bight, north of the Goban Spur, was lower throughout the water column in 2009 than determined in 1997 for a WOCE transect a little further to the south and the ASH appears to be shallower by several hundred metres. Salinity and temperature data indicate that this may be due to physical factors, such as difference in geographical spread of sampling points and water mass mixing (O'Dowd *et al.*, in press).
- Over the Bay of Biscay measurements with good temporal (monthly) resolution show that in the spring bloom the uptake of carbon and nitrate are tightly constrained by the Redfield ratio (Hydes *et al.*, 2011).
- In NW European shelf waters the annual cycle of change in pH is modelled to range from <0.2 to > 1.0 pH units (Blackford and Gilbert, 2007).
- Off the Pacific coast of the USA, Wootton *et al.* (2008) reported a rate of change over 8 years to be 20 times the predicted rate and Feely *et al.* (2008) found a substantial decrease in the depth of the aragonite lysocline.
- The North Sea was estimated to be a substantial sink for CO<sub>2</sub> (Thomas *et al.*, 2005). Recycling of nutrients faster than DIC produces enhanced uptake of CO<sub>2</sub> (Bozec *et al.*, 2006).
- Thomas *et al.* (2009) suggested alkalinity produced by nitrification may support up to 25 % of the North Seas up take capacity for CO<sub>2</sub>.
- In contrast new data from the UK DEFRApH study suggest removal of alkalinity by calcification in the northern North Sea and English Channel (Hydes *et al.*, 2011) is significant. Similar results have been reported in the Bay of Biscay by Suykens *et al.* (2010).
- The analysis of data on pH in Dutch coastal water (Provoost *et al.*, 2010) appears to confirm the hypothesis (Gypens *et al.*, 2009; Borges and Gypens, 2010) that changes related to eutrophication have had a larger impact on the carbonate system in certain regions than any change induced by increases in atmospheric concentrations of CO<sub>2</sub>.
- In some regions organic alkalinity may be present and generate errors in carbonate system calculations (Hydes *et al.*, 2010).

- Measurements off the Shannon estuary suggest that there is a significant presence of organic alkalinity (O'Dowd *et al.*, in press).

## References

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Further results are expected for presentation and discussion at MCWG 2012, from recently started projects on pH measurements in Sweden, Belgium, France (Mediterranean Sea) and Germany (Baltic Sea).

Elisabeth Sahlsten informed about the Swedish project “Ocean acidification – the state of the Baltic Sea and the Skagerrak-Kattegat” run by SMHI and the University of Gothenburg and funded by the Swedish EPA. The project will determine pCO<sub>2</sub> and pH in the surface waters from a Voluntary Observing Ship (VOS) line and pH and AT in depth profiles from a research vessel. A commercial system will be used in which the headspace CO<sub>2</sub> is analysed with a non-dispersive infrared detector, which measures the CO<sub>2</sub> mole fraction instantaneously. The analyzer is calibrated with four CO<sub>2</sub> standard gases at regular intervals. The method is designed to be accurate within 2 µatm for seawater pCO<sub>2</sub> and 0.1 µatm for atmospheric pCO<sub>2</sub>.

Highly accurate spectrophotometric methods based on the indicator m-cresol purple or phenol red are available that provide a precision of ca ± 0.002 pH units in oceanic waters. The project aims to adjust the method to low saline Baltic Sea water. Furthermore, a new fluorometric approach to determine pH in a continuous mode will

be developed. This involves immobilization of a fluorescent dye on a film which is exposed to a continuous flow of seawater, and the resulting fluorescence emission is recorded with a CCD camera. Due to the size of the film a large number of spectra can be recorded per time interval, each of them having an individual calibration. With this system problems of low buffering capacity (and of other confounding factors such as humic substances) are minimized.

Patrick Roose informed about a Belgian ferry-box project on the research vessel Belgica. Following instalments of a continuous measurement system, HAT and SAT, the analytical set-up will be operational in April 2011. The project includes automated analysis of salinity, temperature and fluorescence as well as nutrient analyses (nitrate, nitrite, phosphate, silicate and ammonium) every 20 minutes, using nutrient sensors.

### **5.9.3 Report on recent developments in quality assurance issues in the measurement of carbonate system parameters**

Quality assurance issues for the study of acidification arise from three areas: (1) Access to appropriate standards; (2) Limitations of the techniques and equipment available; (3) Calculation of secondary determinand concentrations (such as carbonate ion) from primary measurements (TA, DIC, pCO<sub>2</sub> and pH).

(1) Well established certified standards are available for the measurement of DIC and TA in water and pCO<sub>2</sub> in the gas phase. A single value certified standard has recently been introduced for pH (a TRIS buffer) while a second is required.

(2) Measurements of pH are currently limited by both the availability of appropriate equipment and lack of well tested best procedures for use of existing equipment (pH electrodes) and systems that are being developed (colorimetric and fluorometric), see also section 5.9.1 and Annex 10.

(3) Concerns have been raised that there may be problems in the calculation of carbonate components. This may be due to: (i) the presence of a component(s) of the measured total alkalinity that is (are) not included in the equations used in the calculations (ii) that the different equations used in the calculations may not be reliable at the artificially high concentration of pCO<sub>2</sub> used in experimental systems.

Key to understanding potential biological effects of ocean acidification is gaining a knowledge of concentrations of carbonate and bicarbonate ions in solution and of the saturation states of appropriate carbonate minerals. The information that is used to compute (for example) carbonate ion concentration is based on experimental measurements with associated uncertainties. In addition, other errors can occur caused by an incomplete (or incorrect) model of the acid-base chemistry appropriate for particular samples. The presence of organic acids has been identified as cause for concern here as has the concentration of calcium ions not being conservative with respect to salinity in some lower salinity waters such as the Baltic Sea.

Consequently we must: (1) ascertain if our knowledge of the marine carbonate system, gained largely from measurement in open ocean waters, is adequate for work in coastal waters and experimental systems with high levels of organic matter and CO<sub>2</sub>; and (2) ascertain if the constants used in equations used for calculations are reliable in experimental system with artificially high concentrations of pCO<sub>2</sub> and waters of intermediate salinity.

These considerations have lead to the following findings (Hydes *et al.*, 2010):

- 1) Three of the four components of the carbonate system - DIC (total dissolved inorganic carbon),  $p\text{CO}_2$  and pH - can be measured by direct techniques, so that uncertainty in the quantity measured is limited only by experimental error. Errors in measurements of DIC and  $p\text{CO}_2$  are well constrained because of the existence of well characterised reference standards, with precision and accuracies appropriate for measurements designed to detect changes related to increased atmospheric concentrations of  $p\text{CO}_2$ . Measurements of pH are presently not fit for this purpose.
- 2) Total alkalinity is measured by titration with strong acid. Carbonate alkalinity is then arrived at indirectly by calculation based on the measurement of total alkalinity. This requires that all the components of the sample, which will be titrated in the pH range 3.6 to 3.0 are known and accounted for in the equations used to calculate carbonate alkalinity (Dickson, 1981; Wolf-Gadrow *et al.*, 2007). Three independent studies show titrateable organic matter can be present in samples from coastal waters and mesocosms at levels equivalent to a few 10s of  $\mu\text{M kg}^{-1}$  of alkalinity (Kim and Lee, 2009; Hernandez-Ayon *et al.*, 2007; Muller and Bleie, 2008). Because of non-linearity in the equations, when such quantities of organic alkalinity are present, equivalent errors of 10s of % will occur in the values of  $p\text{CO}_2$  calculated from measurements of total alkalinity and total dissolved inorganic carbon.
- 3) Discrepancies between direct measurements of  $p\text{CO}_2$  and values calculated from the other components (DIC, TA and pH) have also been reported in a notionally low organic system (Hoppe *et al.*, 2010) used for experiments at high (1000  $\mu\text{atm}$ ) concentrations of  $p\text{CO}_2$ . This study raised concerns that the available sets of equations and constants used in the calculations may not be appropriate for work at high levels of  $\text{CO}_2$ . Reviews of this study severely questioned the quality of the experimental procedures used by the authors.
- 4) Three different software packages (CO2SYS, CO2SW and SEACARB) are freely available for the calculation of  $\text{CO}_2$  system variables. These have been tested and give identical results when calculations are done with the same input parameters (Hydes *et al.*, 2010). At a  $p\text{CO}_2$  of 1000  $\mu\text{atm}$ , the maximum sensitivity to the choice of constants was found to be 5%.

**Our recommendations are that:**

- 1) Researchers in experimental systems carrying out experiments at high levels of  $p\text{CO}_2$  should be aware of how errors in the calculation of  $p\text{CO}_2$  from measurements of DIC, TA and pH propagate. Hydes *et al.* (2010) provide maps of the change in relative errors with concentration. If discrepancies are found beyond the likely experimental error they should be reported to the community.
- 2) Further work should be carried out using state of the art techniques in a range of environments - coastal water to laboratory experiments - to determine the locations and scale of the contribution of organic material to measured total alkalinity.
- 3) Where possible the carbonate system should be over-determined to provide evidence of problems. The simplest way to do this is by measuring three carbonate variables – where possible DIC, TA and  $p\text{CO}_2$ .

- 4) To assist with the development of high quality pH measurements outside the core community of carbonate chemists a more closely specified standard operating procedure (SOP) than the current CO<sub>2</sub>-SOP-6a (Dickson *et al.*, 2007) for the electrode based measurements of pH is recommended – this would be based on experience already available in the community on the most appropriate pH electrodes and temperature sensors to use and the appropriate design of a measurement cell.
- 5) Development of instruments for the automated colorimetric determination of pH should be encouraged as these offer the possibility of making high precision measurements (down to < 0.001 pH unit) with small (< 5 ml) volumes of sample). But as with potentiometric measurements of pH rigorous SOPs will need to be followed precisely to obtain accurate measurements.
- 6) An SOP appropriate to sampling experimental systems is needed; this would include recommendations on the collection of small volume samples (< 100 ml) and filtering of samples. Research is needed into reliable and easy to use (by non expert) storage containers particularly for the storage of small samples (10 to 100 ml).
- 7) Research is needed to find a “safe” efficient biocide to replace the use of mercuric chloride. Note: The testing of biocides and containers must be done in ways that the results are statistically valid.
- 8) Appropriate meta-data for all measurements of carbonate data in natural waters and experimental systems should be recorded. This is to enable carbonate system errors to be assessed and experiments replicated within known limits of reproducibility. A model template for such reporting is provided in Hydes *et al.* (2010).

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#### **5.9.4 Review new information for determination of pH and carbonate parameters in estuarine and brackish water and the associated calculations**

COSG discussed this agenda point and decided to move it to MCWG 2012 as more information will be available from recently started projects.

### **5.10 Revise MCWG 2010 guideline on monitoring of ocean acidification in view of publication as an ICES Cooperative Research Report (CRR)**

MCWG 2010 prepared detailed advice in response to an OSPAR request for specific information on monitoring ocean acidification. Subsequently MCWG considered that this information would be of interest to a broader scientific community and would be widely available if published as an ICES Cooperative Research Report (CRR). COSG restructured and updated the information presented in Annex 8 of the MCWG 2010 report with a view to publication as a CRR and added new relevant information, beyond the OSPAR area. COSG developed a work plan to finalise this intersessionally. A resolution for submission to SCICOM 2011 for publication of this CRR is presented in Annex 5.

### **5.11 OSPAR request: Discuss revision of JAMP Eutrophication Monitoring Guideline, in terms of i) comments by Review Group and ii) Marine Strategy Framework Directive**

COSG revised the JAMP guidelines for nutrient monitoring at MCWG 2009 following a request from OSPAR for additional information on specific sections. The Advice Drafting Group (ADG) in 2009 passed on elements of the MCWG 2009 advice but not the updated nutrient guidelines. ADG observed that given the activities undertaken developing criteria and methodological standards by the Task Group on Eutrophication (TG5) for the Marine Strategy Framework Directive, the ICES Advice Group recommended that OSPAR await the outcome from this activity before seeking further advice.

COSG considered the comments from the Review Group (see MCWG 2009). COSG feel that provision of standards and protocols for the use of moored instrumentation, beyond that which was given in 2009, would be premature due to the still rapidly developing area of this work. COSG are aware of activities which will be undertaken within the EU funded project JERICO which should contribute to this section of the guidelines in the future.

[http://ec.europa.eu/research/infrastructures/index\\_en.cfm?pg=ri\\_projects\\_fp7](http://ec.europa.eu/research/infrastructures/index_en.cfm?pg=ri_projects_fp7)

COSG considered that the guidelines need to be broadly applicable to the wide range of sea areas currently monitored by the OSPAR contracting parties and broad user needs. COSG considered the Commission Decision 2010/477 on Criteria and Methodological Standards (Descriptor 5) and the Task Group 5 report. COSG identified no material changes required to the nutrient guidelines as a consequence of these developments. Further clarification from ICES regarding inclusion of specific information arising from the MSFD relevant to nutrients sampling is therefore required.

COSG considered the work carried out by the IOC-ICES Study Group on Nutrients Standards (SGONS) during 2010 (see 5.7) and the availability of the recently published GO-SHIP repeat hydrography manual. COSG will review and update the nutrient guidelines at MCWG 2012 taking into account any new information. Specifically this will ensure that advice on reporting of meta data and units of concentration within the JAMP guidelines are consistent with the advice given in the GO-SHIP repeat hydrography manual. This will include a table of suggested meta data in the JAMP guidelines and verify that this is consistent with the ICES database.

#### **5.12 Contribute, as may be required, to ICES activities on integrated chemical and biological effects monitoring and review new information on effect directed chemical analysis**

##### **Patrick Roose: Integrated risk assessment and monitoring of micropollutants in the Belgian coastal zone (INRAM)**

The project had been presented at MCWG 2010 and Patrick Roose was asked to give an update at MCWG 2011. The project has been running for 4 years and in the original scheme, the final report was due in January of 2011. However, the Science Policy office granted an extension to the programme of 6 months and the new deadline for final reporting is June 2011. The final report will therefore be available at the MCWG 2012 meeting.

The project focussed on integrated monitoring of contaminants in the Belgian coastal zone and the major harbours. For the purpose of this meeting, only the developments and concentrations of certain chemical substances, and work related to passive sampling were presented.

The concentrations of pharmaceuticals were of particular interest to the group. These included the antibiotics Sulfamethoxazole with concentrations of up to 96 ng L<sup>-1</sup> and Trimethoprim concentrations of up to 29 ng L<sup>-1</sup>. Other antibiotics were not detected. Also, there was some surprise that salicylic acid was detected in more than 90% of all samples at a concentrations of up to 855 ng L<sup>-1</sup>.

In the project, passive samplers were used both to determine the time-integrated concentrations of chemicals and to perform ecotoxicity tests. In the latter, test organisms were exposed to samplers collected in the field. A clear and significant effect could be observed when the organisms were exposed to samplers, for instance, from the harbour of Oostende. In the future, the project will investigate the applicability of passive samplers as a reference phase linking the different compartments (sediment, water, biota) with the effects of contaminants by means of equilibrium modelling.

There was a clear interest for this approach and it can be expected that more information related to this topic will appear in the next few years.

##### **Koen Parmentier: Integrated pollution monitoring - a case study of TBT in shrimp**

Koen Parmentier presented results on TBT effects in shrimp, a self-financed part of a research proposal, taking comprehensive monitoring of different groups of organic chemicals (PCBs, PBDEs, organotins, PFCs and trace metals) into account. The project focusses on effects on the economically important benthic scavenger brown shrimp (*Crangon crangon*), which is also very important in the coastal food chain (up to 80% of the coastal biomass). The integrative part of the research is in picking up the EcR-RXR heterodimeric nuclear receptor complex, crucial for activating genes involved in molting and sexual development, and the construction of a microarray to screen for up- or downregulation of genes in response to exposure.

The first part of the work, picking up the EcR and RXR genes, has been carried out successfully. The influence of TBT on this nuclear receptor complex was demonstrated both by an *in-vitro* reporter assay and an *in-silico* docking experiment, based on the known human RXR 3D-structure.

In the latter part, environmental organotin concentrations were initially determined. The study area stretches from the Belgian coastal zone up to Denmark. Samples were collected in collaboration with research institutes in the adjacent countries, mainly via WGCRAN. In the MUMM Marchem lab, directed by Patrick Roose, samples were analyzed for TBT and TPhT content, together with their degradation products. It was shown that TBT levels in the North Sea coastal region were not elevated and that levels in the Schelde estuary had decreased by a factor 5 in the last 3 years, most probably due to the TBT ban on ship hulls. During the last three years, the LPUE (Landings Per Unit Effort, an estimate for abundance of the organism) for *Crangon crangon* has increased significantly, whilst the normal pattern is a year of increase followed by a year of decrease. There is evidence that the decrease of brown shrimp in the Belgian Part of the North Sea since the 1970s was not caused by fisheries or predation mortality only.

The research part to follow includes an exposure study of brown shrimp, the development of a microarray with 600 genes already identified and sequenced based upon a Suppression Subtractive Hybridization-PCR (SSH-PCR).

The group appreciated this kind of research and is interested in an update.

#### **Jocelyne Hellou: Integrated monitoring**

Jocelyne Hellou (Bedford Institute of Oceanography, Fisheries and Oceans Canada) could not participate in the MCWG 2011 meeting, but had provided the following two papers which Katrin Vorkamp briefly presented to the group:

J. Hellou (2011): Behavioural ecotoxicology, an "early warning" signal to assess environmental quality. *Environ. Sci. Pollut. Res.* 18, 1-11.

J. Hellou and F. Gagné (2011): Integrated impact assessment of mussel health. In: McGevin (ed). *Mussels: Anatomy, Habitat and Environmental Impact*. in press.

#### **ICES/OSPAR Study Group on Integrated Monitoring of Contaminants (SGIMC)**

The SGIMC 2010 report had not been available at the MCWG 2010 meeting and was therefore presented at MCWG 2011. Katrin Vorkamp summarised the main points and outcomes of the report:

A number of background documents had been developed in cooperation with WGBEC, to be incorporated as annexes into the OSPAR JAMP Background Document on Biological Effects Monitoring Techniques. These documents address the biomarkers and methods Cytochrome P4501A activity, lysosomal stability, DNA adducts, PAH metabolites in bile, fish diseases and water bioassays.

Furthermore, WGBEC had produced first drafts of several other background documents, to be completed by SGIMC 2011, including acetylcholinesterase, micronucleus assays and comet assay; other documents are under preparation. SGIMC has also produced background documents on reproductive success in eelpout and stress on stress in bivalves.

SGIMC members had presented data on PAH metabolites in bile, stressing that this was a biomarker of exposure rather than effect. These results showed that there were

larger differences between areas than between species. This spatial heterogeneity will have to be taken into account in the BAC and EAC values to be developed. Similarly, it was emphasised for EROD results that background response/levels and assessment criteria were restricted to the same sampling conditions and fish size.

SGIMC 2010 also produced and reviewed the following technical annexes to the guidelines for the integrated monitoring and assessment of contaminants and their effects:

- Sampling and analysis for integrated chemical and biological effects monitoring in fish and shellfish.
- OSPAR integrated monitoring of mussels.
- Packages of chemical and biological methods for monitoring on a contaminant basis.

In addition, a discussion document was produced on survey design for integrated monitoring. The report also discusses progress made on integrating/aggregating data assessment strategies, with examples from the HELCOM area (approaches and results of the research project Biological Effects of Anthropogenic Chemical Stress (BEAST), the ICES Study Group on Ecosystem Health in the Baltic Sea (SGHE) and the HELCOM thematic assessment of hazardous substances) and the OSPAR area (traffic light system and integrated assessment in the Quality Status Report 2010).

MCWG discussed possible interactions with SGIMC and highlighted MCWG expertise of relevance for integrated monitoring of contaminants. This discussion was summarised in section 5.7.

### **Recommendation**

ICES/OSPAR initiatives on integrated monitoring should not cease with the final meeting of SGIMC in 2011 as this is a field of increasing importance in research and monitoring.

## **5.13 Report on new information regarding emerging contaminants in the environment**

### **5.13.1 Zhiyong Xie: Alternative flame retardants in the marine environment**

Marine boundary layer air and seawater samples were collected onboard the German research vessel *R/V Polarstern* during the expedition cruises ARK-XXIV/3 in the East Greenland Sea in 2009 (69–80.5° N) and ANT-XXV/1+2 along the cruise leg Bremerhaven, Germany – Cape Town, South Africa – Neumayer Station in the Antarctic in 2008. The samples were analysed in order to compare the occurrence, distribution and fate of polybrominated diphenyl ethers (PBDEs) with other brominated flame retardants (BFR) as well as Dechlorane Plus (DP). In the Atlantic transect and the Southern Ocean, the sum of PBDEs ( $\Sigma_9$ PBDEs, including BDE-28, -47, -66, -85, -99, -100, -153, -154 and -183) ranged from 0.40 to 3.3 pg m<sup>-3</sup> in the atmosphere and from 0.09 to 2.19 pg L<sup>-1</sup> in seawater. In the Arctic, the sum of PBDEs ( $\Sigma_{10}$ PBDEs, BDE-28, -47, -66, -85, -99, -100, -153, -154, -183 and BDE-209) ranged from 0.09 to 1.8 pg m<sup>-3</sup> in the atmosphere and from 0.03 to 0.46 pg L<sup>-1</sup> in seawater.

From the Arctic to the Antarctic, alternate BFRs, especially hexabromobenzene (HBB), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) and pentabromotoluene (PBT), were detected in similar concentrations and with similar spatial trends as PBDEs. In addition, DP isomers were detected from 0.05 to 4.2 pg m<sup>-3</sup> in the atmosphere and from below detection limits to 1.3 pg L<sup>-1</sup> in sea water, even in the remote

areas of the Arctic and Antarctic, indicating that DP is susceptible to long-range atmospheric transport (LRAT).

The high atmospheric concentrations observed in the Arctic might result from continental air masses passing Western Europe, while the elevated atmospheric concentrations in the tropic Atlantic might be related to increased emissions from the growing industry for recycling of electronic goods in the Africa. The air-seawater exchange indicates strong deposition, especially of alternate BFRs, as well as dry particle-bound deposition of BDE-209 and DP into the ocean. Overall, these results highlight the important processes of the long-range atmospheric transport and air-sea exchange of PBDE, alternative BFRs as well as DP in the marine environment.

#### **5.13.2 Philippe Bersuder: Occurrence of organophosphorous flame retardants in UK sediment**

Philippe Bersuder reported on initial results from an on-going survey on the presence of organophosphorus flame retardants (OPFRs) in various marine compartments, funded by the UK Department for Environment, Food and Rural Affairs (Defra). OPFRs are a heterogeneous family of chemicals, amongst which organophosphate (OP) esters are the most widely used, as flame retarding compounds for combustion inhibition but also as plasticisers, as additives in plastics, rubber, lubricants and hydraulic fluids and as antifoaming agents. OP esters are listed as EU High Production Volume chemicals, and their consumption throughout Western Europe has increased from 58 000 tons in 1998 to 83 000 tons in 2001. There is increasing evidence of their environmental occurrence, but a general lack of data on the effects and toxicity of these chemicals.

A simple extraction, clean up and sensitive liquid chromatography-tandem mass spectrometry (LC-MS/MS) methodology was developed for the determination of OPFRs in sediment samples. The approach permits the determination of thirteen compounds including three alkyl phosphates, two aryl phosphates, chlorinated alkyl phosphates/phosphite, synthetic intermediates and non-derived alkyl phosphates. Sediment samples are extracted using accelerated solvent extraction followed by gel permeation chromatography clean-up, and LC-MS/MS in electrospray ionisation mode. The recoveries of selected determinants ranged between 71 and 112 % (relative standard deviations between 4 and 23 %). Analytical limits of quantification (LOQs) ranged between 1 to 11 ng/g dry weight for sediments, making the method suitable for trace level environmental analysis.

Subsequently, a pilot study of 15 selected sediments from historically impacted locations was undertaken: twelve UK marine sediments (from Liverpool Bay, Tees Bay, off the Tyne/Tees estuaries and Thames estuary) and three riverine sediments (from the River Mersey). Eight of the thirteen targeted OPFRs were found in these samples (tris-(2-chloropropyl) phosphate (TCPrP), tributyl phosphate (TBP), tris-(2-chloroethyl phosphite (TCEPhi), tricresyl phosphates (TCP), tris(2 ethylhexyl) phosphate (TEHP), triphenyl phosphate (TPP), tributyl phosphine oxide (TBPO), tris-(2-butoxyethyl) phosphate (TBEP)) with concentrations ranging from 1.2 to 179 ng/g dry weight. Tris-(2-chloropropyl) phosphate (TCPrP) was detected at all sites and systematically the dominant compound, with concentrations ranging from 25–179 ng/g (dry weight) and a median concentration of 47 ng/g.

### 5.13.3 Norbert Theobald: Retrospective monitoring of PFCs in fish

Norbert Theobald reported on first results of a project funded by the German Environmental Protection Agency (UBA) on “Retrospective Monitoring of Perfluorinated Organic Acids in Fish Samples from the German Specimen Bank”.

In the project some 200 archived muscle and liver samples of bream from the German Specimen Bank were analysed for PFCs. Samples originated from all major German rivers, from the German Bight and the Baltic Sea. The time range was 1995 to 2009. Five Perfluorosulfonates (C4 to C10), ten Perfluorocarboxylates (C4 to C14) and Perfluorooctylsulfonamid were determined.

The results showed individual local and temporal differences in concentrations and patterns. Generally, concentrations increased in the following order: Baltic Sea < German Bight = Belauer See < Saale < Danube < Elbe < Rhein. In all samples PFOS was the main component: PFOS-concentrations in muscle ranged from 0.5 ng/g (Belauer See) to 91 ng/g (Elbe at Blankenese, Hamburg). In fish liver, PFOS-concentrations ranged from 7.2 ng/g (Belauer See) to 496 ng/g (Elbe at Blankenese, Hamburg). PFOA was detected in the Danube River only.

PFOS and PFOSA generally showed decreasing temporal trends while longer chain PFCs (C>9) exhibited increasing trends.

### 5.14 Discuss the role of atmospheric transport and deposition for the assessment of inputs of PFOS and other PFCs to the marine environment

Perfluorooctane sulfonate (PFOS) and perfluorooctane carboxylate (PFOA) are presently considered to be the environmentally most relevant perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs). Whether or not PFOS and other perfluorinated compounds should be monitored in the atmosphere, with regard to inputs into the marine environment, was discussed at MCWG 2010. The conclusion was that the present state of knowledge was insufficient to recommend atmospheric monitoring for marine assessments. In order to follow up on this topic at MCWG 2011, Ralf Ebinghaus reviewed the literature and addressed the comments made by the Review Group (see MCWG 2010, Annex 11).

PFCAs and PFSAs can be transported directly by oceanic currents or by neutral, volatile precursors, such as fluorotelomer alcohols (FTOHs), fluorinated sulfonamides, and sulfonamidoethanols (FOSAs and FOSEs), that could undergo long-range atmospheric transport and be degraded in remote regions to PFCAs and PFSAs (e.g. Ellis *et al.*, 2004; McMurdo *et al.*, 2008; Armitage *et al.*, 2006). For example, PFCAs and PFSAs have been detected in Arctic snow samples, which indicates a direct atmospheric deposition of these compounds or a degradation of their volatile precursors (Young *et al.*, 2007).

Information on environmental levels of PFOS and PFOA associated to particles is very scarce. Jahnke *et al.* (2007) have reported concentration ranges for PFOS (0.4–1.6 pg m<sup>-3</sup>) and PFOA (< 0.2–2.6 pg m<sup>-3</sup>) for urban aerosols collected in metropolitan Hamburg.

Aerosol-mediated transport of PFCAs and PFSAs has been considered as a potential pathway of long-range transport, however, knowledge of the importance of long-range atmospheric transport on sea-spray in relation to other potential transport pathways is still very limited (McMurdo *et al.*, 2008; Webster *et al.*, 2010a; Jahnke *et al.*, 2007; Barber *et al.*, 2007).

Based on a model exercise Webster and Ellis (2010) concluded that direct PFOA/PFOS transport in aerosols did not contribute significantly to the occurrence of these compounds in remote regions. However, gas-phase PFOA released from oceans may help to explain observed concentrations in remote regions.

This model result is supported by recent experimental data. Chaemfa *et al.* (2010) published evidence of atmospheric transport of PFOS and PFOA based on passive air sampling, in particular for PFOA in samples taken close to the coastline of the North Sea. Furthermore they concluded that there is reasonable level of agreement between their observed distributions and levels with the few published data from active samplers.

In a very recent study, Reth *et al.* (2011) have published evidence derived from an experimental sea spray simulator, that perfluorinated alkyl acids (such as PFOA and PFOS) are effectively transferred from water to air, indicating that these compounds can have potential for long range atmospheric transport. The authors also point out and conclude that before a semi-quantitative assessment can be undertaken, further research must be conducted to explore the effects of other sea-water constituents on the transfer efficiency and to validate the sea spray simulator experiments under natural marine conditions (Reth *et al.*, 2011).

Ahrens *et al.* (2010) conducted a study in high Alpine lakes and tried to establish a link between atmospheric transport and deposition and resulting accumulation in fish. For this purpose, fish liver samples were collected from four high-mountains lakes that had no direct source for PFCs and therefore received these contaminants mainly by wet or dry atmospheric deposition. The atmospheric deposition of PFOS or its precursors in the lakes was homogeneous, i.e. PFOS concentrations in fish livers were very similar in all four lakes, whereas the deposition of PFCAs depended strongly on local contamination sources, i.e. the PFCA concentrations in the reference lakes was significantly lower than in those lakes potentially affected by emissions from the wider urban area of Grenoble.

However, uncertainties in the flux estimates are large and continued laboratory and field studies are required to understand the mechanisms responsible for the fluxes of PFCs between the atmosphere and aqueous systems such as the high-mountain lakes. In particular, dry deposition of particles and volatilisation of PFCs from the lake surfaces are the major sources of uncertainty for mass balance calculations.

In summary, MCWG's 2010 conclusion was confirmed, i.e. it was still premature to recommend atmospheric monitoring for assessment of PFC inputs into the marine environment. Pathways for long range atmospheric transport of either PFCs or precursor compounds are not fully understood today, including the role of sea spray. Evin McGovern informed that the Norwegian monitoring programme now included atmospheric monitoring of PFOS. As MCWG considers this a relevant and scientifically interesting topic, attempts will be made at MCWG 2012 to further follow up on this question, including results from the Norwegian monitoring initiative.

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## 5.15 Complete guidelines for publication in TIMES series

### 5.15.1 Determination of polychlorinated dibenzo-p-dioxin, polychlorinated dibenzofurans and dioxin-like PCBs in biota and sediment

A draft TIMES manuscript on the analysis of dioxins/furans and dioxin-like PCBs was reviewed by MCWG 2011. A couple of queries, mainly relating to references had still to be addressed. This was looked at in 2011 during subgroup sessions. The missing references were added. Additional changes were also suggested, but few issues were raised, and only minor changes required.

Patrick Roose is going to forward the draft manuscript to the Working Group on Marine Sediments (WGMS) for their comments and Katrin Vorkamp will contact the co-authors who were not present at MCWG 2011 for their comments. It is expected that the manuscript will be finalised shortly after the meeting.

### 5.15.2 Determination of polychlorinated biphenyls in biota and sediment

At MCWG 2010 it was agreed that a TIMES draft manuscript on PCB analysis would be prepared for the meeting in 2011. This would be based on the technical guidelines on PCB analysis on sediment and biota prepared previously by MCWG and WGMS. The TIMES draft manuscript for PCB analysis in sediment and biota was prepared intersessionally for review at MCWG 2011.

The document was reviewed by the subgroup during the meeting. A number of issues were raised. This included authorship, as previous guidelines were used as a starting point all authors may not have been included. There was also concern that there was too much information on older techniques and not enough on more recent developments. It was highlighted that a TIMES paper for PCBs in sediment already exists.

These comments will be taken into account for a new version which the subgroup will continue to work on intersessionally, for finalisation at MCWG 2012. The subgroup consists of Lynda Webster (lead), Jacek Tronczynski, Katrin Vorkamp, Michael Haarich, Michiel Kotterman, Patrick Roose and Philippe Bersuder.

### 5.15.3 Passive sampling based on silicone rubber

An updated version of the guidelines for silicone passive samplers was discussed, and only few suggestions for changes were proposed. It is expected that a final version of this guideline can be submitted within the next three months. Kees Booij will be in charge of this.

## 6 Plenary discussion of draft report

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The plenary discussion of the draft report took place on Friday 4<sup>th</sup> March 2011. The final draft version of the report was circulated by e-mail after the meeting, for approval by MCWG.

## 7 Any other business

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MCWG members are asked to check their accounts on the SharePoint site to make sure that all contact details are correct.

Elisabeth Sahlsten will continue as informal chair of COSG.

## 8 Recommendations and action list

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Recommendations are listed in Annex 4.

The following actions have arisen from MCWG 2011:

Action	Who
Send comments on WGBEC TIMES draft manuscript on dioxin bioassays to chair of WGBEC.	Katrin Vorkamp
Provide information on initial assessments under MSFD for individual member states.	All
Provide information on national/regional activities on pH measurements.	Klaus Nagel, Jacek Tronczynski, David Pearce, Patrick Roose, Evin McGovern, Elisabeth Sahlsten
Compile information on organochlorine monitoring in seabird eggs.	Michael Haarich, Katrin Vorkamp
Present new information on atmospheric transport of PFCs and on PFCs in the marine environment.	Ralf Ebinghaus
Approach NILU to see if monitoring information is available on atmospheric inputs of PFCs to the marine environment.	Evin McGovern
Forward TIMES manuscript on dioxin/furans and dl-PCBs to WGMS, for	Patrick Roose

their comments.	
Revise TIMES manuscript on dioxins/furans and dl-PCBs and submit to ICES.	Katrin Vorkamp
Revise TIMES manuscript on PCBs for review at MCWG 2012.	Lynda Webster (lead), Jacek Tronczynski, Katrin Vorkamp, Michael Haarich, Michiel Kotterman, Patrick Roose, Philippe Bersuder
Revise TIMES manuscript on passive sampling (silicone rubber) and submit to ICES.	Kees Booij
Inform MCWG about EMODNET workshop or other EMODNET activities that involve MCWG subgroup.	Carlos Borges
Follow up on suitable statistical methods for compliance checking.	Patrick Roose
Present the final report of INRAM to MCWG.	Patrick Roose
Review and present information on recent developments within passive sampling in the marine environment.	Kees Booij and Philippe Bersuder
Provide any deep core preindustrial dated sediment data for parent and alkylated PAH, dioxins, mercury, cadmium and lead to WGMS.	All
Collate any additional data on contaminants in eel for WGEel 2011. Michiel Kotterman agreed to act as a link between MCWG and WGEel.	All
Provide information on organic contaminants and metals in plankton from the Mediterranean Sea.	Jacek Tronczynski
Provide draft of seawater guideline for review at MCWG 2012 (OSPAR request).	Katrin Vorkamp
Present information on chemical fingerprinting in fish.	Katrin Vorkamp
Report on developments at SGIMC 2011 to MCWG 2012.	Katrin Vorkamp

## 9 Date and venue of the next meeting

MCWG received and welcomed an invitation from David Hydes to host MCWG 2012 at the National Oceanography Centre at Southampton, England. Dates to be confirmed.

## 10 Closure of the meeting

The meeting was closed at 1 p.m. on Friday, 4 March 2011.

## Annex 1: List of participants

Name	Address	Phone/Fax	Email
Anders Grimvall	Department of Computer and Information Science Linköping University 58783 Linköping Sweden	Ph: + 46-(0)13- 281482 +46-(0)13-281000	anders.grimvall@liu.se
Anja Duffek	Federal Environment Agency Laboratory for Water Analysis Bismarckplatz 1 14193 Berlin Germany	Ph: +49-(0)30- 8903-5740	anja.duffek@uba.de
Carlos Borges	Instituto Hidrográfico Divisão de Química e Poluição de Meio Marinho Lisbon Portugal	Ph: +351-210 943 118	carlosborges@hidrografico.pt
Carmen Menchu Rodriguez	Instituto Español de Oceanografía Centro Oceanográfico de Santander Apdo. 240 39080 Santander Spain	Ph: +34 942 291060 Fax: +34 942 275072	carmen@st.ieo.es
David J. Hydes	National Oceanography Centre Southampton University of Southampton Waterfront Campus European Way Southampton SO14 3ZH UK	Ph: +44 (0) 23 80596547	djh@noc.soton.ac.uk
David Pearce	Centre for Environment, Fisheries and Aquaculture Science (Cefas), Pakefield Road, Lowestoft, Suffolk NR33 0HT, UK.	Ph: +44 (0) 1502 524504 Fax: +44 (0) 1502 513865	david.pearce@cefas.co.uk

Elisabeth Sahlsten	SMHI Sven Källfelts g. 15 42671 V. Frölunda Sweden	Ph: +46 (0)31-751 89 90 Fax: +46 31 751 8980	elisabeth.sahlsten@smhi.se
Evin McGovern	Marine Institute Marine Environment and Food Safety Services Rinville Oranmore, Galway Ireland	Ph: +353 91 387200 Fax: +35 391 387 201	evin.mcGovern@marine.ie
Gert Asmund	National Environmental Research Institute (NERI) Aarhus University Frederiksborgvej 399 4000 Roskilde Denmark	Ph: +45-46 30 19 25 Fax: +45-46 30 11 14	gas@dmu.dk
Jacek Tronczynski	Labortoire Biogéochimie des Contaminants Organiques (LBCO) IFREMER DCN-BE Rue de l'Île d'Yeu BP 21105 44311 Nantes Cedex 03 France	Ph: +33-(0)2 40 37 41 36 Fax: +33-(0)2 40 37 40 75	jacek.tronczynski@ifremer.fr
Katherine Langford	Norwegian Institute for Water Research (NIVA) Gaustadalleen 21 0349 Oslo Norway	Ph: +47-22 18 51 00 +47-45 09 82 38 Fax: +47-22 18 52 00	katherine.langford@niva.no
Katrin Vorkamp (Chair)	National Environmental Research Institute (NERI) Aarhus University Frederiksborgvej 399 4000 Roskilde Denmark	Ph: +45 46301859 Fax: +45 46301114	kvo@dmu.dk
Kees Booij	NIOZ PO Box 59 1790 AB Texel The Netherlands	Ph: +31 222 369463 Fax: +31 222 319674	kees.booij@nioz.nl

Klaus Nagel	Leibniz - Institut für Ostseeforschung Warnemünde - Sektion Meereschemie - Seestr. 15 18119 Rostock - Warnemünde , Germany	Ph: +49 381 5197 331 Fax : +49 381 5197 302	klaus.nagel@io-warnemuende.de
Koen Parmentier	Instituut voor Landbouw- en Visserij Onderzoek ILVO Visserij Ankerstraat 1 B-8400 Oostende Belgium	Ph: + 32(0)59 5698.57 + 32(0)59 3422.50 Fax: + 32 (0)59 33.06.29	koen.parmentier@ilvo.vlaanderen.be
Lars Förlin	Department of Zoology Faculty of Science University of Gothenburg Box 100 40530 Gothenburg Sweden	Ph: +46-(0)31- 786-3676	lars.forlin@zool.gu.se
Lynda Webster	FRS Marine Laboratory 375 Victoria Road Aberdeen AB11 9DB UK	Ph: +44 1224 295 624 Fax: +44 1224 295 511	websterl@marlab.ac.uk
Michael Haarich	Johann Heinrich von Thünen- Institut Institut für Fischereiökologie Marckmannstraße 129b D-20539 Hamburg Germany	Ph: +49 4042817612 Fax: +49 4042817600	michael.haarich@vti.bund.de
Michiel Kotterman	Institute for Marine Resources and Ecosystem Studies (IMARES) PO Box 68 1970 IJmuiden The Netherlands	Ph: +31255 564 607	michiel.kotterman@wur.nl

Naomi Greenwood	Centre for Environment, Fisheries and Aquaculture Science (Cefas) Lowestoft Laboratory Pakefield Road, Lowestoft, Suffolk NR33 0HT, UK	Ph: +44 (0)1502 524417 +44 (0)1621 787212 Fax: +44 (0)1502 526212	naomi.greenwood@cefas.co.uk
Norbert Theobald	Bundesamt für Seeschifffahrt und Hydrographie Bernhard – Nocht Str. 78 D-22305 Hamburg Germany	Ph: +49 4031903340 Fax: +49 4031905033	norbert.theobald@bsh.de
Pam Walsham	FRS Marine Laboratory 375 Victoria Road Aberdeen AB11 9DB UK	Ph: +44 1224 295 624 Fax: +44 1224 295 511	P.Walsham@marlab.ac.uk
Patrick Roose	Management Unit Mathematical Models of the North Sea 3e en 23e Linierementsplein 8400 Oostende Belgium	Ph: +32 59242054 Fax: +32 59704935	patrick.roose@mumm.ac.be
Philippe Bersuder	Centre for Environment, Fisheries and Aquaculture Science (Cefas) Lowestoft Laboratory Pakefield Road, Lowestoft, Suffolk NR33 0HT, UK	Ph: +44 (0)1502 524417 +44 (0)1621 787212 Fax: +44 (0)1502 526212	philippe.bersuder@cefas.co.uk
Ralf Ebinghaus	Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research Department for Environmental Chemistry Max-Planck-Str. 1 21502 Geesthacht Germany	Ph: +49-4152-87-2354 Fax: +49-4152-87-2332	ralf.ebinghaus@hzg.de
Solveig Olafsdottir	Marine Research Institute Skulagata 4 121 Reykjavik	Ph: +354 575 2000 Fax: +354 575 2001	solveig@hafro.is

Iceland			
Stepan Boitsov	Research Group 429 "Marine Environment Quality" Institute of Marine Research Nordnesgaten 50 P.b. 1870 Nordnes N-5817 Bergen Norway	Ph: +47-55236394 Fax: +47- 55238555	stepan.boitsov@imr.no
Victoria Besada	Instituto Español de Oceanografía Centro Oceanográfico de Vigo Apartado 1552 36200 Vigo Spain	Ph :+34 986 492 111 Fax :+34 986 498 626	victoria.besada@vi.ieo.es
Zhiyong Xie	Helmholtz- Zentrum Geesthacht Centre for Materials and Coastal Research Department for Environmental Chemistry Max-Planck-Str. 1 21502 Geesthacht Germany	Ph: +49-4152-87- 2330 Fax: +49-4152-87- 2332	zhiyong.xie@hzg.de

## Annex 2: Agenda

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### ICES Marine Chemistry Working Group: 33<sup>rd</sup> meeting

Swedish Meteorological and Hydrological Institute (SMHI)  
Gothenburg, Sweden  
28<sup>th</sup> February – 4<sup>th</sup> March 2011

#### 1 OPENING OF THE MEETING

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

#### 2 ADOPTION OF THE AGENDA

#### 3 REPORT OF THE 98<sup>th</sup> ICES STATUTORY MEETING

- i) 2010 Advice Drafting Group
- ii) 2010 Annual Science Conference
- iii) Internal ICES information

#### 4 PLENARY PRESENTATIONS

- 4.a Lars Förlin (University of Gothenburg): *Integrated fish monitoring in coastal areas*
- 4.b Kristin Andreasson (SMHI): *Monitoring of primary production in the Baltic Sea*

#### 5 MAIN AGENDA

##### General

- 5.a **Development of a JAMP guideline on monitoring of contaminants in seawater:** Develop the general text for a JAMP guideline on monitoring contaminants in seawater, which could act as the overarching chapeau to technical annexes concerning specific substances. The technical annex on analysis of PFC compounds in seawater developed by ICES in 2009 is the first such document. The development of the overarching text should take into account the need to address the following issues: purposes; quantitative objectives; sampling strategy; sampling equipment; storage and pre-treatment of samples; analytical procedures; analytical quality assurance; reporting requirements.(OSPAR request 2011/1).
- 5.b Report on developments with regard to quality assurance of marine chemistry, in particular with respect to QUASIMEME.

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

- i) General overview of WFD and MSFD and their key parameters.
- ii) OSPAR updates: New OSPAR structure and QSR 2010
- iii) Report on the developments in Water Framework Directive monitoring programmes
- iv) Report on the developments under the Marine Strategy Framework Directive.
- v) Discuss suitable statistical methods of compliance checking of Environmental Quality Standards (WFD)

**5.d** MCWG members to report information on projects of relevance to MCWG activities.

*Michiel Kotterman: Contaminant concentrations and biological effects in eel*

*Philippe Bersuder: Applicability of passive samplers for contaminant monitoring in the marine environment.*

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

**5.f** Discuss the European Marine Observation and Data Network (EMODet) chemical portal, with input from the ICES Data Centre.

**5.g** Describe MCWG interests and activities on the interface to other expert groups (e.g. WGMS, WGEel, WGBEC, SGIMC, SGONS). Evaluate potential for collaboration with other EGs in relation to the ICES Science Plan and report on how such cooperation has been achieved in practical terms (e.g. joint meetings, back-to-back meetings, communication between EG chairs, having representatives from own EG attend other EG meetings).

## **Chemical Oceanography**

**5.h** Discuss the need and availability of certified reference materials for the analysis of nutrients in seawater.

**5.i** Ocean acidification:

- i) Report on recent developments in methodology of pH measurements and required standardisation procedures.
  - ii) Report on recent results of measurements of pH in marine systems (especially in the OSPAR area).
  - iii) Report on recent developments in quality assurance issues in the measurement of carbonate system parameters
  - iv) Review new information for determination of pH and carbonate parameters in estuarine and brackish water and the associated calculations.
- 5.j Revise MCWG 2010 guideline on monitoring of ocean acidification in view of publication as an ICES Cooperative Research Report (CRR).
- 5.k OSPAR request: Discuss revision of JAMP Eutrophication Monitoring Guideline, in terms of
  - i) comments by Review Group
  - ii) Commission Decision on good environmental status of marine waters (Marine Strategy Framework Directive).

## Contaminants

- 5.l Contribute, as may be required, to ICES activities on integrated chemical and biological effects monitoring and review new information on effect directed chemical analysis.
- 5.m Report on new information regarding emerging contaminants in the marine environment.
 

*Norbert Theobald: Retrospective monitoring of PFCs in fish.*

*Zhiyong Xie: Alternative flame retardants in the marine environment.*

*Philippe Bersuder: Organophosphorous and new brominated flame retardants in sediment and water.*
- 5.n Discuss the role of atmospheric transport and deposition for the assessment of inputs of PFOS and other PFCs to the marine environment.
- 5.o Complete guidelines for publication in TIMES series:
  - i) Determination of dioxins/furans and dioxin-like PCBs in biota and sediment.
  - ii) PCBs in biota and sediment

iii) Passive sampling based on silicone rubbers

**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**

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The **Marine Chemistry Working Group** (MCWG), chaired by Katrin Vorkamp, Denmark, will meet in Southampton, UK, **DATE** 2012 (to be announced) to:

- a) Review and finalise the JAMP draft guideline on monitoring of contaminants in seawater (OSPAR request 2011/1);
- b) Report on developments with regard to quality assurance of marine chemistry, in particular with respect to QUASIMEME;
- c) Water Framework Directive and Marine Strategy Framework Directive:
  - i) Report on the developments in Water Framework Directive monitoring programmes, including statistical methods for compliance checking of Environmental Quality Standards;
  - ii) Report on developments under the Marine Strategy Framework Directive, including information on initial assessments in member states;
- d) Report on information on projects of relevance to MCWG activities;
- e) ICES Data Centre:
  - i) Provide expert knowledge and guidance to the ICES Data Centre, as may be requested;
  - ii) Report on developments in EMODNET, in particular on intersessional MCWG subgroup activities regarding EMODNET;
- f) Report on activities in other expert groups on the interface to MCWG (e.g. WGMS, WGEel, WGBEC, SGIMC, SGONS);
- g) Chemical oceanography, with focus on ocean acidification:
  - i) Present and discuss new chemical oceanographic data relating to ocean acidification;
  - ii) Review new information for determination of pH and carbonate parameters in estuarine and brackish water and the associated calculations;
  - iii) Report on latest developments in *in situ* chemical oceanographic sensor;
  - iv) Discuss the need for and feasibility of proficiency testing for carbonate parameters (total alkalinity and dissolved inorganic carbon);
  - v) Review progress on interconnectivity of databases with respect to carbonate system data;
- h) Revise JAMP Eutrophication Monitoring Guideline as outlined by MCWG 2011 (OSPAR request);
- i) Contribute, as may be required, to ICES activities on integrated chemical and biological effects monitoring and review new information on effect directed chemical analysis;
- j) Emerging contaminants:
  - i) Report on new information regarding emerging contaminants in the marine environment;
  - ii) Discuss the role of atmospheric transport and deposition for the assessment of inputs of PFOS and other PFCs to the marine environment;

- k) Report on new information and experiences of using seabird eggs as a monitoring matrix for trace metals and persistent organic pollutants;
- l) Report on new information on passive sampling of contaminants in the marine environment;
- m) Discuss recent developments in trace metal analyses;
- n) Complete TIMES manuscript on PCB analysis in biota and sediment.

MCWG will report by **DATE** 2012 (via SSGHIE) for the attention of ACOM and SCI-COM.

## Supporting Information

Priority:	<p>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.</p> <p>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.</p>
Scientific justification and relation to action plan:	<ul style="list-style-type: none"> <li>a) OSPAR request</li> <li>b) 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.</li> <li>c) This work was initiated by MCWG and will be of interest to EU/OSPAR/HELCOM. It will also tie into STGMSFD.</li> <li>d) MCWG members are interested in receiving reports on relevant projects and activities from other members.</li> <li>e) This is in direct response to possible requests by the ICES Data Centre. An EMODNET subgroup with potential intersessional tasks was requested by the ICES Data Centre at MCWG 2011.</li> <li>f) Collaboration between expert groups, as highlighted by SSGHIE at ASC 2010.</li> <li>g) This follows up on OSPAR request 2010/2 at MCWG 2010. These items were identified by MCWG 2011 as important questions under ocean acidification and will be of direct interest to OSPAR</li> <li>h) OSPAR request</li> <li>i) With SGIMC being discontinued, MCWG will continue reviewing relevant information in this field.</li> <li>j) 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. The review of PFC-related research follows up on OSPAR request 2010/6.</li> <li>k) This was initiated by MCWG 2011 as an item of general interest to the group.</li> <li>l) This follows up on previous MCWG work on guidelines on passive sampling. Being a promising technique of potentially wide applicability, MCWG wishes to be kept informed about new developments.</li> <li>m) This was initiated by MCWG 2011 as an item of general interest to the group.</li> <li>n) This work was initiated by MCWG with a view to achieving wider dissemination of guidelines initially prepared in response to an OSPAR request for technical annexes.</li> </ul>
Resource requirements:	The resource required to undertake activities within the framework of this group is negligible.
Participants:	The Group is normally attended by some 20–30 members.

Secretariat facilities:	None.
Financial:	No financial implications.
Linkages to advisory committees:	ACOM
Linkages to other committees or groups:	SCICOM STGMSFD WGMS, WGBEC, WGEel, SGIMC, SGONS
Linkages to other organizations:	The work of this group is closely aligned with work being undertaken within EU Working Groups under the Water Framework Directive. The group provides the basis for some advice to OSPAR.

## Annex 4: Recommendations

RECOMMENDATION	FOR FOLLOW UP BY:
1. Note MCWG's proposal of a theme session for the Annual Science Conference 2012. Preliminary title "Physico-chemical aspects of ocean acidification in the ICES area"	ICES
2. Note MCWG's comment on QUASIMEME proficiency testing scheme	QUASIMEME
3. Note MCWG's comments with regard to revisions of priority substances, priority hazardous substances and related EQS values (Water Framework Directive).	EU Working Group E on Chemical Aspects (Chair: Jorge Rodriguez Romero, DG Env. D.1. jorge.rodriguez-romero@ec.europa.eu) OSPAR, HELCOM
4. Make changes to the database, as described by MCWG 2011, in order to accommodate passive sampling data.	ICES Data Centre
5. ICES/OSPAR initiatives on integrated monitoring should not cease with the final meeting of SGIMC in 2011 as this is a field of increasing importance in research and monitoring.	ICES, OSPAR
6. Provide feedback on current draft guideline (Annex 6), in order to direct further work towards completion at MCWG 2012	ICES, OSPAR

## Annex 5: Draft resolution for a publication (Category 1) and a Theme session proposal

### Draft resolution for a publication (Category 1)

The following reports are proposed for publication as an ICES Cooperative Research Report (CRR).

PUBLICATION TITLE	MCWG LEAD	ESTIMATED PAGE NUMBERS
Chemical aspects of ocean acidification monitoring in the ICES aea [working title]	David Hydes	40

The Marine Chemistry Working Group agrees to submit the final draft of the proposed publication by October 2011.

### Supporting Information

Priority	There has been rapidly increasing interest in assessing spatial and temporal changes to the ocean carbon system. In 2010 MCWG contributed detailed advice in response to an OSPAR request on monitoring ocean acidification. Updating this advice as a CRR will make this information more widely available to organisations in this rapidly developing field.
Scientific justification	The potential threat from ocean acidification is widely recognised and organisations such as regional sea conventions (e.g. OSPAR) are as a matter of high priority considering how best to approach monitoring ocean acidification. As a first step it is essential to determine the spatial and temporal variability of the carbonate system across offshore, shelf, coastal, brackish and estuarine waters. In this rapidly developing field this presents substantial technical challenges to laboratories and agencies charged with delivering this. The report will address key considerations required for developing a monitoring programme such as sampling approaches, key information needs, measurement criteria and quality assurance, developments in instrumentation and data management issues. The report also will describe current and past studies, specifically outlining activities that provide a good starting point for building a coordinated ocean acidification monitoring programme. An overview of the recent information on the variability of the carbonate system in the ICES area will also be incorporated.
Resource requirements:	Cost of production and publication of 40-page CRR.
Participants:	Approximately 3 months part time work is required by the authors to finalise the draft.
Secretariat facilities:	About one month of the services of Secretariat Professional and General Staff will be required?
Financial:	Publication costs.
Linkages to advisory committees:	The requested advice to OSPAR (MCWG 2010) on which this CRR is based was delivered via ACOM
Linkages to other committees or groups:	SCICOM
Linkages to other organizations:	These will be based on guidelines produced by MCWG on request for OSPAR. They will also be of interest to HELCOM and relevant to the EC MSFD (Annex III of which stipulates pCO <sub>2</sub> and pH as parameters).

**Theme Session proposal for the 2012 ASC**

The Marine Chemistry Working Group (MCWG) proposes a Theme Session for the 2012 Annual Science Conference:

**Title:** Physico-chemical aspects of ocean acidification in the ICES area

**Conveners:** David Hydes (UK).

Marta Alvarez (Spain) has also agreed to convene this theme session.

Suggestions: Alberto Borges (Belgium), Jon Olafsson (Iceland), PICES?

## **Annex 6: Draft guideline for seawater analysis (to be completed at MCWG 2012)**

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### **OSPAR request 2011/1**

Development of a JAMP guideline on monitoring of contaminants in seawater: Develop the general text for a JAMP guideline on monitoring contaminants in seawater, which could act as the overarching chapeau to technical annexes concerning specific substances. The technical annex on analysis of PFC compounds in seawater developed by ICES in 2009 is the first such document. The development of the overarching text should take into account the need to address the following issues: purposes; quantitative objectives; sampling strategy; sampling equipment; storage and pre-treatment of samples; analytical procedures; analytical quality assurance; reporting requirements.

### **Sampling and treatment of seawater for subsequent analysis of trace metals and organic contaminants**

#### **1. Purposes**

The monitoring of contaminants in seawater provides information on the chemical status of water masses, which may be sought in relation to pollution including its spatial and temporal variability, exposure to contaminants, or their fate in the environment, e.g. transformation, partitioning and transport processes. Contaminants enter the oceans via the atmosphere, rivers and direct point sources, in dissolved form, associated with particles or in colloidal complexes. They can be transported with ocean currents, partition into other compartments (e.g. sea-air exchange, biota uptake) and subjected to transformation in e.g. hydrolytical, photolytical or biological processes. The monitoring purpose is likely to differ for different water masses, e.g. estuaries, offshore waters and the open ocean.

Seawater analysis is a complex task which requires carefully designed and conducted sampling campaigns, appropriate equipment and its correct handling as well as suitable pre-treatment and storage methods for the analysis in question, i.e. numerous steps which will affect data quality prior to the chemical analysis itself.

This guideline will provide general advice on these initial steps, bearing in mind subsequent chemical analysis of trace elements and organic contaminants. This means that for several pre-analytical steps, different techniques will be discussed for either metals or organics. This also means that the analysis of nutrients will not be considered, neither *in situ* measurements of physical and chemical parameters such as salinity, oxygen, carbon dioxide etc. Analytical protocols for chemical analysis are available in guidelines for specific groups of compounds and will not be included in this document.

This guideline provides a general summary of techniques available for the sampling of trace elements or organic contaminants in seawater. The techniques selected are useful for routine monitoring and ship-campaign based work. However, this guideline is not intended as a complete laboratory manual. If necessary, guidance should be sought from specialized laboratories.

## 2. Quantitative objectives

The quantitative objectives are to provide concentrations of target analytes in the water or particulate phase, which are representative of the location and time of sampling.

[more text to be added?]<sup>1</sup>

## 3. Sampling strategy

The sampling strategy should answer where and when samples are taken, at what frequency, how they are taken and what exactly will be analysed.

Analyte concentrations in seawater (water or particulate phase) will vary between locations and with water depth, due to various physical and biogeochemical processes. The expected spatial variability is an important factor in the development of an adequate geographical sampling scheme, i.e. the outline of the station grid and its vertical resolution (Brügman and Kremling, 1999). Likewise, the temporal variability to be expected for the analyte concentrations will have to be considered in a strategy for sampling times (i.e. at what time of year) and frequencies. The analyte in question (its physical-chemical characteristics and expected concentration) as well as environmental conditions will further determine how samples are taken, e.g. what equipment is used and what volumes are required. However, sampling strategies also include compromises between scientifically advisable approaches and the economical and logistical frames of the sampling effort.

Purely statistical procedures for optimal design of environmental sampling programmes require detailed information about both the spatial and temporal variation in the measured variables, i.e. the analytes. Because the analysis of trace organics and heavy metals is expensive such information is rarely available for the variables considered here. Accordingly, the design must be based on a combination of general statistical principles and expert knowledge about sources and fate of the studied substances in the investigated sea basin. In most cases, this implies that one tries to apply the principles of stratified sampling. First the sampling area under consideration is partitioned into smaller more homogeneous areas, so-called strata, and then the allocation of samples to these strata is optimised.

The partitioning of the study area into homogeneous strata can be based on simple information, such as depth, distance to land, or measured or modelled salinity. A successful stratification is characterized by a small variation of the measured concentrations within each stratum and a substantial variation between strata. For optimal allocation of the samples we first determine the size (volume or area) of each stratum. Assuming that we have  $m$  strata with volumes  $V_1, \dots, V_m$  and that the standard deviation of the target variable is about the same in all strata, the number of samples  $n_j$  in stratum  $j$  shall be taken approximately proportional to the volume  $V_j$ , i.e.

$$n_j \approx n \frac{V_j}{V}$$

where  $V$  is the total volume of the investigated sea basin and  $n$  is the total number of samples.

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<sup>1</sup> Working notes - hereinafter

If the standard deviation of the target variable varies from stratum to stratum it is recommended to take more samples in strata with high standard deviation. More specifically, we shall aim at making  $n_j$  proportional to  $S_j V_j$  where  $S_j$  is the standard deviation in the  $j$ th stratum, i.e. letting

$$n_j \approx n \frac{S_j V_j}{\sum_{j=1}^m S_j V_j}$$

Finally, the average concentration in the study area is estimated to be

$$\sum_{j=1}^m V_j \bar{X}_j / V$$

where  $\bar{X}_j$  is the average observed concentration in the  $j$ th stratum.

In many cases, the target variable is correlated to the salinity of the sample or some other covariate that can be measured or modelled at a grid of points (see Figure 1). Then this covariate can be used to define suitable strata. Furthermore, the estimated relationship between the target variable and the covariate (the dotted line in Figure 1) can be used to estimate the target variable at an arbitrary grid point.

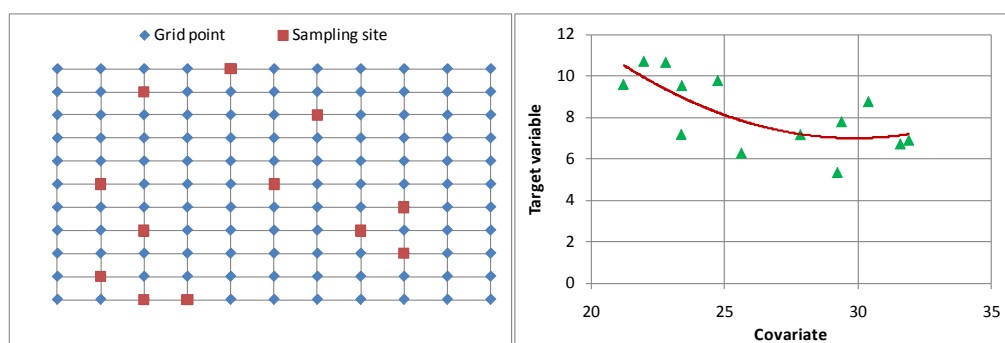


Figure 1. Location of sampling sites (left panel) and scatter chart of the measured target variable vs. a covariate.

#### 4. Sampling equipment

Which equipment to use for sampling strongly depends on the analytes, their physicochemical characteristics and expected concentrations, the depth and location for sampling and the infrastructure available. In order to account for the different requirements for sampling of trace metal and organic contaminants, their sampling equipment will be discussed separately.

Concentrations of organic contaminants in seawater are usually very low. Consequently, large volumes of water must be sampled or an enrichment step must be included *in situ*. Furthermore, contamination is a serious issue (including memory effects of equipment). One has to be particularly careful to avoid contamination from the ship (e.g. from paint, rust). For analyses of e.g. trace elements and oil in the water, clean lab (containers) onboard the ship are highly recommended. Hydrophobic compounds occur in a continuum of dissolved, colloidal and particulate-bound forms. Unless a total concentration is to be determined, the compound partitioning should not be altered during sampling and subsequent treatment, which is challenging. Ideally, filtration should occur online while sampling or immediately after sampling.

#### 4.1 Trace elements (including MeHg)

As a prerequisite for subsequent analysis of trace metals, all contact between the seawater sample and metal must be avoided. The use of polyethylene gloves is imperative for all sampling handling, to avoid contamination. Sampling equipment should be stored under clean conditions (e.g. plastic bags) until deployment. Generally, contamination from the ship has to be avoided at all times.

##### 4.1.1 Discrete samplers

An example of a discrete sampler is the GoFlo sampler (Figure 2). It is a cylinder with inward Teflon-coating which can be closed and lowered into the water column. This avoids contact of the sample with the water surface. At the desired depth, measured as water pressure, a messenger is sent on the hydrographic wire (in teflonized inox, polymer or better Kevlar) to release the closing valves in both ends of the sampler. Thus, it opens automatically at a certain depth, which, however, renders this sampler less suitable for surface sampling.

A variety of the GoFlo sampler is the reversing water sampler. The messenger releases the sampler from the upper attachment, it rotates, and closes the two valves. At the same time one can have a thermometer that when reversed fixes the temperature. Also a new messenger can be released that can trigger the next reversing sampler. There can be several samplers on one hydrographic wire. Both systems have to be cleaned before use by acid washing.

[Nansen samplers? E.G. Hydrobios Nansen sampler ---General Oceanic]

A Niskin sampler appears less suitable, due to rubber parts which cannot be acid-cleaned, moreover, it cannot be closed before deployment. The contact with the water surface increases the risk of contamination or at least unrepresentative sampling.



**Figure 2. Picture of a GoFlo sampler (IFREMER, France).**

The MERCOS sampler is made completely of Teflon and small silicone tube ends (Figure 3). It is lowered in the sea filled with air (so deployment depth is restricted to 100m), with both silicone tubes bended, thereby closing the Teflon bottle. When the bottle has reached the desired depth, a messenger is sent on the wire to release the two bended silicone tubes. Water is flowing into the Teflon bottle through one of the tubes and air is blown out through the other tube. Usually two bottles are used in the system, thus giving duplicate samples for every depth. The Teflon bottles and the silicone tubes have to be acid washed before use.



Figure 3. Picture of a MERCOS sampling bottle (IFREMER, France).

#### 4.1.2 Pumping

For depths down to 100 m, perhaps even 200 m, seawater can be pumped up through silicone or Teflon tubing. In that case one can introduce online filtration. The tubings have to be cleaned by pumping acid (e.g. 10% hydrochloric acid) through the tubing. The first litres of seawater must be discarded. The pumping could either be a peristaltic pump or a Teflon piston pump. The peristaltic pump can be placed between the sampling tube and the filter. The outflow from the online filter can be collected in polyethylene bottles, Teflon bottles, or for mercury analyses glass or quartz bottles.

#### 4.1.3 Centrifuge collection of SPM

[text to be added]

#### 4.2 Organic contaminants

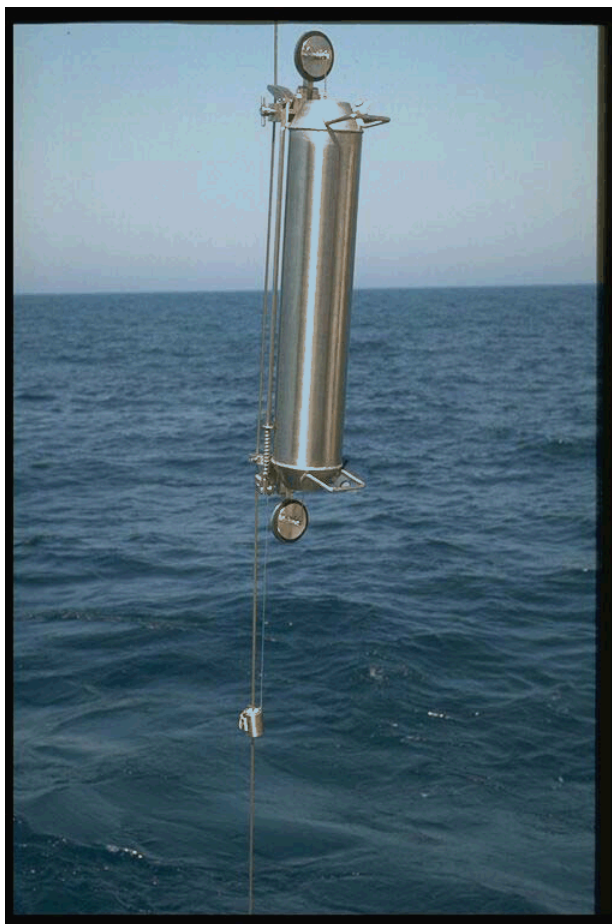
For subsequent analysis of organic contaminants, the preferred sampling equipment for seawater is made of glass or stainless steel. Before use, the equipment has to be cleaned thoroughly, e.g. rinsed with organic solvents.

##### 4.2.1 Discrete sampling and pumping

Usually large volume seawater samples are needed for the analysis of organic contaminants. Typically 30 litres are collected. Samples of water and of sub-surface suspended matter (to a depth of 5 m approximately) can be collected by pump, down to a depth of about 140 m. The samples are collected in stainless steel vessels or in glass bottles holding about 25 litres.

Collecting samples at greater depth is done with stainless steel bottles (Figure 4) holding about 30 litres. This type of sampler was developed following the models of

Niskin and GoFlo type bottles, and has been used for analyzing dissolved herbicides in water samples collected down to 3000 m depth (Ref.?).



**Figure 4.** A stainless steel sampling bottle, for subsequent analysis of organic contaminants in seawater.

An all-glass bottle sampler for smaller volumes is shown in Figure 5. It is fixed on a stainless steel cage and lowered by a hydrographic wire down to the desired sampling depth and opened under water. After filling, the sampler is brought on deck of the ship and can be extracted with a non-polar solvent immediately (see chapter 5 - Storage and pre-treatment of samples).



Figure 5. BSH all-glass bottle water sampler.

Sampling by pump is performed with compressed air Teflon pumps (which, however, are not suitable for subsequent analysis of perfluorinated compounds). In order to balance the system with the sampling water, the water is pumped for about ten minutes, before the actual sampling begins. Then the recipients are thoroughly rinsed along with the sample, before beginning the sampling itself. During the rinsing stages of the system and during the collection of the sub-surface samples, the hose is kept away from the ship's hull.

#### 4.2.2 Surface sampling

Surface seawater samples must be collected from a small boat, e.g. a RIB, by dipping the sampling bottle into the water while the boat is sailing slowly forward against the wind. The sampling bottles have to be cleaned as mentioned above.

#### 4.2.3 *In situ* filtration and extraction

*In situ* filtration and solid-phase extraction sampling devices may minimize the risk of sample contamination during sampling, and allow spatial or temporal variability studies, or water depth profiles. A typical *in situ* pump system, Kiel In-Situ Pump (KISP), has been widely applied to the extraction of organic contaminants in seawater (Petrick *et al.*, 1996). A modified KISP has been described for seawater sampling on board research vessels (Ebinghaus and Xie, 2006). Briefly, as shown in Figure 6, KISP includes a filter holder, a polymeric resin column, a pump and a flowmeter. A glass fiber filter (pore size 0.7  $\mu\text{m}$ ) is used for the particulate phase and a glass column packed with polymeric resin for the dissolved phase. The KISP can be easily operated onboard by connecting it to the ship seawater-intake system for sampling surface seawater at certain depth. The pump system assembly with batteries can be deployed at different depths by hydrographic wire, and the pump starts and ends by remote control.

The original KISP consists of some plastic parts and connections, which may present a contamination risk for some organic contaminants, such as brominated flame retardants, alkylphenols and plasticizers. Although low blanks and extremely low detection limits have been obtained from KISP samples for reliably detecting legacy persistent organic pollutants (POPs), such as PCBs, DDTs and HCHs (Lakaschus *et al.*, 2002; Sobek and Gustafsson, 2004), it is recommended to replace these parts by stainless steel or glass if KISP is applied for sampling seawater for the determination of emerging organic contaminants. Surrogate standards can be added to the resin column before sampling to control the extraction recoveries and storage. It should be noted, that the validation of the in situ pump sampling method is difficult, and extraction efficiency may depend on dissolved organic matter and humic substances.

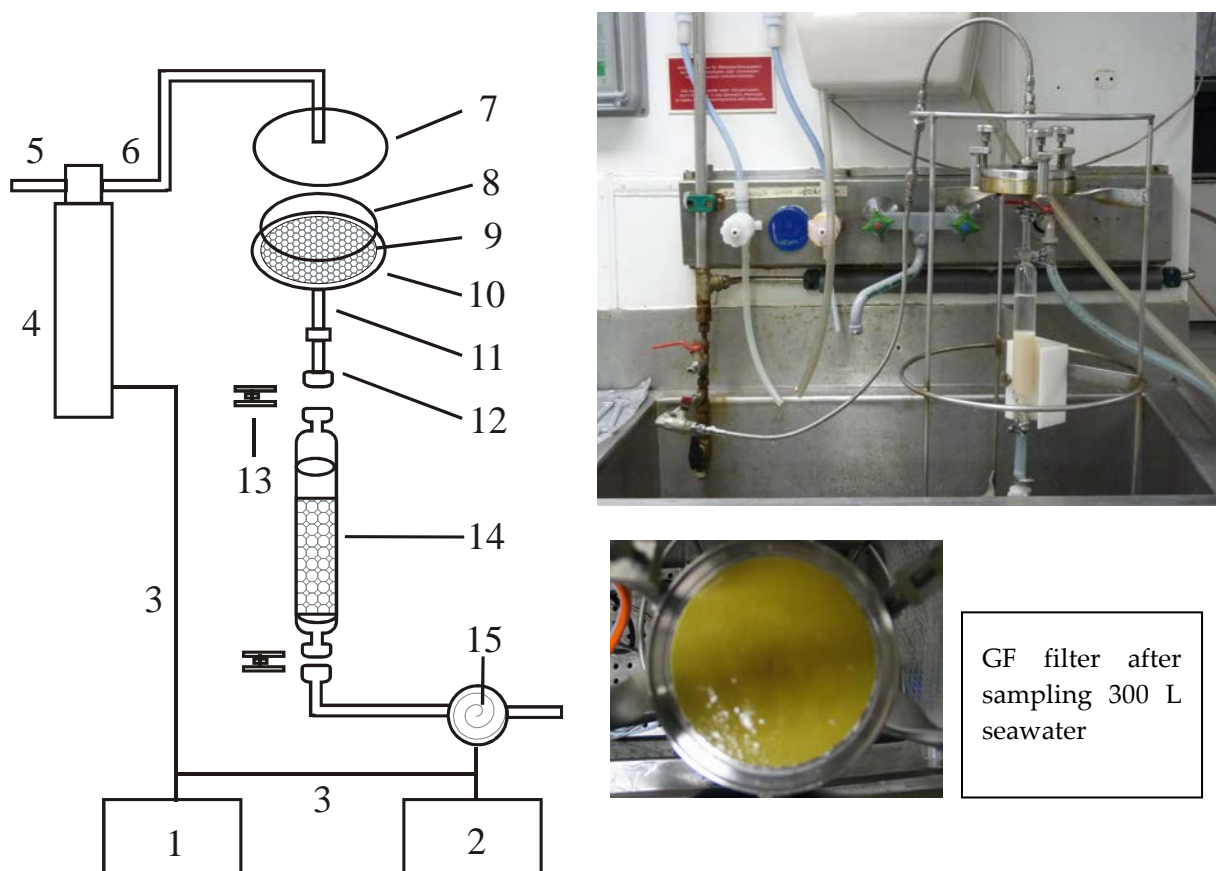


Figure 6. Schematic of the Kiel In-Situ Pump. 1: flow meter controller; 2: flow meter; 3: cable connections; 4: pump; 5: pump inlet; 6: pump outlet; 7: stainless steel deck of filter holder; 8: GF 52 filter; 9: glass plate; 10: filter holder; 11: stainless steel tubing; 12: glass connect; 13: adjustable clip; 14: resins column; 15: counter of flow meter.

#### 4.2.4 Centrifuge collection of SPM

[text to be added]

#### 4.3 Passive sampling devices (PSD)

Passive sampling devices (PSDs) consist of a sorption phase that is separated from the water by a microporous or semipermeable membrane. At large distance of the membrane surface, transport to the sampler takes place by convection and eddy diffusion. Close to the membrane surface, water motion is reduced and molecular diffusion becomes the rate limiting process, and the same holds for transport through the membrane.

Different PSD layouts exist for trace metals, non-polar organic contaminants and polar organic compounds. Passive samplers for trace metals consist of a chelating sorbent that is covered by a hydrophilic membrane. Examples are the diffusive gradients in thin films (DGT) sampler (Davison and Zhang, 1994) and the metals version of the Chemcatcher (Greenwood *et al.*, 2007). The polar organic chemical integrative sampler (POCIS) employs a polar sorbent (e.g., Oasis HLB) that is covered by a polyethersulfone (PES) microporous membrane (Alvarez *et al.*, 2004). The polar Chemcatcher consists of an Empore extraction disk (e.g., C18 bonded silica, sulfonated poly(styrene-co-divinylbenzene)), covered by a PES membrane (Kingston *et al.*, 2000; Greenwood *et al.*, 2007). Non-polar organic contaminants may be sampled by semipermeable membrane devices (SPMD, Figure 7), which consist of a low-density polyethylene (LDPE) lay-flat tubing that is filled with the lipid triolein (Huckins *et al.*, 1990). A Chemcatcher configuration with a C18 extraction disk plus a volume of 1-octanol, covered by an LDPE membrane has also been used for sampling these compounds (Vrana *et al.*, 2005). In addition, non-polar polymer sheets have been successfully used for sampling non-polar compounds, notably LDPE (Adams *et al.*, 2007) and silicone rubbers (Smedes, 2007; Rusina *et al.*, 2010). An overview of other passive sampler designs can be found elsewhere (Kot *et al.*, 2000; Stuer-Lauridsen, 2005).

During the initial stage of the PSD exposure, the sampler acts as an infinite sink, and the accumulated amounts reflect the time-weighted average of the aqueous concentrations. During prolonged exposure, some contaminants may reach sorption equilibrium with the sampler, depending on the sorbent amount, the exposed surface area of the sampler, and the sampler-water sorption coefficient of the analytes. These sorption coefficients are well defined in the case of non-polar PSDs, but not for samplers that target trace metals and polar contaminants. Consequently, the latter PSDs are exposed for relatively short exposure times (~ days to weeks), whereas the non-polar samplers may be exposed for periods of several weeks up to 2 years.

Uptake rates of trace metals by the DGT sampler are typically controlled by transport through the membrane, allowing laboratory calibrations to be used for calculating aqueous concentrations from the absorbed amounts (Garmo *et al.*, 2003). By contrast, the uptake of hydrophobic compounds by non-polar PSDs is typically controlled by transport through the water boundary layer near the membrane surface, which depends on the local temperature and water flow rates. The uptake rates by these samplers can be calibrated *in situ*, by measuring the dissipation rates of performance reference compounds (PRCs), i.e., compounds that do not occur in the environment, and that are spiked into the samplers before exposure (Huckins *et al.*, 2006; Booij and Smedes, 2010). The factors that control the uptake rates of polar PSDs (compound properties and the effects of flow, temperature, and salinity) are presently poorly understood, but semi-quantitative concentration estimates may be obtained by using compound specific calibration parameters that are determined in the laboratory (Alvarez *et al.*, 2004; Macleod *et al.*, 2007).

A number of issues should be considered before making a choice between filtration/extraction methods (FE) and passive sampling.

- The use of PSDs in marine monitoring requires the availability of suitable deployment sites. These can be jetties, buoys, bottom landers, long-term moorings, among others. If no such sites can be selected, then FE methods are the only choice.

- Travel cost to the sampling sites is higher when PSDs are used, because each site has to be visited twice. In addition, the risk of sampler loss due to fisheries and extreme weather conditions should be considered.
- PSDs yield time-integrated average aqueous concentrations, whereas FE methods are only integrative over the period of sample intake. It depends on the research question whether or not this is desirable. For example, FE should be selected if short-term variability is studied, and PSDs should be chosen for assessing average exposure levels.
- FE methods and PSDs may target different contaminant speciations. First, contaminant concentrations in suspended particulate matter can only be determined by FE. Second, the fraction of dissolved contaminants is operationally defined for FE, and includes the contaminant fraction that is bound to small particles and colloids that pass the filter. By contrast, PSDs for organic contaminants only sample the freely dissolved contaminants, and DGT targets the freely dissolved metals and the labile metal complexes. Differences between FE and PSDs may be large or small, depending on the affinity of the contaminants for small particles. In the case of regulatory monitoring, the contaminant fraction to be determined may be determined by the monitoring programme.
- Detection limits of PSD based methods may be smaller or larger than those of FE, depending on the compound properties, the exposure conditions, and the exposure time. An approximate a priori estimate of the detection limits with PSDs can be obtained by combining equivalent water sampling rates ( $R_s$ ) and the amounts that are found in the field control samples (i.e., samplers that receive the same treatments as the exposed samplers, except for the exposure to water). The sampling rate forms the conceptual link between passive sampling and FE. Typical  $R_s$  values that have been observed are 12 mL d<sup>-1</sup> for DGT (Garmo *et al.*, 2003), ~10 L d<sup>-1</sup> for 100 cm<sup>2</sup> non-polar samplers (Huckins *et al.*, 2006; Rusina *et al.*, 2010), and ~100 mL d<sup>-1</sup> for POCIS (Alvarez *et al.*, 2004; Macleod *et al.*, 2007; Mazzella *et al.*, 2007). For example, a 30-d exposure of a nonpolar PSD would yield a contaminant signal that is equivalent with a 10 L d<sup>-1</sup> × 30 d = 300 L water sample. This equivalent water volume can be combined with the amounts that are detected in the field control samples to yield an estimate of the detection limits. The equivalent water volume that is extracted by PSDs is smaller for compounds that reach (partial) equilibrium between water and the sampler (Booij *et al.*, 2007).
- The PSD calibration parameters that are needed to calculate aqueous concentrations should be available for the target analytes. Sufficient calibration data is available for metal sampling with the DGT sampler (Garmo *et al.*, 2003). Sampling rates of many polar contaminants have been determined for the POCIS (Alvarez *et al.*, 2004; Macleod *et al.*, 2007; Mazzella *et al.*, 2007). Sampling rates of many other polar compounds still should be determined experimentally, because  $R_s$  values cannot be calculated from compound properties yet. By contrast, the sampling rate calibration of non-polar PSDs is well understood (Booij and Smedes, 2010). Accurate partition coefficients between non-polar samplers and water are only needed for compounds that reach (partial) equilibrium during the exposure (typically, compounds with logK<sub>ow</sub> < 6). These partition coefficients can be found in the literature, or can be calculated from correlations with molecu-

lar properties, such as molar weight and hydrophobicity (Huckins *et al.*, 2006; Adams *et al.*, 2007; Smedes *et al.*, 2009, and references cited therein).

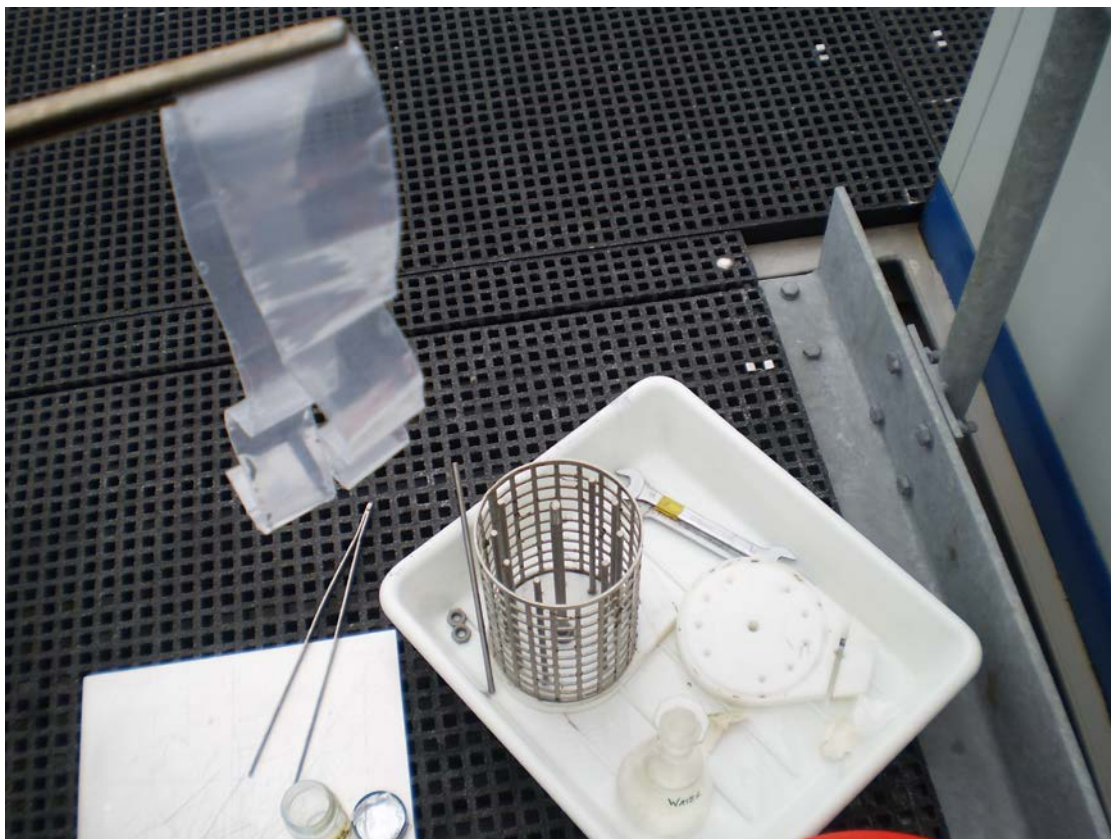


Figure 7. Semipermeable membrane device (SPMD) ready to be mounted in PDS cage.

## 5. Storage and pre-treatment of samples

If appropriate laboratory facilities are available onboard the ship, it will be advisable to process samples immediately, rather than store them for return onshore.

### 5.1 Trace elements (including MeHg)

Seawater samples have to be filtrated to separate dissolved and particle-bound metals. A suitable filter for trace element analyses would be a 0.4 µm polycarbonate filter. Filters must be stored individually and frozen (-20°C) until further analysis. The liquid phase must be conserved with acid. For mercury analyses, acid washed bottles of glass or Teflon should be used, no polyethylene. For other elements, polyethylene and Teflon is suitable, but no glass containers should be used.

### 5.2 Organic contaminants

Whole seawater samples can be extracted directly without filtration if the sample volume is less than 10 L. For high volume seawater sampling, filtration is typically done by glass fibre filter (pore size 0.7 µm). As for the sampling equipment, glass or stainless steel containers should be used, cleaned thoroughly, e.g. by solvent extraction, prior to use. If analytical methods include other chemicals or materials (e.g. sodium sulphate, silica gel), care should be taken to clean these as well.

Liquid-liquid extraction (LLE) and solid phase extraction (SPE) are common extraction techniques for organic contaminants in seawater. LLE should be applied if the

analytes are currently used in polymeric material or strongly retained on polymeric material used for SPE. If the analytes are collected on a polymeric resin column (see 4.2.3 *In situ* filtration and extraction), they can be eluted directly (“cold” elution) or connected to a modified Soxhlet extraction unit (Ehrhardt, 1987; Xie *et al.*, 2011).

## 6. Analytical procedures

[Text to be added. Not quite clear what is expected here, as specific analyses will be described in annexes to this guideline?]

## 7. Analytical quality assurance (QA)

Generally, all procedures including laboratory, field and on-line methods must be validated and controlled on a regular basis, including specific issues like contamination, sampling and extraction recoveries.

For this purpose, each laboratory must establish a quality assurance / quality control system. This should include the participation in interlaboratory or national proficiency testing programmes, procedures to ensure the long term stability of the laboratory’s performance, analyses of reference materials that are representative of the collected water samples, and the documentation required.

To minimise the risk of contamination or the loss of determinands during sampling, storage, pre-treatment or analysis (and so to avoid the generation of false data) QA measures should be applied to the sample from first contact to final measurement and data reporting. The use of a second (and different) sampling method, carried out simultaneously to the routine procedure, is recommended for validation. All QA data should be recorded.

## 8. Reporting requirements

Concentrations of trace elements in seawater should be given in weight per volume (e.g. ng/L) for the dissolved fraction and weight per weight (e.g. ng/g) for particle-bound metals. Organic contaminants?

Further information that should be reported include the sampling method, filtration, storage / conservation and analytical method, including relevant QA data (e.g. measurement uncertainty).

Coordinates of the sampling stations should be reported as well as sample depth and physicochemical parameters at the time of sampling, such as air and water temperatures, salinity, pH and weather conditions.

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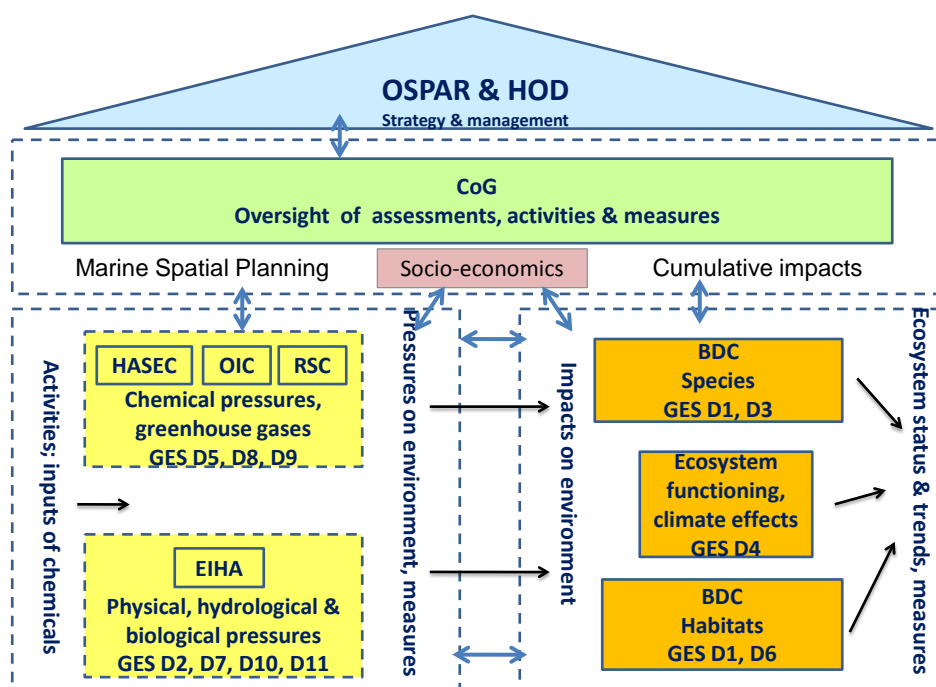
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## Annex 7: Post 2010 OSPAR structure



## Annex 8: Draft lists of reviewed and new priority substances and related EQS under WFD

### Review of existing EQS

Priority Substance	AA-EQS		MAC-EQS		Biota-EQS
	µg/l		µg/l		
	Inland /other surface water		Inland /other surface water		
Anthracene			0.1	0.1	
Benzene	0.08		80	8	1.1
Fluoranthene	0.0063	0.0063	0.12	0.12	30
Lead	1.2	1.3	14.25		
Naphthalene	2.0	2.0	130	130	
Nickel	2	8.6			Sediment-EQS not finalised
PAHs					Sum PAHs Fish: 2 Crustaceans: 5 Molluscs: 10
Benzo(b)pyrene			0.27	0.027	
Benzo(b)fluoranthene			0.017	0.017	
Benzo(k)fluoranthene			0.017	0.017	
Indeno(1,2,3-cd)pyrene					
Benzo(g,h,i)perylene	0.0082	0.00082	0.0082	0.00082	
PBDE	4.5 E-08	2.3 E-09	0.14	0.014	0.016

### Identification of new Priority Substances

Priority Hazardous Substances	Priority Substances
Dichlorvos	Bifenox
17 alpha Ethinylestradiol	Cyanides
17 beta Estradiol	Cybutryne (Irgarol®)
Aclonifen	Cypermethrin
Dicofol	Diclofenac
Dioxin	Terbutryn
PFOS	Ibuprofen
HBCDD	Zinc
Heptachlor/Heptachlor epoxide	
PCBs	
Quinoxifen	

## Draft EQS of new Priority Substances

Priority Substance	AA-EQS µg/l		MAC-EQS µg/l		Biota-EQS µg/kg ww
	Inland	/other surface water	Inland	/other surface water	
Dichlorvos	6 E-04	6 E-05	7 E-04	7 E-05	
17 alpha Ethinylestradiol	3.5 E-05	3.5 E-06			
17 beta Estradiol	5.3 E-04				
Aclonifen	0.12	0.012	0.12	0.012	
Dicofol	1.5 E-04	1.5 E-05			7.7
Dioxin					Sum of PCDD + PCDF + PCBDL 8.0 E-03 µg/kg TEQ biota ww
PFOS	0.00065	0.00013	36	7.2	0.0091 mg/kg biota ww
HBCDD	1.6 E-03	0.8 E-03	0.52	0.052	167
Heptachlor/Heptachlor epoxide	2.1 E-07	1.0 E-08	3 E-04	3 E-05	6.7 E-03
Quinoxifen	0.15	0.015	2.7	0.54	
Bifenox	0.0125	0.00125	0.04	0.04	

## Draft EQS of new Priority Substances

Priority Substance	AA-EQS µg/l		MAC-EQS µg/l		Biota-EQS µg/kg ww
	Inland	/other surface water	Inland	/other surface water	
Cyanides	0.1	0.01	0.8	0.8	
Cybutryne (Irgarol®)	0.0025		0.016		
Cypermethrin	8.2 E-05	8.2 E-08	5.8 E-04	5.8 E-05	Sediment EQS Inland: 0.033 µg/kg dw Other: 0.0033 µg/kg dw
Diclofenac	0.10	0.01	75	7.5	1
Terbutryn	0.065	0.0065	0.34	0.034	
Ibuprofen	0.01				
Zinc	10.9		33		

### Annex 9: List of Certified Reference Materials available for analysis of nutrients in seawater

Producer	Code	Analyte	Matrix	Conc. ( $\mu\text{mol l}^{-1}$ )	Certified (CRM)
Eurofins ( <a href="http://www.eurofins.dk">www.eurofins.dk</a> )	QC SW3.1	Ammonium	Seawater (Sal ~11)	~2	Yes
		Nitrite	- " -	~1	Yes
		TOxN (Nitrite+Nitrate)	- " -	~10	Yes
		TN	- " -	~15	Yes
	QC SW3.2	Orthophosphate	- " -	~2	Yes
		TP	- " -	~2	Yes
		Silicate	- " -	~20	Yes
	QC SW4.1	Ammonium	Seawater (Sal ~35)	~2	Yes
		Nitrite	- " -	~0.2	Yes
		TOxN	- " -	~5	Yes
		TN	- " -	~12	Yes
	QC SW4.2	Orthophosphate	- " -	~1	Yes
		TP	- " -	~1	Yes
		Silicate	- " -	~5	Yes
National Research Council of Canada ( <a href="http://www.nrc-cnrc.gc.ca/eng/services/inms/reference-materials.html">http://www.nrc-cnrc.gc.ca/eng/services/inms/reference-materials.html</a> )	MOOS-1 (Temporarily out of stock, Feb-2011)	Orthophosphate	Seawater (off NS, Canada)	$1.56 \pm 0.07$	Yes
		Silicate		$26.0 \pm 1.0$	Yes
		Nitrite		$3.06 \pm 0.15$	Yes
		TOxN		$23.7 \pm 0.9$	Yes
Ocean Scientific Intl. ( <a href="http://www.osil.co.uk">http://www.osil.co.uk</a> )	NSSPO	Orthophosphate	Deionised water	100	No
	NSSNI	Nitrite	- " -	100	No
	NSSNA	Nitrate	- " -	1000	No
	NSSSI	Silicate	- " -	1000	No
	LNS	All nutrients	Ocean water (S=35)	<1	-

## Annex 10: pH measurements in marine waters – current methods, developments and challenges

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Essentially two methods are in use for pH, the electrometric determination with standards based on TRIS and AMP buffers and the spectrophotometric determination using *m*-cresol purple.

### pH scales

It is important to remember to compare pH data on the same scale. For work on the carbonate system the “total scale” should be used for reporting pH data. The numerical values output by the different scales are significantly different. For example, at T=25°C and salinity=35, pH(free scale) can be ~0.11 higher than pH(total), while the difference between pH(total scale) and pH(seawater scale) is smaller ~0.01. In every case, the pH scale used must be reported, together with salinity, temperature and pressure, which will allow conversion between scales to be calculated if necessary.

### Electrometric determination

For Ocean Acidification (OA) monitoring, pH may appear to be the ideal parameter to measure. However, knowing pH alone does not let you understand the carbonate system. Moreover, the direct measurement of sufficiently accurate pH values in the marine environment is extremely challenging.

As electrodes need regular calibration, the first requirement for using pH electrodes is the availability and use of suitable buffers that span the range of pH to be measured. In theory only one buffer is required, if the electrode follows a Nernstian behaviour. In practise two buffers are used: In the marine environment these are TRIS and AMP pH buffers made up in artificial seawater of known salinity. The pH of these buffers is dependent on salinity (the AMP value is only known for a salinity of 35) and temperature and an empirical equation is used to assign the pH. The current state-of-the-art method is described in SOP 6a “Determination of the pH of sea water using a glass/reference electrode cell” of Dickson *et al.* (2007). However, Dickson advises that pH electrodes should only be used to analyse field-collected samples under well-controlled laboratory conditions. Following current best practise, the top reference laboratories should obtain an accuracy of 0.003 in pH when the salinity of the buffer is matched to that of the sample seawater.

A high level of analytical expertise required for making up seawater buffers and it is important to check regularly against certified reference materials (CRMs). The availability of certified TRIS buffers from Dickson’s laboratory means that the routine use of electrode measurements should be re-evaluated. However, at present there is not source of the second required buffer AMP (2-aminophenol). A good supply of both buffers would reduce the uncertainty in the measurement of marine pH. Detailed information on the shelf life of CRMs (sealed and once opened) is required together with recommendations on storage.

The next requirement concerns the choice of electrodes (hydrogen ion and reference) and measurement systems. There is a wide range of hydrogen electrodes available from a number of manufactures. Conventional electrodes use a glass membrane, which, provided they are treated with care, will provide reliable measurements. Before use (and at regular intervals thereafter) it is important to check that the slope of the electrode is within 1% of theoretical Nernstian slope. Although using two buffers will allow the calibration of the pH cell, a reduction in the theoretical slope will re-

duce maximum accuracy and may indicate a potential fault with the electrode. Other types of hydrogen electrodes are currently in development, e.g., Ion-selective field effect transistors (ISFETs). These alternative electrodes may afford advantages in the future; possibly for autonomous flow-injection systems requiring only small quantities of sample and buffer. However, at present these can only be considered a research tool.

Although the selection of hydrogen electrode is important, the choice of reference electrode is critical to the accuracy and stability of the pH measurements. Generally, the reference electrode consists of the Ag/AgCl type. When designing a reference electrode, the main concern is the junction between this electrode and the seawater being measured. Various designs of junction are available including glass frit, single junction, double junction, PTFE ring and free-diffusion liquid junction. Ideally, the junction should afford a fixed reference potential regardless of the sample's temperature, salinity and other physical and chemical properties. However, this is not the case and the selection of reference electrode is generally a compromise between ease of use and accuracy desired; no "best buy" can be recommended. Typical laboratory based systems use a double junction reference electrode. Butler *et al.* (1985) and Whitfield *et al.* (1985) introduced the concept of a capillary free-diffusion liquid junction, which consisted of a potassium chloride (KCl) salt bridge solution in a capillary between the reference electrode and the hydrogen electrode cell. Changes in seawater sample composition had no effect on the reference electrode and the liquid junction in the capillary could be reformed reproducibly. Again, to obtain the highest accuracy, the seawater buffers used should match the seawater salinity as closely as possible and certainly within about 5 salinity units.

The final requirement is for the electronics and pH cell design. The hydrogen ion electrode requires a very high impedance input to the voltage measurement system to ensure that the current flowing through the glass membrane is extremely low. However, under these conditions glass electrodes act as aerial for electromagnetic interference and extreme care must be taken with design of analogue electronics, screening and earthing. A standard pH meter generally measures to 0.1mV (equivalent to 0.002pH). However, to be certain of obtaining accuracies approaching 0.003 pH it is strongly advised to measure the voltage to 0.01mV (approximately ten-fold higher resolution in voltage than required for the target pH precision). In the laboratory it is recommended to use a high accuracy, calibrated digital voltmeter (5 1/5 digit) fitted with very high impedance input.

For an autonomous or field-based system the requirement for expert design of analogue electronics, screening and earthing should not be under-estimated. Add to these the choice of hydrogen and reference electrodes and issues with electrode measurement stability on *in-situ* samples as this provides an insight into why it is so difficult to take field measurements at accuracies better than about 0.02 pH. One system that has attempted to minimise these issues is the estuarine pH system described by Pearce and Wood, 1997. This vessel-fitted flow-through system used the free-diffusion liquid junction design, where the reference electrode was maintained at a fixed temperature ( $\pm 0.1^{\circ}\text{C}$ ) and the capillary connection to the hydrogen electrode measurement cell contained 3.5M KCl. The system used 20ppt TRIS buffer and an accuracy of 0.02 pH was obtained for estuarine water of salinity from about 5 to 35. Careful design of the electronics ensured good quality voltage measurements with minimal noise and no voltage offset. During use, the system refreshed the liquid junction automatically at a programmed interval and electrode calibrations were carried

out before and after a survey and every four to six hours during a survey. Improvements in accuracy should be possible by the additional use of AMP buffers.

Currently there is no recognised, recommended standard pH electrode-based system (including electrodes, buffers, electronics and software) for autonomous or shipboard continuous flow measurements. The development of an automated calibration regime, (based on TRIS and AMP based buffers of suitable salinities), are required for long-term stability in autonomous systems. Flow injection systems using ISFET-based electrodes and requiring small quantities of buffers may afford cost-effective, reliable systems with satisfactory accuracy.

From the preceding discussion, it is clear that there are several sources of errors in the electrometric determination of pH. The combination of these errors, especially for autonomous measurements, contributes to lower accuracies obtainable in the field than under controlled laboratory conditions. Such sources of error include:

- 1 ) Reference electrode selection and use (changes in liquid junction potential affecting measured cell voltage).
- 2 ) Seawater buffer pH uncertainties (absolute values and drift).
- 3 ) Hydrogen electrode selection and use (including Nernstian response checks).
- 4 ) Noise and voltage offsets brought about by poor earthing and/or electronics design.

Therefore in conclusion, the direct measurement of sufficiently accurate pH values using electrometric techniques in the marine environment is extremely challenging. To improve the accuracy of *in-situ* and other autonomous measurements of pH using electrometric techniques, development work is required to overcome the many issues highlighted. The following recommendations are made:

- 1 ) Electrodes are not currently recommended for autonomous use on moorings and ship flow through systems where data accuracy greater than about 0.02pH is required.
- 2 ) Only with extreme care and training it is possible to obtain accuracies approaching 0.005 pH for field-collected seawater samples (salinity ca. 35) that are subsequently analysed in the laboratory. An enhanced and more detailed version of SOP 6a would improve this situation, increasing the confidence in measurements made in non-reference laboratories.
- 3 ) There is a requirement for further sources and increased quantities of CRMs (TRIS and AMP), which will help improve confidence in electrode-based pH measurements.
- 4 ) Further developments are required before reliable, accurate autonomous measurements can be made. The aim should be to produce recommended, accredited electrodes and electronics/software systems to ensure inter-comparability between monitoring organisations.
- 5 ) Interlaboratory checks with reference seawater solutions of known pH would ensure reliability and accuracy of these measurements.

### **Spectrophotometric determination**

Several laboratories are working on the automation of the spectrophotometric method. The colorimetric method is described in SOP 6b "Determination of the pH of sea water using the indicator dye *m*-cresol purple" of Dickson *et al.* (2007). The man-

ual method has been used successfully over a number of years by some laboratories (Perez and Fraga, 1987; Perez *et al.*, 2010). To obtain accurate data, biases due to contamination of the dye need to be taken into account (Yao *et al.*, 2007). The method has been automated (e.g. Friis *et al.*, 2004) but work is on-going in a number of laboratories to produce reliable systems that can be run autonomously. A system is available from Sunburst Sensors (<http://www.sunburstsensors.com/>, Seidel *et al.*, 2008). Wang *et al.* (2007) reported on an autonomous multi-parameter flow-through CO<sub>2</sub> system measuring surface seawater pH, carbon dioxide fugacity (fCO<sub>2</sub>), and total dissolved inorganic carbon (DIC). All three measurements are based on spectrophotometric determinations of solution pH at multiple wavelengths using sulfonephthalein indicators. The field precisions were reported to be 0.0008 units for pH, 0.9 µatm for fCO<sub>2</sub>, and 2.4 mol kg<sup>-1</sup> for DIC.

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## Annex 11: Review of recent results of pH measurements in the OSPAR area

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“Ocean Acidification” – decreasing pH – of ocean waters is an inescapable consequence of the rising concentration of carbon dioxide in the atmosphere. Orr *et al.* (2005) suggested an average decrease of 0.0015 to 0.002 pH units per year in the open ocean. Regional differences in this rate are likely to be large. Coastal and shelf regions because of their heterogeneity are likely to show the largest deviation from the projected average trend. This includes factors such as atmospheric deposition of nitrogen and sulphur oxides which induce additional acidification at the sea surface (Doney *et al.*, 2007; Duce *et al.*, 2008). Similarly conditions in shallow seas unlike ocean waters will be affected by interactions at the sea bed (Soetaert *et al.*, 2007). Observations are now beginning to be published that show that there are distinct regional patterns.

Evidence is available from time-series, basin-scale measurements and models that indicate that surface water pH varies substantially - seasonally, inter-annually and decadal. For acidification research, these observations are important because their magnitude sets a boundary for what might constitute damaging pH change. The periods of variations in pH need to be quantified if we are to be able to detect permanent changes. Similarly spatial variability needs to be quantified. For example, it is believed that the polar and sub-polar ecosystems are particularly at risk because they are presently the closest to undersaturation with respect to aragonite (Bellerby *et al.*, 2005).

### Ocean waters

Time series data in the North Atlantic are enabling the characteristics of the variability of the oceanic carbonate system to be established. The sites are BATS near Bermuda, and two near Iceland, with data starting in the early eighties; the ESTOC site near the Canary Islands established in 1995, and work on the SOO route from the UK to the Caribbean which has measurements beginning in 1994, and is near-continuous since 2002 (Watson *et al.*, 2009).

In the subtropical gyre, both the BATS (Bates, 2007) and ESTOC (Santana-Casiano *et al.*, 2007) time series stations report a decline in pH which is consistent with that predicted by Orr *et al.* (2005). The time series near Iceland show a different behaviour however: Olafsson *et al.* (2009a; 2009b) report a pH decline for the period 1983–2008 of 0.0014 units yr<sup>-1</sup> for the Irminger Sea but 0.0024 units yr<sup>-1</sup> for the Iceland Sea – significantly different from one another and from the quasi-steady state picture. In the Iceland Sea deep water regime (>1500 m), the rate of pH decline is 25 % of that observed in surface waters. The aragonite lysocline is currently at water depth of 1750m and rising at 4 m yr<sup>-1</sup>.

An Irish project carried out eight surveys covering the waters from the coast to the outer shelf and into the Rockall Trough off western Ireland in 2008 to 2010. Surface and deeper waters were sampled, with some repeats in different seasons and years. This has provided an important and large baseline data set and also one which can be compared with the smaller amounts of data collected on World Ocean Circulation Experiment (WOCE) surveys in 1996/1997. Winter (February) surface seawater in the outer shelf and Rockall Trough in 2010 was observed to be more acidic by 0.02–0.04 pH units than surface seawater sampled in the same area in November 1996 during the WOCE surveys. However, nutrient concentrations show that seasonal stratification may not have fully broken down during WOCE sampling and that biological

activity may, at least in part, explain the pH differences. The Aragonite Saturation Horizon (ASH) was calculated to be at about 2500 m. Little or no change is evident in aragonite saturation state in the southern Rockall Trough between 1996 and 2010. 2009 summer data on shelf edge of the Rockall Trough and of the Porcupine Seabight showed a more complex picture when compared with 1997 WOCE data. The saturation state in summer in the Porcupine Sea Bight, north of the Goban Spur, is lower throughout the water column in 2009 than determined in 1997 for a transect further to the south, and the ASH appears to be shallower by several hundred metres. Salinity and temperature data indicate that this may be due to physical factors, such as difference in geographical spread of sampling points and water mass mixing. These findings demonstrate the need for consistent regular integrated biogeochemical and oceanographic surveys, as the underlying physical and biological processes provide a natural variability which must be understood to get a true picture of changes to the overall acidification state of our marine waters (O'Dowd *et al.*, in press).

In the UK DEFRApH study data collected over the deep water of the Bay of Biscay was examined for monthly observations made from 2008 and 2010. These show a clear picture of continued substantial uptake of dissolved CO<sub>2</sub> by plankton growth after the end of the spring bloom when there were apparently no nutrients in the water to support growth. This demonstrates that changes in the stability of the thermocline from year to year and consequently different transfer of nutrients across the thermocline support different degrees of summer production. This disconnects the drawdown of CO<sub>2</sub> by biological production from that which can be predicted from knowledge of concentrations of nitrate present before the spring bloom (Hydes *et al.*, 2011). Equally importantly the molar ratio of carbon and nitrate uptake during the spring bloom appears to be tightly constrained by the Redfield ratio.

### Shelf seas

Progressive change as noted above can be identified in open ocean waters but in shelf seas a clear picture has yet to emerge. In part this is because of the lack of suitable time series but also because of the greater complexity of shelf sea environments which produce a large "background" variability from which progressive change needs to be distinguished. The scale of possible variability in greater North Sea has been illustrated by Blackford and Gilbert (2007) who made estimates using the POLCOMS/ERSEM model of the current seasonal range of pH and rate of acidification to be expected over coming decades, for UK shelf waters. Through a year the model shows that pH varies over ranges of between <0.2 and >1.0 pH units, depending on location. They also showed that over the next 50 years, pH change from increasing atmospheric CO<sub>2</sub> emissions was likely to exceed 0.1 pH units, on average.

On the US west coast two recent reports have highlighted substantial changes. Wootton *et al.* (2008) reported an extensive pH dataset for a shoreline site on the Washington coast showing substantial variation in pH values across multiple time scales over 8 years of observations. The pH varied ~0.25 unit over 24 hours, up to ~1.0 unit over the seasons, and ~1.5 unit over the entire dataset. Over the 8 year period a significant underlying trend was found, with a mean pH decrease of 0.045 (0.039 to 0.054) unit per year. In more open waters Feely *et al.* (2008) sampled on 13 lines of stations across continental shelf waters into Pacific deep water off the North American west coast from Canada to Mexico (51 to 25 °N). They observed seawater that was undersaturated with respect to aragonite that had upwelled onto large portions of the continental shelf, to depths of 40 to 120 meters, along most transect lines and all the way to the surface off northern California. Although seasonal upwelling of the undersaturated

waters onto the shelf is a natural phenomenon in this region, the ocean uptake of anthropogenic CO<sub>2</sub> has increased the extent of the affected area. This has resulted in the depth of the aragonite lysocline being 50 to 100 shallower than in pre-industrial times.

These continental shelf waters of Western North America studied by Wootton *et al.* (2008) and Feely *et al.* (2008) are subject to upwelling and it remains to be seen whether similar pH dynamics occur off the Iberian margin.

### North Sea

Presently no regular wide area surveys of the carbonate system in the North Sea are being carried out. Dutch groups led by work at NIOZ conducted seasonal surveys between the Dover Straits and 61°N in 2001 and 2002 (Thomas *et al.*, 2005) during which pCO<sub>2</sub> was measured continuously and TA and DIC were measured on a grid of stations. The grid was repeated in summer in 2005 and 2008 with the addition of continuous pH measurements. A further repeat is planned for summer 2011. These reveal a complex pattern of apparent change with rapid increases in pCO<sub>2</sub> (similar to those observed in the open NE Atlantic) in some areas but not in others. The NIOZ work has indentified two key processes. One is what has recently been termed the “biological shuttle” by K.K. Liu. Bozec *et al.* (2006) identified that the recycling of nutrients in stratified areas of the North Sea leads to a draw down of DIC into the deep water in proportion to the number of times the nutrients are recycled during the productive part of the year. This will give a larger decrease pH in bottom water than would be predicted by the winter load of nitrate. This process has been indentified in model results (Blackford and Glibert, 2007) to generate a region specifically more sensitive to acidification. The other key process identified by Thomas *et al.* (2009) is the in-situ generation of alkalinity. They found evidence that anaerobic degradation of organic matter generates total alkalinity (TA) and so increases the CO<sub>2</sub> buffer capacity of seawater. Effectively if TA increases relative to DIC, at fixed values of DIC the corresponding pCO<sub>2</sub> of the water decreases and the pH increases. They estimated that TA generation in the North Sea’s tidal mud flat areas and benthic denitrification in the North Sea, may be supporting 20–25% of the North Sea’s overall CO<sub>2</sub> uptake.

In contrast the DEFRApH study (Hydes *et al.*, 2011) has found indications of relatively strong decreases in alkalinity resulting from the calcification. In the northern North Sea this may be associated with the growth of coccolithopores. In the English Channel it may be associated with the growth of benthic calcifiers such as brittle stars (Davoult, 2009). Such strong calcification has previously been suggested as being a feature of these waters by Borges and Frankignoulle (2003).

RIKZ (now Deltares) have collected regular data on values of pH on their grid of stations through Dutch waters since 1975. The dataset consists of results mainly obtained by simple, direct electrode measurements on board the survey vessel. A review of the dataset by Provoost *et al.* (2010) showed a seasonal variability consistent with model estimates (cf. Blackford & Gilbert, 2006). Long-term trends are difficult to interpret reliably because of changes in methodology. The results suggest that not only atmospheric CO<sub>2</sub>, but also other factors affect long-term trends of surface seawater pH. Recent observations and modelling studies help deconvolute some of the observed complexity and suggest that eutrophication-related biogeochemical changes by affecting the alkalinity of the waters can mask atmospheric CO<sub>2</sub>-induced pH decreases (Gypens *et al.*, 2009; Borges and Gypens, 2010). The analysis of data on pH in Dutch coastal water reported by Provoost *et al.* (2010) appears to confirm Gypens *et*

*al.*'s hypothesis and clearly indicates a need to assess changes in nutrient status of waters when assessing their potential to be affected by acidification.

The possibility that errors in the calculation of carbonate alkalinity from measurements of total alkalinity can occur has been raised in recent publication (e.g. Kim and Lee, 2009). A desk study has assessed the likely sources of error in these calculations (Hydes *et al.*, 2010). The presence organic matter in some types of samples is considered to be a likely sources of such error (Kim and Lee, 2009). This is most likely to be a problem in coastal waters and experimental incubations. The DEFRApH sampling in Liverpool Bay found that changes in total alkalinity did not need the presence of organic to be evoked to explain the observed changes. In contrast new Irish measurements in the Shannon estuary can only be explained if the River Shannon carries a high load of organic alkalinity.

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## **Annex 12: Technical minutes of the Review Group MON2 2011 (RGMON2)**

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### **Review of the ICES Marine Chemistry Working Group 2011 Report**

**6 May 2011**

Reviewers: Paul Keizer, Canada (Chair); Jose Fumega, Spain; Michiel Kotterman, NL; Jordi Dachs, Spain

Chair WG: Katrin Vorkamp, Denmark

Secretariat: Claus Hagebro

### **Guidance on the design of a regional monitoring programme for contaminants in sediments**

This report provides technical comments on the preliminary draft advice from MCWG on the request from OSPAR to develop a JAMP guideline on monitoring of contaminants in seawater:

To develop the general text for a JAMP guideline on monitoring contaminants in seawater, which could act as the overarching chapeau to technical annexes concerning specific substances. The technical annex on analysis of PFC compounds in seawater developed by ICES in 2009 is the first such document. The development of the overarching text should take into account the need to address the following issues: purposes; quantitative objectives; sampling strategy; sampling equipment; storage and pre-treatment of samples; analytical procedures; analytical quality assurance; reporting requirements.

RGMON2 realised that the material in the MCWG 2011 report was very preliminary in nature, the intention being to provide the requested advice to OSPAR in June of 2012. **The comments of RGMON2 are therefore focused on the general content of the MCWG 2011 report rather than the detailed content.** RGMON2 hopes that these comments will assist MCWG with its intersessional work on this guidance document. This document uses the same organisation as the MCWG 2011 report.

### **Draft guideline for seawater analysis (to be completed at MCWG 2012)**

#### **Sampling and treatment of seawater for subsequent analysis of trace metals and organic contaminants**

##### **1. Purposes**

There needs to be an introductory piece that describes seawater, contaminants, and their dynamics. Some of the aspects of seawater composition that need to be considered are its salinity and its dissolved and particulate components. The particulate component needs to be described in terms of its biotic and abiotic components and how these might affect sampling strategy and procedures, and also how they might affect the distribution of contaminants in a seawater sample. Whether it is here or in the section on sampling strategy the case needs to be made for collecting contextual information along with the seawater sample, e.g. CTD, biological sampling, etc.

The general purpose for monitoring contaminants in seawater also needs to be discussed, i.e. to protect the health of marine organisms. This should then lead to the

need for integrated monitoring and the role that measuring of contaminants in seawater has.

## **2. Quantitative objectives**

As noted in the document more text has to be added here. Of particular importance here is the clarity of the objectives and the feasibility of obtaining sufficient data to meet the objectives. This ties in with the next section on Sampling Strategy but there needs to be some rationalising of objectives to account for the realities of sampling logistics and costs. Chemists need to challenge the stated objectives if there is no reasonable expectation of achieving the objectives as stated. Much can be learned in this regard from OSPAR's experience with the QSRs.

## **3. Sampling strategy**

The text seems to focus entirely on sampling for a contaminant from a non-point source or in an area beyond the localised impact of a point source. Presumably this would be the case with respect to the MSFD but would there not be cases where the sampling was being conducted to monitor receiving water levels of a point source contaminant?

The sampling and analysis of organics (and metals) should be done in parallel to as good as possible assessment of the physical, chemical and biological status of the region. In terms of organic pollutants, it is very important to quantify the different organic matter pools and the trophic status. For example, it is now known that concentrations of organics in seawater and plankton depend on the eutrophic or oligotrophic status of the sampled waters.

Of course, all these will be limited due to financial limitations. For organics, there are very few assessments of open sea pollution with more than 30 samples of dissolved concentrations of some priority substances such as PCBs, or PBDEs, and even less for PCDD/F, etc. This practical limitation needs to be considered. Depending on the budget available, the monitoring will be limited to few dozens of samples. The variability issue and significance of this monitoring should be designed taking into account these limitations.

## **4. Sampling equipment**

The second paragraph of this section (beginning with "Concentrations of organic contaminants in seawater are usually very low") is best left to the individual discussions of trace metals and organics; it seems out of place here.

### **4.1 Trace elements (including MeHg)**

There should be a discussion of the potential sources of trace metal contamination. Also some discussion of sample size, i.e. as a function of expected analyte concentration and analytical detection limits, is needed. This would also be an appropriate place to discuss the potential sources of sample contamination and possible loss of analyte. There also needs to be a discussion of the potential problems of filtration methods, e.g. sample contamination, effectiveness and impacts, etc.

#### **4.1.1 Discrete samplers**

This is more of an editorial comment but has some general application. Rather than starting out with an example of the type of sampler, describe the properties/characteristics and pros and cons of a type of sampler and then offer the example.

#### **4.1.2 Pumping**

This is the first mentioning of filtering samples. There needs to be some text in the introduction section or perhaps a new section of seawater properties that provides the background and rationale for filtering samples. The directions on purging the pump lines prior to sample collection needs to be more specific, e.g. how many “tubing or system volumes” should be discarded before the first sample is collected.

#### **4.1.3 Centrifuge collection of SPM**

Should this be a section on collection of SPM in general and then comments on specific methods including centrifugation?

### **4.2 Organic contaminants**

The comments on Section 4.1 also apply here.

Concerning organics the cleaning procedures will be chemical dependent, the protocols are not the same for PCBs than for PFOA. The materials of the equipment will also be dependent on the chemical. Teflon is often used for legacy POPs, while it cannot be used for some emerging pollutants such as PFOS and PFOA.

#### **4.2.1 Discrete sampling and pumping**

Sample volume is dictated by potential concentration of contaminant and the detection limits for the analytical method. However sample volume is also dictated by operational considerations, i.e. size of containers for discrete samplers, time for pumping for pumped samples, and ability to process large volumes, etc.

It is true that discrete (stainless steel and glass) samplers have sometimes been used. However, they are only useful for coastal waters when smaller volumes of water are needed because the seawater concentrations are higher. The truth is that these samplers give a lot of problems if one aims at analysing contaminants for which the ship can be a source of pollution. For example, ships are a point source of PBDEs to the ship atmosphere, and from there the sample can be contaminated. The use of “bottle samplers” was halted by many research groups due to blank problems. To use these types of samplers requires a very specific expertise in order to get good results. See Lohmann *et al.* (EST 2004) for an assessment of ships as a source of pollutants to the ship atmosphere.

Due to these limitations, most assessments of organic pollution in open waters use the pumping systems, since they allow seawater to be sampled without being in contact with the ship atmosphere, this minimizing the blank problems.

#### **4.2.2 Surface sampling**

This is a very superficial (please excuse the unintended pun) of this issue. The brief text speaks to collecting a sample of water from near the surface but there should be some discussion of contaminants that may be concentrated in surface films. This then raises the issues of sampling that film and avoiding contamination of subsurface samples by that film. Of course this all relates back to the goals of the sampling program.

#### **4.2.3 *In situ* filtration and extraction**

Significant editing of this text is needed.

#### **4.2.4 Centrifuge collection of SPM**

As per 4.1.3.

#### **4.3 Passive sampling devices (PSD)**

This material needs to be reorganised, presumably there will be a section 4.1.4 and a 4.2.5.

This section is so heavily laden with acronyms that it is very difficult to read and understand. In many cases it would help to convert some of the lists to bullet form or tables. This is an emerging technique that needs to be handled carefully. It would be useful to separate established methodologies from developmental work. While PSDs have been shown to be suitable for coastal site, for open sea, their applicability has not been proven. The passive sampling allows an integrated sample, but due to temporal variability, the “average concentrations” does not provide information of peaks in concentrations.

### **5. Storage and pre-treatment of samples**

The present brief text suggests that sampling will always be done from a vessel/ship. Since these guidelines could also apply to shore-based sampling the language could be made more general.

#### **5.1 Trace elements (including MeHg)**

Should there be reference to guidelines for specific metals or groups of metals for further details? For example there needs to be more guidance than “(T)he liquid phase must be conserved with acid.” Also for the filtration process I believe more details are required since there are large differences in the performance of filters of different makes..

#### **5.2 Organic contaminants**

Superficial treatment of an important subject, much can be drawn from some of the existing guideline documents. Again it is important to clarify the issue of filtering or not since the filtration process can have significant impact on the analysis for highly SPM-bound contaminants. The decision can be due to goals of the sampling program and/or operational considerations.

It is very important to filter the samples on the ship. If the dissolved phase is to be analyzed, it is very important to concentrate it on an adsorbent as soon as possible. Generally speaking, it is important to minimize the time that a water sample is on deck due to a modification of the “environmental” concentrations due to bacterial degradation, sorption to container walls, etc.

### **6. Analytical procedures**

Is there any general guidance on analytical procedures or will this section simply refer to information in guidance documents for specific chemicals?

### **7. Analytical quality assurance (QA)**

It is suggested that this section should be called “Quality Assurance (QA)” since it is relevant to more than the analytical process. QA for the analytical process will presumably be addressed in detail in the chemical-specific guideline documents. What is needed here is a detailed discussion of QA for the sampling design, sampling procedures, sample pre-treatment, and storage; i.e. a detailed expansion of the last paragraph in this section. When assessing marine pollution for organics, especially a few

miles from the coast, or at open sea, a very high portion of the work is related to QA. Full sets of samples can be easily discarded due to blank problems. A complete assessment on how to deal with field blanks needs to be included as well as information on laboratory blanks, recoveries, etc.

#### **8. Reporting requirements**

This section should address the issue of data storage and access. It would be appropriate to make recommendations with regard to preferred or required databases. Selection of the database to be used will then dictate the details such as units, sample location, etc. For example, the concentrations in the particulate phase should be given in weight per weight (e.g.  $\text{ng g}^{-1}$ ) and in weight per volume (e.g.  $\text{ng L}^{-1}$ ). The two ways of showing the concentrations are complementary and allow complementary assessments.

The concentrations in the water column depend on various factors. The sea can be stratified, or not, the amount of particles varies depending on the season. In near bottom waters, contaminated waters diffusing from the sediment will enhance the concentrations, etc. Complete information on the sample and environmental setting should be provided. Also complete information on blanks should be provided, including not only the levels, but how they were obtained, etc.

#### **9. References**