

OSPAR request on information for use in selecting and deselecting hazardous substances of concern

Advice summary

ICES provides a list of projects, activities, and sources of information for substances of emerging concern in the OSPAR area. For five groups of these substances, ICES provides further information on current knowledge and identifies data gaps.

Request

Following discussion in HASEC [2017], ICES will finalise development of the list of (recent and current) projects, activities and sources of information for new and emerging substances. This list will of course be as far as possible kept up to date but could never be regarded as complete. The main outstanding item is a deeper review of recent literature to determine if any further projects and activities should be added; it is not thought at this stage that this review will add many projects. It must also be noted that a lot of these projects are still ongoing, so new info will be available during the coming years.

In order to identify substances of emerging concern for wider consideration by OSPAR, the groups will focus on:

- *dechlorane+,*
- *alternative brominated flame retardants,*
- *phosphorous flame retardants,*
- *antifoulants,*
- *per- and polyfluorinated substances (not PFOS, PFOA),*
- *benzotriazoles,*
- *siloxanes,*
- *anticorrosion agents, especially those applied in windmill parks*

ICES will likely at this stage not review

- *warfare agents on historic marine dumping sites*
- *pharmaceuticals and daily care products*

Information on these substances (or groups of substances) will be reviewed for data gaps and a prioritisation will be attempted. It must be recognised that this process cannot be comprehensive and is (as with much current work on hazardous substances) heavily resource constrained. A full review would take more time/resources than are currently available.

Elaboration on the advice

1. List of (recent and current) projects, activities, and sources of information for new and emerging substances

The list of sources in Annex 1 is an update of information provided to OSPAR in early 2017. It includes two UK Environment Agency reports on alternative brominated flame retardants and a new Arctic Monitoring and Assessment Programme (AMAP) report on chemicals of emerging concern in the Arctic, which has been published in 2017 together with a supporting database of the properties of 684 substances identified as being of potential concern as Arctic contaminants.

The work of Tornero and Hanke (2016) is highlighted as being of particular importance. It established a list of 276 substances that might be released from sea-based (not land or freshwater) sources, including 22 antifouling biocides. It also provided an overview of those substances which have already been considered in European regulations.

2. Knowledge on substances of emerging concern

Files for each of five substance groups are attached as annexes 2–6, with information generally being provided for 3 to 27 substances in each group. These annexes indicate where the data are not complete due to knowledge gaps and research needs, such as on toxicity or environmental concentrations/behaviour. The key findings for each substance group are:

- a) 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.
- b) Alternative brominated flame retardants (aBFRs)
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, and/or potentially endocrine disrupting.
- c) Organophosphorous flame retardants (OPFRs) The molecular structure of OPFRs is diverse and hence their hydrophobicity and other physico-chemical properties are very wide ranging. This means that it is not possible to summarize the environmental behaviour or risk of OPFRs; many are thought not to be bioaccumulative or persistent, although some are neurotoxic, reprotoxic, or suspect carcinogenic.
- d) Per- and polyfluoroalkyl substances (PFASs) other than PFOS or PFOA
Many PFASs are considered to be highly 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). Overall, there is a high uncertainty of the production volume and emission data for PFASs.
- e) Corrosion protection agents
Much research is needed on the release of corrosion inhibitors from resins and anodes, and on the concentrations and effects of these in the marine environment. Due to the high number of wind turbines and platforms for offshore wind production, these may be an increasingly significant sea-based source of chemical substances.

ICES does not at present advise on new anti-foulants, benzotriazoles, siloxanes, warfare agents from historic marine dumping sites, or pharmaceuticals and daily care products.

Suggestions

It was unclear to ICES as to how OSPAR plans to use the information in this advice. This may mean that ICES has not been able to provide all relevant information, nor to identify all relevant data gaps. At present, for those OSPAR Contracting Parties that are EU Member States, all substances manufactured or imported (>1 tonne/year per producer or importer) need to be registered by May 2018 under the REACH Directive. Hazardous substances are identified based on information provided by industry (PBT, vPvB) and risk assessment potentially performed (e.g. PEC/PNEC). This information can be used under the Water Framework Directive (WFD) and the Marine Strategy Framework Directive (MSFD) to identify new priority substances. Since these directives apply to Member State waters, these substances should be evaluated for their use and effects in marine waters. ICES has not evaluated to what extent this is occurring, but does note a paucity in information on effects of many substances on marine organisms. ICES also notes in this advice that some substances may have a predominantly marine usage. OSPAR may wish to consider how to help remedy these information gaps.

Basis of the advice

Background

This advice forms the formal part of a two part process. In 2016, OSPAR made the following request:

"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 [OSPAR's Hazardous Substances and Eutrophication Committee] is aware that a similar exercise is already established under the Water Framework Directive 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."

A summary and a verbal report was given to HASEC 2017 (ICES, 2017a). That meeting provided ICES with the more detailed request stated above.

Results and conclusions

- a) Dechlorane Plus
ICES reviewed the properties, usage, and environmental (especially in biota) concentrations of three dechloranes, including Dechlorane Plus.
- b) Alternative brominated flame retardants (aBFRs)
ICES provides information on the physico-chemical properties, usage, toxicity and environmental concentrations of 16 different substances including brominated aromatic compounds, brominated phthalates, brominated alkanes and brominated ethers.
- c) Organophosphorous flame retardants (OPFRs)
ICES reviewed the physico-chemical properties, usage, toxicity, and environmental concentrations of 27 substances.
- d) Per- and polyfluoroalkyl substances (PFASs) other than PFOS or PFOA
ICES reviewed the physico-chemical properties of 25 perfluoroalkyl substances (PFASs) (including PFOS and PFOA for context) and summarizes reported environmental concentrations and toxicity of PFASs.
- e) Corrosion protection agents
Two types of corrosion protection agents were reviewed by ICES, one for organic substances and one for galvanic anodes as they relate to use in offshore renewable energy installations.

It should be noted that the decimal places and units vary between studies reported upon, so there are inevitably differences within and between the Annexes in relation to this issue.

Methods

Prior to the receipt of the request from OSPAR, ICES (2017b) had already considered the following substance groups (of chemicals) of emerging concern:

- Antifoulants: Irgarol (cybutryn), Sea-Nine (4,5-dichloro-2-n-octyl-4-isothiazolin-3-one), diuron and pyriithione (both Zn and Cu)
- Phosphorylated Flame Retardants
- Alternative Brominated Flame Retardants
- Per- and poly-fluorinated compounds (not PFOS/PFOA)
- Benzothiazoles
- Short-chain chlorinated paraffins (SCCPs)
- Siloxanes
- Radiopaque substances
- Anticorrosion agents, especially those used in windmill parks
- Dechlorane Plus

This list was taken as the starting point to answer the request. SCCPs were eliminated because they were already on the priority list, and radiopaque substances were also removed as they are considered less relevant for and little studied in the marine environment.

Many projects aiming at identifying substances of emerging concern were listed, mainly based upon the expertise of the representatives and reflecting the ongoing research in the respective countries.

Experts were sought from within the ICES community (ICES 2017c, 2017d) to complete a template for each of the groups of substances. For two groups (siloxanes and benzotriazoles), no experts were found and for a third (antifoulants), the expertise was identified but the group did not have the time to complete the template. ICES did not have the resources to consider warfare agents from historical marine dumping sites, pharmaceuticals, and daily [personal] care products.

Sources and references

ICES 2017a. 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.

ICES. 2017b. Interim Report of the Marine Chemistry Working Group (MCWG), 7-10 March 2016, Galway, Ireland. ICES CM 2016/SSGEPI:10. 18pp.

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

ICES. 2017d. Report of the Working Group on Marine Sediments in Relation to Pollution (WGMS), 6–10 March 2017, Ancona, Italy. ICES CM 2017/SSGEPI:08. 52 pp.

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.

Annexes

1. List of (recent and current) projects, activities and sources of information for new and emerging substances
2. Dechlorane Plus and related compounds
3. Alternative brominated flame retardants (aBFRs)
4. Organophosphorous flame retardants (OPFRs)
5. Per- and poly- fluoroalkyl substances (PFASs)
6. Corrosion protection systems in offshore wind farms

Annex 1. List of recent and current projects, activities, and sources of information for new and emerging substances

Table 1 List of recent and current projects, activities, and sources of information for new and emerging substances

Project name	Approach	Topic	Matrix	Location (estuary, inshore, offshore)	Contaminants noted as present in marine env	Website	Reference
Norwegian screening programme	Targeted screening	Production and import of chemicals (PBT and others)	Effluent, sediment, and biota			http://www.miljo.direktoratet.no/no/Tema/Kjemikalier/Miljogifter/	Norwegian Environmental Agency yearly reports
Swedish screening programme	Targeted screening	Occurrence of compound classes	Effluent, coastal water, and biota			Miljögiftsamordning - DiVa portal	
Non-targeted screening – a powerful tool for selecting environmental pollutants	Non-targeted screening	GC/LC-HRMS of environmental samples	Wastewater, sediment, sludge, and biota samples			http://www.miljo.direktoratet.no/no/Tema/Kjemikalier/Miljogifter/	Norwegian Environmental Agency reports M-27 2013
Non-targeted screening of point sources in city areas in Nordic countries.	Non-targeted screening	GC/LC-HRMS of environmental samples	Wastewater effluent, sediment, and fish samples			www.Nordicscreening.org	
Effects of dredged spoil disposal in the Belgian part of the North Sea	Targeted screening	Pesticides in marine sediment with GC/LC-MS	Sediment				Lauwaert <i>et al.</i> , 2016.
Impact of regulated and emerging pollutants and microplastics in marine ecosystems (IMPACTA) Project code: CTM2013-48194-C3	Targeted screening	Pharmaceuticals, perfluorinated compounds, organophosphorus pesticides, triazines, other current use pesticides, personal care products, nonylphenols, and alkylated PAHs	Seawater, marine sediment	Coastal lagoon, estuary, and offshore	Pharmaceuticals and current-use pesticides in coastal lagoon	http://www.impacta2014.blogspot.com.es/	Moreno-González <i>et al.</i> , 2015 Moreno-González and Leon, 2017
Veille-POP	Targeted screening	Occurrence, levels, and trends of emerging pollutants in the coastal environment	Marine shellfish			http://wwz.ifremer.fr	Annual reports, publications, e.g. Munsch <i>et al.</i> , 2013
MICRO	Targeted screening	GC-MS screening of a broad range of organic compounds on and from marine plastics	Marine litter				Gauquie <i>et al.</i> , 2015

Project name	Approach	Topic	Matrix	Location (estuary, inshore, offshore)	Contaminants noted as present in marine env	Website	Reference
Chemical contaminants entering the marine environment from sea-based sources	Literature search	Antifouling biocides, aquaculture medical products, warfare agents, etc.					Tornero and Hanke, 2016
Screening in urban fjords	Targeted screening	UV stabilizers, PFAS, organophosphorus compounds	Wastewater effluent, sediment, and biota			http://www.miljo.direktoratet.no/no/Tema/Kjemikalier/Miljogifter/	Norwegian Environmental Agency yearly reports
Non-targeted biomonitoring of organochlorines in bottlenose dolphins	Non-targeted screening	Halogenated compounds	Marine mammal blubber				Shaul <i>et al.</i> , 2015 Alonso <i>et al.</i> , 2017
Review of existing knowledge on emerging contaminants: focus on nanomaterials and microplastics in the aquatic environment	Literature review	Nanomaterials and microplastics	Nanomaterials and microplastics				Hartl <i>et al.</i> , 2015
Organic polar pollutants in surface waters of inland seas	Targeted screening	UV filters (personal care), polar pesticides	Seawater				Orlikowska <i>et al.</i> , 2015
Identifying bio-accumulative halogenated organic compounds using a non-target analytical approach: seabirds as sentinels	Non-targeted screening	Halogenated compounds	Black skimmer				Millow <i>et al.</i> , 2015
Study of TNT and degradation products in sediment of the Belgian World War ammunition	Targeted screening	TNT and degradation products	Sediment	Coastal waters	TNT and degradation products		Belgian National DG Environment, (in Dutch)

Project name	Approach	Topic	Matrix	Location (estuary, inshore, offshore)	Contaminants noted as present in marine env	Website	Reference
dumping site "Paardenmarkt"							
New strategies for monitoring and risk assessment of hazardous chemicals in the marine environment with passive samplers	Targeted screening	Priority substances, pharmaceuticals, phtalates, hormones, personal care products, metals	Water, sediment, and passive samplers	Harbours and coastal waters	Priority substances, pharmaceuticals, phtalates, hormones, personal care products, metals	www.newstheps.be	Ongoing project until mid-2019
New strategies for monitoring and risk assessment of hazardous chemicals in the marine environment with passive samplers	Non-targeted screening	Polar and non-polar organics, metals	Water, sediment, and passive samplers	Harbours and coastal waters	Polar and non-polar organics, metals	www.newstheps.be	Ongoing project until mid-2019
UK marine passive sampling survey	Non-targeted screening	Priority substances (PAH, PCB, PBDE), pesticides, herbicides, pharmaceuticals, alkylphenols	Water (passive sampling)	Estuarine/ inshore	Pharmaceuticals (beta-blockers, anti-epileptics)		Balaam <i>et al.</i> , 2011
UK marine passive sampling survey	Non-Targeted screening			Estuarine/ inshore	Herbicides		
UK marine passive sampling survey	Non-Targeted screening			Estuarine/ inshore	Fungicides		
UK marine passive sampling survey	Non-Targeted screening			Estuarine/ inshore	Pesticides		
UK marine passive sampling survey	Targeted screening			Estuarine/ inshore	Clotrimazole		
UK marine passive sampling survey	Targeted screening			Estuarine/ inshore	Pesticides		
UK marine passive sampling survey	Targeted screening			Estuarine/ inshore	diethyl hexyl phthalate		
UK marine passive sampling survey	Targeted screening			Estuarine/ inshore	pentachlorophenol		

Project name	Approach	Topic	Matrix	Location (estuary, inshore, offshore)	Contaminants noted as present in marine env	Website	Reference
UK marine passive sampling survey	Targeted screening			Estuarine/ inshore	alkylphenols		
DECOMAR project: Sources, distribution and biological effects of regulated and emerging micropollutants in the Mar Menor lagoon (Murcia)	Targeted screening	Pharmaceuticals, surfactants, organophosphorus pesticides, triazines, and other current use pesticides	Seawater, marine sediment	Mediterranean coastal lagoon	Anionic and nonionic surfactants and current-use insecticides and herbicides		Moreno-González <i>et al.</i> , 2013a Traverso-Soto <i>et al.</i> , 2015 Campillo <i>et al.</i> , 2013. Moreno-González <i>et al.</i> , 2013b Moreno-González <i>et al.</i> , 2014
EMERCONFO – Novel methodologies to assess the impact of emerging contaminants on marine ecosystems and food consumers.	Targeted screening	Emerging contaminants including some key metabolites and transformation products	Biota (mussels and fish) and estuarine water			https://www.ehu.es/es/web/ibea/emerconfo	
ECsafeSEAFOOD	Targeted screening	Assess and evaluate food safety issues related to contaminants of emerging concern present in seafood as a result of environmental contamination	Biota (seafood)			http://www.ecsafe seafood.eu/	Vandermeersch <i>et al.</i> , 2015 (Others. see web page)
XENOMETABOLOM IC 2017-2019	Targeted screening	Identification of bioaccumulative XENObiotics in mussel following a METABOLOMIC approach: human and environmental exposure, etc.	Biota (mussels)			damqam@cid.csi.c.es dbarcelo@icra.cat	Diana Alvarez-Muñoz Damian Barceló
Fuentes, transporte y alcance de la contaminación por compuestos orgánicos regulados y emergentes en áreas protegidas del litoral andaluz.	Targeted screening	Pollutants in Andalusian coastal areas	Seawater, sediment, and biota	Estuarine and coastal areas	NP, OTNE, galaxolide, and tonalide		Pintado-Herrera <i>et al.</i> , 2016

Project name	Approach	Topic	Matrix	Location (estuary, inshore, offshore)	Contaminants noted as present in marine env	Website	Reference
Project P09-RNM-5417							
Origen, distribución y persistencia de productos farmacéuticos y de higiene personal (ppcps) en sistemas acuáticos de la región suratlántica. Project P10-RNM-6613	Targeted screening	Pharmaceuticals and personal care products in Gulf of Cadiz	Seawater				Baena-Nogueras <i>et al.</i> , 2016
UK CEMP Monitoring programme 2014 west 2015 east	Targeted		Sediment	Offshore	PFAS		Cefas- Thi Bolam (thi.bolam@cefas.co.uk)
UK CEMP Monitoring programme dab livers 2014 west 2015 east	Targeted		Biota	Offshore	PFAS		Cefas- Thi Bolam (thi.bolam@cefas.co.uk)
UK Stranded mammals (51 UK wide harbour porpoises from 2012-14	Targeted		Biota (mammals)	Stranded	PFAS		Cefas- Thi Bolam (thi.bolam@cefas.co.uk) Barber et al (in prep)
UK CEMP Monitoring programme, disposal site and estuarine sediments from 2010-12	Targeted		Sediment	Offshore	NBFRs		Cefas- Thi Bolam (thi.bolam@cefas.co.uk)
UK Stranded mammals (20 UK wide harbour	Targeted		Biota (mammals)	Stranded	NBFRs		Law <i>et al.</i> , 2013

Project name	Approach	Topic	Matrix	Location (estuary, inshore, offshore)	Contaminants noted as present in marine env	Website	Reference
porpoises from 2008)							
UK CEMP Monitoring programme (sediments from 2013)	Targeted		Sediment	Offshore	NBFRs		Suhring <i>et al.</i> , 2015.
20 UK wide harbour porpoises from 2012	Targeted		Biota (mammals)	Stranded	OPFRs		Papachlimitzou <i>et al.</i> , 2015
A few Thames sediments and silicone rubber passive samples from 2013	Targeted		Sediment (passive sampling)	Estuary	OPFRs	www.cefas.co.uk	Cefas (Thi Bolam)
Identifying new persistent and bioaccumulative chemicals among chemicals of commerce	Literature study	Database search, identification of substances was based on EPISuite Software and expert judgment					Howard and Muir, 2010
Identifying new persistent and bioaccumulative chemicals among chemicals of commerce II: Pharmaceuticals	Literature study	Database search, identification of substances was based on potential bioaccumulation or persistence using quantitative structure property relationships (QSPR) or scientific judgment.					Howard and Muir, 2011
Identifying new persistent and bioaccumulative chemicals among chemicals of commerce III: Byproducts, Impurities, and Transformation Products	Literature study	Evaluation of the 610 chemicals from part I as well as high production volume chemicals and identified 320 chemicals (39 byproducts and impurities, and 281 transformation products)that could be potential PB chemicals.					Howard and Muir, 2013

Project name	Approach	Topic	Matrix	Location (estuary, inshore, offshore)	Contaminants noted as present in marine env	Website	Reference
	Literature study and database	Prioritization of flame retardants for environmental risk assessment				http://www.environment-agency.gov.uk/	Fisk <i>et al.</i> , 2003
Environmental risk assessment of ethane-1,2-diyl)bis(penta-bromobenzene (EBP)	Literature review					http://www.environment-agency.gov.uk/	Dungey and Akintoye, 2007
Chemicals of emerging Arctic Concern Database currently includes physico-chemical properties of 684 substances	Literature review and database		Air, biota		16 major groups of 'emerging chemicals' as well as micro-plastics	https://chemicals.amap.no	AMAP, 2017
Chemical Emissions from Offshore Wind farms (2017-2019, Germany)	Target	Environmental analyses of potential emissions from corrosion protection systems used in offshore wind farms	Seawater, marine sediment, and biota	Offshore			Project starting in late 2017
BMVI Network of Experts, SPT 204 - Emissions from transport infrastructures (2016 – 2019, Germany)	Target and Screening	Emissions from corrosion protection systems	Laboratory experiments			http://www.bmvi-expertennetzwerk.de/EN/Topics/Topic2/Topic2_no.de.html	Luft <i>et al.</i> , 2017
Transfers of metallic elements from ALuminium-INDium galvanic anodes to marine Environment (TALINE - 2012-2017, France)	Target	Metal emissions from galvanic anodes	Tank experiments, seawater		Metals		Deborde <i>et al.</i> , 2015

Project name	Approach	Topic	Matrix	Location (estuary, inshore, offshore)	Contaminants noted as present in marine env	Website	Reference
Effective Operations in Ports - WP 2.2.2: Aluminium pollution related to the protection of ports infrastructures from: Sub-Project 2: Ports and Environment WP 2.2: Water pollutions related to ship reception, (EFFORTS 2006 - 2009)	Target	Metal emissions from galvanic anodes	Seawater, sediment	Harbour	Metals	http://cordis.europa.eu/publication/rcn/11323_en.html	Gabelle <i>et al.</i> , 2012:

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Annex 2. Dechlorane Plus and related compounds

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Description

Dechloranes are a group of compounds arising from Diels-Alder reactions of hexachlorocyclo-pentadiene. They were first patented in the 1960s as replacements for the hazardous pesticide and flame retardant Mirex (Sverko *et al.*, 2011). The primary replacements for Mirex were Dechlorane 602 (DDC-DBF), Dechlorane 603 (DDC-Ant), Dechlorane 604 (HCTBPH), and Dechlorane Plus (DDC-CO). The technical product of DDC-CO consists of about 75% anti- DDC-CO and 25% syn- DDC-CO (Sverko *et al.*, 2011). Further dechloranes patented in the 1970s are the so called "experimental" flame retardants such as the mixed brominated-chlorinated dibromoaldrin (DBALD) (European Commission, 2011). The dechloranes discussed in this report are the ones most frequently detected in environmental samples.

Table 1 Abbreviations (PRAbs), names and CAS ID numbers of the discussed dechloranes (Zhang *et al.*, 2016)

Abbreviation	Chemical name (common chemical dynonym)	CAS #
DDC-DBF	1,4:6,9-Dimethanodibenzofuran, 1,2,3,4,6,7,8,9,10,10,11,11-dodecachloro-1,4,4a,5a,6,9,9a,9b-octahydro- (Dechlorane 602)	31107-44-5
DDC-Ant	1,4:5,8:9,10-Trimethanoanthracene, 1,2,3,4,5,6,7,8,12,12,13,13-dodecachloro-1,4,4a,5,8,8a,9,9a,10,10a-decahydro- (Dechlorane 603)	13560-92-4
DDC-CO	1,4:7,10-Dimethanodibenzo[a,e]cyclooctene, 1,2,3,4,7,8,9,10,13,13,14,14-dodecachloro-1,4,4a,5,6,6a,7,10,10a,11,12,12a-dodecahydro- (Dechlorane Plus)	13560-89-9

Physio-chemical properties (K_{ow} , etc)

Dechloranes are strongly hydrophobic with octanol-water partitioning coefficients ($\log K_{ow}$) above 5; they are poorly water-soluble and semi-volatile (Sverko *et al.*, 2011; Zhang *et al.*, 2016) (Table 2).

Table 2 Physical-chemical properties of dechloranes, including molecular weight (MW), water solubility ($\log SI$), vapour pressure ($\log PI$), air-water partitioning coefficient ($\log K_{AW}$), octanol-water partitioning coefficient ($\log K_{OW}$), and octanol-air partitioning coefficient ($\log K_{OA}$) (Zhang *et al.*, 2016).

Compound	MW [g mol ⁻¹]	$\log SI$ [mg L ⁻¹]	$\log PI$ [Pa]	$\log K_{AW}$	$\log K_{OW}$	$\log K_{OA}$
DDC-DBF	614	-4.8	-4.2	-7.0	8.1	15.0
DDC-Ant	638	-7.6	-4.7	-4.0	11.2	15.2
DDC-CO	654	-7.8	-5.1	-3.5	11.3	14.8

There is a lack of experimental data concerning the persistence of dechloranes. Screening models however indicate that dechloranes are not readily biodegradable in water or soil and might meet the P-criteria of the Stockholm Convention and REACH legislation (Sverko *et al.*; 2011, Zhang *et al.*, 2016) (Table 3).

Table 3 Environmental degradation half-lives [h] in water, soil, and sediment of dechloranes (Zhang *et al.*, 2016).

Compound	MW [g mol ⁻¹]	$t_{water, 1/2}$ [h]	$t_{soil, 1/2}$ [h]	$t_{sediment, 1/2}$ [h]
DDC-DBF	614	4320	87600	38904
DDC-Ant	638	4320	87600	38904
DDC-CO	654	4320	87600	38904

As lipophilic compounds with a molecular weight below 700, they furthermore have a potential to accumulate in the foodweb and magnify through trophic levels (Shen *et al.*, 2011, Sverko *et al.*, 2011, Wu *et al.*, 2010). DDC-DBF has the highest bioaccumulation potential of the discussed dechloranes, with biota sediment accumulation factors of up to 270: more than ten times higher than the other dechloranes (Feo *et al.*, 2012; Shen *et al.*, 2011 Sühning *et al.*, 2014). The reported biomagnification factors as well as biological half-lives in fish are typically higher for syn- DDC-CO (Feo *et al.*, 2012; Sühning *et al.*, 2014; Sverko *et al.*, 2011; Wu *et al.*, 2010).

Production and usage

After the ban of Mirex in the late 1970s, dechloranes and especially DDC-CO, have increasingly been applied as additive flame retardants (Sverko *et al.*, 2011). DDC-CO is a high production volume chemical mostly used in hard plastic connectors in televisions and computer monitors, wire coatings, and furniture (Sverko *et al.*, 2011). It is produced by OxyChem in the US. The only listed importer to the European Union is BASF (Germany) (European Commission, 2011).

There are no data available concerning the production or importation of DDC-DBF, DDC-Ant, or the experimental flame retardants to the European Union. Many of them have, however, been detected in biota and abiotic media within the European Union (Guerra *et al.*, 2011; Möller *et al.* 2012) (see details below). Uses of DDC-DBF and DDC-Ant include fibreglass-reinforced nylon and silicone grease, respectively (Shen *et al.*, 2010).

Environmental concentrations

Water

Dechloranes are highly lipophilic and poorly water soluble. Therefore, dechlorane concentrations are generally very low in the water-phase and, if detected, almost exclusively particle bound (de Wit *et al.*, 2010). Consequently, literature regarding water concentrations of dechloranes is scarce. No data for dechloranes in effluents or transitional waters are available. However, there are reports on elevated dechlorane plus concentrations in sediments close to industrial effluent discharges in South Korea with up to 451.2 pg g⁻¹ dry weight (Fang *et al.*, 2014) as well as in sewage sludge (75.1 ng g⁻¹ dry weight) (de la Torre *et al.*, 2011b) indicating that the discharge of industrial and municipal wastewater could be a significant source for dechloranes in the marine environment.

Möller *et al.*, (2012) were one of the few reporting seawater concentrations of dechloranes. They reported concentrations of up to 17.7 pg L⁻¹ DDC-CO in the particulate phase of seawater samples from the German Bight of the North Sea. The isomer ratio of syn- and anti- DDC-CO was close to the technical mixture indicating limited isomer-specific degradation/depletion or proximity to active sources (Möller *et al.*, 2012). For offshore seawater, Möller *et al.*, (2010) sampled transects from the East Greenland Sea to Antarctica. Again, DDC-CO was primarily detected in the particulate phase with concentrations of up to 1.3 pg L⁻¹. Interestingly, Möller *et al.*, (2010) found an increase of the syn-isomer contribution to sum DDC-CO with decreasing latitude, indicating a stereoselective depletion of the anti-isomer with distance from the emission regions.

Biota

Santín *et al.*, (2013) reported the two stereoisomers of DDC-CO, DDC-DBF, and DDC-Ant in various fish species from Iberian rivers and estuaries. DDC-DBF was the dechlorane of highest concentration in all fish samples (up to 174 ng g⁻¹ lipid weight (lw)). The concentrations even exceeded those of most of the banned polybrominated diphenylether (PBDE) congeners (apart from BDE-47) (Santín *et al.*, 2013). DDC-Ant was significantly lower in fish tissue, with concentrations up to 11.8 ng g⁻¹ lw, but still more concentrated than the DDC-CO congeners (syn: 1.25 ng g⁻¹ lw and anti: 4.86 ng g⁻¹ lw) even though DDC-CO is supposedly the only dechlorane used in the European Union (Santín *et al.*, 2013).

Sühning *et al.*, (2015b) reported DDC-DBF in coastal European eels of up to 0.66 ng g⁻¹ wet weight (ww) and up to 0.46 ng g⁻¹ ww for DDC-CO. Interestingly, they found that DDC-CO had higher transfer rates into gonads and eggs than DDC-DBF which seemed to primarily accumulate in muscle tissue (Sühning *et al.*, 2015b).

Concentrations of dechloranes offshore in dabs from the German Bight were lower than in proximity to the coast with DDC-DBF levels of up to 0.087 ng g⁻¹ ww and up to 0.015 ng g⁻¹ ww for syn-DDC-CO (Sühring *et al.*, 2016). Similarly, DDC-DBF was the dechlorane observed in highest concentration in Franciscana dolphins from the southern coast of Brazil reaching 0.94 ng g⁻¹ lw and 0.71 ng g⁻¹ lw for DDC-CO (De la Torre *et al.*, 2011a). Law *et al.*, (2013) detected both stereoisomers of DDC-CO in the blubber of 21 harbour porpoises (*Phocoena phocoena*) stranded or bycaught around UK coasts during 2008, with concentrations ranging from <0.14 – 0.36 ng g⁻¹ ww for anti-DDC-CO and <0.12-0.17 ng g⁻¹ ww for syn-DDC-CO. In oysters from Northern China DDC-CO was higher than DDC-DBF with levels of 4.1 ng g⁻¹ lw and 0.21 ng g⁻¹ lw, respectively. DDC-Ant was detected at 0.12 ng g⁻¹ lw (Jia *et al.*, 2011).

Further research on the uptake pathways, sources, and behaviour of dechloranes in the foodweb is needed, particularly for the highly bioaccumulative DDC-DBF.

Sediment

Data on environmental concentrations of dechloranes in marine sediments are very limited. Most studies focus on the Great Lakes (near the OxyChem facility) or on regions close to potential sources in China.

Sühring *et al.*, (2015a) analysed dechloranes in sediments from the estuaries of the rivers Elbe and Weser, from the German and UK coasts, and offshore in the North Sea. In general, anti-DDC-CO had, on average, the highest reported concentrations in transitional, coastal, and offshore sediments with up to 0.24 pg g⁻¹, 0.61 pg g⁻¹, and 0.037 pg g⁻¹ dry weight (dw), respectively. Syn-DDC-CO concentrations were between 0.011 pg g⁻¹ dw offshore in the North Sea to 0.918 pg g⁻¹ dw in the English Channel. DDC-DBF concentrations ranged from 0.011 pg g⁻¹ dw offshore in the North Sea to 0.279 pg g⁻¹ dw in the Weser estuary (Sühring *et al.*, 2015a).

Further research is needed on the distribution, levels, and trends of dechloranes in sediments.

Toxicity

Toxicity data are scarce for all dechloranes discussed in this study. The few results suggest a low acute toxicity of DDC-CO for wildlife or humans (Sverko *et al.*, 2011). However, DDC-CO shares structural features with compounds, such the organochlorine pesticides dieldrin and heptachlor, which are known to cause cancer or are developmentally toxic (CECBP 2008). DDC-CO was found to have a higher genotoxic potential in marine mussels than the classic brominated flame retardant BDE-209 (Barón *et al.*, 2016). DDC-CO did not induce changes in hemocyte DNA strand breakage, phagocytosis rate, or viability in blue mussels at up to 1 µg L⁻¹ exposure, while lipid peroxidation levels increased at exposure levels of 0.01 µg L⁻¹ indicating that oxidative stress may be a primary toxicological effect of DDC-CO in blue mussels (Gagné *et al.*, 2017). In embryo-larval zebrafish DDC-CO was reported to induce behavioural anomalies, inhibit the development and induce oxidative stress at exposure levels of 30 µg L⁻¹ and more (Chen *et al.*, 2017).

Neither genotoxic effects nor mutagenic effects were observed at environmental concentrations of DDC-DBF (up to 10 pg L⁻¹), using the umuC test and Ames fluctuation test, however results for higher concentrations are lacking (Santín *et al.*, 2013).

There is a lack of acute as well as chronic and sublethal toxicity results for dechloranes in general and particularly for aquatic organisms.

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Annex 3. Alternative brominated flame retardants (aBFRs)

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Description

For full names, the CAS numbers referred to in this text, and additional information, please see the table in section “Additional information”. Following on from the substitution of PBDEs with alternative flame retardants (FRs), lots of different alternative brominated FRs (aBFRs) are being reported in the environment. Some of the alternative BFRs most commonly analysed and found in the environment (and for that reason selected here) are EH-TBB and BEH-TEBP, TBBPA-DBPE, DBHCTD (HCDBCO), PBEB, TBECH (mainly α and β congeners), PBT, TBP-DBPE (DPTE), TBP-AE (ATE) and BATE, TBP and DBP, BTBPE, DBDPE, and HBBz. A harmonized naming system has been suggested by Bergman *et al.*, (2012), but some of the previous names are still used. BB-153 (as the main compound in technical hexabromobiphenyl) is a doubt for inclusion as an “emerging” flame retardant, as it is on the OSPAR List of Substances of Possible Concern and has been included in the Stockholm Convention since 2009; however, being persistent, toxic, bio-accumulative and found in the environment at relatively high concentrations (Vorkamp *et al.*, 2005). More information regarding the evaluation of environmental risks from DBDPE can be found in Dungey and Akintoye (2007) and on various FRs in Fisk *et al.*, (2003).

Physio-chemical properties (K_{ow} , etc)

Table 1 Summary of physicochemical properties of alternative brominated flame retardants (Howard and Muir, 2010; Covaci *et al.*, 2011; Bergman *et al.*, 2012; Papachlimitzou *et al.*, 2012; Vorkamp and Rigét, 2014; Liagkouridis *et al.*, 2015; Zhang *et al.*, 2016b). Blank cells indicate that no information was available.

	Additive / Reactive	MW	$logK_{ow}$	K_{oc}	$logK_{aw}$	Vapour pressure (Pa)	Persistence	Bioaccumulation - Biomagnification		
									BCF (L/kg) (Howard and Muir 2010)	Log BCF (Howard and Muir 2010)
EH-TBB	A	549.92	6.3, 5.6, 8.8, 7.73, 8.75, 8.28	3.82E+05	-1.8, -3.59, -3.7, -8.6, 6.3	549.92	Pov 173.03 h (Liagkouridis <i>et al.</i> , 2015)	Possible bioaccumulation (Vorkamp and Rigét, 2014)		
BEH-TEBP	A	706.14	5.7,6.8, 10.2, 9.34, 11.95, 10.92	2.88E+06	-3.7, -4.91, -6.3, 6.1, -7.0	1.55E-11-2.28E-09	Pov 173.04 h (Liagkouridis <i>et al.</i> , 2015)	No evidence of biomagnification (Sagerup <i>et al.</i> , 2010)	3	0
TBBPA-DBPE	A	943.61	12.99, 11.52, 12.24, 12.2, 12.8, 20.3	1.00E+07	-8.78, -8.18, -9.78, 11.5, -8.2, -8.3	1.60E-07, 2.85E-15, 6.36E-15	Yes (Covaci <i>et al.</i> , 2011) Pov 518.97 h (Liagkouridis <i>et al.</i> , 2015)		3	0
DBHCTD	A	540.76	7.62, 4.4, 6.0, 8.0	3.32E+05	-3.8, -2.8, 5.2	8.27E-07				
PBEB	A	500.65	6.76, 7.48, 6.78, 7.0, 10.0	1.14E+05	-2.49, -2.75, -3.49, 7.5	1.56E-04, 3.2E-04, 6.20E-04	Pov 516.59 h (Liagkouridis <i>et al.</i> , 2015)	Yes (Covaci <i>et al.</i> , 2011)	14 140	4

	Additive / Reactive	MW	logK _{ow}	K _{oc}	logK _{ow}	Vapour pressure (Pa)	Persistence	Bioaccumulation - Biomagnification		
									BCF (L/kg) (Howard and Muir 2010)	Log BCF (Howard and Muir 2010)
TBECH	A	427.8	4.82, 5.24, 8.01, 12.2, 12.6, 19.2	10 000	-2.77, -5.6, -6.0	2.97E-03 – 1.40E-02	Pov 106.76 h (Liagkouridis <i>et al.</i> , 2015)	2153	3	
PBT	A	486.62	5.43, 6.25, 6.99, 6.42, 9.6	60 200	-2.61, -2.82, -2.5, 7.0	1.22E-03, 6.00E-04	Pov 513.97 h (Liagkouridis <i>et al.</i> , 2015) Not readily biodegradable (Covaci <i>et al.</i> , 2011)			
TBP-AE	A/R	370.8	5.04, 9.56, 5.6, 5.1, 8.6	13 100	-3.97, -2.3, -3.2, 5.6	2.40E-02, 1.35E-02, 4.9E-02	Pov 170.16 h (Liagkouridis <i>et al.</i> , 2015)	4019	4	
BATE										
TBP	A/R	330.8	4.24, 4.13, 3.7, 4.4, 4.18, 3.96, 10.0	pH-dep.	-4.90, -5.83, -2.63, -4.3, 4.2	0.41, 2.00E-01, 4.04E-02	Pov 170.35 h (Liagkouridis <i>et al.</i> , 2015)	120	2	
DBP	A/R	251.9	3.47, -0.1, 2.2, 7.6	pH-dep	-7.86, -7.9, -6.7, 0.9	3.65E+00	Pov 104.44 h (Liagkouridis <i>et al.</i> , 2015)			
TBP-DBPE	A	530.67	5.82, 6.5, 6.4, 11.1	35 000	-4.1, -4.5, 6.3	1.26E-05	Pov 517.82 h (Liagkouridis <i>et al.</i> , 2015)	Possible bioaccumulation (Vorkamp and Rigét, 2014)		

	Additive / Reactive	MW	logK _{ow}	K _{oc}	logK _{ow}	Vapour pressure (Pa)	Persistence	Bioaccumulation - Biomagnification		
									BCF (L/kg) (Howard and Muir 2010)	Log BCF (Howard and Muir 2010)
BTBPE	A	687.64	8.31 7.88±0.86 9.15 4.7	7.92E+05		3.88E-10	Pov 518.96 h (Liagkouridis <i>et al.</i> , 2015) Degrade to 2,5,6-tribromophenol Half-life in atmosphere 5.9h Half-life in air 8.6h Half-life in water 4320h (Zhang <i>et al.</i> , 2016a) 13 photochemical transformation products identified (Zhang <i>et al.</i> , 2016b) Half life 1.5-17.1 days Suspected persistent in the environment: Ready biodegradability model (IRFMN) in VEGA (Q)SAR platform predicts that the chemical is NON Readily Biodegradable (moderate reliability);The Danish QSAR database contains information indicating that the substance is predicted as non-readily biodegradable	Yes (TMF of 1.8)		

	Additive / Reactive	MW	logK _{ow}	K _{oc}	logK _{aw}	Vapour pressure (Pa)	Persistence	Bioaccumulation - Biomagnification		
									BCF (L/kg) (Howard and Muir 2010)	Log BCF (Howard and Muir 2010)
DBDPE	A	971.22	11.1 7-10 12.3	1.00E+07		6.0E-15	Pov 518.97 h (Liagkouridis <i>et al.</i> , 2015) Half-life in air 54h, in water 4320h (Zhang <i>et al.</i> , 2016a)	Yes (TMF of 8.6) BAF 6.1-7.1		
BB-153	A	627.59	6.39							
HBBz	A	551.49	6.11 6.07 5.85±0.67	50 300		1.14E-04 3.17E-04 7.5E-04 2.24E-06	Pov 517.86 h (Liagkouridis <i>et al.</i> , 2015) Half-life in air 11,207h, in water 4320h (Zhang <i>et al.</i> , 2016a) Not readily biodegradable	Suspected bio-accumulative: Bioaccumulation Canada database in the toolbox reports at least one value above the B threshold of 2000 L/Kg (3.3 log units)	Very high bio-concentration factor	

Log K_{ow}: Octanol-water partition coefficient. Indicates tendency to adsorb to sediments and to bio-accumulate. Chemicals with log K_{ow} > 5 (Stockholm Convention), ≥4 (OSPAR) or >4.5 (REACH) have potential to bio-accumulate in organisms (Gottardo *et al.*, 2014).

K_{oc}: Soil organic carbon-water partitioning coefficient, predicting the mobility of organic soil contaminants; higher K_{oc} values correlate to less mobile organic chemicals while lower K_{oc} values correlate to more mobile organic chemical.

Log K_{aw}: Atmosphere-water partition coefficient. Describes air-water partitioning. Compounds with log K_{aw} >-5 and <-1 have long range transport potential. Further, under the Stockholm Convention, airborne compounds with a half-life in air of >2 days are classed as having long range transport potential

P-: Overall persistence.

BCF: Bio-concentration factor. It is an estimate of bio-accumulative with values >5000 (Stockholm Convention), >2000 (REACH), and ≥500 (OSPAR), and very accumulative with values > 5000 (REACH) (Gottardo *et al.*, 2014).

Log BCF: $logBCF = mlogK_{ow} + b$

Production and usage

Table 2 Information on production/origin and on main uses of alternative brominated flame retardants (de Wit *et al.*, 2010; Covaci *et al.*, 2011; EFSA 2012a; Vorkamp and Rigét, 2014).

	Production	Use	Listed
EH-TBB		Used in Firemaster 550 in a mixture with BEH-TEBP as an alternative to penta-mix PBDE products in polyurethane foam.	Pre-registered at ECHA
BEH-TEBP	US production volumes of TBPH were 450 to 4500 tonnes/year from 1990 to 2006, but no production information is available after 2006. Degradation could generate bis(2-ethylhexyl)-phthalate (DEHP), a plasticizer which is currently restricted or banned for specific uses in many countries.	Used primarily in PVC and neoprene, as well as in wire and cable insulation, film and sheeting, wall coverings and adhesives.	Pre-registered at ECHA
TBBPA-DBPE	The production volume in China in 2006 was 4000 tonnes. US production in 2006 was <4500 tonnes. Degradation can produce TBBPA.	Used mainly in plastic products such as pipes, kitchen hoods, and electronics.	Listed as an LPV chemical in the EU. Pre-registered at ECHA for CoRAP.
DBHCTD		Has been reported to be used as a flame retardant in “styrenic polymers”.	
PBEB	Low production volume chemical (10–1000 tons) in 2002 according to OSPAR but is not currently produced or used by any OSPAR signatory states. Produced in the US until 1986. Production in France continued until 2002, in a quantity of up to 1000 tonnes year.	Used in circuit board resins, textiles, adhesives, wire and cable coating, and polyurethane and thermoplastic resins.	Classified as a LPV chemical in the EU and is included in the OSPAR list of Chemicals for Priority Action, being ranked as persistent, liable to bio-accumulate and toxic, but not currently produced. The European Food Safety Authority includes this compound as relevant to be addressed in further investigations. Pre-registered at ECHA for CoRAP.
TBECH	The US production volumes were 4.5 to 230 tonnes/year from 1986 to 2002. No production information is available after 2002.	Used primarily in extruded polystyrene, but also in electrical cable coatings, high impact plastics, fabric adhesives, and construction materials.	Pre-registered at ECHA
PBT	Produced in quantities estimated between 1000 to 5000 tonnes per year at the global level. In China, 600 tonnes of PBT per year are produced. Might also be a degradation product of DBDPE and TBBPA.	Used mostly in unsaturated polyesters, polyethylene, polypropylene, polystyrene, SBR-latex, textile, rubbers, ABS (acrylonitrile butadiene styrene terpolymer) in textiles, polyester resins, and paint emulsions.	Listed as an LPV chemical in the EU. Pre-registered at ECHA.
TBP-AE	The US production volume in 2006 was <227 tonnes. Likely degradation product of TBP-DBPE.	A reactive FR, when it is co-polymerized together with the monomer and an additive FR commonly used in expandable polystyrene (EPS) and PS foam.	Listed as an LPV chemical in the EU.
BATE	Likely degradation product of TBP-DBPE.		

	Production	Use	Listed
TBP	US production was 4500 to 23 000 tonnes in 2006 and it is considered a HPV in the EU. Japanese production in 2001 was 3600 tonnes. It can be formed naturally. It could also be a degradation product of BDE-100/154 and it is a by-product in BTBPE production.	Used as a reactive flame retardant in epoxy resins, phenolic resins, polyester resins, polyolefins, and vinyl-aromatic polymers. It is also an antifungal agent (e.g. wood treatment), and as a chemical intermediate. Moreover, 2,4,6-TBP is a common precursor for other BFRs.	The European Food Safety Authority (EFSA, 2012b) recently reviewed the literature on 2,4-DBP and 2,4,6-TBP in environmental samples, food and feed in the context of a risk assessment, but generally noted a lack of data.
DBP	It can also be formed naturally. It could also be degradation product of BDE-47.	Used as reactive flame retardants in epoxy resins, phenolic resins, polyester resins, polyolefins and vinyl-aromatic polymers.	The European Food Safety Authority (EFSA, 2012b) recently reviewed the literature on 2,4-DBP and 2,4,6-TBP in environmental samples, food and feed in the context of a risk assessment, but generally noted a lack of data.
TBP-DBPE	Produced in Germany until 1985		
BTBPE	In the US 450–4500 tonnes/year after 1998 Worldwide production/usage 16,710 tonnes in 2001	Replacement for octaBDE acrylonitrile butadiene styrene, high-impact polystyrene, thermoplastics, thermoset resins, polycarbonate, coatings	Low production volume in the EU Annex III inventory in REACH
DBDPE	Not produced in Europe but imported mainly to Germany (1000–5000 tonnes in 2001) Echa.europa.eu website: manufactured and/or imported in the European Economic Area in 10 000–100 000 tonnes per year Second highest current use additive FR in China (12 000 tonnes in 2006)	Replacement for decaBDE Additive to polymeric materials (high-impact polystyrene, acrylonitrile butadiene styrene, polypropylene) and in textiles	Pre-registered at ECHA
HBBz	350 tons in Japan in 2001; 600 tonnes/year in China; not currently produced in EU; US: 5–250 tonnes in 1998	Additive FR to paper, woods, textiles, electronic and plastic goods	OSPAR list of substances of possible concern – section A Annex1, Dir 67/548/EEC Annex III inventory in REACH
BB-153	Forbidden in Europe in 1984	Synthetic fibres and polymers (thermoplastics in office equipment)	Hexabromobiphenyl: POP of strict elimination (in Cruz <i>et al.</i> , 2015) OSPAR list of substances of possible concern – section C

ECHA: European Chemicals Agency

CoRAP: Community rolling action plan (substances for evaluation by the Member State Competent Authorities under the substance evaluation process of the REACH Regulation (EC) No 1907/2006).

LPV: Low production volume

HPV: High production volume, i.e., substance produced or imported in quantities in excess of 1000 tonnes per year.

Environmental concentrations

Water and air

Table 3 Concentrations of alternative brominated flame retardants in water and air

	Offshore waters	Air
EH-TBB	<LD (Xie <i>et al.</i> , 2011)	<LD–1.4 pg/m ³ (Schlabach <i>et al.</i> , 2011) <LD–8.9 pg/m ³ (Möller <i>et al.</i> , 2011a) <LD (Xie <i>et al.</i> , 2011) Increasing in the Great Lakes region (Ma <i>et al.</i> , 2012) <0.09–28 pg/m ³ (Lee <i>et al.</i> , 2016) 0.024–1.2 pg/m ³ (Yu <i>et al.</i> , 2015) 0.17–58 pg/m ³ (Salamova <i>et al.</i> , 2014)
BEH-TEBP	<LD (dissolved) <LD–0.12 pg/L (particulate) (Möller <i>et al.</i> , 2011b) <LD–0.2 pg/L (Möller <i>et al.</i> , 2011a)	<LD–1.7 pg/m ³ (Schlabach <i>et al.</i> , 2011) <LD–3.4 pg/m ³ (Möller <i>et al.</i> , 2011a) <LD pg/m ³ (gas) <LD–0.08 pg/m ³ (particulate) (Möller <i>et al.</i> , 2011b) <0.04–6.6 pg/m ³ (Lee <i>et al.</i> , 2016) 0.028–5.55 pg/m ³ (Yu <i>et al.</i> , 2015) 0.27–14 pg/m ³ (Salamova <i>et al.</i> , 2014)
TBBPA-DBPE		
DBHCTD	<LD (Xie <i>et al.</i> , 2011)	<LD (Xie <i>et al.</i> , 2011) <0.02–7.2 pg/m ³ (Lee <i>et al.</i> , 2016)
PBEB		0.039–0.25 pg/m ³ (Schlabach <i>et al.</i> , 2011) <0.02–0.81 pg/m ³ (Lee <i>et al.</i> , 2016) 0.01–0.24 pg/m ³ (Salamova <i>et al.</i> , 2014) 0.002–0.078 pg/m ³ (Yu <i>et al.</i> , 2015)
ΣTBECH		3.2–42 pg/m ³ (Schlabach <i>et al.</i> , 2011)
PBT	<LD (dissolved & particulate) (Möller <i>et al.</i> , 2011b) <LD–0.4 pg/L (Möller <i>et al.</i> , 2011a) <LD (Xie <i>et al.</i> , 2011)	0.16–0.73 pg/m ³ (Schlabach <i>et al.</i> , 2011) 0.1–4.5 pg/m ³ (Möller <i>et al.</i> , 2011a) 0.001–0.02 pg/m ³ (gas) (Möller <i>et al.</i> , 2011b) <LD–0.04 pg/m ³ (Xie <i>et al.</i> , 2011) <0.02–0.81 pg/m ³ (Lee <i>et al.</i> , 2016)
TBP-AE	<LD (Xie <i>et al.</i> , 2011)	<0.018–0.27 pg/m ³ (Schlabach <i>et al.</i> , 2011) <LD (Xie <i>et al.</i> , 2011) 0.007–0.102 pg/m ³ (Yu <i>et al.</i> , 2015) <0.008–8.3 pg/m ³ (Lee <i>et al.</i> , 2016)
BATE		0.049–0.051 pg/m ³ (Schlabach <i>et al.</i> , 2011) 0.004–0.021 pg/m ³ (Yu <i>et al.</i> , 2015)
TBP		17–27 pg/m ³ (Schlabach <i>et al.</i> , 2011)
DBP		6.0–21 pg/m ³ (Schlabach <i>et al.</i> , 2011)

	Offshore waters	Air
TBP-DBPE	<LD (dissolved) <LD-0.002 pg/L (particulate) (Möller <i>et al.</i> , 2011b) <LD-1.6 pg/L (Möller <i>et al.</i> , 2011a) <LD-0.77 pg/L (Xie <i>et al.</i> , 2011)	0.16–3.2 pg/m ³ (Schlabach <i>et al.</i> , 2011) 0.1–2.5 pg/m ³ (Möller <i>et al.</i> , 2011a) <LD-1.7 pg/m ³ (gas) 0.005-0.05 pg/m ³ (particulate) (Möller <i>et al.</i> , 2011b) 0.01–1.89 pg/m ³ (Xie <i>et al.</i> , 2011) <0.01–7.6 pg/m ³ (Lee <i>et al.</i> , 2016) 0.006–0.201 pg/m ³ (Yu <i>et al.</i> , 2015)
BTBPE	European Arctic <LD dissolved, <LD-0.002 pg/L particulate (Möller <i>et al.</i> , 2011b)	0.1–30.7 pg/m ³ (Covaci <i>et al.</i> , 2011) European Arctic <LD-0.06 pg/m ³ gaseous, <LD-0.02 pg/m ³ particulate (Möller, <i>et al.</i> , 2011b) Canadian Arctic 0.16–1.9 pg/m ³ (Xiao <i>et al.</i> , 2012) Svalbard 0.01–0.09 pg/m ³ (Salamova <i>et al.</i> , 2014) Greenland <2 pg/m ³ (Vorkamp <i>et al.</i> , 2015) 0.024–0.222 pg/m ³ (Yu <i>et al.</i> , 2015) 0.006–0.6 pg/m ³ (Lee <i>et al.</i> , 2016)
DBDPE		1–1916 pg/m ³ (Covaci <i>et al.</i> , 2011) Nordic environment <2.4–44 pg/m ³ (Schlabach <i>et al.</i> , 2011) 0.04–2.2 pg/m ³ (Salamova <i>et al.</i> , 2014)
BB-153		
HBBz	European Arctic <LD-0.003 pg/L dissolved, <LD-0.002 pg/L particulate (Möller <i>et al.</i> , 2011b)	European Arctic 0.04–0.66 pg/m ³ gaseous, 0.001–0.005 pg/m ³ particulate (Möller <i>et al.</i> , 2011b) Nordic environment <0.93–2.3 pg/m ³ (Schlabach <i>et al.</i> , 2011) Canadian Arctic mean 0.35 pg/m ³ (Xiao <i>et al.</i> , 2012) Svalbard 0.01–1.7 pg/m ³ (Salamova <i>et al.</i> , 2014) 0.003–0.104 pg/m ³ (Yu <i>et al.</i> , 2015) World oceans <LD-26 pg/m ³ gaseous and particulate (Katima <i>et al.</i> , 2017)

<LD: Below the limit of detection

Biota

Table 4 Concentrations of alternative brominated flame retardants in biota in coastal and offshore waters

	Coastal waters	Offshore waters
EH-TBB	Arctic biota 0.44–3.5 ng/g ww (Sagerup <i>et al.</i> , 2010) Mussel 0.0043–0.0049 ng/g lw (Schlabach <i>et al.</i> , 2011) Biota San Francisco <LD (Klosterhaus <i>et al.</i> , 2012) Porpoise < 0.61–3.44 ng/g ww (Law <i>et al.</i> , 2013) Greenland seabirds and mammals <0.064–1.46 ng/g ww (Vorkamp <i>et al.</i> , 2015) Polar bear <LD (Letcher <i>et al.</i> , 2017)	Cetaceans <LD–70 ng/g lw (Lam <i>et al.</i> , 2009) Fish <LD–0.12 ng/g (Schlabach <i>et al.</i> , 2011)
BEH-TEBP	Arctic biota <LD–1.8 ng/g ww (Sagerup <i>et al.</i> , 2010) Mussel 0.032–0.057 ng/g lw (Schlabach <i>et al.</i> , 2011) Biota San Francisco <LD (Klosterhaus <i>et al.</i> , 2012) Arctic biota <0.01–3.87 ng/g ww (Harju <i>et al.</i> , 2013) Porpoise <LD ng/g ww (Law <i>et al.</i> , 2013) Eel <LD–0.1 ng/g ww (Sühring <i>et al.</i> , 2013) Ringed seal <LD–0.34 ± 0.20 ng/g lw (Houde <i>et al.</i> , 2017) Greenland seabirds and mammals <0.025–0.40 ng/g ww (Vorkamp <i>et al.</i> , 2015) Polar bear <LD (Letcher <i>et al.</i> , 2017)	Cetaceans <LD–3860 ng/g lw (Lam <i>et al.</i> , 2009) Fish 0.002–0.2 ng/g lw (Schlabach <i>et al.</i> , 2011) Fish <LD–13 ng/g lw (Houde <i>et al.</i> , 2014)
TBBPA-DBPE	Arctic biota <LD (Sagerup <i>et al.</i> , 2010)	
DBHCTD	Porpoise <LD–2.66 ng/g ww (Law <i>et al.</i> , 2013) Polar Bear <LD (Letcher <i>et al.</i> , 2017)	Cetaceans <LD (Lam <i>et al.</i> , 2009)
PBEB	Gulls <LD (Verreault <i>et al.</i> , 2007) Gull eggs 0.03–0.23 ng/g ww (Verreault <i>et al.</i> , 2007) Arctic biota <LD (Sagerup <i>et al.</i> , 2010) Polar bear <0.05–1.7 ng/g lw (McKinney <i>et al.</i> , 2010) San Francisco biota <LD (Klosterhaus <i>et al.</i> , 2012) Harbor seal <0.08–0.5 ng/g lw (Klosterhaus <i>et al.</i> , 2012) Porpoise <0.34–35 ng/g ww (Law <i>et al.</i> , 2013) Eels <L –0.027 ng/g ww (Sühring <i>et al.</i> , 2013) Ringed seal 0.003–0.12 ng/g lw (Houde <i>et al.</i> , 2017) Polar bear <LD (Letcher <i>et al.</i> , 2017)	Fish <LD–0.00028 ng/g lw (Schlabach <i>et al.</i> , 2011) Fish <LD–2.21 ng/g lw (Houde <i>et al.</i> , 2014) Fish 0.9–2.9 ng/g lw (Poma <i>et al.</i> , 2014) Dolphin <LD (Baron <i>et al.</i> , 2015)
ΣTBECB	Mussel <LD–0.68 ng/g lw (Schlabach <i>et al.</i> , 2011) Porpoise <LD ng/g ww (Law <i>et al.</i> , 2013) Polar bear <LD (Letcher <i>et al.</i> , 2017)	Beluga (βTBECB) 1.1–9.3 ng/g lw (Tomy <i>et al.</i> , 2008)
PBT	Gulls < LD–0.15 ng/g ww (Verreault <i>et al.</i> , 2007) Gull eggs <LD–0.12 ng/g ww (Verreault <i>et al.</i> , 2007) Arctic biota <LD (Sagerup <i>et al.</i> , 2010) Mussel 0.002–0.0035 ng/g lw (Schlabach <i>et al.</i> , 2011) Porpoise <LD–1.8 ng/g ww (Law <i>et al.</i> , 2013) Eels Nd–0.19 ng/g ww (Sühring <i>et al.</i> , 2014) Polar bear <LD (Letcher <i>et al.</i> , 2017)	Fish 0.0017–0.021 ng/g lw (Schlabach <i>et al.</i> , 2011)

	Coastal waters	Offshore waters
TBP-AE	Seal 3.1–10 ng/g ww (von der Recke and Vetter 2007) Arctic biota <LD (Sagerup <i>et al.</i> , 2010) Mussel <0.0022–0.0045 ng/g lw (Schlabach <i>et al.</i> , 2011) Porpoise <LD ng/g ww (Law <i>et al.</i> , 2013) Eel <LD (Sührling <i>et al.</i> , 2014) Seabird eggs <LD (Huber <i>et al.</i> , 2015) Ringed seal <LD (Houde <i>et al.</i> , 2017) Polar bear <LD (Letcher <i>et al.</i> , 2017)	Fish < 0.002–<0.044 ng/g ww (Schlabach <i>et al.</i> , 2011)
BATE	Seals 1.9–8.0 ng/g ww (von der Recke and Vetter 2007) Mussel <LD (Schlabach <i>et al.</i> , 2011) Porpoise <LD ng/g ww (Law <i>et al.</i> , 2013) Seabird eggs <LD (Huber <i>et al.</i> , 2015) Ringed seals <LD (Houde <i>et al.</i> , 2017)	Fish <LD (Schlabach <i>et al.</i> , 2011)
TBP	Arctic biota <LD -0.9 ng/g ww (Sagerup <i>et al.</i> , 2010) Mussel 11-13 ng/g lw (Schlabach <i>et al.</i> , 2011) Arctic biota < 1.01 - 297 ng/g ww (Harju <i>et al.</i> , 2013)	Fish 0.58 – 86 ng/g lw (Schlabach <i>et al.</i> , 2011)
DBP	Mussel 0.75 - 0.97 ng/g lw (Schlabach <i>et al.</i> , 2011)	Fish <LD–6.4 ng/g lw (Schlabach <i>et al.</i> , 2011)
TBP-DBPE	Seals 130–470 ng/g ww (von der Recke and Vetter 2007) Arctic biota <LD (Sagerup <i>et al.</i> , 2010) Mussel 0.026–0.042 ng/g lw (Schlabach <i>et al.</i> , 2011) Porpoise <LD–<1.25 ng/g ww (Law <i>et al.</i> , 2013) Eels 0.026–0.22 ng/g ww (Sührling <i>et al.</i> , 2013) Eels <LD–2.0 ng/g ww (Sührling <i>et al.</i> , 2014) Greenland seabirds and mammals <0.013–0.096 ng/g lw (Vorkamp <i>et al.</i> , 2015) Seabird eggs <LD (Huber <i>et al.</i> , 2015) Ringed seals 0.02–0.2 ng/g lw (Houde <i>et al.</i> , 2017) Polar bear <LD (Letcher <i>et al.</i> , 2017)	Fish <0.003–<0.13 ng/g (Schlabach <i>et al.</i> , 2011)
BTBPE	Shellfish Iceland Norway 0.0085-0.033 ng/g ww (Schlabach <i>et al.</i> , 2011) Fish France <LD-1.4 pg/g ww (Munsch <i>et al.</i> , 2011) Shellfish Asia <0.1-13 ng/g lw (Isobe <i>et al.</i> , 2012) Shellfish US 0.21 ng/g dw (Dodder <i>et al.</i> , 2013) Greenland shark <0.16–8.1 ng/g lw (Strid <i>et al.</i> , 2013) Arctic biota <0.0005-1.125 ng/g ww (Vorkamp and Rigè, 2014) Seafood 0.014-518 ng/g lw (Cruz <i>et al.</i> , 2015) Seabird eggs < LD (Huber <i>et al.</i> , 2015) Shellfish France 0.7-37.3 pg/g ww (Munsch <i>et al.</i> , 2015) Ringed seal blubber Greenland <0.063-0.21 ng/g ww (Vorkamp <i>et al.</i> , 2015)	Nordic environment <0.0052-0.2 ng/g ww (Schlabach <i>et al.</i> , 2011)

	Coastal waters	Offshore waters
DBDPE	Fish <0.03–3.7 µg/kg lw (Covaci <i>et al.</i> , 2011) Fish France <LD–3.5 pg/g ww (Munschy <i>et al.</i> , 2011) Shellfish Iceland Norway 0.036–0.086 ng/g ww (Schlabach <i>et al.</i> , 2011) Shellfish Asia <0.3–22 ng/g lw (Isobe <i>et al.</i> , 2012) Arctic biota 0.19–38.7 ng/g ww (Harju <i>et al.</i> , 2013) Arctic biota <0.0016–0.58 ng/g ww (Vorkamp and Rigèt, 2014) Seafood 3.30–338 ng/g lw (Cruz <i>et al.</i> , 2015) Shellfish France <0.84–20.1 pg/g ww (Munschy <i>et al.</i> , 2015) Ringed seal blubber Greenland <0.12–0.30 ng/g ww (Vorkamp <i>et al.</i> , 2015)	Nordic environment <0.082–0.12 ng/g ww (Schlabach <i>et al.</i> , 2011)
BB-153	Fish Baltic and North Sea <0.90–179 pg/g ww (Gieron <i>et al.</i> , 2010) Fish France 0.1–4.5 pg/g ww (Munschy <i>et al.</i> , 2011) Seafood 0.041–14 ng/g ww (Cruz <i>et al.</i> , 2015) Shellfish France <0.05–81.8 pg/g ww (Munschy <i>et al.</i> , 2015)	
HBBz	Fish France <LD–5.1 pg/g ww (Munschy <i>et al.</i> , 2011) Shellfish Iceland Norway 0.0082–0.011 ng/g ww (Schlabach <i>et al.</i> , 2011) Arctic biota <0.0016–0.072 ng/g ww (Vorkamp and Rigèt, 2014) Whales 8–14 ng/g lw (Vorkamp and Rigèt, 2014) Seafood 0.118–2451 ng/g lw (Cruz <i>et al.</i> , 2015) Shellfish France 0.1–2.3 pg/g ww (Munschy <i>et al.</i> , 2015)	Nordic environment 0.0058–0.072 ng/g ww (Schlabach <i>et al.</i> , 2011)

<LD: Below the limit of detection

ww: Wet weight

lw: Lipid weight

Sediment

Table 5 Concentrations of alternative brominated flame retardants in sediments

	Sludge	Coastal waters
EH-TBB	<LD–2.6 ng/g dw (Schlabach <i>et al.</i> , 2011)	<LD (Schlabach <i>et al.</i> , 2011) <LD (Klosterhaus <i>et al.</i> , 2012) <LD–3.44 ng/g dw (Losada <i>et al.</i> , 2013)
BEH-TEBP	3.8–42 ng/g dw (Schlabach <i>et al.</i> , 2011)	<LD (Schlabach <i>et al.</i> , 2011) <LD (Klosterhaus <i>et al.</i> , 2012) <LD (Harju <i>et al.</i> , 2013) <LD (Losada <i>et al.</i> , 2013)
TBBPA-DBPE		
DBHCTD		<LD–3.33 ng/g dw (Losada <i>et al.</i> , 2013)
PBEB	<LD–0.11 ng/g dw (Schlabach <i>et al.</i> , 2011)	<LD–0.0075 ng/g dw (Schlabach <i>et al.</i> , 2011) <0.03–0.1 ng/g dw (Klosterhaus <i>et al.</i> , 2012) <0.34–13.2 ng/g dw (Losada <i>et al.</i> , 2013) 0.007 ng/g dw (Wu <i>et al.</i> , 2017a, b)
ΣTBECH	<LD–9.0 ng/g dw (Schlabach <i>et al.</i> , 2011)	<LD–0.17 ng/g dw (Schlabach <i>et al.</i> , 2011) <LD (Losada <i>et al.</i> , 2013)

	Sludge	Coastal waters
PBT	0.027–5.2 ng/g dw (Schlabach <i>et al.</i> , 2011)	<0.011–2.7 ng/g dw (Schlabach <i>et al.</i> , 2011) <LD–1.43 ng/g dw (Losada <i>et al.</i> , 2013) 0.002 ng/g dw (Wu <i>et al.</i> , 2017a, b)
TBP-AE	<LD–27 ng/g dw (Schlabach <i>et al.</i> , 2011)	<LD (Schlabach <i>et al.</i> , 2011) <LD (Losada <i>et al.</i> , 2013)
BATE	<LD–4.1 ng/g dw (Schlabach <i>et al.</i> , 2011)	<LD (Schlabach <i>et al.</i> , 2011) <LD (Losada <i>et al.</i> , 2013)
TBP	<LD–101 ng/ dw (Schlabach <i>et al.</i> , 2011)	0.21–1.5 ng/g dw (Schlabach <i>et al.</i> , 2011) 2.47 ng/g dw (Harju <i>et al.</i> , 2013)
DBP	<LD–40 ng/g dw (Schlabach <i>et al.</i> , 2011)	0.096–1.02 ng/g dw (Schlabach <i>et al.</i> , 2011)
TBP-DBPE	<LD–120 ng/g dw (Schlabach <i>et al.</i> , 2011)	<LD (Schlabach <i>et al.</i> , 2011) <LD–<1.25 ng/g dw (Losada <i>et al.</i> , 2013)
BTBPE	Nordic environment <0.075–3.9 ng/g ww (Schlabach <i>et al.</i> , 2011)	0.05–6.7 µg/kg dw (Covaci <i>et al.</i> , 2011) Nordic environment <0.0081–1.7 ng/g ww (Schlabach <i>et al.</i> , 2011)
DBDPE	Sweden 32 ng/g dw; 52 ng/g dw (Kierkegaard <i>et al.</i> , 2004) Nordic environment <0.25–160 ng/g ww (Schlabach <i>et al.</i> , 2011)	Western Scheldt 24 ng/g dw (Kierkegaard <i>et al.</i> , 2004) <LD–95 pg/g dw (Ricklund <i>et al.</i> , 2009) 24–364 µg/kg dw (Covaci <i>et al.</i> , 2011) Nordic environment <0.00001–2.4 ng/g ww (Schlabach <i>et al.</i> , 2011) Arctic sediment <LD–452.57 pg/g dw (Cai <i>et al.</i> , 2012) 0.24 ng/g dw (Harju <i>et al.</i> , 2013) Marine sediment China <0.176–1.57 ng/g dw (Zhu <i>et al.</i> , 2013)
BB-153		
HBB	Nordic environment <0.14–0.72 ng/g ww (Schlabach <i>et al.</i> , 2011)	Nordic environment <0.022–0.19 ng/g ww (Schlabach <i>et al.</i> , 2011) Marine sediment China <0.040 ng/g dw (Zhu <i>et al.</i> , 2013)

<LD: Below the limit of detection

dw: Dry weight

Toxicity

Table 6 Toxicity of alternative brominated flame retardants

	Genotoxic	Endocrine disruptor	Toxicity	ECOSAR LC ₅₀ ^a (mg/L) (Howard & Muir, 2010)	Carcinogenic potential ^b (Howard & Muir, 2010)
EH-TBB		Potential (Vorkamp and Rigét 2014)	DNA affected (Firemaster mix) (EFSA, 2012a)		
BEH-TEBP	Yes (Barr <i>et al.</i> , 2010)	Potential (Vorkamp and Rigét 2014)	Metabolite (TBMEHP) is toxic (Vorkamp and Rigét 2014) DNA affected (Firemaster mix) (EFSA 2012a)	5.08E-04	
TBBPA-DBPE		Potential endocrine disruptor (ECHA 2017)		4.10E-02	
DBHCTD					
PBEB		Potential endocrine disruptor (ECHA 2017)	Not mutagenic (EFSA 2012a)	1.51E-05	Low-moderate
TBECH	Potentially (Vorkamp and Rigét 2014)	Yes (Vorkamp and Rigét 2014) Potential (Pradhan <i>et al.</i> , 2015)	Yes (Vorkamp and Rigét 2014) Mutagenic (EFSA 2012a)	8.00E-03	Low-moderate
PBT			Not mutagenic (EFSA 2012a)		
TBP-AE		Potential (Pradhan <i>et al.</i> , 2015)	Teratogenic, potential neuronal disrupter (Pradhan <i>et al.</i> , 2015)	1.60E-02	Marginal
BATE		Potential (Pradhan <i>et al.</i> , 2015)	Teratogenic, potential neuronal disrupter (Pradhan <i>et al.</i> , 2015)		
TBP	No (EFSA 2012b)	Potential (EFSA 2012b)	Chromosomal aberrations (EFSA 2012b)	2.37E00	Low-moderate
DBP					
TBP-DBPE		Potential (Pradhan <i>et al.</i> , 2015)	Teratogenic, potential neuronal disrupter (Pradhan <i>et al.</i> , 2015)		
BTBPE		Yes for the degradation product 2,5,6-tribromophenol	PNEC water 0.53 µg/L PNEC sediment 1.55 mg/kg dw Echa.europa.eu website: Suspected hazardous to the aquatic environment: DEMETRA Daphnia Magna toxicity model in VEGA (Q)SAR platform predicts that the chemical has a 48h EC50 of 0.0255 mg/L (moderate reliability); Fish toxicity classification (SarPy/IRFMN) model in VEGA (Q)SAR platform predicts that the chemical is Toxic-2 (between 1 and 10 mg/L) (moderate reliability)		
DBDPE			PNEC water ≥0.2 µg/L PNEC sediment ≥ 127 mg/kg dw EC50 (<i>Daphnia magna</i>) invertebrate, 48 hrs: 19 µg/L Echa.europa.eu website: hazard assessment under evaluation		

	Genotoxic	Endocrine disruptor	Toxicity	ECOSAR LC ₅₀ ^a (mg/L) (Howard & Muir, 2010)	Carcinogenic potential ^b (Howard & Muir, 2010)
BB-153			On fish early life stage: yolk sac edema, pericardial edema, multifocal hemorrhages, reduced growth, and craniofacial malformation (Cruz <i>et al.</i> , 2015)		
HBB			<p>Aquatic toxicity: very toxic (<0.1 mg/L) PNEC water 0.53 µg/L PNEC sediment 1.55 mg/kg dw EC50 (<i>Tetrahymena pyriformis</i>), invertebrate, population growth rate, 24 hrs: 20 mg/L NOEC (<i>Nitocra spinipes</i>) invertebrate, larvae development, 6 days: 33.4 mg/L; mortality 6 days: 33.4 mg/L; LC50 (<i>Nitocra spinipes</i>) invertebrate, 96 hrs: >100 mg/L Echa.europa.eu website: may cause long lasting harmful effects to aquatic life; Suspected hazardous to the aquatic environment: Fish toxicity classification (SarPy/IRFMN) model in VEGA (Q)SAR platform predicts that the chemical is 'Toxic-1 (less than 1 mg/L) (moderate reliability)' # Suspected persistent in the environment: Ready biodegradability model (IRFMN) in VEGA (Q)SAR platform predicts that the chemical is NON Readily Biodegradable (EXPERIMENTAL value);The Danish QSAR database contains information indicating that the substance is predicted as non-readily biodegradable</p>		

^a: ECOSAR Lowest LC₅₀ values for all species obtained from predicted 96-hour EC50 in freshwater fish or in mysid shrimp. ECOSAR download available at <https://www.epa.gov/tsca-screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model>.

^b: OncoLogic carcinogenic potential estimate. OncoLogic download available at <https://www.epa.gov/tsca-screening-tools/oncologictm-computer-system-evaluate-carcinogenic-potential-chemicals>.

Additional information

Table 7 Names, CAS number, and commercial mixture for the compounds selected in this review (Covaci *et al.*, 2011; Bergman *et al.*, 2012; EFSA 2012a, b; Vorkamp and Rigét, 2014).

	Name	CAS	Commercial mix	Other names
EH-TBB	2-ethylhexyl 2,3,4,5-Tetrabromobenzoate	183658-27-7	Flammex 5BT Firemaster® 550 Firemaster® BZ-54	EHTBB, TBB
BEH-TEBP	Bis(2-ethylhexyl)-tetrabromophthalate	26040-51-7	DP 45 Pyronil 45 Uniplex FRP 45 Firemaster® 550 Firemaster® BZ-54	TBPH, TBDEHP
TBBPA-DBPE	Tetrabromobisphenol A bis(2,3-dibromopropyl) ether	21850-44-2	TBBPA-DBPE	TBBPA-BDBPE
DBHCTD	5,6-Dibromo-1,10,11,12,13,13-hexachloro - 11- Tricycle [8.2.1.02,9] tridecene	51936-55-1	Saytex BC 26 Citex BC 26	HCDBCO
PBEB	2,3,4,5,6-Pentabromoethylbenzene	85-22-3	EB 80 FR-105	
TBECH	4-(1,2-Dibromoethyl)-1,2-dibromocyclohexane	3322-93-8	Saytex BCL 462 Citex BCL 462	DBE-DBCH
PBT	2,3,4,5,6-Pentabromotoluene	87-83-2	Flammex 5BT FR-105	
TBP-AE	2,4,6-Tribromophenyl allyl ether	3278-89-5	PHE-65 Pyroguard FR 100 NSC 35767 Bromkal 64-3AE	ATE
BATE	2-Bromoallyl 2,4,6-Tribromophenyl ether			
TBP	2,4,6-Tribromophenol	118-79-6	Bromkal Pur 3 Bromol Flammex 3BP NSC 2136 PH 73 PH-73FF FR-613	
DBP	2,4-Dibromophenol	615-58-7	NSC 5723 NSC 6213	
TBP-DBPE	2,4,6-Tribromophenyl 2,3-dibromopropyl ether	35109-60-5	Bromkal 73-5PE	DPTE
BTBPE	1,2-bis(2,4,6-tribromophenoxy)ethane	37853-59-1	FF680 FI 680 FM 680 FireMaster 680 FireMaster FF 680	TBEHxBrPoxE

	Name	CAS	Commercial mix	Other names
DBDPE	Decabromodiphenyl ethane	84852-53-9	Saytex 8010 Firemaster 2100 DBDPE/RDT-3 Ecoflame B-971 Firemaster 2100R SAYTEX 4010 Flame Retardant SAYTEX 4010 ZD SAYTEX 402 Flame Retardant (no longer marketed) SAYTEX 8010 SAYTEX 8010 Flame Retardant SAYTEX 8010 ZD SLFR-2 YCFR-03	DBDE EBPE EBP DeBrPylE
BB-153	2,2',4,4',5,5'-hexabromobiphenyl	59080-40-9	Firemaster FF1	
HBBz	1,2,3,4,5,6-hexabromobenzene	87-82-1	AFR 1001 FR-B HBB-S NSC 113975 Perbromobenzene Plasafety HBB	HBB Hexabromobenzene HxBrBz

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Annex 4. Organophosphorous flame retardants (OPFRs)

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Substance (or substance group) description

Tri-substituted organophosphorus compounds (OPCs) are a group of chemicals extensively used as flame retardants, plasticizers and anti-foam agents in variety of household products such as textiles, furniture, plastics, and electronics (Hou *et al.*, 2016; Wei *et al.*, 2015). Organophosphorus flame retardants are generally based on three chemical structures: the organophosphate esters, the phosphonates, and the phosphinates. Some of these OPCs can be halogenated. Including halogen atoms increases the lifetime of the chemical in the product since it helps reduce the diffusion of OPCs in polymers. In general, organophosphorus flame retardants used as additives (i.e. mixed in the polymer as opposed to chemically bound) comprise the following groups: polyols, phosphonium derivatives, phosphonates, and phosphate esters (including trialkyl, triaryl, or aryl-alkyl derivatives). An extensive review of the physico-chemical properties, production, environmental occurrence, toxicity, and analysis of organophosphorus flame retardants can be found in van der Veen and de Boer (2012) or Wei *et al.*, (2015).

Physio-chemical properties (K_{ow} , etc)

The list of relevant OPCs includes 20–30 different chemicals (see Additional Information). The range of reported and predicted values for the physico-chemical properties of the different OPCs spans orders of magnitude. The solubility (at 25°C) of OPCs ranges from the g L^{-1} level to practically insoluble in water and is related to the molecular mass and the functional groups of the chemicals (van der Veen and de Boer, 2012). Compounds such as triethyl phosphate (TEP) and tri-*n*-butyl phosphate (TnBP) for example have a reported solubility in water of $5 \times 10^5 \text{ mg L}^{-1}$ and 280 mg L^{-1} , respectively, while organophosphate esters with longer side chains, such as trioctyl phosphate, have extremely low solubility in water ($6.47 \times 10^{-6} \text{ mg L}^{-1}$). The hydrophobicity of OPCs will also be dependent on their molecular structure. Increasing octanol-water partition coefficients ($\log K_{ow}$) are related to increasing length and branching of the OPCs, reaching a $\log K_{ow}$ as high as 10.6 for trioctyl phosphate. $\log K_{ow}$ values for chlorine-containing OPCs tend to be in the range of 3–6. As for solubility and hydrophobicity, Henry's law constants, vapour pressure (Brommer *et al.*, 2014), and boiling and melting points vary widely depending on the nature of the OPC. This means that the environmental distribution of the different OPCs can vary widely with some found preferentially in water, sorbed to soil and sediment or in the vapour phase in air. Persistence (P_{ov}) in air and water has been modelled from partition coefficients and environmental half-lives using the "OECD P_{ov} and LRTP Screening Tool" (Sühling *et al.*, 2016). The persistence in air ranged from 12 h (TnBP) to 13 800 h (TDCP). The corresponding values for water ranged from 288 h (TnBP) to 4704 h (TCPP). In general, the halogenated OPCs were found to be more persistent in water than the non-halogenated OPCs, as they were assumed to be less readily hydrolyzed.

Production and usage

OPCs generally have many different applications. Major applications include use as flame retardants or plasticizers with polymers such as polyurethane, polyvinyl chloride (PVC), epoxy, and phenolic resins. They are also used in textiles, as antistatic agents, in cellulose and cotton, cutting oils and in electronic equipment (van der Veen and de Boer, 2012). Non-halogenated OPCs can facilitate recycling printed circuit boards. The restrictions imposed on the production and use of the pentabrominated diphenyl ether flame retardant formulation in Europe in 2004 and decabromodiphenyl ether in 2008, may have contributed to the increase use in organophosphorus flame retardants. Furthermore, increasing demands for certain products (e.g. polyurethane foam) has also led to an increased use of flame retardants (EU, 2008a).

According to CEFIC (2007), organophosphorus compound consumption in Europe represented 20% of the total use of flame retardants in Europe in 2006, i.e. over 90 000 metric tonnes. In the USA, the production of the chlorinated OPCs tris(1,3-dichloropropyl) phosphate (TDCP), tris(2-chloro-1-methylethyl) phosphate (TCPP), and tris(2-chloroethyl) phosphate (TCEP) increased from less than 14 000 tonnes per year in the mid-1980s to about 38 000 in 2012 (Schreder *et al.*, 2016).

In most cases the halogenated OPCs are used for their flame retarding capacity while the non-halogenated chemicals are used as plasticizers. Examples of alkyl phosphates used as plasticisers or lubricants include tri-*n*-butyl phosphate (TnBP), tri-iso-butyl phosphate (TiBP), triphenyl phosphate (TPhP) or tris-(butoxyethyl)-phosphate (TBEP). In 2000, 20 000–30 000 tonnes of TPhP were produced or used in Europe (excluding Eastern Europe). In many cases, OPCs are used in mixtures with other flame retardants. OPCs used for hydraulic fluids application include TBP, TPhP, tris(methylphenyl) phosphate/tricresyl phosphate (TMPP), isopropylated triphenyl phosphate, or 2-ethylhexyl diphenyl phosphate (EHDPP). Compounds such as TEP, TPhP, or TCEP are often used as plasticizers in PVC.

Environmental concentrations

Water

A significant pathway for release of these chemicals into the aquatic environment is through wastewater treatment effluents. Reported concentrations for inlet waters (O'Brien *et al.*, 2015) for different wastewater treatment plants showed concentrations close to or above the $\mu\text{g L}^{-1}$ range for TBEP, TCPP, TiBP, TCEP, and TDCP. River water concentrations in the ng L^{-1} range have often been reported for some of the most widely used OPCs (e.g. Gorga *et al.*, 2015). Barceló *et al.*, (1990) reported concentrations of TiBP, TnBP, and TCEP in waters of estuaries of the West Mediterranean in the range 70–150 ng L^{-1} . The concentrations of TCPP, TCEP, TDCP, TEP, TiBP, or TBEP in waters from Dutch-German tributaries of the North Sea ranged from a few to a couple of hundred ng L^{-1} in August 2010 (Bollman *et al.*, 2012). The authors estimated a riverine input of approximately 50 tonnes per year. The sum of OPCs monitored in water of the German Bight in the same study was also in the ng L^{-1} range. Li *et al.*, (2017) reported sums of concentrations of nine OPCs in open seawater samples from the North Atlantic-Arctic generally not exceeding 5–6 ng L^{-1} . Concentrations generally decreased with increasing latitude. This gradient is the result of ongoing emissions of these chemicals around Europe. In a discussion of long-range transport, Sührling *et al.*, (2016) calculated characteristic travel distances in water of 22 km (tris(2-ethylhexyl)phosphate (TEHP) to 445 km (TDCP). The characteristic travel distance describes the distance a chemical can travel from its source region (Bennett *et al.*, 1998) and is typically used in assessments of long-range transport. The calculations for OPCs were based on partition coefficients and half-lives and as described for persistence above, using the “OECD P_{ov} and LRTP Screening Tool” (Sührling *et al.*, 2016). For the chlorinated OPCs, these exceeded the corresponding values for air; for the non-chlorinated OPCs the travel distances by air were greater. However, their water transport was limited by hydrolysis (in these model calculations), whereas new results indicate that hydrolysis of the organophosphate flame retardants mainly occurred at basic pH values (Su *et al.*, 2016).

Biota

Reported concentrations of the most widely used OPCs in mussel and cod liver from the Norwegian coast were mostly below limits of detection (Green *et al.*, 2008). The latest monitoring data confirms this, with most data found below limits of detection. Only TCPP was consistently detected in blue mussel samples (Green *et al.*, 2015). A wide range of biota is sampled in the inner Oslofjord on a yearly basis for the “urbanfjord” project (Ruus *et al.*, 2015). Despite sampling a relatively contaminated environment in this urbanized fjord, OPCs are most often below limits of detection for many biota samples. Concentrations of OPCs in gull egg and blood were consistently below limits of detection. Only TBEP was found consistently in individual cod liver samples. The remaining compounds (EHDPP, TEHP, TPP, DBPhP, TnBP, TDCP, TEP, TCEP, TPrP, TCPP, and TiBP) were almost always below limits of detection. The highest number of different OPCs was recorded for polychaete (these were depurated for 6–8 hours prior to preservation/analysis) and included TCPP, TPP, TDCP, TBEP, TMPP, TEHP, and EHDPP. TEP, TCPP, TPP, TBEP, and TEHP were all found in mussel samples; only TCEP and TEHP were found above limits of detection in prawn samples while TEP, TCEP, TCPP, TBEP, and TEHP were also measured in herring.

Two studies from the Norwegian Arctic including fish, seabirds, and mammals identified TCEP and EHDPP as the main OPCs (Evenset *et al.*, 2009; Hallanger *et al.*, 2015). Arctic fox liver was found to contain a high level of TBEP, with a median concentration of 955 ng g^{-1} lipid weight (Hallanger *et al.*, 2015). In general, the concentrations and detection frequencies were higher in fish than in high trophic level animals, in contrast to bio-magnification patterns of persistent organic pollutants. In a recent study on polar bear fat (Hudson Bay, Canada), OPCs were detected at sub-ppb levels in some of the samples. The highest detection frequency was that of TEHP, followed by TBEP, and TnBP (Letcher *et al.*, 2018). In contrast to these findings,

Brandsma *et al.*, (2015) noted indications of trophic magnification for TCPP, TCEP, and TBEP based on a foodweb study in the Western Scheldt estuary of the Netherlands. Tentative trophic magnification factors for these three compounds were 2.2, 2.6, and 3.5. OCPs were also detected in human samples, but Sundkvist *et al.*, (2010) concluded that the main exposure occurred from the indoor environment. This was based on analyses of fish in Swedish lakes and the Swedish coast. TCPP and TPhP were generally the main OPCs in fish, but concentrations and patterns varied, probably related to local sources. For example, fish collected downstream of a wastewater treatment plant contained higher levels of TBEP than samples from reference locations.

Sediment

Leonards *et al.*, (2011) measured concentrations of TPhP, tris(methylphenyl) phosphate / tricresyl phosphate (TMMP), TCPP, TCEP, and TDCP in the range <0.1–6.8, <0.05–288, <0.15–54, <0.16–8.5, and <0.09–1 ng g⁻¹ respectively in sediment samples from a fjord on the west coast of Norway and lake Mjøsa. TCCP was the most prominent OPC in sediments from Liverpool Bay and the Rivers Mersey and Tees (UK) with concentrations up to 180 ng g⁻¹ (van der Veen and de Boer, 2012). Concentrations of OPCs measured in sediments in the vicinity of a car demolishing and landfill sites were 1–3 orders of magnitude higher than those found in lake and marine sediments. In the Western Scheldt estuary, TBEP, TiBP, and TCPP were the main OPCs in sediment, with median concentrations of 7.0, 8.1, and 1.8 ng g⁻¹ respectively (Brandsma *et al.*, 2015).

Toxicity

The three chlorinated OPCs, TDCP, TCPP, and TCEP have been assessed by the European Union with regard to their environmental and health risks (EU, 2008a; 2008b; 2009). The overall conclusions include a need for risk reduction and for more information, mainly related to consumers and workers. TDCP and TCEP are classified as carcinogenic, and there is concern that TCPP is also carcinogenic (EU, 2014). The EU (2014) prohibits the use of these compounds in children's toys. Among the non-chlorinated OPCs, TnBP, and TPhP were described as neurotoxic, and TBEP was suspected to be carcinogenic (Reemtsma *et al.*, 2008). TnBP may be considered a non-genotoxic carcinogenic substance (ECHA, 2012) and has a harmonized classification according to CLP regulation as a suspected carcinogen (Carc. 2).

The evaluation of the literature on ecotoxicological data for a set of nineteen OPCs was conducted by NIVA on behalf of the Norwegian Environment Agency (Løken *et al.*, 2016). Several OPFRs have been reported as presenting high hazard with regards to human health effects and/or acute or chronic aquatic toxicity (e.g. TCEP, TCPP, TDCPP, TCP, CDPP, TPhP) (US EPA, 2015; Lassen *et al.*, 2016). For some of them, such data are currently not available. In terms of acute and chronic toxicity, TCEP has been shown to be toxic to zebrafish embryo with an EC₅₀ of 0.0018 mg L⁻¹ (Noyes *et al.*, 2015). The lowest effect recorded for mortality of zebrafish larvae exposed to tris(methylphenyl) phosphate/tricresyl phosphate (TMPP) was for an exposure concentration of 0.002 mg L⁻¹ (Noyes *et al.*, 2015). Trixylyl phosphate (TXP) has a harmonized classification according to CLP regulation as reprotoxic (Repr. 1B). The lowest effect level for mortality of zebrafish larvae is 0.003 mg L⁻¹ for isopropylated triphenyl phosphate (Noyes *et al.*, 2015). Some OPCs remain without existing acute or chronic toxicity data. That is the case for EHDPP or dibutylphenyl phosphate. Most OPCs are not expected to accumulate substantially in biota. TMPP, EHDPP, TXP, and isopropylated triphenyl phosphate may present a slighter higher bioaccumulation potential. The two substances identified to have the highest bioaccumulation potential were tris(*p*-tert-butylphenyl) phosphate (TBPP) and tris(2-ethylhexyl) phosphate (TEHP).

Additional information

Table 1 List of acronyms of organophosphorous flame retardants and their CAS number

Acronym	Substance	CAS no.
BCIPP	bis(1-chloro-2-propyl) phosphate	789440-10-4
BDCIPP	bis(1,3-dichloro-2-propyl) phosphate	72236-72-7
BDPP	butyl diphenyl phosphate	2752-95-6
CDPhP/CDPP (DCP)	cresyl diphenyl phosphate	26444-49-5
DBPhP	dibutylphenyl phosphate	2528-36-1
EHDPP	2-ethylhexyl diphenyl phosphate	1241-94-7
ip-DPHP	isopropyl diphenyl phosphate	60763-39-5
IPP	isopropylated triphenyl phosphate	68937-41-7
TBEP/TBOEP	tris(2-butoxyethyl) phosphate	78-51-3
TBP/TnBP/TNBP	tri- <i>n</i> -butylphosphate	126-73-8
TBP/TiBP	tri- <i>iso</i> -butylphosphate	126-71-6
TBPP	tris(<i>p</i> -tert-butylphenyl) phosphate	78-33-1
tb-DPHP	<i>t</i> -butyl diphenyl phosphate	56803-37-3
TCEP	tris(2-chloroethyl) phosphate	11596-8
TCPP/TCIPP	tris(2-chloro-1-methylethyl) phosphate	13674-84-5
TDCP/TDCPP/TDCIPP	tris(1,3-dichloro-2-propyl)phosphate	13674-87-8
TCP/TMPP/TCrP	tris(methylphenyl) phosphate / tricresyl phosphate	1330-78-5
TEHP	tris(2-ethylhexyl) phosphate	78-42-2
TEP	triethyl phosphate	78-40-0
	tri(<i>isopropyl phenyl</i>) phosphate	26967-76-0
TmCP	tris(<i>m</i> -methylphenyl) phosphate	1330-78-5
	trioctyl phosphate	1806-54-8
ToCP	tris(<i>o</i> -methylphenyl) phosphate	78-30-8
TpCP	tris(<i>p</i> -methylphenyl) phosphate	78-32-0
TPrP	Tripropyl phosphate	513-08-6
TPP/TPhP	triphenyl phosphate	115-86-6
TXP	trixyllyl phosphate	25155-23-1

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Annex 5. Per- and poly- fluoroalkyl substances (PFASs)

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Description

Per- and poly- fluoroalkyl substances (PFASs) have received global public attention because of their persistence, bioaccumulation potential, and possible adverse effects on wildlife and humans (Ahrens and Bundschuh, 2014; Giesy *et al.*, 2010; Martin *et al.*, 2003). The substance group of PFASs are characterized by their fully or partially fluorinated hydrophobic carbon chains of different lengths and a hydrophilic group consisting of, for example, sulfonate (PFSAs, $C_nF_{2n+1}SO_3^-$) or carboxylate (PFCAs, $C_nF_{2n+1}COO^-$) (Ahrens, 2011). “Long-chain” PFASs refers to PFSAs and PFCAs with a perfluorocarbon chain length of $n \geq 6$ and $n \geq 7$, respectively (including their precursor compounds) (Buck *et al.*, 2011). The fluorotelomer alcohols (FTOHs) form another large subgroup of PFASs. They are neutral precursors of the more stable PFCAs. Other potential precursors include perfluoroalkyl phosphates (PAPs), phosphonates (PFPA), and acrylates (PFACs) (Buck *et al.*, 2011). Furthermore, a number of alternative PFASs have been discussed lately, potentially replacing PFOA and PFOS (Wang *et al.*, 2013). Gomis *et al.*, (2015) provide a list of compounds i) replacing PFOA (ammonium 4,8-dioxa-3H-perfluorononanoate (ADONA), 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy) propanoic acid (HFPO-DA/GenX), perfluorotriethyl carboxylic acid (PFTECA), perfluoro((2-ethoxy-ethoxy)acetic acid) ammonium salt (EEA), and 6:2 fluorotelomer carboxylic acid (6:2 FTCA)), ii) replacing PFOS (F-53, F-53B, perfluorobutane sulfonamide with phosphoric acid (PFBSaPA)), and iii) replacing FTOH and other substances. Perfluorobutane sulfonamide (FBSA), possibly a precursor of PFBS, has been detected in the Arctic environment, as well as perfluoro-4-ethylcyclohexane sulfonate (PFECHS) (AMAP, 2017). Other emerging PFASs are introduced below.

Physio-chemical properties

PFASs have unique physico-chemical properties that vary depending on the chain length and functional group (Table 1) (Ahrens *et al.*, 2012; Du *et al.*, 2014; Rahman *et al.*, 2014; Rayne and Forest, 2009; Wang *et al.*, 2016). In general, the perfluorocarbon chain (“tail”) is hydrophobic and also lipophobic, whereas the functional group (e.g. sulfonate or carboxylate) is hydrophilic and is ionized at typical environmental pH. Furthermore, short-chain PFASs are predominantly hydrophilic and are generally more mobile in the environment whereas long-chain PFASs, which have a higher hydrophobicity, tend to bind more strongly to particles and have a higher bioaccumulation potential (Ahrens, 2011; Ahrens and Bundschuh, 2014). In organisms, ionic PFCAs and PFSAs primarily bind to proteins and phospholipids (Armitage *et al.*, 2013).

Table 1 Physio-chemical properties of selected PFASs, including their acronyms, molecular formulas, molecular weights (MW), water solubility (S_w), acid dissociation constant (pK_a) values, and octanol-water partition coefficient ($\log K_{ow}$)

Substances	Acronym	CAS No.	Molecular formula	MW (g mol ⁻¹)	S_w (mg L ⁻¹)	pK_a	$\log K_{ow}$ (L kg ⁻¹)
PFCAs							
Perfluorobutanoate	PFBA	375-22-4 / 2218-54-4	C ₃ F ₇ CO ₂	214	563 ^a	0.05 ^b 0.4 ^c	2.91 ^d 2.82 ^a
Perfluoropentanoate	PFPeA	2706-90-3	C ₄ F ₉ CO ₂	264	113000 ^a	-0.10 ^b	3.69 ^d 3.43 ^a
Perfluorohexanoate	PFHxA	307-24-4	C ₅ F ₁₁ CO ₂	314	15700 ^c 21700 ^a	-0.17 ^b -0.16 ^c	4.50 ^d 4.06 ^a
Perfluoroheptanoate	PFHpA	375-85-9	C ₆ F ₁₃ CO ₂	364	118.0 ^e 4180 ^a	-0.20 ^b	5.36 ^d 4.67 ^a
Perfluorooctanoate	PFOA	335-67-1	C ₇ F ₁₅ CO ₂	414	4340 ^e 3400 ^c	-0.21 ^{b,c}	6.26 ^d 5.30 ^a
Perfluorononanoate	PFNA	375-95-1	C ₈ F ₁₇ CO ₂	464	131 ^a	-0.21 ^b	7.23 ^d 5.92 ^a
Perfluorodecanoate	PFDA	335-76-2	C ₉ F ₁₉ CO ₂	514	260 ^e 25 ^a	-0.22 ^b	8.26 ^d 6.50 ^a

Substances	Acronym	CAS No.	Molecular formula	MW (g mol ⁻¹)	S _w (mg L ⁻¹)	pK _a	Log K _{ow} (L kg ⁻¹)
Perfluoroundecanoate	PFUnDA	2058-94-8	C ₁₀ F ₂₁ CO ₂	564	92.3 ^e 4.13 ^a	-0.22 ^b	2.32 ^e 7.15 ^a
Perfluorododecanoate	PFDoDA	307-55-1	C ₁₁ F ₂₃ CO ₂	614	0.71 ^a	-0.22 ^b	7.77 ^a
Perfluorotridecanoate	PFTriDA	72629-94-8	C ₁₂ F ₂₅ CO ₂	664	0.17 ^a	-0.22 ^b	8.25 ^a
Perfluorotetradecanoate	PFTeDA	376-06-7	C ₁₃ F ₂₇ CO ₂	714	0.027 ^a	-0.22 ^b	8.90 ^a
Perfluorohexadecanoate	PFHxDA	67905-19-5	C ₁₅ F ₃₁ CO ₂	814	n.a.	-0.22 ^b	n.a.
Perfluorooctadecanoate	PFOcDA	16517-116	C ₁₇ F ₃₅ CO ₂	914	n.a.	-0.22 ^a	n.a.
PFASs							
Perfluorobutane sulfonate	PFBS	375-73-5/ 59933-66-3/ 45187-15-3	C ₄ F ₉ SO ₃	300	510 ^e 46200 ^c	0.14 ^{b,c}	3.90 ^a
Perfluorohexane sulfonate	PFHxS	355-46-4/ 108427-53-8	C ₆ F ₁₃ SO ₃	400	1400 ^c	0.14 ^{b,c}	0.97 ^e 5.17 ^a
Perfluorooctane sulfonate	PFOS	1763-23-1/ 45298-90-6	C ₈ F ₁₇ SO ₃	500	570 ^{c,e}	0.14 ^b -3.27 ^c	4.67 ^d 7.66 ^a
Perfluorodecane sulfonate	PFDS	335-77-3/ 126105-34-8	C ₁₀ F ₂₁ SO ₃	600	n.a.	0.14 ^b	7.66 ^a
FOSAs							
Perfluorooctane sulphonamide	FOSA	754-91-6	C ₈ F ₁₇ SO ₂ NH ₂	499	1850000 ^a	6.56 ^b	2.56 ^e
Others							
Ammonium 4,8-dioxa-3H-perfluorononanoate	ADONA	958445-44-8	C ₇ H ₂ F ₁₂ O ₄	378	1540 ^f	0.51 ^f	4.97 ^f
2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid	HFPO-DA/ GenX	62037-80-3	C ₆ HF ₁₁ O ₃	330	7055 ^f	0.06 ^f	4.24 ^f
Perfluorotriethyl carboxylic acid	PFTECA	329238-24-6	C ₁₀ HF ₁₈ O ₅ Cl / C ₁₁ HF ₂₀ O ₅ Cl	578.5 / 628.5	13.6 ^f / 5.60 ^f	0.5 ^f / 0.35 ^f	6.60 ^f / 6.79 ^f
Perfluoro((2-ethoxyethoxy)acetic acid) ammonium salt	EEA	908020-52-0	C ₆ HF ₁₁ O ₄	346	1901 ^f	0.40 ^f	4.60 ^f
6:2 fluorotelomer carboxylic acid	6:2 FTCA	53826-12-3	C ₇ H ₃ F ₁₃ O ₂	366	430 ^f	2.82 ^f	3.94 ^f
1,1,2,2-tetrafluoro-2-(perfluorohexyloxy)ethane sulfonate	F-53	754925-54-7	C ₈ HF ₁₇ O ₃	468	16.6 ^f	0.14 ^f	6.97 ^f
2-(6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyloxy)-1,1,2,2-tetrafluoroethane sulfonate	F-53B	73606-19-6	C ₈ HClF ₁₆ O ₃	484.5	21.1 ^f	0.14 ^f	7.03 ^f
Perfluorobutane sulfonamide with phosphoric acid	PFBSaPA	120945-47-3	C ₁₄ H ₁₅ PF ₁₈ N ₂ S ₂ O ₇	760	1.52 ^f	0.12 ^f	5.44 ^f

Not available (n.a.). ^aWang *et al.*, 2011. ^bAhrens *et al.*, 2012. ^cDu *et al.*, 2014. ^dRayne and Forest, 2009. ^eRahman *et al.*, 2014. ^fGomis *et al.*, 2015

Production and usage

Based on the production volume, historic emissions are estimated to be 2610–21 400 tonnes of C₄–C₁₄ PFCAs in the period from 1951 to 2015 (Wang *et al.*, 2014). The global historic emissions for perfluorooctylsulfonyl fluoride (POSF) are estimated as 6800–45 300 tonnes (1972–2002), while the majority of the emissions were estimated to have been released to the aqueous environment (~45 000 tonnes) (Paul *et al.*, 2009). However, a more recent study estimated the global historic emissions for perfluorooctanesulfonic acid (PFOS) as 1228–4930 tonnes, and emissions of PFOS precursors as 1230–8738 tonnes (1958–2015) (Wang *et al.*, 2017). Overall, there is a high uncertainty of the production volume and emission data for PFASs.

Environmental concentrations

Water

Main point sources for PFASs and their precursors in the aquatic environment are industrial or municipal wastewater treatment plants (WWTPs), PFAS production facilities, landfill leachate, and fire training areas, while the main non-point sources are dry or wet atmospheric deposition, and soil or street surface runoff (Ahrens, 2011). In general, PFAS concentrations were highest from point sources and ranged between tens and thousands ng/L for individual PFASs (Ahrens *et al.*, 2015; Busch *et al.*, 2010; Zareitalabad *et al.*, 2013). In river surface water, PFAS concentrations ranged from a few to hundreds of ng/L for individual PFASs (McLachlan *et al.*, 2007; Nguyen *et al.*, 2017). In coastal seawater, PFAS concentrations were about one order of magnitude lower, ranging from hundreds of pg/L to tens of ng/L, whereas PFAS concentrations in open surface seawater were in a range of tens of pg/L to a few ng/L for individual PFASs (Ahrens, 2011; Yamashita *et al.*, 2008). PFECHS is used as an abrasion inhibitor for hydraulic fluids and was measured downstream from an international airport, at concentrations up to 23 ng/L (de Solla *et al.*, 2012). A study from China showed a decreasing gradient in river water with distance from Beijing airport (Wang *et al.*, 2016). This study identified several isomers of PFECHS as well as perfluoropropylcyclopentanesulfonate (PFPCPeS) and F-53B in water. PFECHS has also been detected in a high Arctic lake, at a concentration of 4.3 ng/L, probably also related to an airport-related emission source (Lescord *et al.*, 2015). Additionally, fluorotelomer sulfonates (FTS) were detected in Arctic lake water in the same study. HFPO-DA was consistently found in water samples from the river Rhine and the North Sea coastline (Heydebreck *et al.*, 2015).

Biota

PFASs have a high binding affinity to serum albumin, which results in a tissue-dependent distribution in biota (Ahrens *et al.*, 2009a). PFAS were detected globally in biota even in remote regions such as the Arctic and Antarctica (Giesy & Kannan, 2001). PFAS concentrations for individual PFASs in freshwater biota ranged between few ng/g wet weight to hundreds of ng/g wet weight in invertebrates and fish (Ahrens and Bundschuh, 2014). Highest individual PFAS concentrations were detected in top predators in the aquatic foodweb (e.g. polar bears) ranging from hundreds to thousands of ng/g wet weight (Ahrens and Bundschuh, 2014). The studies mentioned above also detected PFECHS in invertebrates and fish (de Solla *et al.*, 2012; Lescord *et al.*, 2015). In the airport-related study from China, logarithmic bioaccumulation factors (BAF) of 4.5, 2.7, and 1.9 were found for F-53B, PFECHS, and PFPCPeS, respectively, in Crucian carp (Wang *et al.*, 2016). The logBAF of F-53B was comparable to that of PFOS. F-53B and PFBS were found in marine mammals from Greenland, but their concentrations were about four orders of magnitude lower than that of PFOS (Gebbink *et al.*, 2016). PAPs were sought for, but not detected in ringed seal liver (Gebbink *et al.*, 2016).

Sediment

The sorption of PFASs to particle and sedimentation depends on the perfluorocarbon chain length and functional group with highest partitioning to sediment for long-chained PFASs and PFSAs (Ahrens *et al.*, 2010; Higgins and Luthy, 2006). Individual PFAS concentrations ranged from a few to hundreds of ng/g wet weight in freshwater systems (Zareitalabad *et al.*, 2013), and hundreds of pg/g wet weight to a few ng/g wet weight in coastal sediment (Ahrens *et al.*, 2009b; Benskin *et al.*, 2012); however there is a lack of data for PFASs in the open marine sediment. PFECHS isomers and PFPCPeS were detected in river sediment (matching water samples described above) downstream from Beijing airport at concentrations up to 2 ng/g dry weight (Wang *et al.*, 2016). Their detection frequency was relatively low compared with other long-chain PFASs. The concentrations decreased with increasing distance from the airport.

Toxicity

PFASs are extremely persistent, particularly PFCAs and PFSAs, which are not biodegradable (Parsons *et al.*, 2008; Frömel and Knepper, 2010). They also have a high bioaccumulation potential and caused acute and chronic effects at individual, population, and community level (Ahrens and Bundschuh, 2014; Giesy *et al.*, 2010). Exposure to PFASs has been associated with a lower birth weight, infertility, and lower than average sperm counts in young men (Rahman *et al.*, 2014). Furthermore, PFAS effects

have been shown on multiple generations and species interactions and can affect the ecosystem structure and function in the aquatic environment (Ahrens and Bundschuh, 2014; Giesy *et al.*, 2010). However, little is known about the toxicity of PFAS mixtures or about interactions with other natural and anthropogenic stressors (Ahrens and Bundschuh, 2014). Very little information is available on specific “emerging” PFASs. For PFECs, endocrine disruption potential was shown in *Daphnia magna* (Houde *et al.*, 2016). However, the effect concentrations were above common environmental levels.

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Annex 6. Corrosion protection systems in offshore wind farms

Part I: Organic coatings

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Description

Epoxy resins and polyurethane based coatings are a commonly used corrosion protection technique in a wide range of marine applications (harbour, shipping, offshore industry). The number of offshore wind farms will increase significantly in the next years (especially in the North Sea region). Due to the high number of wind turbines and platforms for offshore wind production, this is an increasing sea-based source for chemical substances (Tornero and Hanke, 2017).

Leachable substances from coatings were investigated for fresh water applications only. Several compounds were identified: Leaching from epoxy resins by Vermeirissen *et al.*, (2017): bisphenols (BPA, BPF) and BADGE, BADGE H₂O, BADGE 2H₂O. In addition epoxy resins may contain alkyl phenols and other bisphenols. Leaching from polyurethane was investigated by Luft *et al.*, (2017): derivatives of N-(tosyl)carbamate, p-toluenesulfonamide, 4,4'-methylenediphenyl diisocyanate, toluenediisocyanate, and p-toluenesulfonic acid. No data are available to know if these substances are relevant for the marine environment.

Chemical corrosion inhibitors and anti-fouling agents are not applied in (German) offshore wind farms, but organic coatings that are used may be a potential new source for already known substances or new (unknown) substances. These coatings are used in a wide range of applications (offshore industry, harbours, shipping), so offshore winds farms are only an additional source to the marine environment and it will likely be difficult to differentiate the individual sources. Data on leaching behaviour and on impact in the marine environment is unknown for most of these compounds, as a consequence, research in this field is needed.

Physio-chemical properties (K_{ow}, etc)

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Production and usage

Epoxy resins and polyurethane coatings are frequently used techniques for corrosion protection in a wide range of applications. Annual epoxy usage for marine coatings in Europe: 51 000 tonnes (all types of marine coatings; Epoxy Resin Committee, 2017).

Environmental concentrations

Water

Data from offshore wind farms are not available. Research needed.

Biota

Data from offshore wind farms are not available. Research needed.

Sediment

Data from offshore wind farms are not available. Research needed.

Toxicity

Toxicity information is available for the already listed substances (e.g. BPA or alkyl phenols)

Additional information

Bisphenol A (BPA): listed on the OSPAR List of substances of possible concern Section B

Alkylphenols (nonylphenol, octylphenol): listed on the OSPAR List of substances of possible concern Section A/B

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Annex 6. Corrosion protection systems in offshore wind farms

Part II: Galvanic anodes

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Description

Galvanic cathodic protection systems are a commonly used corrosion protection technique in a wide range of marine applications (harbour, shipping, offshore industry). Also offshore wind farms are using this technology and the number of offshore wind farms will increase significantly in the future years (especially in the North Sea region).

These structures will be protected by galvanic sacrificial aluminium-based anodes that use tonnes of anode material. Typically, a monopole will use 1.3 tonnes of anode material over a 25-year life span. Depending on the specific alloy and the manufacturer, aluminium anodes also contain Zinc (2.5–5.75%), Indium (0.015–0.04%) and impurities such as cadmium, manganese, iron, silicon, copper, and other trace metals. These anodes will dissolve over their lifetime and the metals will enter the marine environment. The fate of the metals leached from these anodes and their speciation has only been partially investigated in harbour environments or laboratory experiments. These experiments demonstrated enrichment of aluminium on suspended matter and sediments near to the anodes (Deborde *et al.*, 2015; Gabelle *et al.*, 2012). Water concentrations did not increase, due to the dilution effects. Data from offshore wind farms is missing and thus spatial and temporal effects are unknown. Research is necessary for the better understanding of the impact of this new source on the marine environment, especially the effects of Indium.

Physio-chemical properties (K_{ow} , etc)

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Production and usage

-

Environmental concentrations

Water

Data from offshore wind farms are not available. Research needed.

Biota

Data from offshore wind farms are not available. Research needed.

Sediment

Data from offshore wind farms are not available. Research needed.

Toxicity

Toxicity of galvanic anodes was partially investigated in the publications listed below in Sources and references.

Additional information

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