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SCICOM STEERING GROUP ON ECOSYSTEM PRESSURES AND IMPACTS

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

2–6 March 2015

Lisbon, Portugal



**ICES**  
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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 (MCWG), co-chaired by Katrin Vorkamp, Denmark, and Koen Parmentier, Belgium, met at the Hydrographic Institute of Portugal in Lisbon, 2–6 March 2015. The meeting was attended by 21 participants representing ten countries, and by additional guests and guest speakers.

Winnie van Vark and Steven Crum of the **QUASIMEME project office** visited MCWG to present and discuss new developments at QUASIMEME. This included feedback on MCWG's comments at the 2014 meeting, discussions of suitable test materials and of sample information disclosed in the protocols. The QUASIMEME reports were discussed in terms of content and lay-out. MCWG continued the organization of a workshop on ocean acidification under QUASIMEME management.

QUASIMEME had recently organized a development exercise on **passive sampling** of hydrophobic organic contaminants, scientifically supported by members of MCWG. Preliminary results showed a relatively low interlaboratory variability of polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs), but higher variability for the performance reference compounds. Results of this exercise were used to update **Background Assessment Concentrations (BACs)** which MCWG 2013 had originally derived for these (and other) compounds dissolved in water.

In its final report, the **Study Group on Ocean Acidification (SGOA)** delivered initial assessments of seabed aragonite saturation states for cold water corals and of OA temporal trends in the North Atlantic. MCWG could continue some of SGOA's work, including aspects of QA/QC as initiated with the QUASIMEME OA workshop.

Updates in the context of the **Water Framework Directive (WFD)** and the **Marine Strategy Framework Directive (MSFD)** included outcomes of a recent meeting of the MSFD Expert Network on Contaminants, on which MCWG provided comments.

Updates on activities in **HELCOM** and **OSPAR** included reorganisation of guideline structures bearing MSFD requirements in mind. As MCWG has contributed to these guidelines and has contacts to HELCOM, OSPAR and the MSFD contaminant network, MCWG could act as a scientific link between these groups.

MCWG members presented examples of recent research, on passive sampling, pollutants in Chinese mitten crabs, an invasive species in the European freshwater environment, and on oil spill identification. A guest presentation was given by Marina Carreiro-Silva (University of the Azores) on ocean acidification. Furthermore, two plenary speakers had been invited: Ricardo J. N. Bettencourt da Silva (University of Lisbon) gave a presentation on the evaluation of measurement uncertainty, while Ana Lillebø (University of Aveiro) presented an EU project on coastal lagoon management.

Input to the ICES Data Centre was given on new parameters as requested. MCWG are currently working on TIMES manuscripts on chlorophyll determination methods and the determination of partition coefficients (water-sampler and sampler-sampler) in the context of passive sampling.

## **1 Opening of the meeting**

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The Marine Chemistry Working Group (MCWG), co-chaired by Katrin Vorkamp, Denmark, and Koen Parmentier, Belgium, met at the Hydrographic Institute (Instituto Hidrográfico - IHPT) in Lisbon, Portugal, 2–6 March 2015. Koen Parmentier opened the meeting on 2 March 2015 at 10 a.m. and welcomed the participants to the 37<sup>th</sup> meeting of MCWG. The participants were welcomed to the Institute by its Technical Director, Commander Freitas Artilheiro. After an informative presentation of IHPT's mission and capabilities he wished everybody a pleasant stay and a fruitful meeting.

The participants introduced themselves and their affiliations and described their interests within the field of marine chemistry. The meeting was attended by 21 participants from 10 countries. The list of participants is given in Annex 1. Two guests (Ricardo Silva and Ana I. Lillebø) attended the meeting for plenary presentations, and two representatives of QUASIMEME (Winnie van Vark and Steven Crum) attended the meeting on 5 March 2015.

## **2 Adoption of the agenda**

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The draft agenda was discussed and adopted as shown in Annex 2. No requests had been received prior to the meeting from OSPAR or other organisations. In continuation of previous work at MCWG 2014, MCWG provided comments to the Expert Network on Contaminants of the Marine Strategy Framework Directive (MSFD) on the ongoing process of the technical revisions, as further described in section 5.2.

The action list from MCWG 2014 was updated. The timetable for the meeting was presented and discussed. No formal subgroups were formed at MCWG 2015 as the agenda items were of broad interest and the group sufficiently small for in depth discussions.

## **3 Report of ICES activities**

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### **3.1 MCWG 2014 recapitulation**

Katrin Vorkamp presented a summary of the main work at MCWG 2014, to refresh participants' memory and to provide links to the tasks at MCWG 2015.

### **3.2 Intersessional activities (2014/2015)**

Katrin Vorkamp reported on activities of relevance to MCWG since the MCWG 2014 meeting.

#### **Advice Drafting Group on Monitoring (ADGMON), 28–30 April 2014**

Katrin Vorkamp participated in the ADGMON meeting to finalise work on updates of three technical annexes, which OSPAR had requested as part of the ICES advice to OSPAR. MCWG 2014 had worked on the following technical annexes to the OSPAR JAMP guidelines:

- Metals in biota
- Metals in sediments
- Organotins in sediments

The draft updates were submitted to ICES with the MCWG 2014 report. The drafts were subsequently reviewed by a Review Group on Monitoring (RGMON). Based on the MCWG draft and the comments of RGMON, ADGMON produces a final draft version, for approval by the Advisory Committee (ACOM).

The RGMON comments are available as annexes to the MCWG 2014 report and they are briefly summarised here. RGMON had three general comments on MCWG's draft technical annexes:

- It should be indicated where the old document was changed, by highlighting the changes or providing old and new document versions.
- References to other technical annexes might be difficult for readers who are not familiar with the OSPAR JAMP guidelines. References to TIMES or other easily accessible documents are preferred.
- MCWG should consider the preparations of new or updated TIMES documents, so these are in line with the updated OSPAR JAMP guidelines.

These comments might be relevant for future OSPAR requests as well. In addition, RGMON commented on the length-age relation of fish presented in the draft technical annex on metals in biota, which RGMON did not consider entirely convincing.

Based on these comments and discussions at ADGMON, some changes were made to the draft documents: The sampling section of the technical annex on metals in biota was amended to be in line with the main document. Furthermore, references were added on method details to the draft annexes on metals in biota and metals in sediment.

ADGMON 2014 consisted of Mark Tasker (UK, Chair), Claus Hagebro (ICES), Jos Brils (The Netherlands), Craig Robinson (UK) and Katrin Vorkamp (Denmark). Besides the technical annexes of the OSPAR JAMP guidelines, ADGMON addressed an OSPAR request for advice on the spatial representation of existing CEMP sediment monitoring station, which WGMS had worked on.

### **Preparations for ASC business meetings**

Katrin Vorkamp did not participate in the Annual Science Conference, but provided a summary of MCWG's work for SCICOM. For this, a list of question was answered on the main Terms of References (ToRs) and focus of the work, the working group's products, the number of people attending the meeting and progress with multiannual ToRs.

Katrin Vorkamp highlighted in her correspondence with SCICOM that MCWG would like ICES be more aware of the expertise with environmental contaminants present within ICES and to communicate this at EU level. So far, focus has been on ICES's expertise in fisheries and related disciplines, but several groups (MCWG, WGMS, and WGBEC) have built strong expertise with contaminant-related science.



### **MCWG's comments to MSFD Expert Network on Contaminants**

As described in the MCWG 2014 report, MCWG 2014 provided comments on D8 and D9 to the MSFD Expert Network on Contaminants (Chair: Georg Hanke). Katrin Vorkamp forwarded the comments to Georg Hanke and received the following response (20 March 2014):

“Thanks for your mail. I am aware of the OSPAR advice document. Please note that the prioritization process for chemical pollutants takes place in the WFD chemicals working group. The additional comments you have sent might still be useful in the upcoming process of MSFD COM DEC review, therefore many thanks! Please note that the D8+9 expert network has been set-up for a specific purpose and is part of the MSFD common implementation strategy, therefore Member States have nominated experts through whom they intend to give input. For the time being I propose therefore to be in direct contact within the network members. Of course we should aim to consider all available expertise and I am convinced we will find ways to do this together with you!

Many thanks and best regards,  
Georg Hanke”

MCWG continued this line of work at MCWG 2015, as further described in section 5.2.

### **ICES Science Plan Implementation Exercise**

The working groups were asked to go over a list of 31 Science Plan priorities and to explain to what extent the working groups address these topics.

Koen Parmentier presented the list and his response to MCWG. MCWG members discussed the list and made some amendments.

MCWG members remarked that they would be interested in the conclusions that were drawn from this exercise (see Action list, Section 8).

## **3.3 Annual Science Conference 2014**

The ICES Annual Science Conference (ASC) 2014 took place in A Coruña (Spain).

The ASC 2015 is going to take place in Copenhagen (Denmark), from 21-25 September 2015. MCWG (in collaboration with WGBEC and SGOA) has proposed the following theme session: “Ocean Acidification: Understanding chemical, biological and biochemical responses in marine ecosystems”. Pamela Walsham of MCWG/SGOA will be one of the convenors, along with Silvana Birchenough (UK) and Klaas Kaag (The Netherlands) from WGBEC. Deadline for abstract submission is 30 April 2015.

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

See section 5.8.

## 4 Plenary presentations

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### 4.1 Ricardo J. N. Bettencourt da Silva

(Centro de Química Estrutural (CQE), Universidade de Lisboa):

#### **Relevance and approaches for the evaluation of measurement uncertainty**

All modern human activities, directly or indirectly, depend on reports of measurements in chemistry, such as the assessment of products compliance with a specification, the monitoring of environmental health or the development of a new drug to fight an emerging disease [1]. The understanding of the studied material system depends both on the quality of measurement results and on the knowledge about that quality. Measurement quality is estimated by measurements uncertainty [2] that, together with the best estimation of the measured quantity, allows an objective and sound interpretation of the analytical data. The interpretation of measurement results without the respective uncertainty can be misleading or does not allow the early detection of system trends or characteristics. Competing hypotheses can be easily assessed if supporting analytical information is compared in a metrologically sound way, instead of forcing the expenditure of many resources needed to detect small differences quantified without respective uncertainty. The generalised collection of comparable and metrologically sound data in research is also important to enhance the cumulative effect of research work produced in different groups and/or occasions.

This communication presents the principles, advantages and disadvantages of the most popular approaches of the evaluation of the measurement uncertainty.

The differential approach (DApp) of the evaluation of the measurement uncertainty [3] is the most adequate strategy to develop detailed models of complex measurement in chemistry needed to extract more information from the studied systems. The principles and same applications examples of the DApp are presented.

#### **References:**

B. King *et al.*, Metrology in Chemistry, BCR-EC, EUR 19074, 1999.

JCGM, International Vocabulary of Metrology, JCGM 200, BIPM, 2012.

R. J. N. B. Silva, M. J. Lino, J. R. Santos, M. F. G. F. C. Camões, *Analyst*, 125, 1459-1464, 2000

***E-mail: rjsilva@fc.ul.pt***

### 4.2 Ana I. Lillebø

(Biology Department & CESAM, University of Aveiro, Campus de Santiago, 3810-193 Aveiro Portugal):

#### **Science-Policy-Stakeholder interface towards a pan-European management of coastal lagoons: Lessons learnt from the FP7 LAGOONS project**

LAGOONS - 'Integrated Water Resources and Coastal Zone Management in European Lagoons in the Context of Climate Change' - an EU funded FP7 research project, was developed by a multidisciplinary consortium consisted of nine partner institutes from eight different

countries (Portugal, Norway, Poland, Russia, Ukraine, United Kingdom, Germany and Spain). The main objective of LAGOONS was to develop science-based strategies and a decision support framework for the integrated management of coastal lagoons and its drainage area and, in this context, to enhance connectivity between research and policy-making. To achieve the proposed objectives, the multidisciplinary scientific knowledge in the project group was combined and integrated with the knowledge and views of local stakeholders, using a three steps participatory approach. With this innovative approach, which combined integrate deliberative and analytical dimensions (modelling tools) we developed integrated scenarios of future possible economic development and environmental impacts in the following European coastal lagoons: Ria de Aveiro Lagoon in Atlantic Ocean (Portugal); Mar Menor in the Mediterranean Sea (Spain); Vistula Lagoon in the Baltic Sea (Poland/Russia); Tylygulskiy Lagoon in Black Sea (Ukraine). These scenarios were presented and discussed with stakeholders, giving rise to management recommendations for each case study lagoon. Using a bottom-up approach LAGOONS also provided a set of policy guidelines and proposes initiatives concerning management implementation at pan-European level. More detailed information is available at <http://lagoons.web.ua.pt/>.

## **5 Main agenda**

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### **5.1 Quality assurance of marine chemistry**

#### **5.1.1 Report and discuss new developments in QUASIMEME**

Winnie van Vark and Steven Crum (QUASIMEME Project Office) attended MCWG 2015 on 5 March 2015 and presented an update of activities, including new developments since MCWG 2014. Winnie van Vark introduced herself as the new manager of QUASIMEME following the retirement of Bram Eijgenraam and provided an update on other staffing changes. These changes indicate an increased effort on database maintenance and development, although not resulting in an overall increase of staff effort within QUASIMEME.

#### **Points raised at MCWG2014**

Steven Crum provided a follow up on comments and recommendations made at MCWG 2014.

QUASIMEME were unclear on the level of sample information required in protocols sent out with materials. Protocols currently give information that was agreed with MCWG (i.e. fish species if not used before; if used before then fat content provided within three bracketed ranges; mention if freshwater species are used). Although this information has been given in protocols since 2013, not all participants seem to locate it. As a practical means to help participants, this information has also been provided on material labels since 2014. MCWG commented on inaccuracy issues in protocols which seem to be resulting from 'cut & paste' errors. Additionally, the terminology used for biota materials is not always clear (e.g. tissue vs muscle vs homogenate) and QUASIMEME will look into providing more accurate information without compromising the identity of the material. With regards to determinant concentrations being occasionally outside (higher) the range of likely concentrations provided in the protocol, MCWG advised that these should ideal-

ly be checked before the material is used in the proficiency test, but also understands that costs for doing so can be prohibitive.

Goole harbour (UK) sediment with unusually high levels of BDE-209 and  $\gamma$ -HBCD originally distributed in round 73 were removed from stocks used for brominated flame retardants analysis. QUASIMEME queried whether this material could be used for PAHs rounds, but MCWG 2015 recommended for this particular material to be removed altogether as it constitutes a risk of laboratory contamination with these particular brominated flame retardants.

Steven Crum also reported that the ability of submitting additional metals and PAHs with each round was not taken up by sufficient participants (e.g. only three additional metals reported) and questioned whether there was still a requirement for this. Since this does not represent a particular effort from QUASIMEME, MCWG wishes for this capability to be kept, with the understanding that robust statistical analysis can only be achieved with a minimal number of data submitted.

With regards to progress with a Workshop on Ocean Acidification parameters suggested at MCWG 2013, the event is planned to be held at the National Oceanographic Centre (NOC) in Southampton (UK) in May 2015 and the keynote speaker, Prof. Andrew Dickson (Marine Physical Laboratory, Scripps Institution of Oceanography, University of California, San Diego) is booked.

#### **Other new developments at QUASIMEME and points of discussion**

An update on materials offered for accreditation was provided. There should now be sufficient storage stability data for BT11 (Lipophilic shellfish toxins) and BT12 (PSP shellfish toxins) to be offered for accreditation in 2015, and if the homogeneity of AQ3 (Metals in seawater) and AQ4 (Mercury in seawater) materials can be demonstrated, these will also be submitted for accreditation.

The BE1 imposex/intersex exercise planned in 2014 was cancelled due to the loss of snails which were frozen during transit from the supplier. This exercise will be offered again in 2015. There is also growing interest for the BT3 exercise (Dioxins in biota), but there are still too few participants signing up (at least eight laboratories are required, currently only five subscriptions).

The new QUASIMEME participants website (<http://www.participants.wepal.nl/>) was introduced in 2014, along with a new report format which resulted in several complaints to QUASIMEME. The new report format was however a necessary change, primarily so as to comply with the requirement of ISO 17043. Also, the superseded report formats were published from a QUASIMEME database that was running on an old platform that needed replacing. The superseded reports also had to be produced manually, a time consuming and potentially error prone exercise.

Complaints to the new reports included:

- Sample identification is not unique anymore and old format compatible with OSPAR requirements (e.g. QTM123BT) will be re-introduced.
- z-score are separated from data-assessments which makes comparisons difficult. The z-score section will be removed in 2015.

- There are currently no figures available: this will be re-introduced in round 1 of 2015. The QUASIMEME Scientific Advisory Board (SAB) proposes that the figures should include a z-score histogram, Cofino histogram and results ranked overviews, but that Kilt plot should be removed.
- No laboratory specific reports currently available: laboratory specific reports will be re-introduced within 2 months, and also for 2014 reports.
- Consistent/inconsistent indication currently not provided any more, and this needs to be developed.
- .asc files required for ICES submissions need to be re-introduced.

Reports from the old SharePoint are currently not available online because of complex technical issues, but these are archived and can be issued on request to the QUASIMEME Project Office (QPO). At the suggestion of MCWG 2015, QUASIMEME will look into uploading individual laboratory results for the last 5 years.

The nature of tissues used for biota materials was also discussed, and MCWG 2015 was happy with current practice for BT1 (metals) and BT8 (organotins) materials. For BT2 (organochlorines) and BT9 (BFRs), MCWG 2015 commented that it would be useful to have regular (i.e. once per year) liver materials to reflect OSPAR requirements. QUASIMEME might also need to consider whole fish homogenate to address incoming MSFD requirements.

QUASIMEME also updated MCWG 2015 on new developments and information issued from the QUASIMEME SAB. This included the addition of parameters to existing materials (i.e. particulate nitrogen to MS2, chlorinated organics in sediment, and MS3, polycyclic aromatic hydrocarbons in sediments, PFOS added to BT10 and MS8 exercise on PFAS in biota and sediment, respectively). High background levels for copper in AQ3 materials (Metals in seawater) are being investigated and are probably linked to contamination originating from sampling pumps.

For AQ1 (Nutrients in seawater) and AQ2 (Nutrients in estuarine and low salinity open water) the proportional error for blank samples will be lowered to 6%. For AQ2, the constant error for salinity will be changed from 0.001 to 0.01, while the proportional error will be left at 0.1% as laboratories need to be able to measure the salinity very accurately for oceanographic purposes.

Additional practical information included that QUASIMEME subscription fees were kept unchanged in 2015, for the third year running (since 2013). From round 2014.2 all biota and sediment samples are barcode scanned before being sent out so as to prevent mistakes with sample identity.

QUASIMEME are working on membership rules in the form of a contract to be signed by participants. In particular, no data from the reports may be published. The laboratory's own results can be published, but not results from other laboratories.

Steven Crum further consulted MCWG 2015 with regards to potential future developments:

- QUASIMEME proposed that for biota, cultivated mussels are exposed to all determinants offered in the brochure. MCWG commented that it is interested in updates on progress with this approach.

- For sediments, QUASIMEME suggested for different sediments to be mixed so as to achieve the concentrations specified in the protocol. MCWG did not see any particular issue with this approach, and suggested to have a test round.
- MCWG 2015 was consulted on whether there was an interest in setting up a development exercise for pharmaceuticals. MCWG felt that it was too early to support such a development as more investigations in terms of determinants and matrices are required.
- MCWG2015 was informed that the possibility of running a workshop on Microplastics under the auspices of QUASIMEME is being looked into by Jacob de Boer and Joop Harmsen. MCWG 2015 indicated that a similar workshop was already planned to be held in Ghent in January 2015, with 25 participants registered to date.
- QUASIMEME would like to mark its 25 years anniversary in 2017, and consulted MCWG 2015 on any particular wishes or ideas of format. Coupling this event with MCWG17 might be of interest.

Finally, following the Chlorophyll and Nutrients workshop in 2014, a publication is in preparation and data on HPLC methodology was also presented at a workshop at DHI in Denmark. Wim Cofino also participated in a Eurachem workshop in Berlin in 2014 to present the Cofino statics, and these were deemed to be the most robust.

MCWG appreciates the analysis of the wealth of data available to QUASIMEME to be explored, but understands that it is a lot of work. It might be scope for members of MCWG to contribute to some data analysis and potential publications.

MCWG 2015 stressed the importance of strong links with QUASIMEME and welcomed its continued representation by QUASIMEME Project Office staff at MCWG meetings.

#### **5.1.2 Provide information on other proficiency testing schemes with relevance to MCWG**

A proficiency testing scheme for dioxins in foods run in Norway usually includes fish. This might be of interest to MCWG members and QUASIMEME, and additional information has been provided by Katrin Vorkamp via the ICES MCWG 2015 SharePoint (Background documents/QA-QC).

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

### **5.2.1 Review and discuss developments of WFD, in particular regarding new priority (hazardous) substances and associated EQS values**

Anja Duffek gave a short overview of recent WFD and MSFD implementation processes. The MSFD expert network on contaminants had a second meeting in order to further support the technical review of the Commission Decision 2010/477/EU concerning MSFD criteria for assessing Good Environmental Status (GES).

The review of the Commission Decision aims to define more precisely criteria for GES, including quantifiable boundaries for GES criteria whenever possible, methodological standards and specifications and standardised methods for monitoring and assessment.

The new GES Decision should be simpler, clearer by introducing minimum requirements, self-explanatory and coherent with other EU legislation. The review includes the analysis of all information received in order to fill the Part II of the template. In order to do this, a questionnaire has been circulated among the experts of the MSFD network on contaminants (Descriptor 8 and 9). The template structure is common for all Descriptors to ensure coherence in the review exercise and gives instructions to the review of each descriptor, as per the structure of the Decision.

A compilation of all answers (HELCOM, NO, NL, ES, DE, FR, IT, FI, UK, HR) was discussed during the meeting in order to find a common understanding and develop recommendations. The outcome of the meeting was presented by Anja Duffek.

The final analysis will be prepared by JRC and incorporated into the templates until 13 March 2015, followed by another round of comments before the preparation of the final review template, which is due by 20 March 2015.

In order to support the whole process MCWG will send comments on specific issues addressed in the draft outcome. The comments were drafted at the meeting and discussed in plenary. The final version is included in Annex 5. It was sent to Georg Hanke (chair of the MSFD Expert Network on Contaminants on 4 March 2015).

To support the implementation of the WFD the first Watch List has been voted by the Article 21 Committee – for which union-wide monitoring data shall be gathered for the purpose of supporting future prioritisation exercises. The list includes an indication of the monitoring matrices and possible methods of analysis not entailing excessive costs (incl. maximum acceptable method detection limits). Monitoring starts in September 2015.

Additional guidance for sampling and analysis is in preparation (first draft in March) in order to clarify the technical points taking into account the use and properties of Watch List Substances.

The progress on the recent review of the Priority Substance list has been presented. Identification of substances for prioritisation as well as the derivation of draft EQS will be finished in spring 2016 for the further consultation process. Rapporteur, co-rapporteur for EQS Dossiers are welcome.

The EQS-TGD is under revision by updating technical points e.g. the CRED approach regarding criteria for reporting and evaluating ecotoxicity or the method for deriving biota EQS.

### **5.2.2 Calculate and discuss conversions of EQS<sub>biota</sub> values from fish to mussels**

This topic was raised by Evin Mc Govern in 2014 and briefly discussed again at MCWG 2015. MCWG noted initial discussions had taken place in OSPAR MIME with a view to considering how EQS can be used in OSPAR CEMP assessments for contaminants in biota, aligning to WFD and MSFD. The new guidance document 32 on biota EQS (EC, 2014) states that biota EQS should reflect the trophic level where concentrations peak, such that the predator of species of that level is exposed to the highest food concentrations. In general, this is considered to be fish of trophic level ~4 (TL4), although not for PAH where bivalve molluscs are more appropriate. Moreover, TLs are not fixed for species but may vary across different ecosystems. The implication is that if biota of a different TL is moni-

tored some adjustment is required to assess compliance with the EQS, and the guidance recommends measuring stable isotopes to determine the TL of the sampled biota. Guidance on TL determination and adjustment is given in annex 9 of the guidance document. There are two potential approaches for such adjustments:

- Directive 2013/39 recognizes that alternative biota taxons can be monitored in so far as the EQS applied provides an equivalent level of protection. Therefore, one option is to derive an alternative EQS for mussels to take account of the different trophic level (Mussels are TL2 by definition).

$$EQS_{\text{mussel}} = EQS / TMF^{(4-2)} \quad [\text{Trophic Magnification Factor } (TL_{\text{biotaeqs}} - TL_{\text{mussel}})]$$

- Alternatively, the measured trophic level for the sampled biota should be used to make an adjustment of measured concentrations to TL4.

$$Conc_{\text{CTL adj}} = Conc_{\text{mease}} * TMF^{(4 - TL_{\text{sampled}})}$$

However, both conversion approaches present challenges due to the high uncertainties associated with determining TLs and TMFs

Ireland (and other countries) have great interest in keeping mussels as a key monitoring organism, as they are sedentary, sampling and analysis is time- and cost efficient compared to fish, and the variance is relatively low, and there is an aim to maintain current time series. Moreover, the TL is understood to be 2. Even if fish are sampled, it is likely that representative samples of TL~4 could be difficult to acquire and some determination of TL and TL-adjustment would be required in any case. Therefore, further consideration of how biota EQS can be consistently applied in a pragmatic way and consideration of the uncertainties in TL adjustment is required. The topic will be revisited during MCWG 2016 where any developments in other fora (OSPAR, EC) or experiences in member countries can be reviewed and, if deemed appropriate, advice could be developed by MCWG.

#### References:

EC (2014) Common Implementation Strategy for the Water Framework Directive (2000/60/EC) Guidance Document No. 32 on Biota Monitoring (the Implementation of EQS<sub>biota</sub>) under the Water Framework Directive. Technical Report -2014-083. European Commission, ISBN 978-92-79-44634-4 doi: 10.2779/833200

### 5.2.3 Review and discuss developments in MSFD, in particular regarding the monitoring of descriptors 5, 7, 8 and 9

See section 5.2.1 and Annex 5.



### **5.3 Developments at OSPAR and HELCOM**

#### **5.3.1 Discuss activities at OSPAR and HELCOM with direct relevance to MCWG and consider input from MCWG**

HELCOM is reorganizing and restructuring its guidelines. Two manuals are the basis for this: A first manual focusing on contaminants and their effects, and a second manual, mainly on topics included within other MSFD descriptors such as e.g. biodiversity measures.

OSPAR MIME discussed how to structure its guidelines. Michael Haarich proposed a structure based on a general guideline and strategy, which can easily be interpreted by policy makers, and more specific parts on contaminants, added separately. Michael Haarich tries to put forward the same guidelines within HELCOM and OSPAR. He compiled a table (Nov. 2014), giving an overview of the different guidelines which are present at HELCOM, OSPAR and ICES and the guidelines pending or in revision (Annex 6).

No more interaction with HELCOM is expected in the near future. It is stated that MCWG can be a scientific link between OSPAR and HELCOM.

At OSPAR, the revision of technical annexes done by MCWG in 2014, i.e. on metal determination in sediments, metal determination in biota and mono, di- en tributyltin in sediment, is now under review at OSPAR (see section 3.1). There were no major changes made to the main texts.

Scientists from France had contacted the co-chairs prior to MCWG 2015 with the requests to discuss OSPAR-related questions at MCWG 2015. Specifically, the questions were about the sampling period for biota as recommended in the JAMP guidelines which France proposed to reconsider. France samples mussels outside the recommended period. MCWG concluded that more information would be needed to give advice on this topic. Currently, MCWG has not the scientific basis to assess whether the recommended period can be extended or neglected. MCWG also pointed out that there was a formal way of requesting advice through the OSPAR-ICES channels.

In the discussion, it was suggested that working groups with more biological expertise should provide recommendations on sampling periods since they have information on spawning periods and other essential biological information. There is a table available, but it was unclear whether it is still up to date because of spawning periods can be expected to change due to climate changes. Moreover, sampling periods may be country or region dependent since climate conditions may be different. From a chemical point of view, it is important to have comparable conditions from year to year.

### **5.4 Present projects of relevance to MCWG activities, including information on emerging contaminants**

#### **5.4.1 Stevan van Leeuwen: Dioxins, PCBs and heavy metals in Chinese mitten crabs from Dutch rivers and lakes**

Chinese mitten crab is an invasive species in many European rivers and lakes. Data from the UK indicated high levels of dioxins and PCBs, in particular in the brown meat of the body. This was confirmed by studies in the Netherlands, showing average levels of diox-

ins and PCBs in the meat of 43 pg TEQ/g ww in crabs caught in the large rivers. Levels in crab of lakes in the Northern part of the Netherlands were on average 3.7-fold lower. Analysis of 107 individual crabs showed that data from a single location was quite variable. There was no clear relation of the dioxins and PCBs vs the fat content and neither with the age (size) of the crab. This is different from eel caught at the same locations where such relationships can be found.

Consumption of crabs from polluted areas results in a relatively high dose of dioxins and dl-PCBs and could increase the intake above the tolerable weekly intake (TWI). However, in general, consumption of these crabs is low, even in the Asian sub-population in the Netherlands. Nevertheless consumers with a high background exposure may face an additional risk due to mitten crab consumption. Cadmium and lead levels were higher in crabs from contaminated areas, but for mercury and arsenic there was no clear difference. Levels of cadmium were somewhat higher in the brown meat compared to the white meat, whereas for mercury it was the other way around.

#### 5.4.2 Lutz Ahrens: Passive samplers for pesticides in water

Lutz Ahrens presented results on calibration and field evaluation of five passive samplers for monitoring pesticides in water. The objectives of this study were *i)* to characterize five passive sampler types in a laboratory uptake study, *ii)* to apply three passive sampler types in two Swedish river systems, and *iii)* to compare passive sampling and active sampling. In this study, the passive samplers were characterized for 124 individual pesticides including 18 priority substances of the EU Water Framework Directive (WFD). The passive sampler adsorbents included *i)* POCIS A: Pharmaceutical-POCIS, polar organic chemical integrative sampler (Oasis hydrophilic-lipophilic balance (HLB) sorbent), *ii)* POCIS B: Pesticide-POCIS, triphasic sorbent admixture (Isolute ENV+ and Ambersorb 1500) enclosed in a polyethersulphone membrane, *iii)* Chemcatcher® SDB-RPS: Styrene divinyl benzene Empore™ disk, *iv)* Chemcatcher® C18: Empore™ disk, and *v)* silicone rubber (SR). Sampling rates ( $R_s$ ) and passive sampler-water partition coefficients ( $K_{pw}$ ) were calculated for individual pesticides. SR had a better performance for hydrophobic high  $K_{ow}$  pesticides, while POCIS-A, POCIS-B, Chemcatcher® SDB-RPS were more suitable for low  $K_{ow}$  pesticides. The results showed a good agreement between active and passive sampling. 52 pesticides were detected using active sampling, while 69, 58, and 32 using SR, POCIS-A, and Chemcatcher® C18. 38 pesticides were detected by the passive samplers but not by active sampling. Overall, passive sampling is a promising tool for monitoring of pesticides in water with minimal infrastructure and low contaminant concentrations.

#### References:

- Ahrens, L.; Daneshvar, A.; Lau, A.E.; Kreuger, J. (2015) Characterization of five passive sampling devices for monitoring of pesticides in water. *J. Chromatogr. A* 1405, 1–11.
- L. Ahrens, A. Daneshvar, A.E. Lau, J. Kreuger, Passive sampling as a new monitoring tool for pesticides in water. In preparation.

#### 5.4.3 Catarina Rocha: Oil Spill Identification: IH Methodology

One of the Portuguese Hydrographic Institute's (IHPT) main missions is to investigate episodes of marine pollution caused by hydrocarbons, particularly by oil spills. In this sense, IHPT supports the National Maritime Authority in the resolution of offences aroused by this type of incidents. Due to the large number of marine pollution processes and sample types that arrives to IHPT for analysis, its methodology for Oil Spill Identification (based on the NORDTEST method (NORDTEST, 1991; Faksness *et al.*, 2002)) was recently optimized. While the NORDTEST method is more suited to the analysis of crudes and heavy oil products it has some limitations when applied to the characterization of light and medium derivatives. In these oil products the tetra and pentacyclic biomarkers proposed for analysis by the NORDTEST method are absent because they remain in the heavier fractions during the refining processes due to their high boiling point. In order to fill this gap, IHPT optimized the methodology to make it more robust and increase the legal defensibility of the technical assessment when applied to the analysis of refined products. The changes introduced were: the analysis of bicyclic biomarkers (sesquiterpanes and adamantanes), the elaboration of distribution profiles of biomarkers and the determination of weathering ratios (Wang & Fingas, 1997) that involve compounds with different susceptibilities to weathering effects and diagnostic ratios of dimethylphenanthrenes (Biscaya, 1997), sesquiterpanes (Wang *et al.*, 2005) and adamantanes (Wang *et al.*, 2006). During last year, studies of analysis of sesquiterpanes and adamantanes were conducted in different oil products (Rocha *et al.*, 2014) to prove the discriminatory power of these compounds in source identification.

In this work, some of the results obtained in the referred studies are presented and it is demonstrated, through the presentation of a case study, that the optimized IHPT method improves its applicability when compared to a previous assessment of similarity between the same samples, the weathering evaluation, the flexibility in the selection of diagnostic ratios submitted to correlation analysis and defensibility level.

#### References:

- Biscaya, J.L. (1997). Parâmetros Quimiométricos para Identificação/ Classificação de Derrames de Produtos Petrolíferos. Lisbon: Universidade Nova de Lisboa, PhD Thesis, 310 p.
- Faksness, L.G.; Weiss, H.M.; Daling, P.S. (2002). Revision of the Nordtest Methodology for Oil Spill Identification. Norway: SINTEF Applied Chemistry, Nordtest Technical Report no. 498, 110 p.
- NORDTEST. (1991). NORDTEST Method: Oil Spill Identification. Finland: NORDTEST, (NT CHEM 001), 24 p.
- Rocha, A.C; Borges, C.; Cruz, I. (2014). Aplicação da Análise de Sesquiterpanos e Diamantóides em Processos Forenses de Poluição do Meio Marinho. Acta das 3as Jornadas de Engenharia Hidrográfica, 24-26 June 2014, Lisbon, 259-262.
- Wang, Z. & Fingas, M.. (1997). Developments in the analysis of petroleum hydrocarbons in oils, petroleum products and oil-spill-related environmental samples by gas chromatography. J. Chromatogr. A, 774:1-2, 51-78.
- Wang, Z.; Yang, C.; Fingas, M.; Hollebone, B.; Peng, X.; Hassen, A.B.; Christensen, J.H.. (2005). Characterization, Weathering and Application of Sesquiterpanes to Source Identification of Spilled Lighter Petroleum Products. Environ. Sci. Technol. 39, 8700-8707.

Wang, Z.; Yang, C.; Holleborne, B.; Fingas, M.. (2006). Forensic Fingerprinting of Diamondoids for Correlation and Differentiation of Spilled Oil and Petroleum Products. *Environ. Sci. Technol.* 40, 5636-5646.

## 5.5 Marine litter and its role as a potential source of contaminants

### 5.5.1 Report on new information on marine litter and its role as a potential source of contaminants, with particular focus on field studies demonstrating elevated contaminant levels associated with plastics

Bavo De Witte gave an update on two marine litter research projects at ILVO related to micro plastics and marine litter, Micro (interreg) and Clean Sea (FP7). Within these projects, the focus of ILVO is on reporting of marine litter found in fish tracks, in the study of the bacterial load on plastic, the chemical load on plastic and the exposure of marine species to chemical contaminants loaded on litter.

A chemical screening was performed on several types of marine litter and beach pellets, applying an extraction with hexane/dichloromethane, silica fractionation and GC-MS analysis. More than 200 organic compounds or groups of organic compounds were identified, mostly related to the plastic itself. This suggests that plastic may be a potential source of chemical contaminants. Remarkably, some sunscreen agents and cosmetics were found only on beach pellets.

Determination of PCBs and PAHs on beach pellets revealed a high diversity of chemical load on beach pellets. Pellet watch guidelines were followed, reporting the median of 5 independent analysis. Median concentrations on 5 independent locations varied from 31.4 ng/g to 225.9 ng/g for the ICES 7 PCBs and from 1075.7 to 3006.8 ng/g for PAHs. Weathered pellets were clearly more polluted than black beach pellets.

PCBs were loaded on polyethylene and polystyrene pellets and fed to Norway Lobster. It was found that the PCBs stayed tightly bound to polystyrene, not enhancing the concentration of PCB within the lobster. For polyethylene, however, a clear increase of PCB concentrations within the lobsters was found.

Miguel Caetano gave a presentation entitled 'Microplastics and POPs a double threat to marine life'. This study involved screening beach pellets for POPs. A range of sites were studied with samples collected from industrial and remote sites. Samples were collected monthly for an entire year. Plastic debris and pellets were separated into classes according to plastic type and colour. POPs were extracted using hexane/acetone. There was a wide range of PAH concentrations (0.62 ng/g to 80 µg/g) detected in the pellets, with benzo[*e*]pyrene being the dominant PAH in all samples. Furthermore, the variability in the PAH concentrations in replicate samples from sites was high. Highest PAH concentrations were found in pellets collected close to a petrochemical complex. Seasonal effects were observed in the PAH concentrations. Four types of pellets were analysed with the highest concentrations being found in the coloured and black pellets. The most abundant PCB varied with location, there were no seasonal effects nor did the composition of the plastic influenced the PCB concentration. In addition, a bioaccumulation experiment was undertaken using mussels and a range of pellet sizes doped with PAHs. After 28 days only a minor transfer of PAHs to mussels was observed.

Discussions following the two presentations highlighted that there was efficient transfer of POPs from the water to the mussels but low transfer from the pellets to the mussels, only at the highest concentrations was an increase in PAH concentrations observed in the mussels, however these high concentrations may not be representative of natural conditions. The ILVO bioaccumulation study spiked the plastic pellets by simply adding POP spiking solution in hexane to the pellets and allowing the hexane to evaporate. Approximately 90–100% of the POPs were taken up by the pellets. Miguel Caetano used a range of spikes, with a 45–55% uptake in the pellets. Blanks were also analysed in both studies, PCBs were not detected in the blanks but several PAHs were detected.

Publications in relation to contaminants in microplastics has increased considerably over the last few years, however, there is still little evidence of microplastics being a significant vector for contaminants to marine biota. Publications on contaminants in marine litter tend not to include information on quality assurance, such as details of procedural blanks and limits of detection, therefore there is some doubt about the validity of some of this published data. There is currently no ICES working group for marine litter and microplastics, only the OSPAR Intersessional Correspondence Group on Marine Litter (ICG-ML). Although it is unclear if contaminants in microplastics are a major concern this is a topic that should continue to be dealt with by ICES MCWG.

#### **5.5.2 Present information on contaminant desorption from plastic in the digestive system after plastic uptake by biota, if available**

This agenda point was covered by the presentations described in section 5.5.1.

### **5.6 ICES Data Centre: Provide expert knowledge and guidance to the ICES Data Centre, as may be requested**

#### **New parameters**

Lynda Webster had been contacted by Marilynn Sørensen prior to the meeting with the request to check new parameters that had been entered into the database against existing parameter groups of the environmental database DOME.

MCWG reviewed the new parameters and classified them according to the existing parameter groups. The results are shown in Annex 7. Lynda Webster forwarded the list to Marilynn Sørensen shortly after the meeting.

#### **Marine litter**

Marilynn Sørensen provided the following update on inclusion of litter data in the ICES database: “Unfortunately, we did not receive any test data for microplastics. We did however receive a test litter dataset from a Netherlands trawl survey. This gave rise to a number of questions and conflicts and we therefore sent the draft litter format to OSPAR’s Marine Litter group, ICG-ML. ICG-ML suggestions caused a reworking of the reporting format and the database model for trawl collected data. This means that there will be two formats/databases for litter. Environment Reporting format version 3.2 (ERF3.2) format will include litter (mostly microplastics) and the data will enter DOME. The trawl collected litter will use a new standard format partially based on the current DATRAS format and partially based on ERF3.2. The plan is that the trawl collected litter

will go into a newly created database. Both will use the same vocabularies and both will cover all litter types so a combined litter export can be made. We expect the format to be released in a few months.”

## **5.7 Report on activities in other expert groups on the interface to MCWG**

### **5.7.1 Working Group on Marine Sediments in Relation to Pollution (WGMS)**

Katrin Vorkamp had reviewed the WGMS 2014 report and presented some key issues to MCWG. As the WGMS 2014 meeting was held concurrently with the MCWG 2014 meeting, MCWG felt quite up-to-date with the current WGMS work. MCWG welcomed the close contact with WGMS and expressed a wish of continuing close collaboration with WGMS.

At their 2014 meeting, WGMS had worked on three requests from OSPAR. One of these was the update of technical annexes of the OSPAR JAMP guidelines, which was done in collaboration with MCWG, see section 3.2 on the work of the Advice Drafting Group on Monitoring (AGDMON).

Passive sampling is another shared interest of MCWG and WGMS. Specifically, WGMS is going to continue work on a guideline for passive sampling of hydrophobic compounds in sediments, for which a first draft exists. MCWG would be interested in contributing to this work.

In addition to the recommendations that MCWG directed at QUASIMEME in 2014, WGMS had two recommendations to QUASIMEME: WGMS suggested that QUASIMEME determined the real concentrations in the samples to avoid many concentrations below detection limits. WGMS also suggested to build on QUASIMEME's development exercise on passive sampling to include diffuse gradient in thin films (DGT) formats for sampling metals.

Besides passive sampling and potential requests for advice, the WGMS ToRs 2015–2017 include the following topics: Spatial distribution patterns of contaminants in sediments; Deep sea sediment monitoring; Impacts of renewable energy devices; emerging issues (microplastics etc.).

### **5.7.2 Working Group on Biological Effects of Contaminants (WGBEC)**

In 2014, the WGBEC meeting was held concurrently with the meetings of MCWG (and WGMS). Several areas were of interest to both MCWG and WGBEC, such as questions of marine litter (in particular in relation to contaminant transport), ocean acidification and passive sampling of contaminants in water.

MCWG is interested in collaborating with WGBEC in these and other areas of common interest. As specified in section 5.11, MCWG has raised some toxicity-related questions, such as the mixture toxicity of contaminants and the development of environmental assessment criteria based on freely dissolved concentrations of organic contaminants. MCWG would welcome input from and scientific exchange with WGBEC on these questions.

With regard to ocean acidification, WGBEC specified in their 2014 report that a literature review would be prepared on methods suitable for monitoring ocean acidification. This

report would be of great interest to MCWG. Further work within the field of ocean acidification will include recommendations on suitable species and endpoints for monitoring and combined effects of climate change variables, as described in the WGBEC 2014 report. Given MCWG's interest in ocean acidification and its close link to SGOA, MCWG would also be interested in receiving information about progress with these questions.

#### **5.7.3 Joint EIFAAC/ICES/GFCM Working Group on Eels (WGEEL)**

MCWG had no representative at the WGEEL 2014 meeting.

MCWG still sees an interface with WGEEL in terms of bioaccumulation of organic contaminants and will be interested in collaborations on specific issues and questions.

At MCWG 2014, Katrin Vorkamp had informed about plans of a WGEEL/WGBEC workshop on the topic "Are contaminants in eels contributing to their decline?", to be chaired by Claude Belpaire and John Thain. This workshop will take place in January 2016. MCWG representation would be welcomed as discussions at and outcomes of this workshop will be relevant for MCWG as well.

#### **5.7.4 Working Group on Oceanic Hydrography (WGOH)**

It was discussed at MCWG 2014 that it would be interesting for MCWG to establish contacts to WGOH. Caroline Kivimae was going to inform MCWG 2015 about relevant activities in WGOH, but as Caroline Kivimae was unable to attend MCWG 2015, no information could be provided.

#### **5.7.5 Working Group on Phytoplankton and Microbial Ecology (WGPME)**

Following discussions at MCWG 2014 on chlorophyll measurements, MCWG members proposed establishing contacts to WGPME with regard to overlapping interests and activities. Solveig Olafsdottir had kindly agreed to take action, but as she was unable to attend MCWG 2015, the contact has not been established as yet.

### **5.8 Ocean acidification**

#### **5.8.1 Report from the OSPAR/ICES Study Group on Ocean Acidification and address potential recommendations from this group to MCWG**

Evin McGovern, co-chair of the OSPAR/ICES Study Group on Ocean Acidification (SGOA) presented the Final Report to OSPAR from the SGOA group. SGOA was formed to address eight terms of (ToRs) provided by OSPAR which broadly aimed to support development of an OSPAR Ocean Acidification (OA) monitoring and assessment programme. MCWG noted that ocean acidification chemical parameters are currently within the voluntary OSPAR pre-CEMP. SGOA met three times between December 2012 and October 2014 and the final report to OSPAR is a consolidated output of these three meetings. During this time SGOA had collaborated closely with MCWG, with some overlap in membership, and MCWG had contributed significantly to a number for SGOA products.

The SGOA report presents a summary of national OA-monitoring activities in the North Atlantic and also various national and international research and coordination initiatives.

SGOA noted considerable monitoring/research activities are taking place with scope for more coordination.

It was noted that technical guidelines for monitoring chemical aspects of OA as developed by MCWG/SGOA were adopted by OSPAR 2014. SGOA also drafted a high-level OA-monitoring strategy for OSPAR that sets out monitoring goals, core and extended suite of parameters, quality assurance requirements and data reporting considerations, and an overall assessment framework. This will be considered by OSPAR in 2015. SGOA has considered potential OA-specific biological effect indicators and recognized that suitable species and metrics cannot be recommended for the broad OSPAR area at this stage. Nonetheless, SGOA has recommended archiving specimens of thecosomate pteropods, such as *Limacina helicina* in the Arctic for retrospective analysis once metrics are developed.

A key discussion point at MCWG related to the need for enhanced QA/QC supports to progress OSPAR monitoring of carbonate system parameters. The planned QA/QC workshop (see section 5.8.2) is seen as key to this. It was also noted that ICES reporting requirements were specified by SGOA/MCWG and countries may now report OSPAR OA monitoring to the ICES DOME database using ERF 3.2 formats.

Two assessment products were delivered by SGOA. Firstly, an assessment of modelled current and projected (2100) seabed aragonite saturation states for cold water waters (CWCs) areas in the OSPAR region was presented. This showed that for IPCC RCP8.5 emission pathways, CWC habitats would widely occur in undersaturated waters with risk of dissolution of reef structures (SGOA report Annex 6).

SGOA also reviewed reported information on OA temporal trends in the North Atlantic (SGOA report Annex 7). Various approaches are used to assess trends, e.g. high frequency monitoring stations (Bermuda, Iceland), regular and irregular ship-based sampling campaigns, widespread pCO<sub>2</sub> data synthesis based assessments. Though it is difficult to compare different approaches a pH reduction of ca. 0.02 pH units per decade for open sea surface waters is evident. Acidification of deeper waters is also evident although there are fewer reported information on trends in deep water.

SGOA has now completed its work and there is no decision yet as to whether an OA working group will be continued within ICES. However, a number of key activities were identified where MCWG is expected to have a significant input.

- Ongoing activities to support development of enhanced QA/QC supports for monitoring including development of CRMs, proficiency testing and preservation techniques (noting problems experienced in some countries due to restrictions on availability of mercuric chloride). This should be taken up by MCWG 2016 based on the output of the OA QA/QC workshop.
- Support to ICES data centre concerning reporting OA data (for example reporting high volume sensor data).
- Consider developments in measurement techniques for monitoring the carbonate system and related parameters.
- Review new information pertaining to chemical aspects of ocean acidification in the ICES area.



### **5.8.2 Report on QUASIMEME workshop on ocean acidification and discuss implications of workshop results for OA monitoring**

The planned workshop was unable to progress in 2014 and is now scheduled to take place 19–21 May 2015 at the National Oceanography Centre (NOC) Southampton. Andrew Dickson will attend as an invited speaker. Additional invited speakers have been identified and approached. Sue Hartman (NOC) WebEx'd into the meeting during the OA discussions and confirmed costs. SGOA and QUASIMEME will advertise the workshop shortly.

### **5.8.3 Present and discuss new chemical oceanographic data relating to ocean acidification**

New data relating to ocean acidification were regularly presented at the SGOA meetings and are included in the SGOA reports.

At MCWG 2015, an opportunity arose to be informed about current research into ocean acidification at the University of the Azores. Marina Carreiro-Silva who happened to be at the Hydrographical Institute was invited by MCWG 2015 to give a presentation on her work on ocean acidification.

## **5.9 Chlorophyll**

### **5.9.1 Report on QUASIMEME initiative of assessment of chlorophyll data in the QUASIMEME database, in particular regarding data comparability, and discuss potential implications for existing measurement guidance**

QUASIMEME had contact with DMI in Denmark. They are interested in participating in proficiency testing, which would be a considerable expansion of the limited number of laboratories addressing Chlorophyll analysis through HPLC. The focus will be on the harmonisation of extraction and pretreatment procedures, which is believed to give good results.

The work is going to be put forward in cooperation with Koen Parmentier from RBINS, Belgium.

Steven Crum (QUASIMEME) informed MCWG that a publication was in preparation, based on the chlorophyll results in the QUASIMEME database.

### **5.9.2 Collect information in preparation of TIMES manuscript or similar publication on chlorophyll determination methods**

Pamela Walsham had collected literature on chlorophyll methods prior to the meeting. She proposed to work on a draft TIMES manuscript on chlorophyll determination methods, with a deadline of June 2016.

The following MCWG members expressed their interest to contribute to this draft manuscript: Carlos Borges, Kristin Andersen, Koen Parmentier. Evin McGovern mentioned that a colleague from the Marine Institute of Ireland could be involved as well.

A draft resolution is included in this report (Annex 8).

It was also brought up in the discussion of different chlorophyll determination methods (and the risk of inconsistent results) that this issue should be pointed out to the ICES Data Centre. OSPAR uses the parameters “chlorophyll a” and “total chlorophyll a” and it is not certain that this differentiation is recognized in the database parameters. This is included as a recommendation to the ICES Data Centre (Annex 4). The same issue had been pointed out to OSPAR via a recommendation in the MCWG 2014 report.

### 5.10 Seabird eggs as a monitoring matrix for organic contaminants and trace metals

Since 2012, Michael Haarich and Katrin Vorkamp have provided brief literature reviews at each MCWG meeting, on the use of seabird eggs as a monitoring matrix for contaminants. For MCWG 2015, Michael Haarich had also prepared an overview of the recent literature on this topic.

From a literature research on Google Scholar starting from 2014, a number of 24 new publications could be identified from an overview screening. Although most of the studies have been performed in Arctic regions, there are also some studies from Asia and one from South Africa, indicating that seabird egg monitoring has started to be applied worldwide (see Figure 1).

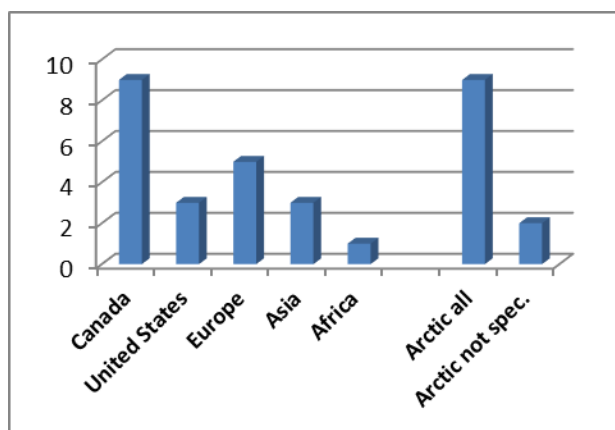


Figure 1. Number of publications on seabird egg monitoring since the beginning of 2014, divided by regions (Search in Google Scholar).

Regarding the target analytes, the majority of studies still address the group of chlorinated compounds, but closely followed by fluorinated and brominated compounds. For single metals, mercury is dominant (see Figure 2).

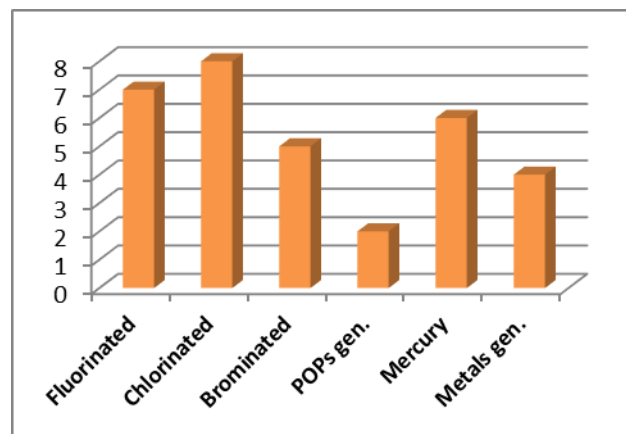


Figure 2. Number of publications on seabird egg monitoring since the beginning of 2014, divided by target analytes (Search in Google Scholar).

We can conclude from multiple years of literature reviews, that contaminant analysis in seabird eggs is widely applied in environmental marine monitoring of coastal areas. For inclusion in monitoring programmes at national and regional level, long term experience has been made in the framework of the Trilateral Wadden Sea monitoring programme (NL, DE and DK), the Arctic Monitoring and Assessment Programme (AMAP) (e.g. Canada, Denmark, Iceland, Norway) and the Swedish monitoring in the Baltic Sea. Guidelines are available e.g. by OSPAR since 1998 (Ospar Publication 99-02e JAMP Guidelines for Monitoring Contaminants in Biota, Rev. 2012).

#### 5.10.1 Review and discuss potential contributions from the Working Group on Seabird Ecology

Following discussions at MCWG 2014 and a presentation by guest expert Anders Mosbech on seabird ecology, Katrin Vorkamp was to contact the Working Group on Seabird Ecology (WGSE) to convey MCWG's interest in this topic. However, ICES informed that WGSE had been combined with a WGBIRD. This new group (JWGBIRD) is a joint OSPAR-ICES group.

Katrin Vorkamp contacted the chair of JGBIRD (Ian Mitchell, UK) on 23 February 2015, but no reply was received.

### 5.11 Passive sampling

#### 5.11.1 Report on QUASIMEME exercise on passive sampling and review data with a view to adjustment of background assessment concentrations

A QUASIMEME development exercise on passive sampling was initially proposed by the Workshop on Passive Sampling and Passive Dosing (WKPSPD) in January 2013 and further discussed with QUASIMEME and scientific experts at MCWG 2013 and MCWG 2014.

The QUASIMEME development exercise on silicone passive samplers (PSDs) was run between October 2014 and January 2015. A first evaluation of the results was presented at

MCWG 2015. Twenty-one out of 25 participants submitted results. Participants were asked to report

- amounts of polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and brominated diphenyl ethers (BDEs) in a field-exposed PSD
- amounts of the same compounds in an unexposed PSD
- limits of detection (LODs) used by participants in these analyses (ng per sampler)
- fractions of performance reference compounds (PRCs) in the exposed PSD relative to the unexposed PSD. (PRCs are used for calibrating the in-situ sampling kinetics.)
- aqueous concentrations calculated from the given amounts of five target compounds and 14 PRCs. (All participants were given the same input values.)

Results for the analysis of the exposed PSD suggested an interlaboratory variability of 20% for PCBs, 14% for PAHs and 28% for BDEs in the high amount range (i.e., the proportional error), and a constant error of 6 ng for PCBs, 10 ng for PAHs and 0.1 ng for BDEs. This is better than expected based on previous experience with other interlaboratory studies.

The reported retained fractions of PRCs showed a relatively high variability of 16%. This may have been caused by the fact that many laboratories do not routinely analyse these compounds. There were also some reports of PRCs interfering with internal standards.

LODs and reported amounts in the unexposed PSDs were used by MCWG to improve the estimates of measurement uncertainty for the derivation of Background Assessment Concentrations (see below).

The calculation exercise showed that the skills for calculating aqueous concentrations from the absorbed amounts were good for 14 out of 18 laboratories, with a scatter of 3% due to minor round off issues in the PSD-water partition coefficients. Four laboratories reported incorrect results, and three laboratories did not submit calculation results. An extended evaluation of the QUASIMEME study is expected by the end of March 2015 when the report will be distributed to the participants.

### **Adjustment of Background Assessment Concentrations (BAC) for dissolved organic contaminants in water**

The text of this section that is written in italics is copied from the MCWG 2013 report, in order to provide continuity and to highlight the changes.

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

In order to test whether or not an actual concentration measurement indicates elevated levels relative to the natural background, *the uncertainty in analytical results* is added to the BC to yield a Background Assessment Concentration (BAC). This uncertainty *consists of a bias that originates from contamination during sampler preparation, transport and analytical procedures, and a precision by which these lowest observed amounts in the samplers can be quan-*

*tified. MCWG chose not to consider the contribution of analytical precision to the uncertainty in the analytical results, because sample contamination (the bias) was considered to dominate the uncertainty in the analytical results.*

During its 2013 meeting, MCWG derived BAC values for freely dissolved nonpolar contaminants (PCBs, PAHs, 4,4'-DDE,  $\alpha$ -HCH,  $\gamma$ -HCH, dieldrin, and hexachlorobenzene). Background Concentrations (BCs) for organochlorine contaminants were set to zero. Background concentrations of PAHs were estimated based on observed low concentrations in remote areas obtained by large-volume batch water sampling, passive sampling, and equilibrium partitioning estimates using dated sediment cores. The conversion from BCs to BACs was based on expert judgement on achievable LODs.

As described above, QUASIMEME organised a development exercise for silicone passive samplers (PSDs) between October 2014 and January 2015. On the request of MCWG, laboratories were asked to quantify the amounts in non-exposed (i.e., field-control) PSDs, even if these were lower than the laboratories' LODs. These results would allow for a better assessment of measurement uncertainty (MU), strengthening the scientific basis of the BACs. However, the data reported by the laboratories was rather difficult to assess because: some laboratories reported "<LOD" for some compounds and the actual amount for other compounds. Some other laboratories reported zeros when no peak was found, while still other laboratories may have quantified the instrumental noise in such cases. MCWG therefore estimated achievable LODs based on:

- 1) reported amounts only, deleting all entries "<LOD" and "0". This method was expected to result in a high estimate of the MU, because some laboratories only reported the actually observed amounts when these were higher than their LOD (e.g., phenanthrene).
- 2) reported LODs. This method was expected to result in a low estimate of the MU in some cases (e.g., when the actual amount was higher than the laboratory's LOD), and in high estimates where laboratories adopted an overprotective LOD. Since not all laboratories have a long standing experience in silicone PSD analysis, many reported LODs may be indicative values only.

In both methods, the robust mean was estimated as the median of all results, and the robust standard deviation was estimated from the mean of absolute deviations (MAD). The MU was obtained as the mean + 2 standard deviations. The results indicate that the two approaches generally yield similar results (Annex 9), with the following exceptions:

- hexachlorobutadiene, phenanthrene, fluoranthene, pyrene. Sample contamination from the laboratory atmosphere are often observed for these compounds, and the amount-based approach is likely the more reliable method.
- Five- and six-ring PAHs and BDEs. The reported LODs appear to be relatively high for these compounds, and it is believed that the amount-based approach is more reliable for these compounds.
- PCB-118. MU based on reported amounts was 5 times smaller than the MU for the other PCBs (~1 ng) and the latter value was adopted for PCB-118.

Overall, MCWG concluded that the amount-based approach yields more reliable estimates of the MU in the low amount range.

MUs in  $C_{\text{free}}$  (pg L<sup>-1</sup> units) were derived from these amounts as described in section 5.12 of the MCWG 2013 report. BACs were estimated from the BCs that were suggested during the 2013 MCWG meeting, amended with observed low concentrations in remote areas for acenaphthene, acenaphthylene, and fluorene. BCs for hexachlorbutadiene and BDEs were set to 0, since no natural sources for these compounds exist. For compounds that were not analysed in the QUASIMEME Laboratory Performance Study, the 2013 estimates of BC and BAC were adopted. The updated BACs are summarised in Annex 9, together with the previously suggested BACs. MCWG wishes to stress that these BACs are indicative values that are subject to the following caveats:

- *The concentrations presented for the use as BCs for the water phase are concentrations that MCWG considers as “low concentrations”. However, they are not proposed as natural background concentrations.*
- *The concentrations are proposed to assist OSPAR in deriving assessment criteria for passive sampling applications in (pre-)CEMP assessments and should not be used for other purposes.*
- Measurement uncertainty in  $C_{\text{free}}$  is site dependent for compounds that do not reach their equilibrium concentrations in the sampler. For these compounds, MU decreases with increasing water flow rates, and with increasing exposure time.
- Measurement uncertainty in  $C_{\text{free}}$  is laboratory dependent. The 75% and 25% percentiles of the MU typically span a factor of 2 to 20.

MCWG recommends to OSPAR to take note of the updated values (Annex 4 and Annex 9).

#### Reference:

OSPAR (2010). Hazardous Substances. The North-East Atlantic Environment Strategy. OSPAR Agreement 2010-03. [www.ospar.org](http://www.ospar.org)

#### 5.11.2 Obtain information from WGBEC and WGMS regarding the use of $C_{\text{free}}$ as a proxy of the effects of non-polar compounds, with a view to determining environmental assessment criteria

Following the joint sessions at MCWG 2014, WGBEC 2014 and WGMS 2014, the three chairs drafted some mutual recommendations, amongst these the recommendation to WGBEC and WGMS to contribute to the data collection and review on toxicity of contaminants of freely dissolved concentrations, with a view to developments of environmental assessment criteria (see recommendations in the MCWG 2014 report).

Katrin Vorkamp contacted the chairs of WGBEC and WGMS on 23 February 2015 with regard to this recommendation, but did not receive a reply.

Since MCWG wishes to keep passive sampling on their agenda as one of the multi-annual terms of references and since the development of environmental assessment criteria is a crucial point in bringing passive sampling forward in a monitoring context, this question will still be highly relevant to MCWG. MCWG members with ecotoxicological expertise are invited to contribute to this topic, as are members from other working groups.

### **5.11.3 Review and discuss information on mixture toxicity derived from passive sampling, supported by WGBEC**

See section 5.11.2.

## **5.12 Publications**

### **5.12.1 Review and comment on TIMES draft manuscript on passive sampling in sediments, produced by WGMS**

This manuscript from WGMS was not yet available, see section 5.7.

The chair of WGMS informed MCWG during the meeting that WGMS was working on a review of passive sampling methods in sediments and recommendations. WGMS asked if MCWG members would be willing to read the review, which was affirmed by MCWG.

### **5.12.2 Review and complete TIMES draft manuscript on the determination of sampler/water and sampler/sampler partition coefficients**

Some progress has been made on the guideline for determining sampler-water partition coefficients. A final draft will be prepared intersessionally with WGMS. This will be presented and discussed at the MCWG 2016 meeting. It is expected to be ready for submission to TIMES by the end of March 2016.

### **5.12.3 Discuss initial work on concluding report on seabird eggs as a monitoring matrix for organic contaminants and trace metals**

As mentioned in section 5.10, Michael Haarich and Katrin Vorkamp have provided annual literature reviews on the use of seabird eggs as a monitoring matrix for contaminants. With its 2015 update, MCWG will conclude its work on this topic (see section 5.10). Michael Haarich and Katrin Vorkamp will consider a concluding publication, subject to time availability.

## **6 Plenary discussion of draft report**

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During the meeting, MCWG's comments to the MSFD Expert Networks on Contaminants were discussed in plenary (Annex 5), to allow a timely submission to the network's chair.

The MCWG 2015 draft report was discussed by e-mail subsequently to the meeting.

## **7 Any other business**

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Katrin Vorkamp thanked MCWG for the pleasant experience of chairing MCWG in the last five years. She thanked the MCWG members for their dedicated efforts and hard work, resulting in productive meetings and scientific progress. She particularly acknowledged the work atmosphere of mutual respect, which, besides MCWG's high scientific competences, is a particular asset of this group.

Katrin Vorkamp thanked Evin McGovern, the previous chair, for his support throughout her term as chair. Koen Parmentier had been elected as incoming chair at MCWG 2014

and had co-chaired the MCWG 2016 meeting. Katrin Vorkamp wished him good luck with this work.

## **8 Recommendations and action list**

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### **8.1 Recommendations**

See Annex 4.

### **8.2 Action list**

#### Carlos Borges:

- Contribute to TIMES draft manuscript on chlorophyll determination methods (first author: Pamela Walsham).

#### Kees Booij:

- Prepare final draft manuscript on the determination of sampler/water and sampler/sampler partition coefficients, for presentation and discussion at MCWG 2016.

#### Kristin Andreasson:

- Contribute to TIMES draft manuscript on chlorophyll determination methods (first author: Pamela Walsham).

#### Koen Parmentier:

- Follow up on ICES Science Plan Implementation Exercise (see Section 3.2) and inform MCWG about the outcomes of this exercise.
- Contribute to TIMES draft manuscript on chlorophyll determination methods (first author: Pamela Walsham).

#### Pamela Walsham:

- Take the lead on a TIMES draft manuscript on chlorophyll determination methods, for presentation and discussion at MCWG 2016.

## **9 Date and venue of the next meeting**

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MCWG was kindly invited by Evin McGovern to hold its next meeting at the Marine Institute of Ireland located in Galway. MCWG thanked Evin McGovern for this invitation and would like to accept it.

The meeting dates were later agreed to be 7–11 March 2016.



## 10 Closure of the meeting

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Katrin Vorkamp and Koen Parmentier thanked Carlos Borges, the host of the MCWG 2015 meeting, for the excellent facilities at the Hydrographical Institute and for his help with smooth meeting procedures. The co-chairs also wished to extend their thanks to the team at the Hydrographical Institute who had assisted Carlos Borges in arranging this meeting.

The MCWG 2015 meeting was closed on Friday, 6 March 2015, at 1 p.m.

## Annex 1: List of participants

Name	Address	Email
Lutz Ahrens	Swedish University of Agricultural Sciences P.O.Box 7050 75007 Uppsala, Sweden	Lutz.Ahrens@slu.se
Kristin Andreasson	Swedish Meteorological and Hydrological Institute SMHI Göteborg Sven Källfelts gata 15 SE-426 71 Västra Frölunda Sweden	Kristin.Andreasson@smhi.se
Philippe Bersuder	Centre for Environment, Fisheries and Aquaculture Science (Cefas) Lowestoft Laboratory Pakefield Road NR33 0HT Lowestoft Suffolk, United Kingdom	Philippe.Bersuder@cefas.co.uk
Victoria Besada	Instituto Español de Oceanografía Centro Ocean- ográfico de Vigo Subida a Radio Faro 50 36390 Vigo (Pontevedra), Spain	Victoria.Besada@vi.ieo.es
Stepan Boitsov	Institute of Marine Research Nordnesgaten 50, Bergen, Norway	Stepan.Boitsov@imr.no
Kees Booij	Royal Netherlands Institute for Sea Research P.O. Box 59 NL-1790 AB Den Burg, Texel, The Netherlands	Kees.Booij@nioz.nl
Carlos Borges	Instituto Hidrografico Rua das Trinas 49 PT-1249-093 Lisbon, Portugal	carlos.borges@hidrografico.pt
Miguel Caetano	IPMA – National Institute of Biological Resources, Av. Brasília, 1449-006 Lisbon, Portugal	mcaetano@ipma.pt
Steven Crum	Alterra Wageningen UR Droevendaalsesteeg 3 6708PB Wageningen The Netherlands	Steven.Crum@wul.nl
Bavo de Witte	Institute for Agricultural and Fisheries Research (ILVO) Ankerstraat 1 8400 Oostende, Belgium	ba- vo.dewitte@ilvo.vlaanderen.be
Anja Duffek	Federal Environment Agency Bismarckplatz 1 14193 Berlin, Germany	Anja.Duffek@uba.de

Ralf Ebinghaus	Helmholtz Centrum Geesthacht Centre for Materials and Coastal Research Department Environmental Chemistry Max-Planck-Straße 1 21502 Geesthacht Germany	Ralf.Ebinghaus@hzg.de
Michael Haarich	Thünen Institute Institute for Fisheries Ecology Marckmannstrasse 129b, Building 4 20539 Hamburg, Germany	Michael.Haarich@ti.bund.de
Ana I. Lillebø	Department of Biology & CESAM University of Aveiro Campus Universitário de Santiago PT-3810-193 Aveiro, Portugal	lillebo@ua.pt
Evin McGovern	Marine Institute Rinville Oranmore Co. Galway, Ireland	Evin.McGovern@marine.ie
Koen Parmentier (Co-chair)	Royal Belgian Institute of Natural Sciences OD NATURE 3 <sup>de</sup> & 23 <sup>ste</sup> Linierregimentsplein 8400 Oostende, Belgium	KParmentier@naturalsciences.be
Catarina Rocha	Instituto Hidrografico Rua das Trinas 49 PT-1249-093 Lisbon, Portugal	Catarina.Rocha@hidrografico.pt
Ricardo Bettencourt da Silva	Departamento de Química e Bioquímica Edifício C8, piso 5, sala 8.5.39 Faculdade de Ciências da Universidade de Lisboa Campo Grande PT-1749-016 Lisbon, Portugal	rjsilva@fc.ul.pt
Stefan van Leeuwen	RIKILT Wageningen UR Akkermaalsbos 2 6708WB Wageningen The Netherlands	Stefan.vanLeeuwen@wur.nl
Winnie van Vark	Alterra Wageningen UR Droevendaalsesteeg 3 6708PB Wageningen The Netherlands	winnie.vanvark@wur.nl
Katrin Vorkamp (Co-chair)	Aarhus University Dept. of Environmental Science Frederiksborgvej 399 4000 Roskilde Denmark	kvo@envs.au.dk
Pamela Walsham	Marine Scotland Science Marine Laboratory 375 Victoria Road P.O. Box 101 AB11 9DB Aberdeen, United Kingdom	Pamela.Walsham@gov.scot

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Lynda Webster

Marine Scotland Science Marine Laboratory 375  
Victoria Road P.O. Box 101 AB11 9DB Aberdeen,  
United Kingdom

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Lynda.Webster@gov.scot

## Annex 2: Agenda

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### ICES Marine Chemistry Working Group 37<sup>th</sup> meeting

Instituto Hidrográfico, Lisbon, Portugal

2 – 6 March 2015

#### 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

*Updates of MCWG action list, discussion of timetable, formation of subgroups.*

#### 3 REPORT OF ICES ACTIVITIES

- i) MCWG 2014 recapitulation
- ii) Intersessional activities
- iii) 2014 Annual Science Conference
- iv) OSPAR/ICES Study Group on Ocean Acidification (SGOA) (*see also 5.8*)

#### 4 PLENARY PRESENTATIONS

- 4.1 Ricardo Silva: Relevance and approaches for the evaluation of measurement uncertainty
- 4.2 Ana Lillebø: Science-Policy-Stakeholder interface towards a pan-European management of coastal lagoons: Lessons learnt from the FP7 LAGOONS project

#### 5 MAIN AGENDA

##### General

##### 5.1 Quality assurance of marine chemistry.

- i) Report and discuss new developments in QUASIMEME.  
*Presentation by Steven Crum and/or Winnie van Vark (QUASIMEME)*  
*(see also 5.8, 5.9 and 5.11)*
- ii) Provide information on other proficiency testing schemes with relevance to MCWG.

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

- i) Review and discuss developments of WFD, in particular regarding new priority (hazardous) substances and associated EQS values.
- ii) Calculate and discuss conversions of EQS<sub>biota</sub> values from fish to mussels.
- iii) Review and discuss developments in MSFD, in particular regarding the monitoring of descriptors 5, 7, 8 and 9.

#### 5.3 Developments at OSPAR and HELCOM.

- i) Discuss activities at OSPAR and HELCOM with direct relevance to MCWG and consider input from MCWG.

#### 5.4 Present projects of relevance to MCWG activities, including information on emerging contaminants.

*Stevan van Leeuwen: Dioxins, PCBs and heavy metals in Chinese mitten crabs from Dutch rivers and lakes.*

*Lutz Ahrens: Passive samplers for pesticides in water.  
(see also 5.11)*

*Catarina Rocha: Oil Spill Identification: IH Methodology*

#### 5.5 Marine litter and its role as a potential source of contaminants

- i) Report on new information on marine litter and its role as a potential source of contaminants, with particular focus on field studies demonstrating elevated contaminant levels associated with plastics.
- ii) Present information on contaminant desorption from plastic in the digestive system after plastic uptake by biota, if available.

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

#### 5.7 Report on activities in other expert groups on the interface to MCWG

- i) WGMS
- ii) WGBEC
- iii) WGEEL
- iv) Working Group on Oceanic Hydrography (WGOH)
- v) Working Group on Phytoplankton and Microbial Ecology (WGPME)

## Chemical Oceanography

### 5.8 Ocean acidification

- i) Report from the OSPAR/ICES Study Group on Ocean Acidification and address potential recommendations from this group to MCWG  
(See also 3 iv)
- ii) Report on QUASIMEME workshop on ocean acidification and discuss implications of workshop results for OA monitoring.  
(See also 5.1)
- iii) Present and discuss new chemical oceanographic data relating to ocean acidification.

### 5.9 Chlorophyll

- i) Report on QUASIMEME initiative of assessment of chlorophyll data in the QUASIMEME database, in particular regarding data comparability, and discuss potential implications for existing measurement guidance.  
(See also 5.1)
- ii) Collect information in preparation of TIMES manuscript or similar publication on chlorophyll determination methods.

## Contaminants

### 5.10 Seabird eggs as a monitoring matrix for organic contaminants and trace metals.

- i) Review and discuss potential contributions from the Working Group on Seabird Ecology.

### 5.11 Passive sampling

- i) Report on QUASIMEME exercise on passive sampling and review data with a view to adjustment of background assessment concentrations.  
(See also 5.1)
- ii) Obtain information from WGBEC and WGMS regarding the use of Cfree as a proxy of the effects of non-polar compounds, with a view to determining environmental assessment criteria.
- iii) Review and discuss information on mixture toxicity derived from passive sampling, supported by WGBEC.

#### 5.12 Publications

- i) Review and comment on TIMES draft manuscript on passive sampling in sediments, produced by WGMS.
- ii) Review and complete TIMES draft manuscript on the determination of sampler/water and sampler/sampler partition coefficients.
- iii) Discuss initial work on concluding report on seabird eggs as a monitoring matrix for organic contaminants and trace metals.

#### 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 multi-annual resolution 2016–2018

The **Working Group on Marine Chemistry** (MCWG), chaired by Koen Parmentier, Belgium, will work on ToRs and generate deliverables as listed in the Table below.

	MEETING DATES	VENUE	REPORTING DETAILS	COMMENTS (CHANGE IN CHAIR, ETC.)
Year 2016	7–11 March	Galway, Ireland	Interim report by 15 April to SSGEPI	
Year 2017			Interim report by	
Year 2018			Final report by	

#### ToR descriptors

ToR	Description	Background	Science Plan topics addressed	Duration	Expected Deliverables
a	Respond to requests for advice from Regional Seas Conventions (e.g. OSPAR, HELCOM, ICES Data Center, EU) as required.	Science or Advisory Requirements.	1, 13, 20, 21, 25, 31	3 years	Advice, revision, as appropriate
b	Review developments in MSFD and WFD, in particular regarding new (emerging) and priority (hazardous) substances and associated EQS values, conversion factors and other issues regarding monitoring for Descriptor 5, 7, 8, 9 & 10.	Follow-up on this matter is key in order to constructively guide the development process for environmental quality criteria.	1, 13, 19, 20, 21, 22, 25, 27, 28, 31	3 years	Advice, Environmental Quality Standards or Environmental Assessment Criteria, conversion factors, scientific review on emerging contaminants and risks involved
c	Report new developments in QUASIMEME (Quality Assurance in Marine Environmental Monitoring in Europe), and provide information on other proficiency testing schemes with relevance to MCWG.	Availability of high quality proficiency testing is vital to produce reliable results.	20, 21, 27, 31	3 years	Provide guidance for proficiency testing
d	Marine litter and its role as a potential source of contaminants: i) Report on new information regarding marine litter as a potential source of contaminants, with particular focus on field studies reporting	Effects of marine litter are poorly understood, and all additional information will increase our understanding of all processes involved.	1, 13, 19, 20, 21, 25, 27	3 years	Review paper in collaboration with the WG on Marine Litter.

	elevated contaminant levels associated with plastics. ii) Present available information on contaminant desorption from plastic in the digestive system after uptake.				
e	Summarise and synthesise relevant information from other expert groups on the interface to MCWG; incl. WGMS, WGBEC, WGEEL, WGSE, WGOH, WGPME	MCWG has always been very active in trying to interconnect different WGs, although response has often been very limited. The collaboration with WGMS is exemplary.	13, 19, 20, 21, 22, 25, 27	3 years	Joint meetings, corporate advice, TIMES paper
f	Ocean acidification: Report from data, research and developments in Ocean Acidification and address recommendations to MCWG	Ocean acidification, understanding how important it is, and being able to quantify its impact is crucial for a variety of scientific disciplines, and for ocean health.	1, 4, 13, 19, 20, 21, 25, 27, 28, 31	3 years	Data overview, TIMES publication
g	Report on QUASIMEME assessment of chlorophyll data, in particular regarding comparability of data and potential implications for existing measurement guidance, and to collect information in preparation of TIMES.	The aim is to solve problems for data comparability that exist for decades concerning chlorophyll measurements.	13, 25, 31	Year 1 & 2	Publication in TIMES: manuscript on chlorophyll determination methods
h	Report on intercalibration exercises on passive sampling and review data with a view to adjustment of background assessment concentrations; obtain information regarding the use of Cfree as a proxy of the effects of non-polar compounds, with a view to determining EACs, and review information on mixture toxicity derived from passive sampling/dosing.	PS seem inevitable in order to assess GES, as several EQS cannot be checked by standard methods. The possibility of Passive Dosing seems key in assessing mixture toxicity.	13, 19, 20, 21, 22, 25, 27, 28, 31	3 years	Improved quality control on delivered data

### Summary of the Work Plan

Year 1	Respond to requests under ToR a Progress work towards completion of the remaining ToRs
Year 2	Respond to requests under ToR a Progress work towards completion of the remaining ToRs
Year 3	Respond to requests under ToR a Report on the remaining ToRs

### Supporting information

Priority	This group maintains an overview of key issues in relation to marine chemistry, both with regard to chemical oceanography and contaminants. 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
Resource requirements	The research programmes which provide the main input to this group are already underway, and resources are already committed.
Participants	The Group is normally attended by some 20–25 members and guests.
Secretariat facilities	None.
Financial	No financial implications.
Linkages to ACOM and groups under ACOM	Yes
Linkages to other committees or groups	WGMS, WGBEC OSPAR/ICES study group on Ocean Acidification (SGOA) ICES Data Centre
Linkages to other organizations	The work of this group is closely aligned with EU working groups under the Water Framework Directive (e.g. Working Group on Chemicals) and EU expert networks with regard to contaminants under the MSFD. Specific agenda points will be directly relevant for QUASIMEME. The group provides the basis for some advice to OSPAR.

## Annex 4: Recommendations

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RECOMMENDATION	ADRESSED TO
1. OSPAR uses two parameters for the determination of chlorophyll a, i.e. “chlorophyll a” and “total chlorophyll a”. These parameters reflect different analytical methods which seem to produce systematically different results. MCWG recommends to the ICES Data Centre to check if this differentiation is followed through in the database.	ICES Data Centre
2. MCWG 2013 had derived Background Concentrations (BCs) and Background Assessment Concentrations (BACs) for dissolved organic contaminants in water. The BACs have been updated by MCWG 2015, using new data from the QUASIMEME development exercise on passive sampling. MCWG recommends to OSPAR to take note of these updates.	OSPAR

## Annex 5: Comments of MCWG 2015 to MSFD Expert Network on Contaminants

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This annex refers to section 5.2.1. The co-chairs forwarded the comments to the chair of the MSFD Expert Network on Contaminants directly after the MCWG 2015.

### Comments to MSFD Expert Network on Contaminants

At the 37th Annual Meeting (2–6 March 2015) of the ICES Marine Chemistry Working Group we discussed the outcome from the 2nd working meeting of the MSFD Expert Network Contaminants. We are interested in supporting the technical revision process with our extensive background in marine monitoring of contaminants. During the last few years, MCWG's reviews and revisions of the OSPAR JAMP Guidelines (including technical manuals and QA/QC) have taken into account WFD and MSFD requirements. There are several activities to harmonize existing monitoring guidelines, e.g. between HELCOM and OSPAR.

We would appreciate your consideration of the following points for further elaboration of the template.

We feel that the information and knowledge gathered and approaches developed in Regional Sea Conventions form a solid basis for the further development of the MSFD Descriptor 8. The link between MSFD and WFD needs a stronger focus on marine aspects in EU working groups dealing with coastal and transitional waters.

We welcome the development of common guidelines for **deselection of WFD substances** and will be happy to contribute with our expertise. Guidelines should also describe a method on how to select and prioritise contaminants of relevance to the marine environment (originating from atmospheric deposition, marine activities, etc.). In addition, a harmonisation of RSCs and WFD prioritisation is probably needed.

### 3.3.2 Sampling strategies

There are comprehensive and widely applied guidelines addressing sampling strategies developed in RSCs. The choice of technique or approach is essentially depending on the specific objectives of the monitoring programme.

Passive sampling is an innovative sampling technique with significant potential for application in MSFD monitoring, and guidelines exist or are under development.

The attached document<sup>1</sup> presents an overview of HELCOM and OSPAR technical annexes in the monitoring guidelines and manuals and ICES technical advice.

#### 3.3.3.1 QA/QC Directive

QA/QC issues are generally addressed in monitoring guidelines. QA procedures have been adopted by the RSCs. The COM DEC should refer to the requirements of Directive 2009/90/EC.

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<sup>1</sup> Included in Annex 6 of this report.

### 3.3.3.2 Proficiency testing schemes

PT schemes need to be suitable for MSFD monitoring, as those developed for the specific WFD requirements may not be appropriate for laboratories performing chemical analysis under the MSFD.

### 3.3.3.3 Open/Deep Sea Areas

It has to be considered that deep sea areas may exist in front of the coast, i.e. within the area covered by the WFD (e.g. in Southern Europe 2000 meters water depth at 5nm from the coastline).

Monitoring of mammals or sea bird eggs can give useful information regarding bioaccumulation and trophic transfer of contaminants, and to assess time trends especially in open sea areas. It is important to consider the spatial representativeness of the monitored species.

The monitoring of open and deep sea areas should be risk based considering potential sources of contaminants and specific ecosystem vulnerabilities.

## 4.1 DESCRIPTOR 9 SCOPE (Q1)

Commission Regulation No 1881/2006 states in recital 61: *Maximum levels are also necessary in foods where environmental pollution may cause high levels of contamination, in particular in fish and fishery products, resulting, for example, from oil spills caused by shipping.*

In this respect there is a link to D 9 of the MSFD. The monitoring and assessment under the MSFD could identify how environmental pollution causes high levels of contaminants in fish for human consumption. It should be clarified how this link to the national food safety authorities is operationalized in order to avoid duplication of activities.

Compliance check of maximum limits as in Commission Regulation (EC) No 1881/2006 is mentioned also in D9. In the case that a fish sample does not comply, the national food safety authorities will follow up by taking that fish from the market and making an EU wide RASFF notification.

The maximum limits in the 1881/2006 are 'trade limits', i.e. fish may not be traded if above these limits. Although the limits have the nature of protecting consumers, a balancing took place compared to other food commodities. Fish is allowed a 'higher' ML because of health benefits of fish consumption.

## Annex 6: Overview of existing OSPAR, HELCOM and ICES guidelines for environmental monitoring

This table was compiled by Michael Haarich and presents the status as of November 2014.

Overview of HELCOM and OSPAR Technical Annexes in the Monitoring Guidelines and Manuals					OSPAR JAMP Guidelines for Monitoring Contami- nants in <b>Biota</b> (agreement 1999-2)	OSPAR JAMP Guidelines for Monitoring Contami- nants in <b>Sediments</b> (agreement 2002-16)	OSPAR JAMP guideline on monitoring of contami- nants in <b>Seawater</b>	OSPAR JAMP Guidelines for Contaminant- specific Biological Effects Monitoring (agreement 2008-9)	OSPAR JAMP Guidelines for General Biological Effects Monitoring (agreement 1997-7)	OSPAR JAMP Guidelines for Monitoring Chemical Aspects of Ocean Acidification (agreement 2014-3)	HELCOM Combine Manual			ICES		
INDICATORS	HELCOM	OSPAR		MSFD	ANNEX (last revision)						ANNEX			ICES Publication		
		CEMP	Common indicator	Descriptor	Biota	Sediment	Water	Organisms			Biota	Sediment	Water	Biota	Sediment	Water
Polybrominated biphenyl ethers (PBDE): BDE-28, 47, 99,100, 153 and 154 (209)	core	CEMP	Biota Sediment	D8.1.	4 (2008)	7 (2008)	(2013)				B-12	B-13	B-11	TIMES 46 (2012)		
Hexabromocyclooctecane (HBCDD)	core	CEMP		D8.1.	5 (2008)	8 (2008)								TIMES 44 (2009)		
Perfluorooctane sulphonate (PFOS)	core	pre-CEMP		D8.1.	6 (2009)	9 (2010)	(2010)							TIMES 48 (2009)		
Polychlorinated biphenyls (PCB) *: CB-28, 52, 101, 118, 138, 153 and 180**	core	CEMP	Biota Sediment	D8.1.	8 (2010)	2 (2010)								TIMES 53 (2013)		
*and dioxins and furans: : **WHO-TEQ of dioxins, furans –dl-PCBs		pre-CEMP				9 (2011)	10 (2011)								TIMES 50 (2012)	
Polyaromatic hydrocarbons and their metabolites: US EPA 16 PAHs	core	CEMP	Biota Sediment	D8.1.	3 (2009)	3 (2009)	(2013)				B-12	B-12	B-11	TIMES 45 (2009)		
/ selected metabolites		pre-CEMP				TIMES 39 (2005)		2 (2007)							TIMES 39 (2005), CRR 315 (2012)	
Metals (lead, cadmium and mercury)	core	CEMP	Biota Sediment	D8.1.	2(2014)	6 (2014)	(2013)				B-12	B-13	B-11	TIMES 1 (1987)	TIMES 3 (1987)	TIMES 2 (1987)
Radioactive substances: Caesium-137 in fish and surface waters	core			D8.1.							MORS Guidelines (2013)					
Tributyltin (TBT)	core	CEMP	sediment	D8.1; 8.2.	TIMES 47 (2010)			3 (2007)						TIMES 47 (2010)		
and imposex																TIMES 24 (1999)
Pharmaceuticals: Diclofenac, EE <span>A2</span> (+E1, E2, E3 + in vitro yeast essay)	pre-core			D8.1.										TIMES 19 (1996)		
Lysosomal Membrane Stability – a toxic stress indicator	pre-core			D8.2.					6 (2013)					TIMES 36 (2004), CRR 315 (2012)		

Fish Disease Index-- a fish stress indicator	pre-core			D8.2.											TIMES in prep.			
Liver histopathology		pre-CEMP							7 (2007)							TIMES 38 (2004), CRR 315(2012)		
Macroscopic liver neoplasms		pre-CEMP							8 (2007)							CRR 315 (2012)		
Externally visible fish diseases		pre-CEMP							9 (2007)							TIMES 19 (1996), CRR 315 (2012)		
Reproductive disorders: Malformed eelpout and amphipod embryos	pre-core			D8.2.					10 (2007)						CRR 315 (2012)			
PCB and dioxins for safe fish to eat	candidate			D9.1.														
Alkylphenols (nonylphenol and octylphenol)	candidate			D8.1.											TIMES 49 (2012)			
Vitellogenin induction	candidate	pre-CEMP		D8.2.				4 (2007)							CRR 315 (2012)			
EROD/CYP1A (Ethoxyresorufin-O-deethylase) induction	candidate	pre-CEMP		D8.2.				2 (2007)	5 (2007)						TIMES 13 (1991), CRR 315 (2012)			
Acetylcholin-esterase inhibition	candidate			D8.2.											CRR 315 (2012)			
Alkylated PAHs	core ?	pre-CEMP		D8.1.	3 (2009)	3 (2009)									TIMES 45 (2009)			
OCPs (HCHs, HCB, DDTs)	Combine			D8.1.	1 (2010)							B-12		B-11	TIMES 10 (1990)			
															TIMES 9 (1990)			
Ocean Acidification (general)		pre-CEMP		D5													CRR 319 (2013)	
pH	Combine			D5										B-14				
Total alkalinity	Combine			D5										B-15				
Carbon dioxide				D5														
Dissolved organic carbon				D5										B-17				
Dissolved inorganic carbon				D5														
Anoxic Waters	Combine			D5										B-10				
Hydrographic parameters	Combine			D7										B-8, C-2				



				OSPAR JAMP eutrophication monitoring guidelines – nutrients (agreement 2013-4)	OSPAR JAMP eutrophication monitoring guidelines – oxygen (agreement 2013-5)	OSPAR JAMP eutrophication monitoring guidelines – benthos (agreement 2012-12)	OSPAR JAMP eutrophication monitoring guidelines - phytoplankton species composition (agreement 1997-5)	OSPAR JAMP eutrophication monitoring guidelines - chlorophyll a (agreement 2012-11)	OSPAR JAMP guidelines on Quality Assurance for biological monitoring in the OSPAR area (agreement 2002-15)	HELCOM Combine Manual	ICES					
INDICATORS	HELCOM	OSPAR		MSFD Descrip-tor	ANNEX (last revision)/ICES publication						ANNEX			publication		
		CEMP	Common indicator		Water		Organisms		Water	Organisms	Organisms	Sediment/ Bottom	Water	Biota	Sediment	Water
Nutrients	Combine	CEMP		D5	(2013)							B-9			TIMES 17 (1996)	
Chlorophyll-a	Combine	CEMP		D4, D5				(2012)		C-4						
Phytoplankton species composition	Combine	CEMP		D1, D2, D4, D5			(1997)			C-6						
Phytoplankton primary production	Combine			D1, D2, D4, D5						C-5						
Mesozooplankton	Combine			D1, D2, D4, D5						C-7						
Bacterioplankton growth	Combine			D1, D2, D4, D5						C-11						
Bacterioplankton abundance	Combine			D1, D2, D4, D5						C-12						
Salinity and Temperature	Combine			D7								B-8/1				
Oxygen		CEMP		D5		(2013)						B-8/2 B-8/3				
Hydrogen sulfide	Combine			D7								B-8/4				
Benthos				D1, D2, (D4), D5, D6										TIMES 42 (2009), TIMES 16 (1991)		
(Macrozoobenthos) soft-bottom	Combine	CEMP		D1, D2, (D4), D5, D6		(2013)				C-8				TIMES 43 (2009)		
(Macrozoobenthos) hard bottom		CEMP		D1, D2, (D4), D5, D6		(2013)										
Phytobenthic plants	Combine			D1, D2, (D4), D5, D6						C-9						
Animal communities	Combine			D1, D2, (D4), D5, D6						C-9						
Sediment traps	Combine										C-3					
Fish Monitoring	Combine			D1, D2, D3, D4						C-10						
Passive sampling															TIMES 52 (2012)	
Quality Assurance										Combine Manual Part B			TIMES 35 (2004)			
General/principles	Combine								(2002)	B-1						
validation	Combine									B-2						
Quality audit	Combine									B-3						
Standard Operating Procedures (SOP)	Combine									B-4						
Sampling	Combine									B-5						
Reference materials	Combine									B-6						
Units and conversion	Combine									B-7						
Co-Factors	Combine									B-16						
Compilation: M. Haarich, Nov. 2014																

## Annex 7: Classification of new parameters for the ICES Data Centre

This annex refers to section 5.6. The table was forwarded to the ICES Data Centre by Lynda Webster, shortly after the MCWG 2015 meeting.

Parameter Code	Name	Parameter Group Code	Name	Comments
AOX-U	absorbable organic halogens - unspecified	OC-CL	Organochlorines (general)	Operationally defined rather than chemically defined parameter.
CEE1	Chloroethene	OC-CL	Organochlorines (general)	
CL-	Chloride ion	I-MAJ	Major inorganic constituents	Major inorganic constituents
CN-	Cyanide ion	I-MAJ	Major inorganic constituents	
CNTOT	Cyanides (as total CN)	I-MAJ	Major inorganic constituents	
CODCr	Chemical oxygen demand (dicromate method)	O-MAJ	Major organic constituents	Operationally defined rather than chemically defined parameter.
CODMn	Chemical oxygen demand (potassium permanganate method)	O-MAJ	Major organic constituents	
CR3+	Chromium ion(3+)	I-MET	Metals and metalloids	Organic esters
DBAC	2-(2-Butoxyethoxy)ethyl acetate	O-ES	Organic esters	
DCFPP	p,p'-Dicofol	O-GPT	Pesticides (general)	
F	Fluorine	I-MAJ	Major inorganic constituents	Not sure- doesn't seem to fit in any group, main use is as a solvent so surprised anyone measuring it. Maybe need new group but not sure what- organic compound (general) or ether?
MTBE	Methyl tertiary butyl ether			
NAPCLD	Naphthalene, chloro derivatives	OC-CL	Organochlorines (general)	Or new group- polychlorinated naphthalenes - PCN, may be better
NOPHE4X	Phenol, 4-nonyl-, branched	O-PHC	Phenols/chlorophenols	
PAM3	3-Methylphenanthrene	O-PAH	Polycyclic aromatic hydrocarbons (PAHs)	Organofluorines
PFTDA	Perfluorotetradecanoic acid	O-FL	Organofluorines	
PFTTrDA	Perfluorotridecanoic acid	O-FL	Organofluorines	Organofluorines
PFUnda	Perfluoroundecanoic acid	O-FL	Organofluorines	
PRCAZL	Propiconazole	O-GPT	Pesticides (general)	Polycyclic aromatic hydrocarbons (PAHs)
PYRM2	2-Methylpyrene	O-PAH	Polycyclic aromatic hydrocarbons (PAHs)	
SRFAN	anionic surfactants			More like a parameter Group than a parameter- loads of anionic surfactants. There may be a method to determine anionic surfactants as methylene blue active substances (MBAS). This might place the parameter closer to the COD/AOX parameters, perhaps?
STYRN	Styrene	O-MAH	Monocyclic aromatic hydrocarbons	Needs new parameter group
TBEP	Tris(2-butoxyethyl) phosphate		Organophosphorus flame retardants	
TBP	Tri-n-butyl phosphate		Organophosphorus flame retardants	Needs new parameter group
TCLEP	Tris(2-chloroethyl) phosphate		Organophosphorus flame retardants	
TCP	Tris(1-chloro-2-propyl) phosphate		Organophosphorus flame retardants	Needs new parameter group
TDCPP	Tris(1,3-dichloro-2-propyl) phosphate		Organophosphorus flame retardants	
TEHP	Tri(2-ethylhexyl) phosphate		Organophosphorus flame retardants	Needs new parameter group
TPP	Triphenyl phosphate		Organophosphorus flame retardants	

## Annex 8: Resolution for a TIMES draft manuscript on methods to determine chlorophyll

This annex refers to section 5.9.2.

The report on “**Methods for the Determination of Chlorophyll in Seawater**”, prepared and edited by Pamela Walsham (UK) and other members of the MCWG, as reviewed and approved by the Chair of the SSGEPI, will be published in the ICES Techniques in Marine Environmental Sciences (TIMES) series. The manuscript will describe and compare different analytical methods and include aspects of quality assurance and quality control as well as data reporting and storage.

The estimated number of pages is 20.

The authors agree to submit the final draft of the proposed publication by 30 June 2016.

### Supporting Information

Priority	Although chlorophyll is included in the OSPAR CEMP programme and many national monitoring programmes as an eutrophication parameter, no TIMES guidelines exist. Updates of and guidance on analytical methods are needed because different methods for chlorophyll a determination seem to lead to systematically different results.
Scientific justification	Two main methods exist for the determination of chlorophyll a: Fluorometric/Photometric method and a method based on high performance liquid chromatography (HPLC) with ultraviolet (UV) or diode array detection (DAD). MCWG 2014 discussed that these methods lead to systematically different results. This conclusion was supported by data analyses performed by QUASIMEME on chlorophyll results in the QUASIMEME database and by scientific presentations at previous MCWG meetings. OSPAR recognises this difference by using different parameters, but this differentiation might not be consistently used in all cases (data analyses, reports etc.). The TIMES manuscript will review the literature, provide guidance on analytical and reporting issues and discuss implications for assessments.
Resource requirements	Cost of production and publication.
Participants	MCWG members, potentially additional experts, external reviewers.
Secretariat facilities	Help with document preparation/publication. Final editing.
Financial	Publication costs.
Linkages to advisory committees	-
Linkages to other committees or groups	-

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Linkages to  
other  
organizations

This documentation is relevant for OSPAR and QUASIMEME, and for other organizations involved in the monitoring of eutrophication.

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## Annex 9: Updates of Background Concentrations (BCs) and Background Assessment Concentrations (BACs) for dissolved organic contaminants in water

The table summarises the results of the work described in section 5.11. It gives the Measurement uncertainty (MU) in ng per sampler derived from amounts reported for non-exposed passive sampling devices and from reported limits of detection (LODs) in connection with the QUASIMEME development exercise on passive sampling. It further provides Background Concentrations (BC) and Background Assessment Concentrations (BAC) as suggested previously (MCWG 2013) and updated BAC estimates.

Compound	MU from reported amounts (ng)	MU from reported LODs (pgL <sup>-1</sup> )	BC <sub>2013</sub>	BAC <sub>2013</sub>	BC <sub>2015</sub>	BAC <sub>2015</sub>
Naphthalene	-	-	160	5760	130	5700
Acenaphthene	5.1	3.8	-	-	38	160
Acenaphthylene	2.5	3.8	-	-	18	105
Fluorene	4.4	3.2	-	-	43	110
Phenanthrene	19	5.1	43	286	31	180
Anthracene	2.6	3.7	6	73	3	20
Dibenzothiophene	-	-	21	78	9	65
Fluoranthene	10	3.4	16	55	12	53
Pyrene	12	3.5	9	46	4	48
Benz[a]anthracene	3.0	2.8	2	10	0.6	9
Chrysene/Triphenylene	3.7	3.8	4	13	3	13
Benzo[b]fluoranthene+ Benzo[j]fluoranthene	2.0	3.8	4	11	4	9
Benzo[k]fluoranthene	1.3	3.8	5	13	5	8
Benzo[e]pyrene	-	-	3	10	3	11
Benzo[a]pyrene	-	-	2	10	1	9
Benzo[ghi]perylene	1.4	3.8	1	9	0.5	4
Indeno[1,2,3-cd]pyrene	0.4	3.8	1	9	1	2
Dibenz[a,h]anthracene	0.3	3.9	0.2	8	0.2	1
PCB 28	1.4	0.9	0	1	0	4
PCB 52	1.3	1.1	0	1	0	3
PCB 101	1.5	1.0	0	1	0	4
PCB 118	0.2	0.88	0	1	0	3
PCB 138	1.1	0.9	0	1	0	3
PCB 153	1.6	1.1	0	1	0	4
PCB 180	0.6	1.0	0	1	0	1
γ-HCH	-	-	0	40	0	45
α-HCH	-	-	0	40	0	45
p,p'-DDE	-	-	0	1	0	1
hexachlorobenzene	1.2	1.1	0	1	0	4

dieldrin	-	-	0	2	0	1
hexachlorobutadiene	34	2.4	-	-	0	180
BDE 28	0.1	0.4	-	-	0	0.2
BDE 47	0.2	0.5	-	-	0	0.5
BDE 99	0.2	0.7	-	-	0	0.4
BDE 100	0.2	0.7	-	-	0	0.5
BDE 153	0.2	0.4	-	-	0	0.4
BDE 154	0.1	0.4	-	-	0	0.3