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

Monica Giulivo [a], Ettore Capri [a], Eleni Kalogianni [d], Radmila Milacic [e], Bruno Majone [f], Federico Ferrari [g], Ethel Eljarrat [b,*], Damià Barceló [b,c]

[a] Institute of Agricultural and Environmental Chemistry, Università Cattolica del Sacro Cuore di Piacenza, Via Emilia Parmense 84, 29100 Piacenza, Italy
[b] Water and Soil Quality Research Group, Dep. of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain
[c] Catalan Institute for Water Research (ICRA), H₂O Building, Scientific and Technological Park of the University of Girona, Emili Grahit 101, 17003 Girona, Spain
[d] Institute of Marine Biological Resources and Inland Waters, Hellenic Centre for Marine Research, 46.7 km Athinon – Souniou Av., 190 13, P.O. Box 712, Anavissos, Greece
[e] Department of Environmental Sciences, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
[f] University of Trento, Department of Civil, Environmental and Mechanical Engineering, Via Mesiano 77, 38123 Trento, Italy
[g] Aeiforia Srl, 29027 Gariga di Podenzano (PC), Italy

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
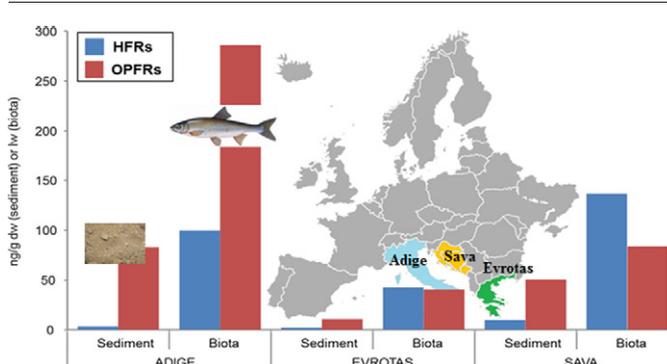
ARTICLE INFO

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.

* Corresponding author.
  E-mail address: eeeqam@cid.csic.es (E. Eljarrat).

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
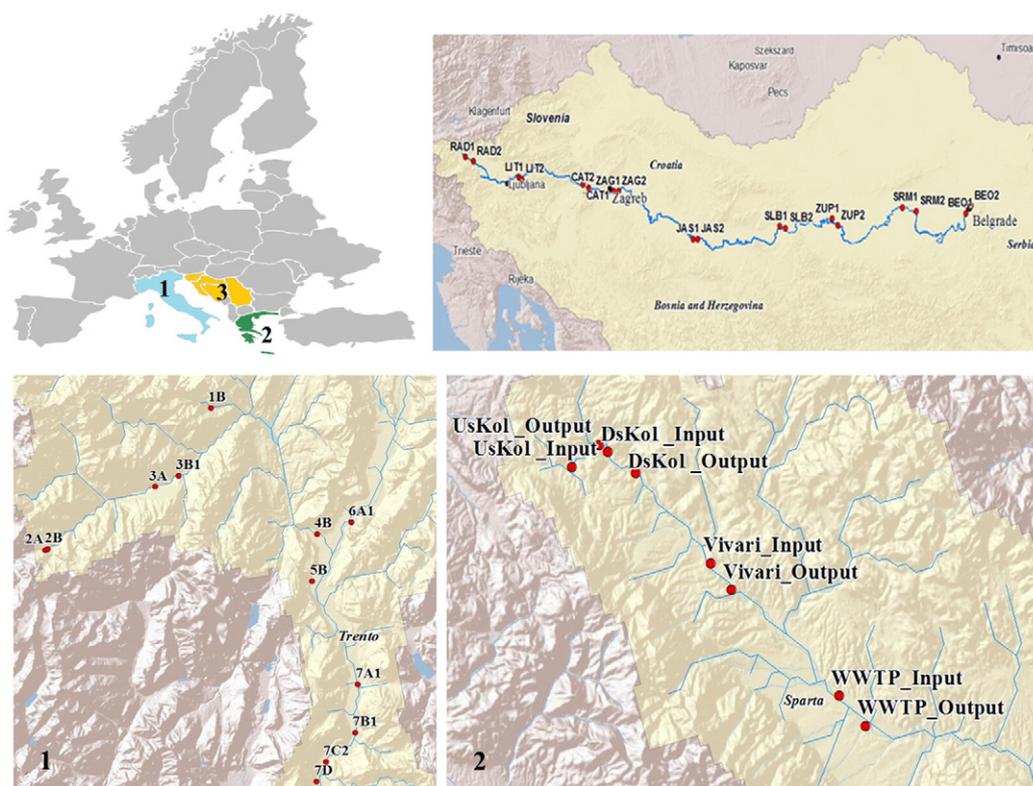
Fig. 1. Sampling locations at each river basin: (1) Adige (Italy); (2) Evrotas (Greece); and (3) Sava (Slovenia, Croatia, Bosnia and Herzegovina and Serbia).

were kept at 4 °C prior to shipment to the laboratory. Once in the laboratory, sediment and fish samples were lyophilised, ground and homogenised, and stored in sealed containers at −20 °C until analysis. Muscle portion was analysed and one fish sample was processed for each sites.

3. Materials and methods

3.1. Standards and reagents

HBB, PBEB and DBDPE were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). Native and ^{13}C-labeled standards mixtures of PBDEs (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209), *syn*- and *anti*-DP isomers and ^{13}C-*syn*-DP were obtained from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). Dec 602 (95%), Dec 603 (98%) and Dec 604 (98%) were purchased from Toronto Research Chemical Inc. (Toronto, ON, Canada). OPFR standards, including Tris(2-butoxyethyl)phosphate (TBOEP), tris(chloroethyl)-phosphate (TCEP), tris(chloroisopropyl)-phosphate (TClPP), trihexyl phosphate (THP) and tris(2-ethylhexyl) phosphate (TEHP), were purchased from Santa Cruz Biotechnology

(Santa Cruz, CA, USA). Isodecyldiphenyl phosphate (IDPP) and 2-ethylhexyldiphenyl phosphate (EHDP) were purchased from AccuStandard (New Haven, CT, USA). Diphenyl cresylphosphate (DCP), tributyl phosphate (TBP), TPHP, triphenylphosphine oxide (TPPO) and tris(1,3-dichloro-2-propyl)phosphate (TDCPP) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Tri-cresyl phosphate (TMCP) was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Isopropyl phenyl phosphate (IPPP) was purchased from Chiron (Trondheim, Norway). d_{15}-TDCPP, d_{27}-TBP, d_{12}-TCEP and ^{13}C$_2$-TBOEP were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada). d_{15}-TPHP was obtained from Cambridge Isotope Laboratories Inc. (Andover, MA, USA).

Al-N cartridges were provided by Biotage (Uppsala, Sweden). Alumina (0.063–0.2 mm) and copper (<63 μm) were obtained from Merck (Darmstadt, Germany). Acetone, dichloromethane (DCM), hexane, methanol, toluene, water and sulphuric acid were purchased from Merck (Darmstadt, Germany).

3.2. Sample preparation

FR analysis was carried out using previously optimised analytical methods (Barón et al., 2012, 2014b; Giulivo et al., 2016).

For HFRs, sediment and biota samples were extracted using a pressurised liquid extraction (PLE) method. Lyophilised samples (1.0 and 1.5 g dry weight (dw)) of sediment and fish respectively were spiked with ^{13}C-PBDEs mixture and ^{13}C-*syn*-DP. Spiked samples were kept in the fridge overnight to equilibrate. In the case of sediment, spiked samples were ground with alumina and copper (1:2:2) and loaded into a 22 mL extraction cell previously loaded with 8 g of alumina. Dead volume was filled with hydromatrix. The extraction cell was filled with a hexane:DCM mixture (1:1) until the pressure reached 1500 psi (1 psi = 6894.76 Pa), and heated to 100 °C. After an oven heat-up time of 5 min under these conditions, two static extractions of 10 min

Table 1
Principal river basin characteristics.

River basin	Length	Drainage basin area	Land coverage
Adige	410 km	12,000 km^2	Forest (56%) Grassland and sparse vegetation (both around 17%) Agriculture (12%)
Evrotas	82 km	2418 km^2	Semi-natural areas 61% Agricultural areas 38% Urban areas account for 1%.
Sava	945 km	97,713 km^2	Forest and semi-natural areas (55%) Agricultural surfaces (42%)

Table 2
Sediment and biota samples collected from the Evrotas, Adige and Sava river basins.

River basin	Sampling campaign	Sediment samples	Biota samples
Evrotas (Greece)	June 2014	$n = 8$	–
	July 2015	$n = 4$	$n = 4$
			Menida (*Squalius keadicus*)
Adige (Italy)	February 2015	$n = 12$	–
	July 2015	$n = 8$	$n = 13$
			Riverine brown trout (*Salmo trutta fario*)
			Marble trout (*Salmo marmoratus*)
			Grayling (*Thymallus thymallus*)
			Bullhead (*Cottus gobio*)
			Chub (*Squalius cephalus*)
Sava (Slovenia, Croatia, Bosnia and Herzegovina and Serbia)	September 2014	$n = 11$	–
	September 2015	$n = 9$	$n = 10$
			Rainbow trout (*Oncorhynchus mykiss*)
			Chub (*Squalius cephalus*)
			Common barbel (*Barbus barbus*)

at constant pressure and temperature were developed. After this static period, fresh solvent was introduced to flush the lines and cell, and the extract was collected in the vial. The flush volume amounted to 100% of the extraction cell. The extraction was cycled twice. The volume of the resulting extract was about 35 mL. Extracts were concentrated to incipient dryness and re-dissolved with toluene for a final volume of 40 μL.

As regards fish, spiked samples were loaded into an 11 mL extraction cell. Dead volume was filled with hydromatrix and PLE was carried out using the same conditions as for sediment samples. Extracts were concentrated to dryness, kept in the oven at 95 °C for 2 h and lipid content was determined gravimetrically. Then the extracts were treated with sulphuric acid in order to remove lipids. After acid treatment, the organic phase was cleaned through solid phase extraction (SPE) using Al-N cartridges (5 g) conditioned with hexane and eluted with hexane:DCM (1:2). Extracts were concentrated to incipient dryness and re-dissolved with toluene for a final volume of 40 μL. Finally, both sediment and fish extracts were analysed using gas chromatography, coupled to tandem mass spectrometry (GC–MS-MS).

For OPFRs, sediment was extracted using PLE: one gram dw was loaded into a 22 mL extraction cell previously filled with copper and hydromatrix, and extracted with hexane:acetone (1:1) at 1500 psi and 100 °C. Extracts were concentrated to incipient dryness and re-dissolved with methanol for a final volume of 500 μL. Ultrasound was chosen for fish samples, mainly because it offers a mild extraction allowing a smaller amount of interfering compounds. 0.5 g dw was extracted with 15 mL of hexane:acetone (1:1). The extract was reconstituted in 5 mL of hexane:methanol (1:3). The solution was centrifuged and 200 μL were collected for instrumental analysis. Prior to analysis using turbulent flow chromatography-liquid chromatography (TFC-LC) coupled to MS-MS, labeled compounds, TCEP-d$_{12}$, TDCPP-d$_{15}$, TBP-d$_{27}$, TPHP-d$_{15}$ and ^{13}C$_2$-TBOEP, were added as internal standards.

3.3. Instrumental analysis

Instrumental analysis of HFRs was carried out with GC–MS-MS using an Agilent Technologies 7890A GC system coupled to 7000A GC/MS Triple Quadrupole. Chromatographic separation was carried out with a DB-5 ms column (15 m × 0.25 mm × 0.1 μm film thickness). For PBDEs, HBB, PBEB and DBDPE, GC–MS-MS using electron ionisation (EI) was applied (Barón et al., 2014b), whereas HNs were analysed with GC–MS-MS using negative chemical ionisation (NCI) (Barón et al., 2012). Due to low sensitivity to decabrominated analytes using GC-EI-MS-MS, BDE-209 and DBDPE were determined with GC-NCI-MS (Eljarrat et al., 2004).

For OPFR analyses, online sample purification and analysis was performed with a Thermo Scientific TurboFlow™ system consisting of a triple quadrupole (QqQ) MS with a heated-electrospray ionisation source (H-ESI), two LC quaternary pumps and three LC columns, two for

purification and one for separation. The TurboFlow™ purification columns employed were: Cyclone™-P (0.5x50mm) and C18-XL (0.5 × 50mm). Chromatographic separation was subsequently achieved using an analytical column: Purosphere Star RP-18 (125 mm × 0.2 mm) with a particle size of 5 μm (Giulivo et al., 2016).

Selective reaction monitoring (SRM) mode was used for all compounds with two transitions monitored for each analyte. The most intense transition was used for quantification, while the second provided confirmation.

3.4. Quality control

Instrumental parameters such as recoveries, method limits of detection (mLODs) and method limits of quantification (mLOQ) are summarised in Supplementary information (Table S2). Recoveries ranged between 48–114% and 49–99% for sediment and fish samples, respectively, always being within the range of acceptability (40–120%) for analytical methods based on quantification by isotopic dilution. For sediment samples, mLODs and mLOQs ranged from 0.0001 to 1.65 and from 0.0003 to 5.49 ng/g dw, respectively. As regards fish samples, mLODs and mLOQs ranged from 0.002 to 19.3 and from 0.008 to 24.8 ng/g dw, respectively.

3.5. Data analysis

One way analysis of variance (ANOVA) and *two-sample t*-tests were carried out, using the *EXCEL* program, to determine significant differences ($p \leq 0.05$) between the three river basins selected.

4. Results and discussion

4.1. Sediment samples

Table 4 summarises the results obtained in the three river basins, indicating the detection frequency and concentration ranges as well as mean values (for individual sample results see Supporting Information, Tables S3, S4 and S5).

4.1.1. HFRs

HFRs were detected in all sediment samples, with the exception of one sample (River Evrotas). ΣHFR levels (ΣPBDEs + ΣEmerging BFRs + ΣHNs) ranged from nd to 6.82, 0.26 to 11.9 and 0.25 to 34.0 ng/g dw for the Evrotas, Adige and Sava respectively.

One-way ANOVA test was applied and statistical differences were observed between the three case studies. Student's *t*-test showed significant statistical differences for the Sava basin in relation to the Adige ($t = 2.06$, d.f 23, $p < 0.05$) and Evrotas river basins ($t = 2.07$, d.f = 22, $p < 0.05$), while insignificant differences were observed between

the Adige and Evrotas river basins ($t = 2.04$, d.f $= 29$, $p > 0.05$). Indeed, significantly higher HFR levels were found in the Sava river basin compared with the Adige and Evrotas basins ($p < 0.05$). This trend is principally correlated to the dominant pressures for the river basins. The Sava is indeed mostly influenced by high pollution from industrial processing, while the principal stressors for the Evrotas and Adige are agricultural activities. The reason also lies in the dense population of the Sava river basin 8.2 million inhabitants. Moreover, the t-test suggests that HFR levels did not change significantly in the first and the second sampling campaign (t-test, $p > 0.05$) for the Evrotas and Adige rivers, whereas for the River Sava significant differences were observed between the two sampling campaigns ($p \leq 0.05$). Significantly higher values were observed for the sampling campaign undertaken in 2014.

It is well known that the properties of sediment, such as total organic content (TOC), can influence the concentration levels of organic pollutants. Nevertheless, the range of TOC values for the River Evrotas (between 2.08% and 7.18%) was similar to that obtained for the other two river basins (between 1.08% and 7.37%). Thus, the reason for the lower contamination levels in the Evrotas is probably more related to the different activities in the basin.

PBDEs contributed between 58–100% (mean value of 93%), 25–100% (mean value of 77%) and 3–100% (mean value of 68%) of total HFR contamination in the Evrotas, Adige and Sava respectively. PBDEs were detected in all sediment samples, with the exception of one sample (River Evrotas). Total PBDE levels ranged from nd to 4.52, 0.26 to 10.8 and nd to 14.0 ng/g dw in the Evrotas, Adige and Sava respectively. Statistical differences in PBDE concentrations in the three river basins were observed. PBDEs behaviour followed the same trend as for HFRs, with significant differences for the Sava basin in relation to the Adige ($t = 2.00$, d.f $= 28$, $p < 0.05$) and Evrotas river basins ($t = 2.03$, d.f $= 22$, $p < 0.05$). However, no significant differences were observed between the Adige and Evrotas river basins ($t = 2.04$, d.f $= 28$, $p > 0.05$). Again, no significant differences between the first and the second sampling campaign ($p > 0.05$ in all case studies) were found. Significantly lower PBDE contribution was found in samples collected along the Sava river basin, in which a high DBDPE contribution was found. Five different PBDE congeners were detected, i.e. BDE-28 (in only one sediment sample), BDE-47, BDE-99, BDE-100 and BDE-209. These results indicate the use of Penta- and Deca-BDE commercial mixtures in the three study areas. Penta- and Deca-BDE are mainly used in mattresses, plastics such as high impact polystyrene, electronic equipment, electrical cable coatings, the construction sector, textiles and furniture. BDE-209 was the most abundant compound in sediment from the Adige and Sava rivers. In the River Adige BDE-209 contributed between 36–100% with a mean value of 46%, while in the River Sava, the contribution was between 12–100%, with a mean value of 41% of total PBDE burden. Their contribution was lower in the case of the River Evrotas, and was not detected or below mLOQ in 67% of sediment samples, indicating less use of the Deca-BDE commercial mixture in this area.

BDE-209 mostly dominates the BDE congener profile in freshwater sediments all around the world, reflecting the fact that use of the Deca-BDE technical formulation accounts for 75% of overall BDE consumption (Martellini et al., 2016). BDE-209 was found to dominate in Taiwan, Korea, Indonesia and Spain freshwater sediments (Hong et al., 2010; Ilyas et al., 2011; Jiang et al., 2011; Lee et al., 2012; Moon et al., 2007; Barón et al., 2014a). A study of Lake Maggiore in Italy also showed high abundance of BDE-209 in the BDE congener profile (Mariani et al., 2008).

In the Evrotas samples, BDE-47 was the most abundant PBDE congener, contributing between 17% and 100% (mean value of 37%) of the total PBDE burden.

As regards emerging BFRs, HBB, PBEB and DBDPE were not detected in any samples collected at the Evrotas and Adige rivers. DBDPE, introduced as a replacement for the Deca-BDE mixture, was detected only in the Sava river basin at concentration levels between nd to 20.8 ng/

dw. In the case of samples in which both BDE-209 and DBDPE were detected, the levels of the latter were higher (with $R_{BDE/DBDPE}$ values between 0.45 and 0.63), and only one sample showed a BDE-209 contribution higher than that of DBDPE ($R_{BDE/DBDPE} = 2.33$).

Frequency detection for HNs was lower than that observed for PBDEs. HNs were detected in 25%, 40% and 55% of the sediment analysed from the Evrotas, Adige and Sava river basins, respectively. Total HN levels ranged from nd to 2.30, nd to 3.67 and nd to 2.80 ng/g dw in the Evrotas, Adige and Sava samples respectively. Dec 602, Dec 603, *syn*-DP and *anti*-DP were detected, both DP isomers being most frequently detected and at the highest concentration levels. F_{anti} values (the isomeric ratio of *anti*-DP relative to the total amount of both isomers) were calculated and compared with those found in commercial mixtures (from 0.64 to 0.80) (Xian et al., 2011). As expected, similar F_{anti} values were obtained for sediment samples.

The ratio between BFRs (PBDEs + Emerging BFRs) and HNs was calculated. In most cases, BFR concentrations were higher than those of HNs, with ratios between 1.36 and 26.9. However, in some samples (especially in some sediment from the Adige), this ratio was reversed, with higher values for HNs.

Our HFR values were compared with those in other published works. Although a large number of published works have reported PBDE levels in river sediments, there are limited data on emerging BFR or HNs (Law et al., 2014; Iqbal et al., 2016). In any case, we focused our comparison on data published in the last three years (Table 4). As shown, our PBDE levels were within the concentration ranges obtained in other European locations (Barón et al., 2014a) and slightly lower than the levels found in China (Zhang et al., 2015). As regards HNs, our concentrations were similar to those obtained in Spanish river basins (Barón et al., 2014a), and slightly higher than those obtained in samples from the River Elbe (North Sea) (Sühring et al., 2015, 2016).

4.1.2. OPFRs

OPFRs were detected in all sediment samples. Table 3 summarises the results obtained in the three river basins, indicating the detection frequency and concentrations ranges as well as mean values (for individual sample results see Supporting Information, Tables S3, S4 and S5). ΣOPFR levels ranged from 0.31 to 31.0, 11.5 to 549 and 10.5 to 248 ng/g dw for the Evrotas, Adige and Sava respectively. On applying the ANOVA test, differences concerning OPFR concentrations in sediment samples in the Evrotas, Adige and Sava river basins were not considered to be statistically significant, with p-values > 0.05. All the 14 OPFRs included in our analytical methodology were detected in at least some sediment samples. In sediment collected along the Evrotas river basin, TPPO was not detected and THP was only detected in some samples, but below the mLOQ. EHDP and TCIPP were the most frequently detected (100%) followed by TPHP and TEHP (92%). Moreover, EHDP and TCIPP were two of the most abundant OPFRs with values ranging from 3.80 to 6.39 and nq to 7.62 ng/g dw respectively. IPPP contribution was also higher with concentration levels ranging from nd to 7.09 ng/g dw. In the case of River Adige sediment, all 14 studied OPFRs were detected in 100% of the sediment samples analysed, with EHDP being the most abundant (between 4.27 to 288 ng/g dw) followed by TCIPP (0.53 to 53.7 ng/g dw) and IPPP (nq to 40.8 ng/g dw). Thus, similar patterns were observed at both river basins. In sediment collected along the Sava river basin, TPPO and TPHP were not detected either. TBOEP, TCIPP, TEHP, IPPP and TMCP were the most frequently detected (100%) followed by DCP and TBP (95%). Moreover, IDPP and IPPP were two of the most abundant OPFRs with values up to 197 and 49.5 ng/g dw, respectively.

Our OPFR values were compared to those presented in other published studies, but it should be pointed out that limited OPFR data are currently available (Table 4). As shown, our OPFR levels were within the concentration ranges detected in sediments from China (between 8.30 and 470 ng/g dw) (Tan et al., 2016) and higher than levels found in the Western Scheldt estuary (Netherlands) (<0.1–19.6 ng/g dw)

Table 3
Summary of HFR levels obtained in sediment (expressed in ng/g dw) and fish (expressed in ng/g lw) collected from the three European river basins.

		Evrotas river basin		Adige river basin		Sava river basin	
		Sediment	Fish	Sediment	Fish	Sediment	Fish
ΣPBDEs	% Positive	91.6	100	100	100	100	100
	Range	nd–4.52	9.32–116	0.26–10.8	18.7–187	nd–16.7	11.9–461
	Mean*	1.68	42.4	2.14	94.9	5.6	135
ΣEmerging BFRs	% Positive	0	0	0	0	35	10
	Range	nd	nd	nd	nd	nd–20.8	nd–2.94
	Mean	nd	nd	nd	nd	9.0	2.94
ΣHNs	% Positive	25	100	40	100	55	90
	Range	nd–2.30	nq	nd–3.67	nq–19.7	nd–2.80	nd–5.08
	Mean	1.60	nq	2.21	7.59	1.20	3.00
ΣHFRs	% Positive	91.6	100	100	100	100	100
	Range	nd–6.82	9.32–116	0.26–11.9	22.3–187	0.25–34.0	11.9–461
	Mean	2.11	42.4	3.02	99.7	9.2	136
ΣOPFRs	% Positive	100	100	100	100	100	100
	Range	0.31–31.0	34.1–55.5	11.5–549	50.6–650	10.5–248	14.4–196
	Mean	10.4	40.1	82.6	286	50.1	84

nd: not detected (below mLODs).
nq: not quantifiable (below mLOQs).
Mean*: values obtained taking into account only positive results.

(Brandsma et al., 2015) and in Bui Dau (Vietnam) (nq–4.5 ng/g dw) (Matsukami et al., 2015).

While much research work has been conducted on HFR pollution in river basins, it is also very important to know the degree of contamination by another group of FRs, OPFRs, which are also widely used and applied. This is why it is important to analyse and compare the concentration levels of both groups (HFRs and OPFRs) in the same series of samples. Concentration levels of OPFRs in sediment samples were higher than those of HFRs in the all river basins studied.

Similar findings were observed by Brandsma et al. (2015) in their study on the Western Scheldt estuary (The Netherlands). In the abiotic compartments (sediment and suspended particular matter) they found that OPFR concentrations were often higher than those of PBDEs.

4.2. Fish samples

4.2.1. HFRs

HFRs were detected in all fish samples as, is evident in Table 3, which that summarises the results obtained in the three river basins, indicating detection frequency, concentration ranges mean values (for individual sample results see Supporting Information, Tables S6, S7 and S8). ΣHFR levels (ΣPBDEs + ΣEmerging BFRs + ΣHNs) ranged from 9.32 to 116, 22.3 to 187 and 11.9 to 461 ng/g lw for the Evrotas, Adige and Sava respectively. Similarly to sediment samples, HFR levels in fish seem to be higher in the Sava river basin, followed by the Adige and Evrotas. However, a statistical analysis with this scope cannot be undertaken, as the fish species in the three rivers are completely different.

Table 4
HFR (PBDE and HN) and OPFR concentrations found in sediment (ng/g dw) and biota (ng/g lw) samples around the world.

Site	Location	ΣPBDEs	ΣHNs	ΣOPFRs	Reference
Sediment					
Spain	Ebro river basin	nd–37.3	nq–3.74		Barón et al., 2014a
Spain	Llobregat river basin	1.50–44.3	0.02–3.68		Barón et al., 2014a
South Africa	Gauteng rivers	0.8–4			Olukunle et al., 2014
Netherlands	Western Scheldt estuary	0.01–111		<0.1–19.6	Brandsma et al., 2015
North Sea	Elbe river	nd–0.04	nd–0.05		Sühring et al., 2015
China	Pearl River estuary	17.7–43.5			Zhang et al., 2015
Vietnam	Bui Dau	100–350		nq–4.5	Matsukami et al., 2016
North Sea	Elbe river	nd–0.20	nd–0.01		Sühring et al., 2016
China	Pearl river delta			8.30–470	Tan et al., 2016
Greece	Evrotas river basin	nd–4.52	nd–2.30	10.5–248	This study
Italy	Adige river basin	0.26–10.8	nd–3.67	11.5–549	This study
Slovenia	Sava river basin	nq–16.7	nd–2.80	0.31–310	This study
Biota					
China	Taihu	1.13–97.5			Su et al., 2014
Tanzania	Tanzania lakes	nd–34	0.09–27		Polder et al., 2014
Netherlands	Western Scheldt estuary			<0.06–17[a]	Brandsma et al., 2015
				<0.06–17[b]	
Belgium	Flanders	94[c]		673[c]	Malarvannan et al., 2015
Italy	Po river	94.9–821			Viganò et al., 2015
China	Pearl river	3.88–59.8	0.18–6.88		Sun et al., 2015
Spain	Llobregat river basin			nq–2423	Santín et al., 2016
China	Pearl river delta	6.9–690			Sun et al., 2016
Vietnam	Bui Dau			<5–300	Matsukami et al., 2016
Greece	Evrotas river basin	9.32–116	nd	34.1–55.5	This study
Italy	Adige river basin	18.6–187	nq–19.7	50.6–650	This study
Slovenia	Sava river basin	11.9–461	nq–3.80	14.4–196	This study

[a] Concentrations expressed in ng/g wet weight (ww) for benthic fish.
[b] Concentrations expressed in ng/g ww for pelagic fish.
[c] Mean values.

Therefore, comparison of HFR levels in pelagic and benthic fish groups in the River Adige and the three fish species living in the River Sava, respectively was undertaken, and no significant differences were found.

PBDEs contributed between 80% and 100% of total HFR contamination in fish. PBDEs were detected in all fish samples at levels ranging 9.32 to 116, 18.7 to 187 and from 11.9 to 461 ng/g lw in the Evrotas, Adige and Sava respectively. On comparing PBDE levels in pelagic and benthic fish groups in the River Adige and the three fish species living in the Sava River respectively, no significant differences were found. Eight different PBDE congeners were detected, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183 and BDE-209. BDE-47 was the most abundant compound in fish samples, contributing between 44–90% (mean value of 58%), 10–75% (mean value of 40%) and 48–82% (mean value of 65%) of total PBDE burden, for the Evrotas, Adige and Sava respectively. The contribution of BDE-99 and BDE-100 was also significant, with contributions of up to 54% and 52% respectively. This PBDE pattern is the same as that presented in previous studies on biota collected from different locations around the world (Van Leeuwen and de Boer, 2008; Van Ael et al., 2013; Santín et al., 2013; Ben Ameur et al., 2011).

BDE-209 was the main contributing PBDE congener in sediments, but due to their large molecule size, its bioaccumulation capacity was lower than that observed for other PBDE congeners with a lower degree of bromination (Eljarrat et al., 2007). As regarding BDE-209 levels, differences between pelagic and benthic fish species were observed, although these differences were not statistically significant ($t = 2.36$, d.f $= 7$, $p > 0.05$). Slightly higher BDE-209 levels were found for benthic species, these results being consistent with a recent study (Brandsma et al., 2015). The reason is probably associated with the living and feeding area of benthic fish, on or near sediment rich in BDE-209. The lower metabolic capability of benthic organisms compared to pelagic ones may also play an important role (Wilson et al., 2013).

As regards emerging BFRs, PBEB and DBDPE, these were not detected in any fish samples. Only HBB was detected in the Sava river basin at concentration levels between nd to 2.94 ng/g lw.

Frequency detection for HNs was lower than that observed for PBDEs. HNs were detected in the Adige and Sava river basins, but not in the Evrotas. Total HN levels ranged from nq to 19.7 and nq to 5.08 ng/g lw in the Adige and Sava respectively. Dec 602 and Dec 604 were detected in the Adige samples, with Dec 602 being the most frequently detected (54% of analysed samples) at levels of up to 8.99 ng/g lw. DP was the only HN detected in the Sava samples. F_{anti} values ranged from 0.35 to 0.66, with a mean value of 0.56, lower than that found in Sava sediment (mean F_{anti} values of 0.65) and in commercial mixtures. This could be due to the higher bioaccumulation capacity of the syn-isomer or because the anti-isomer can be degraded more easily. Similar findings have been reported in biota samples, such as fish or dolphins (Sverko et al., 2011; Barón et al., 2015).

The ratio between BFRs (PBDEs + Emerging BFRs) and HNs was calculated. Similarly to sediment, BFR concentrations were higher than those of HNs, with ratios ranging between 1 and 155 (mean ratio of 15 and 55 for the Adige and Sava respectively).

Our HFR values were also compared to those presented in other published studies. Although a large number of those studies have reported PBDE levels in riverine fish, there are limited data available on emerging BFR or HNs. Nevertheless, we focused our comparison on data published in the last three years (Table 4). As is evident in the table, our PBDE levels were within the concentration ranges obtained in other European locations (Malarvannan et al., 2015; Viganò et al., 2015) and China (Su et al., 2014; Sun et al., 2015, 2016), and higher than those observed in Tanzania (Polder et al., 2014). As regards HNs, our concentrations were similar to those obtained in China (Sun et al., 2015) and Tanzania (Polder et al., 2014).

4.2.2. OPFRs

OPFRs were detected in all fish samples. Table 3 summarises the results obtained in the three river basins, indicating detection frequency, concentration ranges and mean values (for individual sample results see Supporting Information, Tables S6, S7 and S8). ΣOPFR levels ranged from 34.1 to 55.5, 50.6 to 650 and 14.4 to 196 ng/g lw for the Evrotas, Adige and Sava respectively. The highest values were found in the Adige (mean value of 286 ng/g lw), followed by the Sava (mean value of 84 ng/g lw) and the Evrotas (mean value of 40.1 ng/g lw). No significant inter-species differences (River Sava fish species) and fish groups (River Adige) were observed (ANOVA test, $p > 0.05$).

All 14 OPFRs included in our analytical methodology were detected in at least some fish samples. In fish collected along the Evrotas river basin, six OPFRs were detected in all the analysed samples: EHDP, TBOEP, TCEP, TClPP, TDCPP and IPPP. TBP was the most abundant OPFR with values of up to 32.5 ng/g lw, followed by TCEP with values of up to 18.2 ng/g lw and IPPP, with values of up to 7.81 ng/g lw. In the case of River Adige fish, all the 14 studied OPFRs were detected, but TBOEP levels were always below the LOQ. The highest values were for TBP, with a mean concentration of 102 ng/g lw, followed by IDPP (mean value of 52.5 ng/g lw) and EHDP (mean value of 31.8 ng/g lw). For fish samples collected along the Sava river basin, IPPP was the most abundant OPFR with a mean value of 39.5 ng/g lw, followed by TBP (mean value of 25.7 ng/g lw) and TCEP (mean value of 18.0 ng/g lw). Thus, different patterns were observed for the three river basins, but we can conclude that TBP, TCEP and IPPP were among the most abundant OPFRs in European fish.

Although limited information is available on the occurrence of OPFRs in biota samples, our OPFR values, when compared with other published studies (Table 4) appear to be lower than the values reported in 2016 by Santin et al., in Spanish river basins, with concentration levels reaching 2423 ng/g lw. Malarvannan et al. (2015) published OPFR levels in fish samples from Flanders (Belgium) and they too found similar concentrations to those we detected in the Adige. Matsukami et al. (2016) showed levels in biota (<5–300) higher than the values obtained for the Evrotas and Sava river basins.

Comparison between HFR and OPFR mean values obtained for both sediment and biota samples in each river basin shows that, in fish samples, OPFR values were similar to HFR values in the Evrotas, and even lower than HFR values in the Sava. Only in the Adige did HFR and OPFR values in sediment and fish show a similar trend. These findings could indicate higher bioaccumulation power for HFRs as compared to OPFRs.

4.2.3. Biota to sediment accumulation factors (BSAFs)

BSAFs were calculated based on lipid weight concentrations in fish compared to the concentrations in sediment normalised to organic carbon. It was only possible to determine BSAF values for those analytes detected in both sediment and fish matrices. Fig. 2 shows BSAFs for some PBDEs and OPFRs determined in the Sava (two sampling sites, two fish species) and Adige (one sampling site, three fish species) river basins. The same general trends were observed: BSAFs for PBDEs were clearly higher than those obtained for OPFRs. Furthermore, as widely described in the literature, BSAF values for PBDEs decrease as the degree of bromination increases: we found BSAFs of around 10 for tetra-BDE-47, whereas BSAF values for penta-BDEs (BDE-99 and BDE-100) decreased to BSAF values of around 5. Of the different OPFRs tested, DCP, TBP, TCEP and TMCP seem to have the highest bioaccumulation potential, with BSAF values always lower than 1.

It should be pointed out that some compounds are usually found in fish samples, indicating their bioavailability, but no accumulation factor can be determined because they were not detected in sediment. This is the case of THP, detected in sediment samples but at levels below the mLOQ (0.22 ng/g dw), which was found in several fish samples, for instance in 10 out 13 fish collected in the Adige river basin, THP was found at concentration levels ranging between nd and 39.6 ng/g lw,
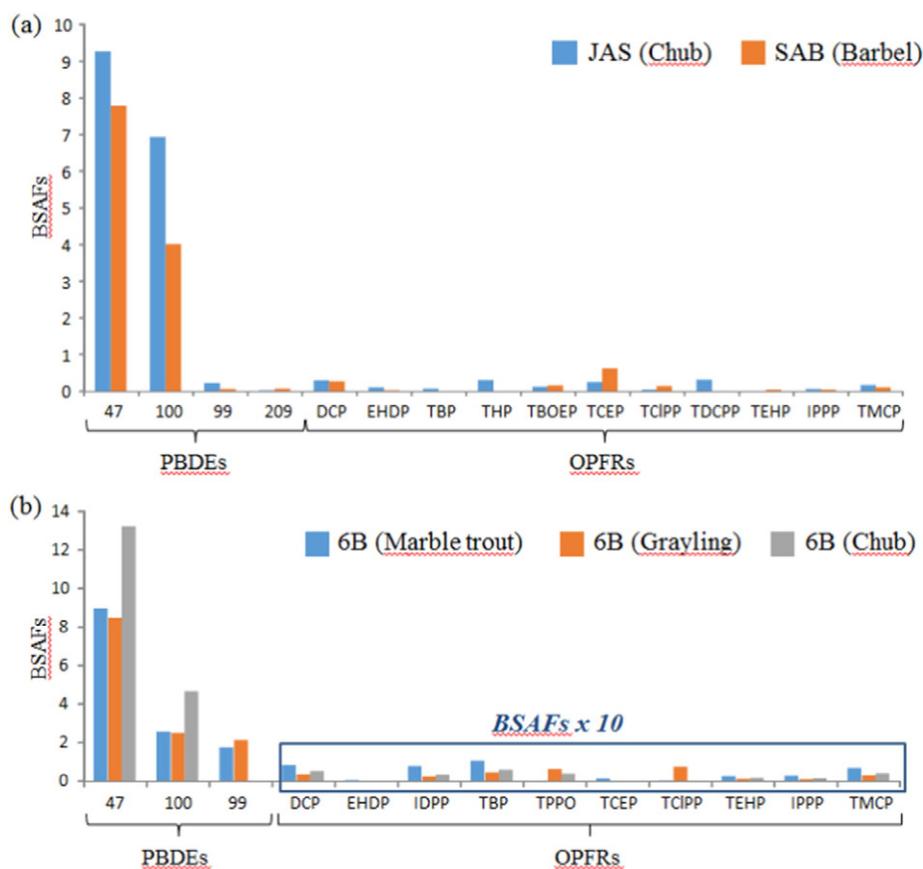
Fig. 2. Biota to sediment accumulation factors (BSAFs) for PBDEs and OPFRs in (a) Sava river basin; and (b) Adige river basin.

with a mean value of 20.3 ng/g lw. Taking into account this mean value in biota, a BSAF of 4 could be assumed for this OPFR, probably the OPFR compound with the highest bioaccumulation potential. However, future studies determining BSAFs for OPFRs in different scenarios must be carried out in order to confirm this behaviour.

5. Conclusion

This is the first time that HFRs (including PBDEs, emerging BFRs and HNs) and OPFRs have been analysed in sediment and biota samples collected from the Evrotas, Adige and Sava river basins. HFRs were detected in practically all the samples, with the Sava basin being the most contaminated, followed by the Adige and Evrotas river basins. PBDEs were the main contributors to HFR contamination, while emerging BFRs were barely detected. HNs were also found, but at concentration levels lower than those of PBDEs. As regards OPFRs, they were also found in all the analysed samples. In this case, the most polluted basin was the Adige, followed by the Sava and Evrotas river basins. Different OPFR patterns were observed in each area studied, but TBP, TCEP and IPPP were commonly the most abundant OPFRs in fish.

This study is one of the few in which these two families of FRs, halogenated and organophosphate, have been analysed in the same samples. This has allowed a comparative study aiming to establish the main contributors to river contamination by FRs. Whereas OPFR values were higher in sediment, similar and even lower concentrations than HFRs were found for OPFRs in fish samples. These findings seem to indicate a higher bioaccumulation power of HFRs versus OPFRs. However, more studies are required in order to better understand the bioaccumulation processes of OPFRs in biota.

It is also important to remark that the increased demand for OPFRs following the ban and phase out of PBDEs may lead to a further increase of environmental levels and a higher exposure of organisms to OPFRs.

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