

# ICES MCWG REPORT 2017

SCICOM STEERING GROUP ON ECOSYSTEM PRESSURES AND IMPACTS

ICES CM 2017/SSGEPI:07

REF. ACOM, SCICOM

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

6–10 March 2017

Hamburg, Germany



**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)

Recommended format for purposes of citation:

ICES. 2018. Interim Report of the Marine Chemistry Working Group (MCWG), 6–10 March 2017, Hamburg, Germany. ICES CM 2017/SSGEPI:07. 47 pp.

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## Executive summary

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The Marine Chemistry Working Group (MCWG) met for the second meeting of its 3-year term on 6–10 March 2017 in Thünen Institute, Hamburg, Germany. The meeting was attended by 16 members from 9 countries and by two local members of the MCWG. In addition, valuable contributions were received from four staff members of the BSH Institute.

The MCWG terms of reference require the group to **(a)** respond to requests for advice; **(b)** review developments in MSFD and WFD, in particular regarding emerging and priority substances (incl. EQS values, conversion factors); **(c)** report on new developments in QUASIMEME and other proficiency testing schemes relevant to MCWG; **(d)** report and present new information on marine litter and its role as potential source of contaminants, incl. desorption in digestive tract of organisms concerned; **(e)** summarise and synthesise relevant info from other expert groups (WGMS, WGBEC, WGEEEL, WGSE, WGOH, WGPME); **(f)** report from data, research and developments in Ocean Acidification; **(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 a TIMES manuscript; **(h)** report on inter-calibration exercises on passive sampling with a view to adjustment of background assessment concentrations; obtain information regarding the use of  $C_{free}$  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; **(i)** OSPAR request: MCWG and WGMS are requested to report on the selection and de-selection of hazardous substances of concern to coastal and marine waters in the OSPAR maritime area. Reporting should: 1) Identify and collate information on projects, activities and sources of information for new and emerging substances; as well as 2) Review the information to identify new and emerging substances, identify information gaps and recommend what further work is needed.

In 2017, there were three requests under ToR a) from the ICES Data Centre. In the first one, MCWG was requested to review the P01 code for chlorophyll *a* analysis and indicate if other P01 codes were necessary to fulfil the requirements of the OCEAN database. The list extracted from the BODC P01 Vocabulary list contains 101 entries and is presented in Annex 3. MCWG did not consider it necessary to add any additional entries to this list. The second request was to consider whether the method fields included in DOME were sufficient. MCWG reviewed the different method Code Types and identified changes which might improve the use of the DOME database. MCWG has recommend two changes to address this. In addition, MCWG noted checks made to data entering the various ICES databases can be viewed at <http://gis.ices.dk/OC/> and participants will encourage their respective National Data Centres to perform the checks. MCWG 2017 was also asked to review Technical Annex 4 of the OSPAR JAMP Guidelines for Monitoring Contaminants in Sediments on the analysis of TBT in sediments.

Under ToR b, MCWG was updated on the MSFD, and noted three inconsistencies. Human health issues must be dealt with under Descriptor 9 and not under Descriptor 8, both for priority and additional substances, so merging the EQS levels for D8 and D9 by picking the lowest value and applying them to both descriptors makes no sense. The EQS

for riverine basin-specific pollutants has to be derived on a national level that may differ an order of magnitude and should be harmonised on a regional level. Practice proves this to be difficult.

Under ToR c, Quasimeme provided MCWG with feedback on the previous year's reporting and the schedule for the upcoming year. QUASIMEME informed the group that tests will be undertaken to determine whether it will be possible to make a test material for OA parameters during 2017. Quasimeme also reported that a Workshop on Organotin analysis was planned for the end of 2017. MCWG members offered to assist Quasimeme with the upcoming review of lab performance against method of analysis.

Under ToR d, Kine Baek (Norway) presented details of Plastox project investigating the uptake of pollutants by microplastics, while Lucia Viñas (Spain) provided details on the BASEMAN and IMPACTA microplastic projects.

Under ToR e, the chairs of WGBEC and WGMS were asked to provide details on "any other relevant information" to MCWG. WGEEL provided feedback by Michiel Kotterman (The Netherlands). On the special ToR i, there were two virtual joint sessions with WGMS (see below).

On ToR f, the outcome of the Quasimeme Workshop on Ocean Acidification was discussed, and the group took note of the development of a Proficiency test for OA parameters, as suggested by the workshop report. MCWG 2017 were also updated on the recent ICES/PICES Workshop on Understanding the Impacts and Consequences of Ocean Acidification for Commercial Species and End-users (WKACIDUSE).

Under ToR g, the drafting of a TIMES publication for chlorophyll analysis was discussed along with the results of the recent study, undertaken by QUASIMEME, to determine the influence of methodology on analytical results for chlorophyll measurements. In addition, MCWG met, via video conferencing, with the co-chair of WGPME who agreed their group would contribute to the revision of the publication. Following review of the current TIMES paper for chlorophyll analysis, it was agreed that the changes required were too substantial to merit a simple revision and a Category 1 resolution for a new paper to SICOM would be required.

The review of the TIMES paper 'Guidelines for determining polymer-water and polymer-polymer partition coefficients of hydrophobic organic compounds' was covered under ToR h. MCWG provided comments and advice on the manuscript which will be progressed intersessionally aiming to have it completed by next year's meeting.

Finally, MCWG received an additional ToR i, requested by ICES ACOM, to report on the selection and deselection of hazardous substances of concern to coastal and marine waters. MCWG 2017 spent a considerable amount of time discussing what the group could offer. There are no ecotoxicologists within MCWG and this advice could not be provided. The list of potential hazardous compounds is vast, and care needs to be taken reducing the number of compounds without losing important ones. MCWG felt the emphasis should be based on risk, potential amounts making it to the marine environment, and compounds that are used or historically present in the marine environment (antifouling, anti-corrosion compounds used on offshore wind farms and dumped chemical warfare agents, etc.). Moreover, although delivery of the ICES advice to OSPAR has a fixed end-point in time, MCWG 2017 felt the continuous update of this kind of work is essential.

## 1 Administrative details

<p><b>Working Group name</b> Marine Chemistry Working Group (MCWG)</p> <p><b>Year of Appointment within current cycle</b> 2016</p> <p><b>Reporting year within current cycle (1, 2 or 3)</b> 2</p> <p><b>Chair(s)</b> Koen Parmentier, Belgium</p> <p><b>Meeting dates</b> 6–10 March 2017</p> <p><b>Meeting venue</b> Hamburg, Germany</p>
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## 2 Terms of Reference a) – z)

ToR	DESCRIPTION	BACKGROUND	SCIENCE PLAN		EXPECTED DELIVERABLES
			TOPICS ADDRESSED	DURATION	
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	Availability of high quality proficiency testing is vital to produce reliable results.	20, 21, 27, 31	3 years	Provide guidance for proficiency testing

	information on other proficiency testing schemes with relevance to MCWG.				
d	<p>Marine litter and its role as a potential source of contaminants:</p> <p>i) Report on new information regarding marine litter as a potential source of contaminants, with particular focus on field studies reporting elevated contaminant levels associated with plastics.</p> <p>ii) Present available information on contaminant desorption from plastic in the digestive system after uptake.</p>	<p>Effects of marine litter are poorly understood, and all additional information will increase our understanding of all processes involved.</p>	1, 13, 19, 20, 21, 25, 27	3 years	Review paper in collaboration with the ICG-ML
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	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

	determining EACs, and review information on mixture toxicity derived from passive sampling/dosing.			
i	<p>OSPAR request: MCWG and WGMS are requested to report on the selection and de-selection of hazardous substances of concern to coastal and marine waters in the OSPAR maritime area.</p> <p>Reporting should:</p> <ol style="list-style-type: none"> <li>1) Identify and collate information on projects, activities and sources of information for new and emerging substances; as well as</li> <li>2) Review the information to identify new and emerging substances, identify information gaps and recommend what further work is needed.</li> </ol>	<p>Reporting should be done to ensure that in the new and emerging hazardous substances in the marine environment (of the OSPAR maritime area) that are of general concern to coastal and marine waters are identified, so that appropriate action can be taken by OSPAR. The work by MCWG and WGMS should build on and be coordinated with the already established EU WFD Watch List process and the relevant OSPAR List. Reporting should also take into account other research programmes that screen substances in the marine environment, e.g. through passive sampling, tissue analysis, sediment sampling etc.</p>	1.5 years	<p>MCWG and WGMS are requested to provide an intermediate report on progress of work by 10 March 2017 for the attention of ACOM.</p> <p>Based on feedback to the ICES Secretariat from OSPAR HASEC, update and finalize their work by 12 October 2017 and report to ACOM.</p>

### 3 Summary of Work plan

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

### 4 List of Outcomes and Achievements of the WG in this delivery period

#### 4.1 ToR A: Respond to requests for advice from Regional Seas Conventions and ICES Data Centre

##### 1) Chlorophyll a parameters reporting to Ocean Database

The ICES Data Centre requested MCWG review current BODC P01 method codes for chlorophyll *a* analysis, as a first approach to the introduction of chlorophyll *a* parameters



into the OCEAN database. The BODC P01 vocab has an extensive list of near 300 entries related to chlorophyll parameters.

This list was reviewed in order to check those that may be needed in the current stage of development of the OCEAN database. MCWG only considered entries regarding chlorophyll *a* in water associated to method of analysis are appropriate. The final list, extracted from BODC P01 Vocab list, contains 101 entries and is presented in Annex 3.

MCWG 2017 did not identify the need for any additional entries to this list currently.

## 2) DOME views

MCWG reviewed the different method Code Types and has identified several changes which might improve the use of DOME database for the end user. Two major changes are recommended:

In the case of Code Type METCX (Method of chemical extraction) MCWG felt that it was not appropriate to include the solvents used and suggest limiting the submission of information to some more general methods (*e.g.* solvent extraction, complexation, acid digestion). METCX would be dedicated solely to extraction methods with a new code type dedicated to extraction chemicals being created which would only become available after the previous field was filled. The new code type would have a list of extraction solvents/chemicals such as , acetone, hexane/DCM, HNO<sub>3</sub> etc.

In the case of CodeType METOA (Method of analysis/assay type), MCWG's advice is to reduce the list of available choices for several hyphenated techniques (*e.g.*, GC and HPLC), in order to simplify data submission and avoid redundancies.

MCWG also considers that some gaps or overlaps of information contained in the methods exist and that they must be solved in order to prevent misinterpretations. This information is summarized in the table in Annex 3 along with MCWG recommendation.

## 3) Comments on the OSPAR JAMP Guidelines for Monitoring Contaminants in Sediments Technical Annex 4: analysis of TBT in sediment

The technical guidelines on analysis of the mono-, di- and tributyl-tin compounds are very comprehensive and (to the knowledge of experts present) covers all essential aspects of analysis of these compounds. MCWG 2017 has only few remarks:

- also refer to the DIN EN ISO 23161:2011–10.
- During the MCWG 2017 meeting there was a discussion with Steven Crum from Quasimeme on potential stability problems of test samples, produced by Quasimeme, possibly as a consequence of organotin degradation. Therefore, with respect to certified reference materials, MCWG 2017 suggests to emphasize in the guideline that their organotin content should be scrutinized on a regular basis, although they should have been checked on stability and storage conditions on beforehand.
- For decimal number, periods have to be used instead of commas.

## 4.2 ToR B: Review Developments in MSFD and WFD

MCWG 2017 was updated with developments on MSFD and WFD monitoring. As part of MSFD monitoring, contaminants from the WFD should be monitored within coastal territories. Reference is made to compounds specified in Directive 2008/105/EC (priority substances) and to river basin-specific pollutants. It is possible to monitor additional compounds if relevant. For these contaminants, the matrix and threshold values used for the assessment shall be representative for the most sensitive species and exposure pathway, including hazards to human health via exposure through the food chain.

The MSFD approach gives rise to some inconsistencies:

- 1) Directive 2008/105/EC specifies biota EQSs for 11 substances, of which 7 have been derived for the protection of human health and four for the protection of top predator from secondary poisoning. Risk to human health should, however, be covered by descriptor 9 instead of descriptor 8.
- 2) For river basin-specific pollutants, the responsibility to derive EQS values is at national level, which may lead to different EQSs for the same substance, which may differ by orders of magnitude. It would be advisable to agree EQSs for those substances on a regional level.
- 3) For additional contaminants, hazards to human health should be considered in derivation of threshold values for those compounds. Again, risk to human health should be covered in descriptor 9 instead of descriptor 8.

The MCWG internal report of the outcome of the Working Group on Chemicals is attached as Annex 4.

## 4.3 ToR C: New developments in Quasimeme or other proficiency testing schemes

- Quasimeme reported the highly contaminated Goole harbour sediment which caused analytical issues for several laboratories, has been removed from stock;
- The test feeding mussels contaminated material (TBT, PAHs and PCBs) proved successful and is likely to be used as test materials in the future;
- BT-10 (PFAS) will be held twice a year from 2017 onwards; MS-8 (PFAS) will be held in April as there are now 8 participants;
- A new parameter code will be added for PAHs: Total benzo-fluoranthene (a+b+j+k) to align with reporting requirements;
- Measurements for Ocean Acidification parameters, Total Alkalinity (TA) and dissolved inorganic Carbon (DIC) will be initiated as a pilot study by Koen Parmentier, RBINS, Belgium in collaboration with Scripps, San Diego;
- An overview of biota and sediment test material for the coming years was presented for approval;
- Quasimeme, noted performance by participating labs for brominated flame retardants in biota samples (BT 9) has improved and as a consequence the constant error for BT9 is to be reduced;
- Quasimeme also reported they have observed degradation of the test materials on long term storage for both organotins and PAHs;

- Quasimeme is considering organising a number of workshops in the near future. An analytical Workshop on Organotin analysis is scheduled for the end of 2017 or early 2018 and will be organised by RBINS, Belgium. VU Amsterdam (Prof. Jacob De Boer) is investigating whether a Workshop on Microplastics, focussing on methodology is required. The need for a workshop on phosphorus Flame Retardants will also be evaluated;
- Quasimeme celebrates 25th anniversary in 2017 and hopes to hold a small symposium to mark this event Jan/Feb 2018. In advance of this meeting, Quasimeme asked MCWG for volunteers to look at data along with the method codes to determine any methodology trends. A number of MCWG members offered to assist with this task: Philippe Bersuder (BFR, TBT & PFAS), Bavo De Witte (PAHs), Lutz Ahrens (PFAS), Lucia Viñas, Peter Lepom, Koen Parmentier (nutrients, PAHs, TBT);
- The calculation of Quasimeme z-scores has been amended to meet the requirements of ISO 13528. Quasimeme presented the new uncertainty calculation for determining z-scores which will be used for reporting from 2016.2 onwards. Quasimeme also presented details of the new Method Information Codes (MICs) providing guidance on how to enter this information into the database along with how this information is presented in the reports.

#### 4.4 ToR D: Marine litter and its role as a potential source of contaminants

MCWG was updated with details of three Marine Litter projects, namely PLASTOX (Torben Kirchgeorg), BASEMAN (Lucia Viñas) and IMPACTA (Lucia Viñas):

- PLASTOX: PLASTOX is one of the four funded 3 years-projects of the JPI Oceans Call on micro plastics. 15 institutions are part of the consortium, coordinated by SINTEF (Norway), working on the direct and indirect ecotoxicological impacts of microplastics on the marine environment. The main targets can be summarized as: a) The investigation of adsorption and desorption behaviour of common POPs, additives and metals on different types of microplastics in the environment and in laboratory tests; b) the uptake through ingestion and other routes by analyses of marine organism tissue; c) the acute and sub-lethal eco-toxicological effects will be investigate for a wide range of marine organisms, covering the food chain of the European marine environment; d) investigation of the food web transfer of microplastics and POPs and metals associated with microplastics.

All partners will use the same microplastic materials for the different experiments. These are provided by the project partner CARAT GmbH (Bocholt, Germany). Different types of materials are available: e.g. LDPE, HDPE, PE, PP, PET and PVC and different stages of their lifetime: pristine pellets, post-industrial pellets, post-consumer, environmental samples. For the different requirements of the planned experiments, different sizes of the material will be produced and additional information (e.g. technical data sheet, metal content) of the material will be provided by CARAT.

First exposure studies in other countries have already started. Biofouling is a challenging problem for the exposure studies. Exposure time between 2 weeks

and 24 months are planned. SOPs were elaborated to guarantee a similar pre-treatment, sampling and analyses of the exposed material.

Further information about the project and the other work packages are available at: <https://www.sintef.no/projectweb/plastox/>

- BASEMAN: BASEMAN, “Defining the baselines and standards for microplastics analyses in European waters”, is one of the four projects funded in the JPI Call on ecological aspects of microplastics for a 3-year period starting in January 2016. It involves 18 partners and 6 associated partners.

At present, microplastics are recognized as an emerging contaminant in the environment but there are still some aspects that need to be standardized such as sampling, extraction, purification and identification if the results of the ongoing projects are to be compared.

The main aim of the BASEMAN project is to overcome this problem by means of validating and harmonizing analytical methods which are indispensable for the identification and quantification of microplastics in the environment.

- IMPACTA: The IMPACTA project (Impact of regulated and emerging pollutants and microplastics in marine ecosystems, CTM2013–48194-C3) main objective is to evaluate the distribution of regulated pollutants as well as pollutants of emerging concern (pharmaceuticals, perfluorinated compounds, phthalates, plastic additives, personal care products, alkylphenols, alkylated PAHs and organophosphorus, triazines and other current-use pesticides) and microplastics and to assess their related biological effects. This project focuses on marine sediments and seawater in two coastal areas (Vigo Ría and Mar Menor lagoon) and some selected stations in the Atlantic and Mediterranean Spanish coastal shelves.

Samples were collected in spring and autumn 2015 to study the pollutant distribution seasonal variations. Sensitive and selective analytical methods have been developed and validated for both matrices. The distribution of emerging organic pollutants in coastal areas was heterogeneous depending on the distance to the source, hydrodynamic, dilution capacity, suspended solids sedimentation, etc. Significant seasonal variations of the current-use pesticides, pharmaceuticals and other pollutants concentrations had been previously found in coastal sediments (Moreno-González *et al.* 2015; 2017), as a consequence of variations in sources discharges, temperature, sun irradiation, etc. The study of the Atlantic and Mediterranean continental shelves sediment samples will allow the identification of those emerging pollutants that can access deeper sediment areas.

#### 4.5 ToR E: Synthesis with other ICES expert working groups

WGMS and WGBEC were contacted via e-mail for an update on “any other relevant information”. ToR I was discussed with WGMS, who were meeting the same week in Ancona, Italy, via teleconference. WGEEL feedback was given through Michiel Kotterman, not present at the meeting, via e-mail. WGEEL reported some members think that lipid concentrations in eels are dropping and that this may be as a consequence of contamination by persistent organic pollutants (POPs) such as PCBs. However, this has not been

confirmed and members want this hypothesis to be confirmed by further data reviews. POP-effects in eel are lacking, rendering support for either one of these theses difficult. WGPME was contacted during a teleconference with Alexandra Kraberg, Co-chair of WGPME, during the meeting (see below: ToR g).

#### 4.6 ToR F: Ocean Acidification

MCWG 2017 were updated with developments with Ocean Acidification. Following on from MCWG 2016, where the outcomes of the Quasimeme Workshop on Quality Assurance for Inorganic Carbon System Measurements in Context of Ocean Acidification (OA) Monitoring were presented, a report on the workshop was prepared and presented to OSPAR. Quasimeme is planning to prepare a reference material for inorganic carbon system measurements which will be tested in 2017 with a view to undertake a development exercise in 2018. This was welcomed by MCWG 2017.

MCWG 2017 were also updated on the recent ICES/PICES Workshop on Understanding the Impacts and Consequences of Ocean Acidification for Commercial Species and End-users (WKACIDUSE). There is increasing concern about the impacts of OA with research suggesting that the effects of OA will vary between groups of marine organisms and in some cases there may be dramatic consequences for ecosystems. Identifying factors responsible for this variability in species/ecosystem sensitivity is a priority. It is therefore important to understand the effects and repercussions of OA for ecosystems, fisheries and aquaculture in conjunction with other stressors such as increasing temperatures, overfishing and pollution. Of specific interest to MCWG were:

- Funding for large scale ocean acidification (OA) ecosystem studies have ended (UKOA program) or are nearing completion (German Bioacid) in the ICES area with only the PICES and AMAP continuing to fund such research. There are still knowledge gaps in OA studies, which cannot be addressed by short time scale studies. Participants highlighted the need to understand OA ecosystem impacts in conjunction with other stressors such as increasing sea temperatures, overfishing and contaminants.
- Prevailing conditions:
  - i) Understanding prevailing conditions is important if any ecosystem response is to be assessed.
  - ii) The Pacific and Atlantic Oceans are showing a consistent annual pH decrease -0.0011/y to -0.0024/y.
  - iii) The downward pH trend in coastal waters is significantly larger than in the open ocean (-0.0012/y to -0.02/y), however this rapid decrease may not be a consequence of OA alone. Several long term OA coastal studies began around the time eutrophication controls were introduced to coastal regions. The limited datasets which pre-date eutrophication controls show increasing pH until eutrophication measures were introduced. It was also noted that the physical and biological conditions should also be considered in conjunction with chemical conditions in coastal areas.
  - iv) Sediment pore water, seasonal & diurnal pH variability is often greater than annual pH trend and may influence adaptability of coastal and benthic communities. However, organisms may currently exhibit resilience

but might be at the edge of their tolerance window (physiological responses) which may become narrower due to other stressors such as increasing temperatures.

#### **4.7 ToR G: Report on Quasimeme assessment of chlorophyll data and implications for revision on the ICES Chlorophyll TIMES paper**

Steven Crum (Quasimeme) reported that Quasimeme had undertaken a review of the analytical techniques and extraction solvents used for the analysis of chlorophyll *a* by participants with a view to identify issues with the methods. A number of laboratories were extracting samples based on the Lorenz method, which includes an acidification step. The acidification step is used to correct chlorophyll *a* from interference from magnesium free chlorophyll derivatives (phaeopigments). The revised OSPAR JAMP Eutrophication Monitoring Guidelines (OSPAR Agreement 2012–11) no longer recommend acidification because it is time consuming and the results are questionable. It is currently not clear whether data reported to Quasimeme has been corrected for phaeopigments. Quasimeme will introduce a new determinant to the chlorophyll *a* round in 2017 for the acidified step. It is expected results will be fed back to MCWG 2018.

Pamela Walsham (Marine Scotland) reported the current ICES TIMES paper for chlorophyll analysis, ICES TIME 30 (Aminot and Ray) had been reviewed. ICES TIME 30 no longer reflects current methodology or reporting practices and revision of this document would prove difficult. The chemical oceanography sub-group met via WebEx with a Co-chair of the ICES working group on phytoplankton and microbial ecology (WGPME) to discuss the chlorophyll TIMES paper with both MCWG and WGPME agreeing a new TIMES paper was required which would also include information provided by Quasimeme. The paper will expand on the information within ICES TIMES 30 and ensure it is relevant for current statutory requirements for drivers such as MSFD and WFD. The paper aims to provide a comprehensive guide to ensure data issues with cross boundary regional assessments are minimised.

The aim was to be completed intersessionally by spring 2018, however since the meeting the MCWG chair was informed a Category 1 Resolution would be required by SCICOM.

#### **4.8 ToR H: Report on intercalibration exercises on passive sampling**

- 1) MCWG 2017 commented on “Guidelines for determining polymer-water and polymer-polymer partition coefficients of hydrophobic organic compounds” written by Kees Booij - Foppe Smedes - Ian J. Allan

The document gives guidance for the measurement of polymer-water and polymer-polymer partition coefficients of hydrophobic organic compounds and is in general well written as equilibrium and kinetic methods are extensively discussed. However, some parts are written like a review article not, as the title implies, as a guidance document. The following issues need to be improved: i) Provide a more clear structure which is typical for a guidance document and make sure that the headlines are precise and reflects the content of the section, ii) use more precise language/terms, iii) provide more examples for the equations, iv) provide units for all equations, and v) give more guidance; this can also build up on other guidance documents (e.g. Smedes, Booij (2007): Guidelines for passive sampling of hydrophobic contaminants in water using silicone rubber samplers).

Overall, the document needs major revisions before submitting to TIMES. General and specific comments are provided in the document uploaded on the ICES share point. MCWG members are happy to provide more comments and offer to help in the further process to finalize the guidance document. The final version should be finish in March 2018.

- 2) MCWG 2017 enquired whether an alternative for the calibrated silicone rubber Altesil was available. After contacting Foppe Smedes, former MCWG and WGMS member and specialist in the matter, two possible alternatives were proposed:

SSP (Specialty Silicone Products (producer)): a material that is likely pure PDMS (with fumed silica) platinum cured, which has been used by Philip Mayer and Anika Jahnke for a number of years. Foppe selected a 0.25 mm, (takes less space in the soxhlet upon extraction),  $K_{pw}$  are lower by a factor 1.5–3 (up to 0.3 log unit), this material was used in the last Quasimeme round.

J-flex: this is not PDMS but silicone rubber like Altesil. In Smedes *et al.* (EST 2009) both a red and a transparent type were tested. The Red type showed  $K_{pw}$  equal to Altesil, the transparent somewhat lower. Good quality, cheap, they do not show of with stable thickness, but so does SSP.

Foppe recommends this last one for further use, because SSP is a pure PDMS and has the lower  $K_{pw}$  (so more polar substances e.g. atrazine, will be even lower for SSP). Atrazine was sampled with Altesil, a silicone rubber, and likely also with j-flex. The red colour might protect for UV-degradation - to be confirmed.

#### 4.9 ToR I: OSPAR request to MCWG and WGMS on hazardous substances

MCWG and WGMS had two joint sessions arranged through Skype. There was agreed on a way forward between the two groups. This involved further intersessional work on a voluntary basis, the time to be devoted is anyway limited. Finally, results are presented as an outcome of the ADGHAZ meeting, attached as Annex 8.

MCWG suggests to use the term “substances of emerging concern” instead of “emerging substances”. MCWG thinks that the emphasis should be on existing prioritization exercises, and scrutinize this information, rather than make new lists. One of the first valuable exercises on marine substances of emerging concern is the work of Tornero and Hanke (2016). They provided a review on substances that might be released from sea-based sources. They established a list of 276 substances including 22 antifouling biocides, 32 aquaculture medical products and 34 warfare agents. They also provided an overview of those substances which have already been considered in European regulations. For the review of the list of priority substances, a prioritization process was conducted by JRC, starting with more than 11000 compounds and ending with a short list. OSPAR should consider this list and approach JRC to check whether marine aspects have been adequately considered. Adaptations to the list may be needed based on marine monitoring data and information on substances released from sea-based sources.

MCWG 2016 considered the following substance groups of emerging concern: dechlorane+, alternative brominated flame retardants, phosphorous flame retardants, antifoulants, per- and polyfluorinated substances (not PFOS, PFOA), benzotriazoles, siloxanes,

radiopaque substances, anticorrosion agents. As per the ICES request, MCWG compiled, in cooperation with WGMS, a non-exhaustive list of projects and sources. This table requires further amendment because access to literature search engines such as Scopus was not available to MCWG during the meeting. In a second step, these projects and sources should be evaluated and prioritized. As a result, a huge number of compounds may be identified. The difficulty will be to identify the relevant substances which may impact the marine environment. This should be based on toxicity, hazard properties, chemical and physical properties, production volumes and use patterns. However, MCWG considers this a knowledge gap as this information will not be available for the vast majority of the compounds. Although the REACH regulation is in place, toxicological information to predict the impact of chemicals on the marine environment is limited. Prioritization of the substances would be easier if from the beginning a more in depth investigation was obligatory.

## 5 Progress report on ToRs and workplan

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**ToR a:** Questions of the ICES Data Centre were addressed and answered. Comments on the Annex 4 analysis of TBT in sediment were delivered.

**ToR b:** There was a yearly update on MSFD. The report of the Expert Group on Chemicals was presented (Annex 4).

**ToR c:** Quasimeme new developments are closely followed; other PT schemes are regularly reported.

**ToR d:** The feedback from and cooperation with the ICG-ML is limited. MCWG have provided valuable information on projects on this topic, however, it is unlikely that a joint paper can be prepared by the 2018 MCWG Meeting.

**ToR e:** Feedback from and cooperation with WGMS is excellent, a joint paper with WGPME is in the pipeline. It should be highlighted that the fact that WGPME and MCWG meet in different periods and have no history in cooperation has had an impact on review and delivery of the chlorophyll TIMES paper.

**ToR f:** MCWG is ready to offer a forum to the OA research community during its yearly meeting.

**ToR g:** Agreement with WGPME for a joint TIMES publication on chlorophyll *a*. Instead of updating the existing document, both groups prefer the withdrawal of ICES TIMES 30 and replacement with a new document. A Category 1 Resolution was submitted to ICES SCICOM (see Annex 6 and section 6 of this report).

**ToR h:** Progress intersessionally on the completion of a TIMES manuscript. Draft document uploaded by Kees Booij (The Netherlands) and reviewed and commented by MCWG (Lutz Ahrens as lead).

**ToR i:** Significant effort was made during the meeting, and subsequently, to address this special ToR (OSPAR request) along with experts from WGMS. An interim report on this ToR was submitted to ICES in March (for reporting to OSPAR in March) and a final report in October 2017.



The special request from OSPAR to ICES for information for use in prioritising contaminants of emerging concern was addressed in plenary and intersessionally by WGMS and MCWG to produce interim and final reports to ICES. Production of these reports involved MCWG members in a number of teleconferences with ICES secretariat and the Advice Drafting Group Chair. The joint report was subject to an ICES Review Group and the MCWG Chair, Koen Parmentier, then attended (along with the WGMS Chair) the ICES Advice Drafting Group on Hazardous Substances (ADGHAZ) to help produce the final advisory document for sending to OSPAR. The report is attached as Annex 8.

## **6 Revisions to the work plan and justification**

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Since the MCWG 2017 meeting, a Category 1 resolution has been submitted to and approved by SCICOM (Annex 6). Prior to this submission MCWG were unable to contact the WGPME chair and agree a date for completion. The date set in the resolution does not meet with the WGPME reporting cycle and they have indicated they require an additional ToR to complete this work with a delivery date of 2 years.

## **7 Next meetings**

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The MCWG will meet in Vigo, Spain, 5–9 March 2018.

## Annex 1: List of participants

Name	Institute	Email
Marion Abraham	Leibniz-Institut für Ostseeforschung, Seestrasse 15, D-18119 Rostock, Germany	<a href="mailto:marion.abraham@io-warnemuende.de">marion.abraham@io-warnemuende.de</a>
Lutz Ahrens	Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences, Gerda Nilssons väg 5, 756 51 Uppsala, Sweden	<a href="mailto:lutz.ahrens@slu.se">lutz.ahrens@slu.se</a>
Kristin Andreasson	Swedish Meteorological and Hydrological Institute SMHI Göteborg Sven Källfelts gata 15 SE-426 71 Västra Frölunda, Sweden	<a href="mailto:kristin.andreasson@smhi.se">kristin.andreasson@smhi.se</a>
Kine Baek	Norwegian Institute for Environmental Research (NIVA), Gaustadalléen 21, 0349 Oslo, Norway	<a href="mailto:kine.baek@niva.no">kine.baek@niva.no</a>
Berit Brockmeyer	Bundesamt fuer Seeschifffahrt und Hydrographie (BSH) Federal Maritime and Hydrographic Agency, Germany	<a href="mailto:Berit.Brockmeyer@bsh.de">Berit.Brockmeyer@bsh.de</a>
Carlos Borges	Instituto Hidrografico Rua das Trinas 49 PT-1249-093 Lisbon, Portugal	<a href="mailto:carlos.borges@hidrografico.pt">carlos.borges@hidrografico.pt</a>
Steven Crum	Alterra Wageningen UR Droevendaalsesteeg 3, 6708PB Wageningen, The Netherlands	<a href="mailto:Steven.Crum@wur.nl">Steven.Crum@wur.nl</a>
Bavo De Witte	Institute for Agricultural and Fisheries Research (ILVO) Ankerstraat 1 8400 Oostende, Belgium	<a href="mailto:bavo.dewitte@ilvo.vlaanderen.be">bavo.dewitte@ilvo.vlaanderen.be</a>
Michael Haarich	Thünen Institute, Institute for Fisheries Ecology, Marckmannstrasse 129b, Building 4 20539 Hamburg, Germany	<a href="mailto:michael.haarich@ti.bund.de">michael.haarich@ti.bund.de</a>
Peter Lepom	Federal Environment Agency Bismarckplatz 1, 14193 Berlin, Germany	<a href="mailto:Peter.Lepom@uba.de">Peter.Lepom@uba.de</a>
Cathérine Munschy	Departement Biological Resources & Environment, Unit Biogeochemistry and Ecotoxicology, Rue de l'Île d'Yeu BP 21105, 44311 Nantes Cedex 03, France	<a href="mailto:cmunschy@ifremer.fr">cmunschy@ifremer.fr</a>
Koen Parmentier (Chair)	Royal Belgian Institute of Natural Sciences, OD NATURE, 3 <sup>de</sup> & 23 <sup>ste</sup> Linierregimentsplein, 8400 Oostende, Belgium	<a href="mailto:kparmentier@naturalsciences.be">kparmentier@naturalsciences.be</a>
Stefan Schmolke	Bundesamt fuer Seeschifffahrt und Hydrographie (BSH) Federal Maritime and Hydrographic Agency, Germany	<a href="mailto:Stefan.Schmolke@bsh.de">Stefan.Schmolke@bsh.de</a>

Name	Institute	Email
Lucia Viñas	Instituto Español de Oceanografía Centro Oceanográfico de Vigo Subida a Radio Faro 50 36390 Vigo (Pontevedra), Spain	<a href="mailto:lucia.vinas@vi.ieo.es">lucia.vinas@vi.ieo.es</a>
Pamela Walsham	Marine Scotland Science, 375 Victoria Road P.O. Box 101 AB11 9DB Aberdeen, United Kingdom	<a href="mailto:pamlea.walsham@gov.scot">pamlea.walsham@gov.scot</a>
Zhiyong Xie	Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research GmbH, Institute of Coastal Research Department for Environmental Chemistry, Max-Planck-Street 01, D-21502 Geesthacht, Germany	<a href="mailto:zhiyong.xie@hzg.de">zhiyong.xie@hzg.de</a>

## **Annex 2: Recommendations**

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None.

### Annex 3: ICES Data Centre Request

MCWG considers that some gaps or overlaps of information contained in the methods exist and that they must be solved in order to prevent misinterpretations. This information is summarized in the table below, along with MCWG recommendation to overcome the situation.

Code	Description	CodeType	Recommended Action	Remarks
HPLC-MS-MS (proposal)	HPLC - mass spectrometry – mass spectrometry	METOA	Add	
HPLC-DA (proposal)	HPLC – diode array detector	METOA	Add	
DFRZ	Freeze dried	METST; METPT	Remove from METST; keep on METPT	Not a method of storage
FRZND	Frozen directly without pretreatment	METPT	Move to METST	Not a method of pretreatment
HYDM	Hydrometer	METPT	Move to METOA	Not a method of pretreatment
PIP	Pipette analysis	METPT;METOA	Needs clarification	If it refers to titration is METOA
PL-GPC-DCM	PL-Gel GPC column with dichloromethane	METPT	Move to METOA	Not a method of pretreatment
SLAC	Silica column	METPT	Move to METPS	Not a method of pretreatment
HPLC	High performance liquid chromatography	METPS;METOA	Remove from METPS; keep on METOA	
GC	Gas chromatography	METPS;METOA	Remove from METPS; keep on METOA	
GC-KAT	Gas chromatography - katharometer	METPS;METOA	Remove from METPS; keep on METOA	
	Preparative Liquid Chromatography	METPS	Add	
	Column Chromatography (including SPE)	METPS	Add	
	Cu Treatment	METPS	Add	
	TBA Treatment	METPS	Add	
	Acid treatment	METPS	Add	
SOX	Soxhlet method	METCX;METOA	Remove from METOA; keep on METCX	Not a method of analysis

Finally, a general review of the codes description should be made in order to correct for mistypes (*e.g.*, for AAS-HB the definition must be corrected from "...hybrid/hybride generation..." to "...hydride generation...")

Data Centre will check and the MCWG members will pass this information to their national data centres.

**Table: BODC P01 Vocab List extract (chlorophyll *a* associated to method of analysis)**

conceptid	Preflabel
CHLADMFA	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >GF/F phase] by filtration, N, N-dimethylformamide extraction and fluorometry
CPHLFEP1	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >GF/F phase] by filtration, ethanol extraction and fluorometry
CPHLFLCF	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate 0.2–10um phase] by cascade filtration, acetone extraction and fluorometry
CPHLFLP1	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >GF/F phase] by filtration, acetone extraction and fluorometry
CPHLFLP2	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >0.4/0.45um phase] by filtration, acetone extraction and fluorometry
CPHLFLP3	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >GF/C phase] by filtration, acetone extraction and fluorometry
CPHLFLP4	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >0.2um phase] by filtration, acetone extraction and fluorometry and summation of size-fractionated values
CPHLFLP5	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >0.2um phase] by filtration, acetone extraction and fluorometry
CPHLFLP6	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >GF/F phase] by filtration, acetone extraction and fluorometry and summation of size-fractionated values
CPHLFLP8	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >0.8um phase] by filtration, acetone extraction and fluorometry
CPHLFLPC	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >unknown phase] by centrifugation, acetone extraction and fluorometry
CPHLFLPZ	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >unknown phase] by filtration, acetone extraction and fluorometry
CPHLFMP1	Concentration of chlorophyll- <i>a</i> {chl- <i>a</i> CAS 479–61–8} per unit volume of the water body [particulate >GF/F phase] by filtration, methanol extraction and fluorometry

CPHLHPP1	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >GF/F phase] by filtration, acetone extraction and high performance liquid chromatography (HPLC)
CPHLHPP2	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >0.4/0.45um phase] by filtration, acetone extraction and high performance liquid chromatography (HPLC)
CPHLHPP4	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >0.2um phase] by filtration, acetone extraction and high performance liquid chromatography (HPLC) and summation of size-fractionated values
CPHLHPP5	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >0.2um phase] by filtration, acetone extraction and high performance liquid chromatography (HPLC)
CPHLHPPB	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-3um phase] by filtration, acetone extraction and high performance liquid chromatography (HPLC)
CPHLHPPC	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 3-20um phase] by filtration, acetone extraction and high performance liquid chromatography (HPLC)
CPHLHPPZ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by filtration, acetone extraction and high performance liquid chromatography (HPLC)
CPHLINTC	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit area of the water body [particulate >0.2um phase] by filtration, acetone extraction and high performance liquid chromatography (HPLC) and profile integration
CPHLMHP1	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >GF/F phase] by filtration, methanol extraction and high performance liquid chromatography (HPLC)
CPHLPL01	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by in-situ chlorophyll fluorometer and laboratory calibration applied
CPHLPM01	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by in-situ chlorophyll fluorometer and manufacturer's calibration applied
CPHLPM02	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by in-situ chlorophyll fluorometer (second sensor) and manufacturer's calibration applied
CPHLPR01	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by in-situ chlorophyll fluorometer
CPHLPRKG	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit mass of the water body [particulate >unknown phase] by in-situ chlorophyll fluorometer
CPHLPRTX	Concentration of chlorophyll (nominal) {Chl CAS 1406-65-1} per unit volume of the water body [particulate >unknown phase] by bench fluorometer
CPHLPS01	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by in-situ chlorophyll fluorometer and calibration against sample data
CPHLSEP1	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >GF/F phase] by filtration, ethanol extraction and

	spectrophotometry
CPHLSP1	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >GF/F phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
CPHLSP3	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >GF/C phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
CPHLSPC	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by centrifugation, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
CPHLSPZ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
CPHLSSP1	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >GF/F phase] by filtration, acetone extraction and trichromatic spectrophotometry following the Jeffrey and Humphrey protocol
CPHLSSP2	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >GF/C phase] by filtration, acetone extraction and trichromatic spectrophotometry following the Jeffrey and Humphrey protocol
CPHLSSP6	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >GF/F phase] by filtration, acetone extraction and trichromatic spectrophotometry following the Jeffrey and Humphrey protocol and summation of size-fractionated values
CPHLSSPC	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by centrifugation, acetone extraction and trichromatic spectrophotometry following the Jeffrey and Humphrey protocol
CPHLSP1	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >GF/F phase] by filtration, acetone extraction and spectrophotometry
CPHLUA01	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by radiometer and computation from the ratio of upwelled irradiance at 440 and 570 nm
CPHLUB01	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by radiometer and computation from the ratio of upwelled irradiance at 490 and 570 nm
CPHLULAQ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by Aquatracka fluorometer immersed in non-toxic supply and laboratory calibration applied
CPHLULTF	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by through-flow fluorometer plumbed into non-toxic supply and laboratory calibration applied
CPHLUMAQ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by Aquatracka fluorometer immersed in non-toxic supply and manufacturer's calibration applied



CPHLUMTF	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by through-flow fluorometer plumbed into non-toxic supply and manufacturer's calibration applied
CPHLUT01	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by through-flow fluorometer plumbed into non-toxic supply and calibration against sample data
CPHLUW01	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >unknown phase] by Aquatracka fluorometer immersed in non-toxic supply and calibration against sample data
CPHLYMP1	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >GF/F phase] by filtration, acetone extraction and fluorometry and processed following the protocol of Yentsch+Menzel
INCAFLP1	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit area of the water body [particulate >GF/F phase] by filtration, acetone extraction and fluorometry and profile integration
INCAFLP4	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit area of the water body [particulate >0.2um phase] by filtration, acetone extraction and fluorometry and summation of size-fractionated values and profile integration
INCAFLP5	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit area of the water body [particulate >0.2um phase] by filtration, acetone extraction and fluorometry and profile integration
SCHLEXP	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of experiment water sample [particulate >5um phase] by filtration, acetone extraction and fluorometry
SCHLEXP	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of experiment water sample [particulate GF/F-5um phase] by filtration, acetone extraction and fluorometry
SCHLEXP	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of experiment water sample [particulate >10um phase] by filtration, acetone extraction and fluorometry
SCHLFLPA	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >5um phase] by filtration, acetone extraction and fluorometry
SCHLFLPB	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >2um phase] by filtration, acetone extraction and fluorometry
SCHLFLPC	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 2-5um phase] by filtration, acetone extraction and fluorometry
SCHLFLPD	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 1-5um phase] by filtration, acetone extraction and fluorometry
SCHLFLPE	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 0.2-1um phase] by filtration, acetone extraction and fluorometry
SCHLFLPF	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 0.2-2um phase] by filtration, acetone extraction and

	fluorometry
SCHLFLPG	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 2-20um phase] by filtration, acetone extraction and fluorometry
SCHLFLPH	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 20-200um phase] by filtration, acetone extraction and fluorometry
SCHLFLPI	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 0.6-5um phase] by filtration, acetone extraction and fluorometry
SCHLFLPJ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-200um phase] by filtration, acetone extraction and fluorometry
SCHLFLPK	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-53um phase] by filtration, acetone extraction and fluorometry
SCHLFLPL	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-20um phase] by filtration, acetone extraction and fluorometry
SCHLFLPM	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-5um phase] by filtration, acetone extraction and fluorometry
SCHLFLPN	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-2um phase] by filtration, acetone extraction and fluorometry
SCHLFLPO	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >10um phase] by filtration, acetone extraction and fluorometry
SCHLFLPP	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-0.8um phase] by filtration, acetone extraction and fluorometry
SCHLFLPQ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >20um phase] by filtration, acetone extraction and fluorometry
SCHLFLPS	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 0.8-2um phase] by filtration, acetone extraction and fluorometry
SCHLFLPT	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 5-20um phase] by filtration, acetone extraction and fluorometry
SCHLFLPU	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 0.2-5um phase] by filtration, acetone extraction and fluorometry
SCHLFLPV	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 2-18um phase] by filtration, acetone extraction and fluorometry
SCHLFLPW	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >18um phase] by filtration, acetone extraction and

	fluorometry
SCHLFLPX	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 5-10um phase] by filtration, acetone extraction and fluorometry
SCHLFLPY	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 10-20um phase] by filtration, acetone extraction and fluorometry
SCHLFLPZ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >30um phase] by filtration, acetone extraction and fluorometry
SCHLHPPF	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 0.2-2um phase] by filtration, acetone extraction and high performance liquid chromatography (HPLC)
SCHLHPPG	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 2-20um phase] by filtration, acetone extraction and high performance liquid chromatography (HPLC)
SCHLHPPQ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >20um phase] by filtration, acetone extraction and high performance liquid chromatography (HPLC)
SCHLSPP4	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >0.4/0.45um phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
SCHLSPPA	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >5um phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
SCHLSPPJ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-200um phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
SCHLSPPK	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-53um phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
SCHLSPPL	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-20um phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
SCHLSPPM	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-5um phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
SCHLSPPN	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-2um phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
SCHLSPPP	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-0.8um phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
SCHLSPPQ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >20um phase] by filtration, acetone extraction and spectrophotometry and processing following the Lorenzen protocol
SCHLSSPA	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate >5um phase] by filtration, acetone extraction and

	trichromatic spectrophotometry following the Jeffrey and Humphrey protocol
SCHLSSPC	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 2-5um phase] by filtration, acetone extraction and trichromatic spectrophotometry following the Jeffrey and Humphrey protocol
SCHLSSPM	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-5um phase] by filtration, acetone extraction and trichromatic spectrophotometry following the Jeffrey and Humphrey protocol
SCHLSSPN	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate GF/F-2um phase] by filtration, acetone extraction and trichromatic spectrophotometry following the Jeffrey and Humphrey protocol
SCHLZP02	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit volume of the water body [particulate 2-10um phase] by filtration, acetone extraction and fluorometry
SINCFLPF	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit area of the water body [particulate 0.2-2um phase] by filtration, acetone extraction and fluorometry and profile integration
SINCFLPG	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit area of the water body [particulate 2-20um phase] by filtration, acetone extraction and fluorometry and profile integration
SINCFLPQ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit area of the water body [particulate >20um phase] by filtration, acetone extraction and fluorometry and profile integration
SINCFLPY	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit area of the water body [particulate >5um phase] by filtration, acetone extraction and fluorometry and profile integration
SINCFLPZ	Concentration of chlorophyll-a {chl-a CAS 479-61-8} per unit area of the water body [particulate 2-5um phase] by filtration, acetone extraction and fluorometry and profile integration

## Annex 4: MCWG internal report of the outcome of the Working Group on Chemicals

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The CIS-Working Group on Chemicals established two subgroups: one group on prioritization of substances, another group on revision of the Technical Guidance for derivation of EQSs.

The subgroup working on prioritization of substances made a draft list of new emerging contaminants that needs consideration for EQS derivation. A list of 11549 compounds was reduced to 6523 after a first screening. For further selection, compounds were split up in two groups, depending on the availability of monitoring data. For the monitoring-based approach, 326 substances were taken into consideration. These compounds were analysed in more than 4 member states, at more than 10 sampling locations, in more than 50 samples. Moreover, a PNEC was available. A STE approach was applied for selection of priority substances. Within a STE approach, the spatial distribution, temporal distribution and the extent of PNEC-exceedance is evaluated for each compound by making a STE-score.

When no monitoring data was available, a modelling based exercise was performed. 6197 compounds were used in the screening phase, reduced to a list of 33 compounds with PNEC that also ended in an intermediate list of four insecticides for EQS consideration. From the two approaches, a list of 10 substances was proposed for further EQS derivation: uranium, omethoate/dimethoate, malathion, selenium, silver, permethrin, nicosulfuron, deltamethrin, bifenthrin, esfenvalerate. It should be stressed that this list is not yet a final selection.

Next to selection of candidate priority substances, a deselection procedure was proposed as well. This is a conservative procedure not deselecting (1) all substances added by Directive 2013/39/EU, (2) all substances added by Directive 2008/105/EC for which the preferred monitoring matrix in Directive 2013/39/EU is biota, (3) priority hazardous substances.

Compounds could be deselected if (1) the STE-score is below 0.6, (2) the substance is measured in more than 20 countries but has exceedances in at maximum four countries and (3) the substance is banned in the EU.

The subgroup working on the revision of the EQS proposed 4 major changes: (1) clarification of the section on deriving bioavailability-based EQS for metals, (2) advice on methods for the assessment of the reliability and relevance of eco-toxicological data, (3) refinement of the methodology for deriving biota quality standards to protect top predators against secondary poisoning, making use of energy normalized EQS-values and (4) revision of the methodology for deriving biota quality standards to protect human health from contamination via consumption of fishery products. Related to the derivation of QS<sub>biota,hh</sub>, a decision still has to be taken whereas limit values from food legislation or toxicological derived standards are preferred.

From 2019, a review of WFD itself is planned. As regards priority substance the Commission suggested a more holistic approach, taken into account mixture toxicity. Focus will be more on group of substances according to their mode of action and on time trends for ubiquitous PBT compounds while member states should maintain/revise their emission

inventories. The commission proposed not to come up with a new proposal for revising the list of priority substances, but to bundle this with the WFD review after 2019. The results of the technical work done so far should be taken into account in the assessment of pressures and impacts to prepare the river basin management plans 2021. Water directors emphasized that when designing the new approach cost and feasibility should be taken into account, that legal and practical issues related to identification and implementation of measures should be tackled, that coordination with other legislation and discussion at expert level in WG chemicals will be important.

Based on articles 4.4 and 4.5, exemptions from achieving good status in 2027 are possible. Article 4.5 states that less stringent objectives are allowed for a substance or group of substances if the original objective is not reachable by 2027 and all possible measures have been taken. However, application of article 4.5 should be exceptional and limited. Article 4.4 states that exemptions are possible due to technical feasibility problems, disproportional costs or natural conditions.

Exemptions due to natural conditions require that it will be impossible to achieve the objective by 2027 even though all feasible measures to reduce pollution have been taken as the recovery of the ecosystem will take a longer time period.

The concept of 'natural conditions' will be further discussed in the relevant CIS-Working Groups ECOSTAT, Chemicals and Groundwater. Member States are invited to provide examples and case studies.

## **Annex 5: Summary of presentations made at MCWG 2017**

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Valuable contributions by both host institute and participants were made during the MCWG 2017 meeting. The presentations, if available and free for viewing, can be found on the SharePoint site or requested, an abstract is presented hereunder.

### **Emissions from corrosion protection systems of offshore wind farms**

#### **Torben Kirchgeorg**

The marine environment is a highly corrosive environment for steel constructions such as offshore wind turbines. Corrosion affects all parts of offshore wind turbines, especially in the submerged and in the tidal- and wave effect zones. These zones are protected with different systems against corrosion processes, often the combination of different techniques. Amongst those are (organic) coatings (e.g. epoxy resins), thicker steel to compensate the loss through corrosion, and galvanic anode cathodic protection systems (GACP, the so called “sacrificial anodes”) or impressed current cationic protection systems (ICCP) for the submerged zones of foundations. All techniques have different potentials of chemical emissions, e.g. sacrificial anodes emitting high amounts of aluminium, zinc and other metals during their consumption, or the leaching of organic substances from organic coatings. Here a short overview about the emissions of corrosion protection systems was given and the potential impact to the marine environment was discussed.

### **Environmental forensic analysis of mineral oil products**

#### **Dr. Uta R. Kraus**

In recent years, intentional maritime oil pollution in Europe is declining due to international regulations and maritime surveillance. However, the probability of an accidental oil-spill incident in European seas is rising due to both an increase in seaborne traffic and the increase and expansion of offshore oil and gas activities resulting in a rising number of oil and gas installations. Furthermore, while the average number of spills per year is declining, large quantities can be spilled in very few accidents due to ever rising vessel size. In case of an oil spill, environmental forensic analysis is extremely helpful in regard of characterizing waterborne oils and the identification of possible sources. Additionally, since large-scale spills often reach across national borders, internationally concerted analysis with comparable results is the most promising way to approach the issue of compensation claims.

Besides the environmental forensic analysis of oil spills, analysis of other mineral oil (by-) products like paraffin wax are recently becoming more important due to a rising number of considerable pollution incidents along maritime shorelines. As international regulations start to take this topic into account, a new field of environmental forensic analysis in maritime environments is rapidly evolving.

## **Sulphur emission compliance monitoring of ships in German waters**

### **Dr. Andreas Weigelt**

Shipping emissions has a significant influence on air pollution in the marine environment. To minimize environmental pollution the International Maritime Organisation (IMO) adopted the MARPOL regulations. Annex VI regulates, among other issues, the sulphur content in shipping fuels, which is transformed into the air pollutant sulphur dioxide (SO<sub>2</sub>) during combustion. Within designated Sulphur Emission Control Areas (SECA) on 1 January 2015 the allowed fuel sulphur content was limited to 0.1%. Inside the SECAs like the North Sea and the Baltic Sea, ships must use more expensive low sulphur fuels or must be operated with exhaust gas treatment systems (Scrubber). This presentation gave an insight to the inspections done to check whether ships are compliant with the sulphur regulations in German waters. The uses of new remote measurement techniques to select ships for on-board inspections were introduced. Some results on compliance rate and air quality improvement since January 2015 were shown.

## **Chemical emissions from offshore windfarms in Germany: An overview**

### **Ingo Weinberg**

Offshore wind energy is one of the emerging techniques in the development of renewable energies in many European countries. In Germany, about 1100 wind turbines and 25 substations and converter platforms have already been constructed/are under construction to achieve the goals of the energy transition towards renewable energies and hence climate protection. The majority of these facilities are situated in the German exclusive economic zones (EEZ) of the North and Baltic Sea.

The presentation gave a short overview of the current state of offshore windfarm development in Germany and presented the different sources of chemical emissions by these offshore installations (*e.g.* corrosion protection, sewage treatment) and how they are examined in the framework of permissions.

## **Screening of Per- and Poly-fluoro-alkyl Substances in the Aquatic Environment**

### **Lutz Ahrens**

Three separate studies were presented focusing on i) PFASs in Swedish rivers (Nguyen *et al.*, 2017), ii) PFASs in surface and groundwater in Sweden, and iii) PFASs in various matrices in Svalbard. In total, 26 different PFASs were investigated including perfluoro-alkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAAs), perfluoro-octanesulfonamides (FOSAs), perfluoro-octanesulfonamido acetic acids (FOSAAs), perfluoro-octane sulfonamido ethanols (FOSEs) and 6:2 fluorotelomer sulfonate (6:2 FTSA). The results from the screening of PFASs in Swedish rivers showed that the annual average environmental quality standard (AA-EQS) value of 0.65 ng L<sup>-1</sup> for PFOS for inland surface waters of the EU WFD was exceeded at 12 of 44 river sites (Nguyen *et al.*, 2017). The results of PFASs in Swedish surface and groundwater showed that the AA-EQS of 0.65 ng L<sup>-1</sup> for PFOS for inland surface waters was exceeded in 42% of the sampling sites (n = 177). Overall, all studies showed an ubiquitously distributed of PFASs in various



matrices (i.e. water, snow, sediment, soil and biota) even in remote regions such as Svalbard.

#### Literature

Nguyen, M. A.; Wiberg, K.; Ribeli, E.; Josefsson, S.; Futter, M.; Gustavsson, J.; Ahrens, L., Spatial distribution and source tracing of per- and poly-fluoroalkyl substances (PFASs) in surface water in Northern Europe. *Environ. Pollut.* 2017, 220, 1438–1446.

#### Zn and Cu increases at the Belgian continental shelf: linked to antifouling?

##### Bavo De Witte

The Belgian Continental Shelf contains 5 dredged spoil disposal sites which are monitored 2 times a year. Results on chemical analyses data from 2005 to 2014 were presented. Data was modelled by a linear mixed-effect model in R. Within the model, the effect of time, season and sludge disposal site, relative to associated reference sites, is studied. PCB concentrations are not decreasing whereas Hg concentrations are increasing at dredged spoil disposal site S2. An increase of Zn concentrations was noticed at dredged spoil disposal sites Oostende and Nieuwpoort, whereas Cu concentrations increased at disposal site Nieuwpoort. Remarkably, these are the least intensively used disposal sites and the dredged spoil at these sites originates from the least industrialised areas. Results suggest that Cu and Zn concentration increase may be related to the use of Cu- and Zn based antifouling agents, which use increased after the TBT-ban. Source investigation revealed different Cu and Zn point sources at harbour Oostende. At Nieuwpoort harbour, no point sources were identified, probably related to adequate measures at boat- and shipyards during blasting or painting of boat hulls.

#### Organophosphate Ester Flame Retardants and Plasticizers in Ocean Sediments from the North Pacific to the Arctic Ocean

##### Zhiyong Xie

The presence of organophosphate ester (OPE) flame retardants and plasticizers in surface sediment from the North Pacific to Arctic Ocean was observed for the first time during the fourth National Arctic Research Expedition of China in the summer of 2010. The samples were analysed for three halogenated OPEs [tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), and tris(di-chloro-isopropyl) phosphate], three alkylated OPEs [tri-isobutyl phosphate (TiBP), tri-n-butyl phosphate, and tri-pentyl phosphate], and tri-phenyl phosphate.  $\Sigma 7\text{OPEs}$  (total concentration of the observed OPEs) was in the range of 159–4658 pg/g of dry weight. Halogenated OPEs were generally more abundant than the non-halogenated OPEs; TCEP and TiBP dominated the overall concentrations. Except for that of the Bering Sea,  $\Sigma 7\text{OPEs}$  values increased with increasing latitudes from Bering Strait to the Central Arctic Ocean, while the contributions of halogenated OPEs (typically TCEP and TCPP) to the total OPE profile also increased from the Bering Strait to the Central Arctic Ocean, indicating they are more likely to be transported to the remote Arctic. The median budget of 52 (range of 17–292) tons for  $\Sigma 7\text{OPEs}$  in sediment from the Central Arctic Ocean represents only a very small amount of their total production volume, yet the amount of OPEs in Arctic Ocean sediment was

significantly larger than the sum of poly-brominated diphenyl ethers (PBDEs) in the sediment, indicating they are equally prone to long-range transport away from source regions. Given the increasing level of production and usage of OPEs as substitutes of PBDEs, OPEs will continue to accumulate in the remote Arctic.

## Annex 6: Resolution for a publication

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An ICES paper on Chlorophyll analysis and reporting prepared by MCWG and WGPME other colleagues (Petra Schilling, Kerry Smith), will be published in the ICES TIMES Report series. MCWG and WGPME reviewed the current chlorophyll ICES TIMES paper (TIMES 30, Aminot and Ray) with a view to amending to take account of new instrumentation and revised OSPAR JAMP recommendations on best practice. MCWG & WGPME concluded the required revisions were sufficient to merit replacement of ICES TIMES 30. The estimated number of pages is 10.

The editors agree to submit the final draft of the proposed publication by 31 December 2017, with publication before the end of the current ICES MCWG term in March 2018.

### Supporting information

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Priority:	The proposed TIMES paper is to replace ICES TIME 30 (Aminot and Ray) which no longer reflects current methodology or reporting practices. The paper will expand on the information within ICES TIMES 30 and ensure it is relevant for current statutory requirements for drivers such as MSFD and WFD. The paper aims to provide a comprehensive guide to ensure data issues with cross boundary regional assessments are minimised.
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Scientific justification:	<p>MCWG 2015 highlighted concerns about the the reporting of chlorophyll data to ICES for MSFD assessments.</p> <p>A range of analytical methods have been used to derive chlorophyll concentrations, including fluorometric, photometric and HPLC determinations. The choice of analytical method used to derive background concentrations has implications for MSFD Descriptor 5 assessments, potentially resulting in difficulties with cross boundary regional assessments.</p>
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Data can be submitted, to the ICES-Data Centre (DC), using three parameter codes; CPHL (Chlorophyll *a*), CPHLC (Chlorophyll *a*, SCOR/UNESCO method) and CPHLL (Chlorophyll *a*, Lorenz acidification method), none of which match the current OSPAR JAMP guidelines. There is currently no parameter code within the ICES for “total chlorophyll *a*”, as listed in the OSPAR JAMP guidelines. The term “total chlorophyll *a*” itself is misleading, the fluorometric method cannot separate different chlorophylls, therefore a more accurate description for this is required. To meet statutory requirements for drivers such as MSFD and WFD, contracting parties are increasingly relying on the use of automatic and remote devices such as buoys, ferryboxes and satellites for inclusion in data sets for their assessments. There is no single analytical technique recommended for the calibration of these devices.

There is a clear need on guidance for the analysis and reporting of chlorophyll data and associated metadata to the ICES datacentre.

Linkages to advisory committees:	NA
Linkages to other committees or groups:	It is expected that the TIMES paper will be of interest to a range ICES working groups.
Linkages to other organizations:	In addition it is expected that the TIMES paper will be of interest to organisations such as OSPAR, HELCOM and AMAP. Members of MGWG are also involved in the Joint Monitoring Programme Eutrophication of the North Sea with satellite data (JMP EUNOSAT) project and this work is of direct relevance.
Draft outline of publication:	Where possible the report will follow standard TIMES paper formats.
Resource requirements:	Currently not required.
Participants:	MCWG will lead on this paper and aim to complete the first draft by December 2017 with publication prior to the end of the current MCWG term in March 2018.
Secretariat facilities:	About two weeks (?) of the services of Secretariat Professional and General Staff will be required
Financial:	Associated publication costs.
Promotion:	The report will be promoted to relevant ICES working group chairs through the ICES publication process.

## **Annex 7: OSPAR Special Request to WGMS and MCWG: Interim Report, March 2017**

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**Joint interim report to ACOM from WGMS and MCWG on progress with the 2017 Special Request from OSPAR on the selection and de-selection of hazardous substances of concern to coastal and marine waters in the OSPAR maritime area**

Prior to the March meetings of the ICES Working Group on Marine Sediment (WGMS) and Marine Chemistry Working Group (WGMS), the Chairs of the two groups were notified that ICES had received this Special Request from OSPAR. The Chairs recognised the importance of this task but noted that the timing of the task may be problematic, since a report had to be prepared by the last day of the meeting week in order to meet the timetable of OSPAR HASEC. The request was amended to presenting an interim report by 10 March 2017 and a final report by 12 October 2017. The Chairs still considered that this timetable remained a risk to the successful completion of the task as they had an expectation that members of both groups would have limited time available for substantive inter-sessional work. The groups consider that the correct term to be applied with respect to “emerging substances”, and that will be used hereafter, is “substances of emerging concern”. The text of the request was is given in Annex 1.

### **Part 1: ICES is requested to identify and collate information on projects, activities and sources of information for new and emerging substances**

During their 2017 meetings, the WGMS and MCWG have collated a list of projects and other sources of information known to those present. Neither group had access to bibliographic search engines (e.g. SCOPUS) during their March meetings and the list principally contains projects that group members present were aware of, plus some important references. The document therefore requires further additions and amendment. This “sources of information” list has been prepared as an Excel spread sheet that is available from the “working documents” folder of the MCWG 2017 SharePoint site. Information relevant to part 2 of the current request (e.g. project name, contact person, substances studied, matrices studied, substances actually detected in the marine environment, publication details) has been extracted from the spread sheet and is presented below as Annex 2. One of the most valuable exercises on marine substances of emerging concern is the work of Tornero and Hanke (2016). They provided a review on substances that might be released from sea-based sources and established a list of 276 substances including 22 antifouling biocides, 32 aquaculture medical products and 34 warfare agents. They also provided an overview of those substances which have already been considered in European regulations. For the recent review of the Water Framework Directive (WFD) list of priority substances, a prioritization process was conducted by JRC, starting with more than 11 000 compounds and ending with a short list of 17. OSPAR should consider this list and approach JRC to check whether marine aspects have been adequately considered. Adaptations to the list may be needed based on marine monitoring data and information on substances released from sea-based sources. During their 2016 meeting, MCWG considered the following substance groups of emerging concern: dechlorane+, alternative brominated flame retardants, phosphorous flame retardants, antifoulants, per- and polyfluorinated substances (not PFOS, PFOA), benzotriazoles, siloxanes, radioactive substances, anticorrosion agents.

**Part 2: Review the information to identify new and emerging substances, identify information gaps and recommend what further work is needed**

In order to identify new substances of emerging concern the groups have identified which substances are already listed as Priority Substances by OSPAR or the European Commission (under the Water Framework Directive); these are NOT considered to be substances of emerging concern. Other substances have been identified as being of potential concern by OSPAR, or by the WFD Watch List and JRC prioritisation process and these have been identified in Annex 3

The list of projects & sources of information in Annex 2 requires to be completed, and the projects/sources of information should be evaluated and prioritized to allow the extraction of a list of substances that should be reviewed as to their environmental significance. To do so, OSPAR will need to obtain additional information for each substance, including toxicity, hazard properties, chemical and physical properties, production volumes and use patterns. However, the availability of this information is expected to be incomplete and a significant knowledge gap for the vast majority of the compounds. Although the REACH regulation is in place, toxicological information to predict the impact of chemicals on the marine environment is limited. Prioritization of the substances would be easier if from the beginning a more in depth investigation was obligatory.

**Annex 1: Text of the OSPAR request to ICES**

OSPAR is keen to ensure that new and emerging hazardous substances in the marine environment that are of **general concern to coastal and marine waters** are identified, so that appropriate action can be taken.

HASEC is aware that a similar exercise is already established under the WFD through the Watch List process and therefore the work for the marine environment would need to build on and be coordinated with this process.

Currently there are research programmes that screen substances in the marine environment, e.g. through passive sampling, tissue analysis, sediment sampling etc.

HASEC's request is in stages:

1. ICES is requested to identify and collate information on projects, activities and sources of information for new and emerging substances;
2. Review the information to identify new and emerging substances, identify information gaps and recommend what further work is needed;
3. Report back to HASEC on the findings of the exercise

HASEC 2017 should be updated on the progress on stage 1 (interim update (summary report as a meeting document to HASEC and presentation of progress, not advice); Stage 2 and the full advice reported to HASEC 2018

**Annex 2: List of projects/ sources of information**



List of  
information sour...

**Annex 3: Lists of substances NOT considered to be of emerging concern, and list of substances already identified as being of potential concern**



List of lists.xls

## **Annex 8: OSPAR Special Request to WGMS and MCWG: Final Report, October 2017**

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**Report to ICES from WGMS and MCWG on the 2017 Special Request from OSPAR on the selection and de-selection of hazardous substances of concern to coastal and marine waters in the OSPAR maritime area**

### **Introduction**

The ICES Working Group on Marine Sediments in relation to pollution (WGMS) and Marine Chemistry Work Group (MCWG) were tasked ahead of their March 2017 meetings to jointly respond to ACOM regarding a Special request from OSPAR on the selection and de-selection of hazardous substances of concern to coastal and marine waters. A preliminary report was submitted in March 2017 that highlighted a number of groups of contaminants of emerging concern to the marine environment. Following feedback from OSPAR Hazardous Substances Committee on their requirements, this report collates information on the physico-chemical properties, production, usage, toxicity and environmental occurrence of many of these substances. The report has been drafted jointly by experts from the two ICES Working Groups working intersessionally.

### **Methods**

The interim report in March 2017 listed eight substance groups as being contaminants of emerging concern to the marine environment. These were: alternative brominated flame retardants (aBFRs), corrosion protection agents, Dechlorane Plus, phosphorous flame retardants (OPFRs), per- and poly-fluoroalkyl substances (PFASs) other than PFOS and PFOA, benzotriazoles, siloxanes and new antifoulants. A template document was designed in order to capture the required information in a systematic manner. Volunteer experts from the two Working Groups have obtained, collated and summarised literature-sourced information on the physico-chemical properties, production, usage, toxicity and environmental occurrence of five of the identified substance groups; there were no volunteers available to produce documents on siloxanes, benzotriazoles, or new antifoulants.

### **Results**

A template file was completed for each of five substance groups, with information generally being provided for more than 15 substances in each group. In a number of cases the data are not complete due to knowledge gaps and research needs, such as on toxicity or environmental concentrations / behaviour. The key findings are summarised in Table 1, whilst the template files are attached as Annexes.



**Table 1: Summary of the template files for each substance group.**

SUBSTANCE GROUP	AUTHOR(S)	COMMENT
Alternative brominated flame retardants (aBFRs)	Sara Losada Rivas <a href="mailto:sara.losadarivas@cefas.co.uk">sara.losadarivas@cefas.co.uk</a> Jon Barber <a href="mailto:jon.barber@cefas.co.uk">jon.barber@cefas.co.uk</a> Catherine Munsch <a href="mailto:Catherine.Munsch@ifremer.fr">Catherine.Munsch@ifremer.fr</a> Katrin Vorkamp <a href="mailto:kvo@envs.au.dk">kvo@envs.au.dk</a>	<p>Template document contains information on the physico-chemical properties, usage, toxicity and environmental concentrations of 16 different substances, which include brominated aromatic compounds, brominated phthalates, brominated alkanes and brominated ethers.</p> <p>aBFRs are a diverse group of compounds, with variable physico-chemical characteristics and toxicity; they tend to be lipophilic and not readily degradable. Some of them are genotoxic, teratogenic, or potentially endocrine disrupting.</p>
Corrosion protection agents	Torben Kirchgeorg <a href="mailto:Torben.Kirchgeorg@bsh.de">Torben.Kirchgeorg@bsh.de</a>	Two templates were received – one for organic substances and one for galvanic anodes. Both are partially completed, noting that much research is needed on the release of corrosion inhibitors from resins and on the concentrations of Potentially Toxic Elements in the marine environment close to marine renewable energy parks.
Dechlorane Plus	Roxana Sühring (Cefas) <a href="mailto:Roxana.suhring@cefas.co.uk">Roxana.suhring@cefas.co.uk</a>	<p>Document received detailing properties, usage, and environmental (especially biota) concentrations of 3 dechloranes, including Dechlorane Plus.</p> <p>Dechloranes are lipophilic and hence bioaccumulative, but there is a shortage of data on their toxicity and persistence; modelling suggests that they are likely to be persistent and they have structural similarities to toxic organochlorine pesticides.</p>
Organophosphorous flame retardants (OPFRs)	Ian Allan <a href="mailto:Ian.Allan@niva.no">Ian.Allan@niva.no</a> Katrin Vorkamp <a href="mailto:kvo@envs.au.dk">kvo@envs.au.dk</a> Karina Petersen <a href="mailto:Karina.Petersen@niva.no">Karina.Petersen@niva.no</a> Philippe Bersuder <a href="mailto:philippe.bersuder@cefas.co.uk">philippe.bersuder@cefas.co.uk</a>	The template document outlines the physico-chemical properties, usage, toxicity and environmental concentrations of ca. 25 substances. As hydrophobicity and other physico-chemical properties are very wide ranging, depending upon the molecular structure (length and branching) and functional group, it is not possible to readily summarise the environmental behaviour or risk of OPFRs; many are not thought to be bioaccumulative, although some are neurotoxic, reprotoxic or suspect carcinogenic.
Per- and polyfluoroalkyl	Lutz Ahrens <a href="mailto:lutz.ahrens@slu.se">lutz.ahrens@slu.se</a>	The template document details the physico-chemical properties of 25 perfluoroalkyl

substances (PFASs) other than PFOS or PFOA	Katrin Vorkamp <a href="mailto:kvo@envs.au.dk">kvo@envs.au.dk</a> Philippe Bersuder <a href="mailto:philippe.bersuder@cefas.co.uk">philippe.bersuder@cefas.co.uk</a>	substances (PFASs) (including PFOS and PFOA) and summarises reported environmental concentrations and toxicity of PFASs (not clear if the summed concentrations included PFOS/PFOA). PFASs are considered to be persistent, bioaccumulative and toxic, although the degree to which this applies for the individual compounds varies depending upon the length of the fluorinated hydrophobic carbon chain and the type of hydrophilic functional group (sulfonate or carboxylate).
New antifoulants	No template completed	
Benzotriazoles	No template completed	
Siloxanes	No template completed	

### Discussion

The documents indicate the vast number of contaminants of emerging concern, and their wide ranging environmental concentrations and behaviours, even within these five substance groups. The documents provide information (where it is available) that will allow OSPAR to assess whether these substances are of sufficient concern to require monitoring through the JAMP/CEMP, or to highlight to Contracting Parties where there are significant knowledge gaps. The work of Tornero and Hanke (2016) is highlighted as being of importance in this field. They established a list of 276 substances that might be released from sea-based sources, including 22 antifouling biocides. They also provided an overview of those substances which have already been considered in European regulations.

### Reference

Tornero, V. and Hanke, G. 2016. Chemical contaminants entering the marine environment from sea-based sources: A review with a focus on European seas. *Marine Pollution Bulletin*, **112**, 17–38. <http://dx.doi.org/10.1016/j.marpolbul.2016.06.091>



01. aBFRs  
template.docx



02. Corrosion  
protection template.doc



03. Dechloranes  
template.docx



04. OPFR  
template.docx



05. PFASs  
template.docx



06. request text.docx

## **Annex 9: Technical Minutes from the Review Group RGHAZ**

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Review of ICES Marine Chemistry Working Group (MCWG) and Working Group on Marine Sediments in Relation to Pollution (WGMS) report on the 2017 Special Request from OSPAR on the selection and de-selection of hazardous substances of concern to coastal and marine waters in the OSPAR maritime area.

### **Special requests from OSPAR**

ICES WGMS and MCWG are requested to report on the selection and de-selection of hazardous substances of concern to coastal and marine waters in the OSPAR maritime area.

- b) identify and collate information on projects, activities and sources of information for new and emerging hazardous substances of concern to coastal and marine waters.
- c) review the information to identify new and emerging substances, identify information gaps and recommend what further work is needed

### **Reviewer: Emma Undeman, Sweden (chair)**

With additional comments provided by Victoria Torneo and Georg Hanke, JRC

Chair WGMS: Celine Tixier, France, and Craig Robinson, UK

Chair MCWG: Koen Parmentier, Belgium

Secretariat: Sebastian Valanko

### **Written for ADGHAZ**

#### **General comments:**

- The report builds on a preliminary interim report that addresses the issues of task a) (see above), i.e. describes the information used to pre-select the 8 substance groups. This brief report describes that members of the two contributing WGs listed various projects or screening efforts they were aware of in a spreadsheet during meetings in 2017, however no systematic literature review or other search for relevant information in scientific databases appears to be conducted. It is commented that this list must be further processed and analyzed, but it not clear how (if) this list of projects and scrutinized compounds was actually used, in particular as the substance groups considered to be of emerging concern appears to have been specified by MCWG already in 2016. Despite the interim report, it is hence unclear how the pre-selection of substance groups was made. A clarification of this circumstance should be given.
- Since no documentation is available to the RG describing the information used and analysis made to decide on substance groups to review more thoroughly in the second part of the request (b above), this makes it difficult to judge if the request from OSPAR is fully addressed by ICES.

- It would indeed be valuable if the information on the approach that was used for scrutinizing substances and selecting specifically these compound groups was available, and to what extent the selection was based on information specifically related to the OSPAR area. It can be noted that JRC is currently reviewing the procedures for identification of emerging contaminants across EU, taking different information sources and responsibilities into account. The OSPAR/ICES experience from this work can be valuable for the JRC review (comment by Georg Hanke).
- Eight substance groups were identified by ICES as of emerging concern, but no volunteers were available to do the data compilation for three of the groups. The request by OSPAR is hence not fully addressed.
- On the other hand, is it not necessarily relevant to present groups or classes of chemicals as being of emerging concern, as inherent properties and associated hazards can be diverse within a group. It appears as if a thorough analysis of the relevance to OSPAR areas of the identified substances in various screening projects and other information sources would have served as a good first selection for both individual substances or substance groups of emerging concern. An information source that can be added to the list of projects, and possibly used as a candidate selection instrument, is the SIN list by ChemSec ([www.sinlist.org](http://www.sinlist.org)) listing chemicals fulfilling REACH criteria for PBT or vPvB substances.
- The intended use of the requested output stated by OSPAR (“Request from OSPAR to support the work on the selection and de-selection of hazardous substances for HASEC”) is rather un-specific and leaves a lot of room for ICES to do their own interpretation and decisions about level of ambition in the report. This is reflected in the templates for information delivery to OSPAR made by ICES, which aim at collecting some basic data for each compounds class. However, it is not specified in detail which data should be included and to what extent the availability or quality of data should be discussed. It is not specified if environmental concentrations should be compiled for e.g. OSPAR region marine or aquatic environments, or any environment. The extent of data compilation and depth of analysis made is therefore variable for the five compound classes.
- The templates designed by ICES requests substance specific information typically used in a risk assessment of a chemical compound. Hence the given information is useful since it provides data that can potentially be used as a basis for selecting chemicals to prioritize in screening/monitoring activities. The information is given either in running text or tables, although the type of information given is often suitable for tables (see e.g. OPFRs).
- It is recommended to consider the WFD prioritizing process as guidance for the templates, and also to consider the work of NORMAN network. For EU members in particular, it is beneficial if ICES/OSPAR work supports fulfilling the commitments under the MSFD (comment by Georg Hanke).
- It can be noted that “de-selection” of compounds would require data compilation not only for emerging contaminants, but also for well-known classical

contaminants that may have ceased to be relevant parameters to monitor due to banned use and low environmental levels.

- The discussion section of the report states that: “The documents provide information (where it is available) that will allow OSPAR to assess whether these substances are of sufficient concern to require monitoring through the JAMP/CEMP, or to highlight to Contracting Parties where there are significant knowledge gaps”, which is the case, although in most cases the provided information is that there seems to be a lack of knowledge. The selection of information to provide (physical-chemical properties, environmental degradation rates and bioaccumulation potential, production/use data, toxicity and observed concentrations in environmental matrices) depends on the risk/hazard criteria or prioritization scheme to be used. OSPAR relies (according to their website) on REACH criteria to identify substances of possible concern, and it is supposedly these criteria that have been considered by ICES when designing the templates. This should be clarified in the report. It can be noted that in the aBFR data sheet, also Stockholm Convention and OSPAR specific criteria are mentioned.
- It is noted in the request details that “HASEC is aware that a similar exercise is already established under the WFD through the Watch List process and therefore the work for the marine environment would need to build on and be coordinated with this process”, a brief discussion about how ICES/OSPAR prioritization activities aligns with the WFD prioritization and Watch List process would be informative. In previous WFD prioritization processes, lists such as the OSPAR priority list has been included in the “list of lists” proposing the initial candidates for further ranking.
- The report is indeed rather brief, and a more detailed description of the method, the design of the templates, the anticipated use of the information by OSPAR and the recommended further work needed would be helpful to any external reader.
- Substance evaluation according to REACH criteria for Substances of Very High Concern (PBT, vPvB) requires the following information:
  - P, vP: Degradation half-life in marine, fresh/estuarine water, sediment or soil. Indication from ready biodegradation tests or other screening tests or QSAR model
  - B, vB: bioconcentration factor in aquatic species. Indication from experimentally determined or QSAR log KOW. Studies of bioaccumulation in terrestrial species, humans, vulnerable/endangered species, chronic toxicity studies, studies on toxicokinetics, studies on biomagnification or measured trophic magnification factors. Molecular size.
  - T: NOEC or EC10 for marine or freshwater organism, or tests to determine if a substance is carcinogenic, mutagenic, toxic for reproduction, have specific target organ toxicity after repeated dose, or evidence of chronic toxicity (e.g. long term toxicity testing in invertebrates or fish), or growth inhibition studies on aquatic plants, long-term or reproductive toxicity testing with birds.

In addition to standardized tests, REACH also allows “other information provided that its suitability or reliability can be reasonably demonstrated” to identify PBT or vPvB substances. As standardized tests are often not performed in scientific studies, much data falls within the “other information” category and requires, if REACH methodology is strictly followed, some judgement of its reliability and relevance is needed.

- On this note, what is generally lacking is an analysis of the collected data. Either in terms of comments on the quality, variability, representativeness, coverage of the literature survey, or the completeness of the data for the purpose of doing some kind of risk assessment or prioritization exercise. The responsible scientists’ judgement about the urgency to include the selected substances on the OSPAR priority list would be valuable.
- The part b) of the request is hence not completed as an analysis of the data to allow identifying substances of emerging concern relevant for the OSPAR area is lacking, and it should in the report be differentiated between general research needs and the needs to clarify the relevance of particular contaminants in the OSPAR area (comment by Victoria Torneo).
- Despite the use of templates, there are inconsistencies between physical chemical properties given for the different compound groups. This should be commented on and justified. E.g. for PFAS no vapor pressure or Henry’s Law constant is given, which is reasonable as these molecules are (judging from the pKa values reported) practically always dissociated at environmentally relevant pH. However, the selection of physical-chemical properties to present (either due to relevance or data availability) should be explained and motivated. The availability of data differs much for the five substance groups, and reasons for this could be highlighted.
- The discussion section of the report states that: “The documents provide information (where it is available) that will allow OSPAR to assess whether these substances are of sufficient concern to require monitoring through the JAMP/CEMP, or to highlight to Contracting Parties where there are significant knowledge gaps”. In many cases, “further research needed” is indeed the recommendation to fill knowledge gaps regarding inherent physical-chemical properties, toxicity or environmental concentrations. It is however not useful to state that more research is needed in a too general manner. To fill all data gaps identified in this report is a formidable task. OSPAR Contracting Parties would therefore be better served if it could be specified *which* data gaps that are most urgent to fill, i.e. recommendations about prioritization.
- The report refers to the review of sea-based sources of chemical substances by Tornero and Hanke. This review article provides a comprehensive list of possible candidates based on use (qualitative), but no other data (quantitative) to base risk assessment on. Hence, for the substances listed in the review, data need to be compiled or produced to allow for a risk assessment or some kind of prioritization. It can also be noted that it is indeed difficult to determine the relative importance of sea-based sources and land based sources for chemicals with diverse applications. Sea based emissions can in many cases be much lower than land based emissions, but on the other hand these emissions occur

directly to the sea, whereas land based emissions are always partly reduced by retention in the terrestrial system.

- It is stressed that the article by Torneo and Hanke is prepared specifically to complement the WFD processes for collecting information on potentially occurring substances in marine waters, but does not provide a complete prioritization of substances (comment by Georg Hanke).
- A final general remark is that an overview of the outcome of the data compilation effort should be given. For example, it would be valuable to indicate for which chemicals there is enough data to do e.g. a PBT/vPvB-assessment and for these indicate the result. When possible, data on the environmental concentrations should be compared to the reported toxicological thresholds. Although the data is scattered and many knowledge gaps need to be filled, this report could state more clearly for which of these compounds there is enough data to do an environmental risk assessment.
- It is acknowledged that this work is done on a voluntary basis with limited resources.

#### **Specific comments in addition to the general comments**

##### Alternative brominated flame retardants

- The data compilation is comprehensive and summarizes many information sources. The data can be used to do e.g. a PBT/vPvB assessment for many of the listed compounds.
- Log KAW values are sometimes very high, it appears as if minus sign is sometimes missing. This should be checked. The for  $\log BCF = m \log KOW + b$ , which values for m and b where used, was this correlation derived for a specific compound class or a broader group of compounds?
- An important comment in this data sheet is that the selected aBFRs are those most commonly analyzed and this also impacts which are found in the environment. It is not clear if there are aBFRs that are extensively used but not analyzed (e.g. due to analytical challenges).
- It is informative that environmental concentrations and range is given, it would have been good to include also some information about geographical location.
- BB-153: measured concentrations is only given for biota, but not water, air, sediment or sludge. As this compound is banned and regulated, one would expect more monitoring data to be available.
- For example, the draft risk profile for hexabromobiphenyl presented at the Persistent Organic Pollutants Review Committee second meeting in 2006 (document UNEP/POPS/POPRC.2/9) includes relevant information (comment by Victoria Torneo).
- There are registration dossiers at ECHA for some aBFRs (e.g. BEH-TEBP, TBBPA-DBPE, TBP) whose information should be considered. For example, according to ECHA, DBHCTD is suspected to be bioaccumulative while TBBPA-DBPE does not bioaccumulate. This info is missing in the template (Comment by Victoria Torneo).

- There are no comments on data or knowledge gaps, or recommendations on future work needed.

#### Corrosion protection

- The purpose of this table seems to be mainly to draw attention to a previously overlooked source of sea-based emissions of chemicals namely leaking from epoxy resins (bisphenols) and polyurethane coatings of submerged constructions such as wind farms. No data to perform risk assessment are provided.
- Very little information is given. No physical chemical properties are listed, although this data is available at least for some compounds. This should be motivated. Some compounds are as pointed out already listed, e.g. bisphenol A (OSPAR) and alkylphenols (OSPAR/WFD prio list).
- There is information that could have been included. For example, there is an ECHA registration dossier for BADGE and 4,4'-methylenediphenyl diisocyanate is in the REACH restriction list (comment by Victoria Torneo).

#### Dechlorane

- The data compilation is comprehensive and summarizes many information sources.

#### Organophosphorous flame retardants

- The data compilation is comprehensive and summarizes many information sources.
- OPFRs are a group of compounds exhibiting diverse physical-chemical properties, environmental behavior and are used in many different applications. A discussion of the risks associated with these compounds as a group is therefore difficult. An important point made is that these compounds are used as replacement for some banned brominated flame retardants and are used in large volumes.
- Physical-chemical properties are not reported, instead references to extensive reviews are made. It is not clear if basic data required for e.g. PBT/vPvB analysis is available.
- It can be noted that there are PBT assessments available at ECHA for some of these substances (e.g. EHDPP, IPP, TBEP/TBOEP, TBP/TiBP); (comment by Victoria Torneo).
- Oftentimes unclear which reference is the source of information.

#### PFAS

- There are hundreds or thousands of compounds that can be classified as "PFAS". The data sheet describes this large compound class and reports data for selected PFASs which have been analyzed or described in the scientific literature.
- Typical use of PFASs is not described.
- Extensive list of physical-chemical properties of a large number of PFAS provided, but information on bioaccumulation potential is not given all though it is stated that "PFASs have high bioaccumulation potential". Bioaccumulation



of PFASs has been an important issue, e.g. difference in bioaccumulation potential for short chained and long-chained PFAS, and the differences in uptake mechanisms (i.e. binding to proteins rather than lipids) compared to classical POPs.

Further research needed is not indicated.