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New priority substances of the European Water Framework Directive: Biocides, pesticides and brominated flame retardants in the aquatic environment of Denmark

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HIGHLIGHTS

- Cybutryn, terbutryn, heptachlor epoxide and HBCD were frequently detected.
- Cybutryn, heptachlor epoxide and HBCD exceeded AA-EQS values.
- Despite sensitive instrumentation, some detection limits were above AA-EQS values.
- Storm- and wastewater seem to be sources of cybutryn, terbutryn and HBCD.
- Non-detects of aclonifen, bifenox and cypermethrin might reflect off-season sampling.

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ABSTRACT

The biocides cybutryn (Irgarol) and terbutryn, the herbicides aclonifen and bifenox, the insecticides cypermethrin and heptachlor/heptachlor epoxide and the brominated flame retardant hexabromocyclododecane (HBCD) are new priority substances of the Water Framework Directive of the European Union. In order to gain knowledge about their presence in the aquatic environment in an off-season situation with regard to pesticide and biocide applications, these substances were analysed in freshwater, seawater and fish samples from Denmark. Aclonifen, bifenox, cypermethrin and heptachlor were below the limits of detection (LODs) in all samples. However, the LODs for cypermethrin and heptachlor exceeded the annual average environmental quality standards (AA-EQSs). Cybutryn, terbutryn, heptachlor epoxide and HBCD were detected in the majority of samples, with detection frequencies of 100% for heptachlor epoxide and HBCD in water and 90% in fish. No concentration was above maximum allowable concentration (MAC)-EQS values, but AA-EQS values were exceeded for all four compounds by several samples, including 100% of the water samples with regard to heptachlor epoxide. Methodological issues remain for cypermethrin, and to a certain extent for heptachlor/heptachlor epoxide, for which water LODs were above AA-EQSs although a water volume of 12 L was combined with very sensitive high resolution mass spectrometry.

1. Introduction

The Water Framework Directive (WFD) of the European Commission (EC 2000/60/EC) describes the monitoring of priority substances and other pollutants in the surface waters of the European Union. It covers freshwater and coastal waters, which is of great relevance for Denmark, with a coastline of over 7000 km. The daughter directive 2008/105/EF of the European Parliament and the Council of the European Union has defined environmental quality standards (EQSs) for priority substances in water, with the aim to protect the aquatic environment from adverse effects of these substances. For some compounds, EQS values have been derived for biota to protect against indirect effects and secondary poisoning. Amongst the priority substances, specific compounds have been classified as priority hazardous substances, with the aim to cease or phase out their discharges, emissions and losses.

The list of priority substances was recently revised (Directive 2013/39/EU). New priority substances were added by the European Commission, amongst these are the biocides cybutryn (Irgarol) and terbutryn, the pesticides aclonifen, bifenox, cypermethrin and heptachlor/heptachlor epoxide and the brominated flame retardant hexabromocyclododecane (HBCD). HBCD and heptachlor/heptachlor epoxide have been characterised as priority hazardous substances, with EQS values for fish of 167 and 0.0067 μg kg^{-1} wet weight, respectively (Table 1), the latter referring to the sum of heptachlor and heptachlor epoxide (EU Working Group E, 2011a). For all compounds, EQS values have been set for water, i.e. EQS values for annual averages (AA-EQS) and maximum allowable

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Table 1
Summary of environmental quality standards (EQSs) for annual averages (AA-EQSs) and maximum allowable concentrations (MAC-EQSs), numbers of samples, detection frequencies, frequencies of AA-EQS exceedance, limits of detection (LODs), minimum and maximum concentrations. ww: wet weight. n.a.: not available (because of LOD > AA-EQS).

Compound	No. of samples	Detection frequency	AA-EQS or biota EQS	MAC-EQS	Exceedance of AA-EQS	LOD	Minimum concentration	Maximum concentration
Aclonifen								
Freshwater	16[a]	0%	120 ng L^{-1}	120 ng L^{-1}	0%	0.1 ng L^{-1}	<LOD	<LOD
Seawater	14	0%	12 ng L^{-1}	12 ng L^{-1}	0%	0.1 ng L^{-1}	<LOD	<LOD
Bifenox								
Freshwater	16[a]	0%	12 ng L^{-1}	40 ng L^{-1}	0%	1.0 ng L^{-1}	<LOD	<LOD
Seawater	14	0%	1.2 ng L^{-1}	4 ng L^{-1}	0%	1.0 ng L^{-1}	<LOD	<LOD
Cypermethrin								
Freshwater	14	0%	0.08 ng L^{-1}	0.6 ng L^{-1}	n.a.	0.42 ng L^{-1}	<LOD	<LOD
Seawater	3	0%	0.008 ng L^{-1}	0.06 ng L^{-1}	n.a.	0.42 ng L^{-1}	<LOD	<LOD
Cybutryn								
Freshwater	16[a]	44%	2.5 ng L^{-1}	16 ng L^{-1}	0%	0.004 ng L^{-1}	<LOD	0.85 ng L^{-1}
Seawater	14	86%	2.5 ng L^{-1}	16 ng L^{-1}	21%	0.004 ng L^{-1}	<LOD	13 ng L^{-1}
Terbutryn								
Freshwater	16[a]	88%	65 ng L^{-1}	340 ng L^{-1}	0%	0.004 ng L^{-1}	<LOD	14 ng L^{-1}
Seawater	14	93%	6.5 ng L^{-1}	34 ng L^{-1}	0%	0.004 ng L^{-1}	<LOD	2.2 ng L^{-1}
Heptachlor								
Freshwater	14	0%	0.2 pg L^{-1}[b]	300 pg L^{-1}[b]	n.a.	0.85 pg L^{-1}	<LOD	<LOD
Seawater	3	0%	0.01 pg L^{-1}[b]	30 pg L^{-1}[b]	n.a.	0.85 pg L^{-1}	<LOD	<LOD
Fish	10[c,d]	0%	6.7 pg g^{-1} ww[b]	–	0%	0.7 pg g^{-1} ww	<LOD	<LOD
Heptachlor epoxide								
Freshwater	14	100%	0.2 pg L^{-1}[b]	300 pg L^{-1}[b]	100%	2 pg L^{-1}	3.4 pg L^{-1}	7.5 pg L^{-1}
Seawater	3	100%	0.01 pg L^{-1}[b]	30 pg L^{-1}[b]	100%	2 pg L^{-1}	6.4 pg L^{-1}	7.5 pg L^{-1}
Fish	10[c,d]	90%	6.7 pg g^{-1} ww[b]	–	70%	1.6 pg g^{-1} ww	<LOD	23 pg g^{-1} ww
HBCD[e]								
Freshwater	5	100%	1.6 ng L^{-1}	500 ng L^{-1}	40%	0.004 ng L^{-1}[f]	0.096 ng L^{-1}	2.9 ng L^{-1}
Seawater	5	100%	0.8 ng L^{-1}	50 ng L^{-1}	0%	0.004 ng L^{-1}[f]	0.052 ng L^{-1}[g]	0.40 ng L^{-1}
Fish	11[d,h]	90%	167 ng g^{-1} ww	–	0%	0.004–0.005 ng g^{-1} ww[f]	<LOD	0.056 ng g^{-1} ww[i]

[a] Including four 24-hour-samples.
[b] The EQS values are valid for the sum of heptachlor and heptachlor epoxide (EU Working Group E, 2011a).
[c] Five samples of perch, 2 samples of flounder, 1 sample each of roach, eelpout and cod.
[d] Pooled samples of 5 individuals, with the exception of cod (2 individuals).
[e] Sum of α-, β- and γ-HBCD.
[f] Individual HBCD isomers.
[g] 1/2 LOD used for α- and β-HBCD because of concentrations < LOD.
[h] Seven samples of perch, 1 sample each of flounder, roach, eelpout and cod.
[i] 1/2 LOD used for β-HBCD because of concentrations < LOD.

concentrations (MAC-EQS) (Table 1). The chemical structures of the compounds included in this study are given as Supplementary data.

Cybutryn and terbutryn are s-triazine compounds primarily used as algaecides/biocides in buildings. Cybutryn has also been used as an antifouling agent on ships, replacing the phased out tributyltin (TBT), and has been detected in marinas of the German coast at μg L^{-1} levels (Biselli et al., 2000). Denmark has numerous small marinas, thus presenting a potential source of cybutryn. Recent studies have also shown the leaching of these biocides from buildings as a significant source to the environment (Burkhardt et al., 2011, 2012; Wangler et al., 2012). Terbutryn might also be emitted to surface waters from wastewater treatment plants (Quednow and Püttmann, 2007).

Aclonifen, bifenox and cypermethrin are current-use pesticides. Aclonifen and bifenox are chlorinated diphenyl ethers used as herbicides, while cypermethrin is a pyrethroid used as an insecticide. The use of bifenox had been decreasing in Denmark and was prohibited in July 2013 (Danish Ministry of the Environment, 2012). Cypermethrin was previously detected in freshwater sediments from Denmark (Bossi et al., 2009), but its sale in Denmark has also been decreasing (Danish EPA, 2012). Heptachlor is a chlorinated insecticide which is mainly degraded to heptachlor epoxide in the environment. Heptachlor epoxide is resistant to biodegradation and is therefore persistent in the environment (INCHEM, 1984). Production and use of heptachlor are regulated globally through the Stockholm Convention on Persistent Organic Pollutants. The use of heptachlor ceased in Denmark in 1972.

HBCD is a brominated flame retardant mainly used in polystyrene material. The technical product consists of several isomers, the most abundant ones being α-, β- and γ-HBCD. While γ-HBCD dominates the technical product, α-HBCD accumulates in the food chain (Covaci et al., 2006). HBCD has been detected in marine and freshwater fish from Europe (e.g. Janák et al., 2005), but only little information is available on HBCD occurrence in surface water (Harrad et al., 2009). Given scientific evidence of bioaccumulation and long-range transport (Vorkamp et al., 2011, 2012), HBCD is an official candidate for the Stockholm Convention.

As very little a priori information was available on the presence of these priority substances in the European aquatic environment, the objective of this study was to obtain initial data from Denmark, focusing on off-season samples, i.e. collected outside typical pesticide and biocide usage seasons, and suitable approaches for monitoring and compliance checking against their EQS values.

2. Materials and methods

2.1. Sampling strategy

As the EQS values refer to surface water, all compounds were analysed in water samples, with varying numbers of freshwater and marine samples, the latter mainly representing harbours and fjords. In addition, heptachlor/heptachlor epoxide and HBCD were analysed in