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Halogenated and organophosphorus flame retardants in European aquaculture samples

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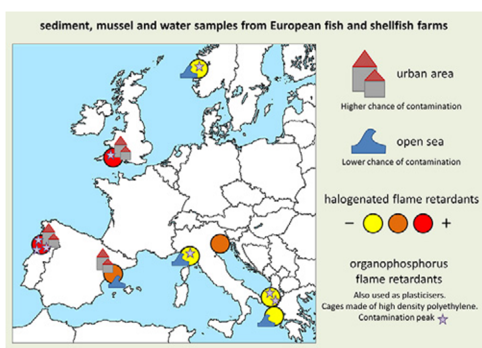
HIGHLIGHTS

- Flame retardants in European fish and shellfish farms: water, sediment, mussels.
- PBDEs were in 95% of the sediments (8.6 ± 23 ng g^{-1} dw) and mussels (<10 ng g^{-1} lw).
- DBDPE was at levels lower than BDE-209 in sediment and similar levels in mussels.
- OPFRs levels were much higher; they are plasticisers and plastics are used in farms.
- Farms away from urban shores and river mouths minimize flame retardants input.

GRAPHICAL ABSTRACT



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ABSTRACT

This work monitors flame retardants in sediment, mussel and water samples from European fish farms. Polybrominated diphenyl ethers (PBDEs) were detected in 95% of the sediment and mussel samples with mean levels of 8.60 ± 22.6 ng g^{-1} dw in sediments and 0.07 ± 0.18 ng g^{-1} dw in mussels. BDE-209 was the main contributor for the sediments and BDE-47 was found in about 60% of the samples of both matrices. Pentabromoethylbenzene (PBEB) and hexabromobenzene (HBB) were detected in 42% of the sediments, but not in mussels. Decabromodiphenyl ethane (DBDPE) was found in about 55% of the samples of both matrices. The same happened for dechloranes in mussels, but they were detected in 92% of the sediments. *Syn*-DP and anti-DP were always the main contributors. Methoxylated PBDEs (MeO-PBDEs) were detected in all mussels and some sediments, mainly 6-MeO-BDE-47 and 2′-MeO-BDE-68. Organophosphorus flame retardants (OPFRs) were found in all matrices with concentrations of 0.04–92.8 ng g^{-1} dw in sediment, 0.50–102 ng g^{-1} dw in mussel and 0.43–867 ng l^{-1} in water. Only OPFRs were analysed in water samples as halogenated flame

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Seafood
Persistent organic pollutants

retardants and MeO-PBDEs are highly unlikely to be detected in water due to their physicochemical properties. Flame retardants have no application in fish farming so results should reflect the impact of human activity on the farm locations. A large majority of the most contaminated samples were collected from sampling spots that were at urban shores or in enclosed water bodies not completely open to the sea.

1. Introduction

Environmental contaminants in seafood are a hot topic for the scientific community and different research projects study seafood contamination or the presence of these compounds in the water surrounding aquaculture systems. This work monitors flame retardants (FRs) in samples from European fish and shellfish farms.

FRs are compounds that applied to plastics, electronic devices, furniture, vehicles, etc. increase the fire resistance of these materials (Alaee et al., 2003). The most used FRs are polybrominated diphenyl ethers (PBDEs). Typically, PBDEs are produced at three levels of bromination, including Penta-BDE, Octa-BDE and Deca-BDE, and are classified according to their average bromine content. Because these compounds are simply blended into polymers instead of covalently bonded, they are constantly released from materials (Alaee et al., 2003). Thus, PBDEs have been found in all kind of environmental matrices like sediment, sludge and water (Gorga et al., 2013; Guerra et al., 2010; Sánchez-Avila et al., 2011), and in biological matrices like seafood (Aznar-Alemany et al., 2017; Lacorte et al., 2010).

PBDEs are considered persistent organic pollutants (POPs) by the Stockholm Convention on Persistent Organic Pollutants (Convention, 2008). Criteria for POPs are for compounds to persist in the environment, to accumulate in food chains, to have potential for long-range transportation and to have toxic effects on the environment and humans. PBDEs can affect hormonal regulation and thyroid, liver and neuronal activity (Branchi et al., 2003; Costa and Giordano, 2011; Mikula and Svobodova, 2006). For these reasons, before the inclusion of Penta-BDE and Octa-BDE in the Stockholm Convention in 2011, their sale was already banned in the European Union (EU) in 2004 under Directive, 2003/11/EC (in concentrations higher than 0.1% by mass) (Directive, 2003). Deca-BDE is currently in the Stockholm Convention as well since summer 2017 and it has been banned in the EU since 2008 by the European Court of Justice, case C-14/06 (Judgment, 2008). On the other hand, in 2010 Deca-BDE was also added to the REACH regulation (Registration, Evaluation, Authorisation and Restriction of Chemicals) (REACH, 2006), which provides a legislative framework for chemicals manufacture and use in Europe. Additionally, the EU Marine Strategy Framework Directive (MSFD) (Directive 2008/56/CE) establishes requirements to achieve a good environmental status of the marine environment by 2020 (MSFD, 2008). One of the MSFD eleven descriptors focuses on meeting the existing regulations on contaminants in seafood. The MSFD also highlights some compounds with no regulated limits that should be monitored, including PBDEs (the 8 congeners in this study), and monitoring decabromodiphenyl ethane (DBDPE) and hexabromobenzene (HBB) is recommended too (Swartenbroux et al., 2010).

DBDPE and HBB, along with pentabromoethylbenzene (PBEB), are emerging flame retardants (EFRs) now used as alternatives to PBDEs. Since their production increased for three decades, they have been included in monitoring programs (Covaci et al., 2011). To meet the REACH regulation requirements, these substitutes should be safer for the environment and human health than PBDEs.

Dechloranes—including Dechlorane Plus (DP) and Dec 602, Dec 603 and Dec 604—are also EFRs (Zhu et al., 2014). Their behaviour and occurrence in the environment have become a topic of interest in the last decade. They have been found in several environmental matrices, including, but not limited to, sediment, sludge, water and seafood (Aznar-Alemany et al., 2017; Hong et al., 2010; Houde et al., 2014; Sverko et al., 2007; Torre et al., 2010).

Apart from halogenated flame retardants (HFRs), there are also organophosphorus flame retardants (OPFRs). They accounted for 20% of the FR use in 2006 in Europe — twice as much as brominated FRs — and have been increasingly applied after the ban on PBDEs (Van der Veen and de Boer, 2012). However, inorganic FRs were preferred, accounting for the remaining 70%. Like PBDEs, OPFRs leak from materials and can access environmental matrices through deposition, washout, infiltration, etc. (Andresen et al., 2004; Schreder and La Guardia, 2014). Additionally, OPFRs are used as plasticisers; hence they can be released from the tones of plastic present in seas and oceans. OPFRs have been found in sediments, fish and water (Chung and Ding, 2009; Gao et al., 2014; Giulivo et al., 2016). OPFRs can have toxic reproductive, systemic and endocrine and carcinogenic effects (Hou et al., 2016; Van der Veen and de Boer, 2012).

On top of anthropogenic compounds, methoxylated PBDEs (MeO-PBDEs) are produced by red algae or sponges and, therefore, occur naturally in the marine environment (Vetter et al., 2002). As the organisms that produce MeO-PBDEs live in the sea, these compounds cause concern only in sea waters. Their concentrations are similar to PBDEs' or even higher at further points away from the shore (Vetter et al., 2002). They have been found in cetaceans or seafood (Alonso et al., 2014; Aznar-Alemany et al., 2017; Losada et al., 2009) around the world.

This work studied the occurrence of PBDEs, HBB, DBDPE, PBEB, MeO-PBDEs, dechloranes and OPFRs in sediment, mussels and water from different European fish and shellfish farming sites. As these compounds have no application in aquaculture activities, this is a study of the environmental contamination at the location of said farms.

2. Materials and methods

2.1. Sampling

Sediment ($n = 24$), mussel ($n = 17$) and water ($n = 27$) samples were collected in summer 2016 from fish farms and shellfish farms from Albania, Greece, Italy, Norway, Portugal, Spain and the United Kingdom (UK). See Table 1 and Fig. 1 for details.

None of the Albanian, Greek or Italian sampling spots were close to urban areas. The Albanian location was in a lagoon connected to the Ionian Sea and the Greek location was in the open Ionian Sea. The Italian fish farm in the northern Tyrrhenian Sea was 1.5 km off-shore and away from two small towns (about 40,000 inhabitants combined). In that location, mussels were collected at the boundary of the farm and between the cages, while sediment and water samples were collected either inside or outside the farm. The set of samples from the Italian shellfish farm were collected from Sacca di Goro, at the Po River Delta, which is separated from the Adriatic Sea by a sandy barrier. The Norwegian fish farm was about 200 m from urbanisation and close to a road, while the shellfish farm was about 1 km away. The Portuguese sampling spot was the closest to urban areas, in fact, quite surrounded by them. Portuguese mussels were collected from natural banks in the area of the shellfish farm. The Spanish sampling spot was by the shore close to both urban and agricultural land. Spanish mussels were unroot cultivated mussels. The three sampling spots in the UK were at the mouth of river Exe after it broadens. Two spots were right next to the opening to the sea; the third one was slightly further up at an urban shore. Mussels from the UK were collected from that third spot.

As OPFRs are also used as plasticisers, plastic was avoided in the sampling using aluminium or glass containers instead in order to