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

DRAFT

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CIEM Conseil International pour l'Exploration de la Mer

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Recommended format for purposes of citation:

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

Contents

Executive summary

Report to be submitted.

1 Administrative details

Working Group name

Marine Chemistry Working Group (MCWG)

Year of Appointment within current cycle

2016

Reporting year within current cycle (1, 2 or 3)

2

Chair(s)

Koen Parmentier, Belgium

Meeting dates

6–10 March 2017

Meeting venue

Hamburg, Germany

2 Terms of Reference a) – z)

Report to be submitted.

3 Summary of Work plan

Report to be submitted.

Annex XX: OSPAR Special Request to WGMS and MCWG: Interim Report, March 2017

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 bibiliographic 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 XX: OSPAR Special Request to WGMS and MCWG: Final Report, October 2017

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 sara.losadarivas@cefas.co.uk Jon Barber jon.barber@cefas.co.uk Catherine Munschy Catherine.Munschy@ifremer.fr Katrin Vorkamp kvo@envs.au.dk	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. 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.
Corrosion protection agents	Torben Kirchgeorg Torben.Kirchgeorg@bsh.de	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) Roxana.suhring@cefas.co.uk	Document received detailing properties, usage, and environmental (especially biota) concentrations of 3 dechloranes, including Dechlorane Plus. 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.
Organophosphorous flame retardants (OPFRs)	Ian Allan Ian.Allan@niva.no Katrin Vorkamp kvo@envs.au.dk Karina Peterson Karina.Petersen@niva.no Philippe Bersuder philippe.bersuder@cefas.co.uk	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 lutz.ahrens@slu.se	The template document details the physico-chemical properties of 25 perfluoroalkyl

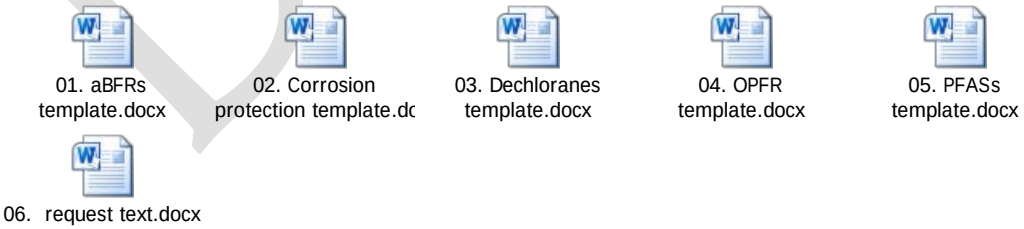
substances (PFASs) other than PFOS or PFOA	Katrin Vorkamp kvo@envs.au.dk Philippe Bersuder philippe.bersuder@cefas.co.uk	substances (PFASs) (including PFOS and PFOA) and summarises reported environmental concentrations and toxicity of PFASs (not clear if the summed concentrations included PFOS/PFOA). 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



Annex XX: Technical Minutes from the Review Group RGHAZ

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.

a) identify and collate information on projects, activities and sources of information for new and emerging hazardous substances of concern to coastal and marine waters.

b) 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) 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.