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Occurrence of halogenated and organophosphate flame retardants in sediment and fish samples from three European river basins

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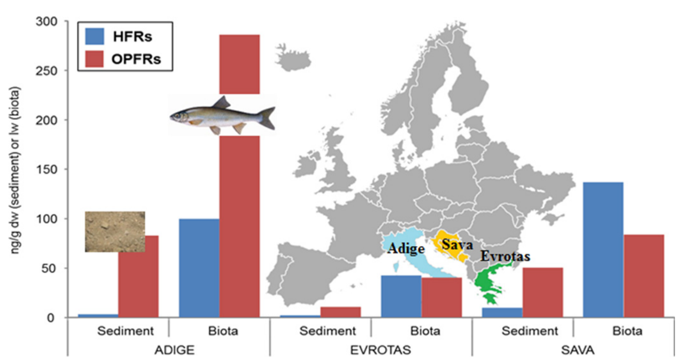
HIGHLIGHTS

- HFRs and OPFRs were analysed in sediments and fish in three European river basins.
- OPFRs were detected in sediment at concentration higher than HFRs.
- Levels in fish suggest a weak bioaccumulation power of OPFRs.
- Adige and Sava showed the higher levels of contamination.

GRAPHICAL ABSTRACT



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ABSTRACT

Classic (polybromodiphenyl ethers, PBDEs) and emerging halogenated flame retardants (HFRs) such as decabromodiphenyl ethane (DBDPE) and halogenated norbornenes, as well as organophosphate flame retardants (OPFRs) were analysed in 52 sediments and 27 fish samples from three European river basins, namely the Evrotas (Greece), the Adige (Italy) and the Sava (Slovenia, Croatia, Bosnia and Herzegovina and Serbia). This is the first time that FR levels have been reported in these three European river basins. The highest contamination was found in the Adige and Sava rivers, whereas lower values were obtained for the Evrotas. The levels in sediment samples ranged between 0.25 and 34.0 ng/g dw, and between 0.31 and 549 ng/g dw, for HFRs and OPFRs respectively. As regards levels in fish, concentrations ranged between 9.32 and 461 ng/g lw and between 14.4 and 650 ng/g lw, for HFRs and OPFRs, respectively. Thus, whereas OPFR values were higher in sediments, similar concentrations (in the Evrotas) and even lower concentrations than HFRs (Sava) were found for OPFRs in the fish samples, indicating the lower bioaccumulation potential of OPFRs. Biota to sediment accumulation factors (BSAFs) were calculated and higher values were obtained for HFRs compared to those assessed for OPFRs.

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1. Introduction

Chemical additives known as flame retardants (FRs) are incorporated into materials such as polymers to meet fire safety standard. There are different types of FRs: (i) halogenated FRs (HFRs), with brominated and chlorinated FRs (BFRs and CFRs, respectively), (ii) organophosphorus-containing FRs (OPFRs) and (iii) inorganic FRs (Van der Veen and De Boer, 2012).

HFRs are commonly used due to their low impact on the polymer's characteristics, thus they are used in many products such as electronics, clothes, toys, plastics, etc. However, in most cases they are not fixed in the polymer by chemical binding, and can therefore freely leak to the surrounding environment. These compounds are now ubiquitous and a number of scientific articles have dealt with their occurrence in different abiotic and biotic matrices such as sediment (Barón et al., 2014a; Brandsma et al., 2015; Matsukami et al., 2015; Sühring et al., 2016; Zhen et al., 2016), air (Newton et al., 2015; Vorkamp et al., 2015; Xu et al., 2016), soil (Wang et al., 2015a; Li et al., 2016) or fish tissue (Barón et al., 2014b; Greaves et al., 2016; Matsukami et al., 2016).

For several decades, polybrominated diphenyl ethers (PBDEs) were extensively used but due to their persistence, bioaccumulation and biomagnification through food webs, long-range transport and toxicity, their use was banned for production and use in the European Union (EU, European Court of Justice, 2008) and subsequently phased out in the USA and other countries (US EPA, 2015). Moreover, PBDEs were classed as persistent organic pollutants (POPs) and included in the list of global elimination compounds under the Stockholm Convention.

Unfortunately, restriction of commercial BDE mixtures has not led to an overall reduction in the application of FRs, but rather to a shift towards the use of alternative FRs, including emerging FRs and some examples are hexabromobenzene (HBB), pentabro-moethylbenzene (PBEB), decabromodiphenyl ethane (DBDPE) (Covaci et al., 2011) and halogenated norbornenes (HNs) such as Dechlorane 602 (Dec 602), Dechlorane 603 (Dec 603), Dechlorane 604 (Dec 604) and Dechlorane plus (DP) (Sverko et al., 2011), and OPFRs, such as tributyl phosphate (TBP), triphenyl phosphate (TPhP) and tris-(butoxyethyl)-phosphate (TBOEP). In 2001, global consumption of OPFRs was 186,000 tons, while it was 300,000 t in 2004, increasing to 500,000 t in 2011 and 680,000 t in 2015 (Wang et al., 2015b).

As regards HNs, DP is the most common in polymeric systems such as electrical hard plastic connectors in televisions and computer monitors, wire coating and furniture (Betts et al., 2006). The commercially available formulation of DP contains two stereoisomers, *syn*-DP and *anti*-DP with an approximate ratio of 1:3. Like BFRs, dechloranes have been found in abiotic and biological matrices such as air (Li et al., 2015), sediment (Yu et al., 2015), sewage sludge (Sverko et al., 2015), fishes (Von Eyken et al., 2016) and humans (Sahlström et al., 2014).

Another group of alternative FRs is OPFRs (Van der Veen and De Boer, 2012). OPFRs are already widely used, not only as FRs but also as plasticizers and antifoaming agents in a wide range of materials, due to their excellent physicochemical properties and low cost.

To date, limited data on sediment have been reported, mainly in studies in Austria, Spain and China (Cao et al., 2012; Cristale and Lacorte, 2013). Limited information is also available on biota samples (Chen et al., 2012; Brandsma et al., 2015; Malarvannan et al., 2015; Greaves et al., 2016).

The aim of this work is thus to provide, for the first time, a survey of FR contamination in sediment and biota samples from three European river basins: a continental river (the Sava, which flows through Slovenia, Croatia, Bosnia and herzegovina and Serbia), a Mediterranean river (the Evrotas, in Greece) and an Alpine river basin (the Adige, in Italy). Finally, biota to sediment accumulation factors (BSAFs) will be evaluated for the different HFRs and OPFRs included in our work, allowing us to compare the environmental behaviour of both FR families.

2. Sampling

2.1. River basin description

Three European river basins were selected for our study: the Adige (Italy), the Evrotas (Greece), and the Sava (Slovenia, Croatia, Bosnia and Herzegovina and Serbia) (Fig. 1). The principal characteristics (length, drainage basin area, land coverage) of the selected river basins are provided in Table 1.

The Sava, Evrotas and Adige river basins encompass a rich set of socio-ecological conditions (agricultural areas and industrial clusters, forested mountainous areas, etc.), and cover a wide geographical area, but they are all affected by water scarcity, due either to climatic or societal reasons. In addition, they are affected by significant environmental pressures. For the River Adige the principal stressors are widespread pollution from agriculture, hydropeaking effects and the release of pollutants accumulated in glaciers.

The dominant pressures for the River Evrotas derive mainly from agricultural activities and include overexploitation of water resources for irrigation, disposal of agro/industrial waste, agrochemical pollution and hydromorphological modifications.

In the River Sava, the upper reaches are largely influenced by hydromorphological pressures, and central stretches by agricultural activities and biological processes related to eutrophication, while the lower reaches are influenced mostly by stressors related to high pollution from industrial processing, along with untreated municipal waste water discharge.

2.2. Sampling and pre-treatment

Two different sampling campaigns were conducted at each river basin. Different sampling points were selected, and sediment and biota samples were collected (Fig. 1, Table 2). Details regarding the main sampling site characteristics for each river basin are provided in Supporting Information (Table S1).

In the case of the Evrotas river basin, sampling campaigns were conducted in June 2014 and July 2015, corresponding to two different flow conditions, as both precipitation and discharge were higher in 2015. Four sampling reaches were selected: two reference sites (Uskol and Vivari), one drought impacted reach (Dskol) and one pollution impacted reach (WWTP). During 2015, 10 Evrotas chub (*Squalius keadicus*) with a sample size of 350–400 g were collected in each Evrotas reach for analysis. In the case of the Adige, sampling campaigns were conducted in February and July 2015, reflecting two extreme situations for the river basin: the winter season, characterised by heavy tourisms and low stream flow, contrasted with the summer period with lower, though appreciable numbers of tourists and high stream flow. Twelve locations pertaining to seven water bodies were selected in order to investigate the effects of different stressors. Fish samples were collected along seven reaches, from riverine brown trout (*Salmo trutta fario*) or marble trout (*Salmo marmoratus*), bullhead (*Cottus gobio*), grayling (*Thymallus thymallus*) and chub (*Squalius cephalus*), as representatives of predator, benthivorous and omnivorous specimens, respectively (Kračun-Kolarević et al., 2016). At each sites 6 to 8 marble trout (250 g) and 1 bullhead, grayling and chub (1 kg) were collected. Finally, sampling at the Sava river was conducted in September 2014 and September 2015, at 11 sampling sites. Fish tissue samples were collected along 10 reaches from rainbow trout (*Oncorhynchus mykiss*), chub (*Squalius cephalus*) and common barbel (*Barbus barbus*). At each reach 4 to 5 individuals weighing 200–300 g were collected.

According to the protocol at each reach, sediment was collected from the river banks, using grab sampling with a stainless steel spade from the top 10 cm layer. At each site, approximately 1–2 kg of sediment was taken, wet sieved first through a coarse 2 mm sieve and afterwards through a 63 µm sieve. Samples were subsequently stored in high-density polyethylene (HDPE) Ø 88 one litre bottles. Sediment samples

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