Environment International 59 (2013) 232–243

Contents lists available at SciVerse ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Priority and emerging flame retardants in rivers: Occurrence in water and sediment, *Daphnia magna* toxicity and risk assessment

Joyce Cristale, Alejandro García Vázquez [1], Carlos Barata, Silvia Lacorte *

Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, 08034 Barcelona, Catalonia, Spain

ARTICLE INFO

Article history:
Received 4 May 2013
Accepted 17 June 2013
Available online xxxx

Keywords:
PBDE
New brominated flame retardants
Organophosphate flame retardant
D. magna toxicity
Risk assessment
River

ABSTRACT

The occurrence, partitioning and risk of eight polybrominated diphenyl ethers (PBDEs), nine new brominated (NBFRs) and ten organophosphorus flame retardants (OPFRs) were evaluated in three Spanish rivers suffering different anthropogenic pressures (Nalón, Arga and Besòs). OPFRs were ubiquitous contaminants in water (ΣOPFRs ranging from 0.0076 to 7.2 μg L^{-1}) and sediments (ΣOPFRs ranging 3.8 to 824 μg kg^{-1}). Brominated flame retardants were not detected in waters, whereas ΣPBDEs ranged from 88 to 812 μg kg^{-1} and decabromodiphenyl ethane (DBDPE) reached 435 μg kg^{-1} in sediments from the River Besòs, the most impacted river. The occurrence of flame retardants in river water and sediment was clearly associated with human activities, since the highest levels occurred near urban and industrial zones and after wastewater treatment plants discharge. *Daphnia magna* toxicity was carried out for OPFRs, the most ubiquitous flame retardants, considering individual compounds and mixtures. Toxicity of nine tested OPFRs differed largely among compounds, with EC_{50} values ranging over three magnitude orders (0.31–381 mg L^{-1}). Results evidenced that these compounds act by non-polar narcosis, since their toxicity was proportional to their lipophilicity (K_{ow}). Furthermore, their joint toxicity was additive, which means that single and joint toxicity can be predicted knowing their concentration levels in water using quantitative structure activity relationships (QSARs) and predictive mixture models. Based on these results, a risk assessment considering joint effect was performed calculating and summing risk quotients (RQs) for the water and sediment samples. No significant risk to *D. magna* (ΣRQs <1) was observed for any of the monitored rivers.

1. Introduction

Flame retardants are chemical substances incorporated to different materials to inhibit or slow down the growth of fire. The use of these substances has proved to be effective for saving lives and preventing injuries and property losses (EFRA, 2005). Despite these benefits, many flame retardants are toxic and potentially harmful to human health and the environment. In this context, polybrominated diphenyl ethers (PBDEs) are developmental neurotoxicants, potential endocrine disruptors (Costa et al., 2008) and bioaccumulate in biota (Wu et al., 2012). Owing to these toxic properties, PBDEs were banned in Europe (ECJ, 2008; OJEU, 2003) and are regulated by EU Water Framework Directive (OJEU, 2008). Because of these bans, PBDEs have been substituted by other compounds, such as new brominated flame retardants (NBFRs) and organophosphorus flame retardants (OPFRs) (Covaci et al., 2011; van der Veen and de Boer, 2012). These compounds are considered as emergent pollutants since they have been detected in all environmental compartments and many of them have toxic properties.

Industrial and Wastewater Treatment Plant (WWTP) discharges (Eljarrat et al., 2007; Meyer and Bester, 2004; Ricklund et al., 2009), releases from materials (Birgul et al., 2012; Brommer et al., 2012), atmospheric deposition (Melymuk et al., 2011; Regnery and Püttmann, 2010a) and runoff (Regnery and Püttmann, 2010b) are indicated as a source of flame retardants to the environment. Consequently, several flame retardants are expected to co-occur in the aquatic environment, and their relative concentration in water or sediment will depend on their production/use/discharge, their persistence and partition properties.

Few studies are available concerning the presence of PBDEs, NBFRs and OPFRs in rivers. Due to their lipophilicity, ΣPBDEs were detected in sediment from 3.67 to 2520 μg kg^{-1} and ΣNBFR ranged from 0.22 to 5270 μg kg^{-1} in the Pearl River Delta (China) (Chen et al., 2013). PBDEs have been also detected in the River Aire (UK) waters, reaching concentrations of 0.295 μg L^{-1} (only BDE-209 detected) (Cristale et al., 2013). Maximum ΣPBDEs were of 0.0043 μg L^{-1} in the River Prédecelle (France) (Labadie et al., 2010). OPFRs are reported as ubiquitous contaminants in river water, present at ng–μg L^{-1} levels (Cristale et al., 2013; Martínez-Carballo et al., 2007; Regnery and Püttmann, 2010a; Rodil et al., 2012). In addition, OPFRs were also detected in river sediments, reaching concentrations of 1300 μg kg^{-1} in the River Schwechat (Austria) (Martínez-Carballo et al., 2007).

---

* Corresponding author. Tel.: +34 934006133; fax: +34 932045904.
E-mail address: slbqam@cid.csic.es (S. Lacorte).

[1] Present address: Dept. of Analytical Chemistry and Organic Chemistry, Universitat Rovira i Virgili, Marcel.li Domingo s/n, 43007, Tarragona, Catalonia, Spain.

0160-4120/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envint.2013.06.011

However, mere knowledge of pollutant concentration has only limited use, unless such data can be related to the assessment of ecological risk (Wu et al., 2008). Various tools can be used for ecological risk assessment and frequently correlate environmental concentrations (either measured environmental concentrations — MEC, or predicted environmental concentration — PEC) to a predicted no effect concentration (PNEC), that is derived from toxicological data (EC, 2003). *Daphnia magna* acute toxicity (LC_{50} or EC_{50}) is commonly used to assess the risk of a particular chemical to freshwater aquatic environment (Verbruggen et al., 2005). Nevertheless, most of the ecotoxicological studies focus on individual substances, and the effect of pollutant mixtures has not received the appropriate attention. Joint toxicity of chemicals at low concentrations can produce significant effects in mixtures (Backhaus et al., 2011; Barata et al., 2007; Payne et al., 2001; Silva et al., 2002). For this reason, combined effects have to be considered for risk assessment and water quality criteria establishment.

The objective of this study was to increase the knowledge about the presence, partitioning, and toxic effect of mixtures of flame retardants (priority and emerging) in river environment. For this purpose, water and sediment collected from source to mouth of three Spanish rivers receiving different pressures (mining, agricultural, industrial, urban) were monitored to determine the impact of a large number of flame retardants. In addition, the most ubiquitous compounds were tested for *D. magna* acute toxicity assays, and the joint effect of mixtures was studied. These results were finally applied to assess the risk of flame retardants for aquatic organisms in rivers with different pressures and anthropogenic impacts.

2. Materials and methods

2.1. Samples

One liter of water and approximately 0.5 kg of surface sediment were collected from the source to mouth in the Spanish rivers Arga (Navarra), Nalón (Asturias) and Besòs (Catalonia) during spring 2012. The source of these rivers is located in mountainous areas, generally in Natural Parks with minor human activities, and their flow through industrial, agricultural and urban areas affects water quality, which highly depends on the geographic and climatologic conditions of each basin. Fig. 1 presents the sampled points in each studied river. Industrial and urban zones, WWTPs and protected natural areas are indicated.

The source of the River Nalón (Asturias, NW Spain) is located at the "Fuente La Nalona" in "Puerto de Tarna" at 1500 m (asl) and within the Natural Park of Redes, far from anthropogenic impacts. Nalón length is of 153 km and flows to Cantabrian Sea forming the Ria de Pravia. The river basin is 3692 km^2, with an average flow of 55.18 $m^3\ s^{-1}$, although the annual maximum is of 1250 $m^3\ s^{-1}$ and the minimum of 3.4 $m^3\ s^{-1}$ (CHCANTABRICO, 2013). The use of water is evident from the source of the river. Upstream, there is a drinking water treatment plant supplying the whole community, an aquaculture factory and several hydroelectric plants. In the middle course, there is a large pharmaceutical factory. Multiple carbon mines, that historically have used Nalón's waters until their almost complete closure just recently, are spread over the basin.

The second river studied is the Arga (Navarra, N Spain), whose source is located at the Urquiaga Hill, in the north of Erro Valley, crosses Pamplona and flows into the River Aragón near Funes, which is a tributary of the River Ebro. Arga length is approximately 150 km, the river basin is 2730 km^2, with an annual average flow of 53.50 $m^3\ s^{-1}$ (CHEBRO, 2013). The river is dammed in the Eugui reservoir, close to the source, that supplies water to the Pamplona metropolitan area. Close to the city of Pamplona, the Arga receives urban wastewaters and effluents from industrial installations with metal and car factories. Through its course to the river Aragón, the basin is highly agricultural, with 275.218 ha of crops including cereals, potatoes, tobacco, beans, asparagus, fruit trees, vegetables and wines, among other less important.

The last river studied is the Besòs (Catalonia, NE Spain), a river with Mediterranean regimen highly affected by high population density. The source of the River Besòs is located in the Natural Park of Montseny, and the Besòs is formed after the confluence of rivers Congost and Mogent. The rivers Caldes, Ripoll and Tenes flow into Besòs. The Besòs discharges into the Mediterranean Sea in "Sant Adrià de Besòs" city. Besòs length is 18.4 km, the river basin is 1026 km^2 (including all the rivers) and its volume is very irregular throughout the year (average flow 4.12 $m^3\ s^{-1}$) (ACA, 2013). The historical agricultural activity carried out in this relatively small area has been totally substituted by industry, with involvement of all sectors, specifically the chemical, metallurgic, plastic, tanneries, textile, construction materials, paper, and food, with almost 10,000 factories potentially contaminating. Besides, the area is surrounded by highways. The Besòs basin is the most densely populated in Catalonia, with more than 2 million inhabitants.

2.2. Chemicals

A solution mixture of BDEs 28, 47, 99, 100, 153, 154, 183 and 209 in n-nonane at 1 μg mL^{-1} was acquired from Cambridge Isotope Laboratories (Andover, USA). Individual solution of 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) at 50 μg mL^{-1} in 5% toluene in nonane, decabromodiphenyl ethane (DBDPE) at 25 μg mL^{-1} in toluene, bis(2-ethyl-1-hexyl)tetrabromo phthalate (BEHTBP), pentabromotoluene (PBT), 2,3-dibromopropyl 2,4,6-tribromophenyl ether (DPTE), hexachloro cyclopentadienyl dibromooctane (HCDBCO) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB) (at 50 μg mL^{-1} in toluene) were acquired from Wellington Laboratories (Guelph, Canada). Pure standards of hexabromobenzene (HBB), pentabromoethylbenzene (PBEB), tris(2-choroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP), tris[2-chloro-1-(chloromethyl)ethyl] phosphate (TDCP), triphenyl phosphate (TPhP), 2-ethylhexyl diphenyl phosphate (EHDP) and tributyl phosphate (TBP) were acquired from Sigma Aldrich (Germany). TCPP was acquired as a mixture of isomers (tris(2-chloro-1-methylethyl) phosphate, bis(1-chloro-2-propyl)-2-chloropropyl phosphate, and bis(2-chloropropyl)-1-chloro-2-propyl phosphate). Tris(2-butoxyethyl) phosphate (TBEP), tris(2-ethylhexyl) phosphate (TEHP) and tricresyl phosphate (TCP) were acquired as pure standards from Dr. Ehrenstorfer (Augsburg, Germany). Tri-iso-butyl phosphate (TiBP) at 1000 μg mL^{-1} was acquired from Chiron (Trondheim, Norway).

The surrogates [$^{13}C_6$]hexabromobenzene (MHBB) at 50 μg mL^{-1} in toluene, 3,3′,4,4′-tetrabromo[$^{13}C_{12}$]diphenyl ether (MBDE-77) at 50 μg mL^{-1} in nonane and decabromo[$^{13}C_{12}$]diphenyl ether (MBDE-209) at 25 μg mL^{-1} in toluene, were acquired from Wellington Laboratories (Guelph, Canada). Solid standard of triphenyl phosphate-D15 (TPhP-D15) was acquired from Sigma Aldrich (Germany). Tributyl phosphate-D27 (TBP-D27) as pure standard was acquired from Cambridge Isotope Laboratories (Andover, USA). The internal standards 2,3,5,6-tetrachlorobiphenyl (PCB-65) and decachlorobiphenyl (PCB-209), both at 10 μg mL^{-1} in iso-octane, were acquired from Dr. Ehrenstorfer (Augsburg, Germany). Acetone, hexane, methanol, dichloromethane, ethyl acetate and toluene were acquired from Merck (Darmstadt, Germany). Cyclohexane was acquired from PANREAC (Castellar del Vallès, Spain).

2.3. Extraction and analysis

Extraction methods for waters and sediments were described in detail in previous studies (Cristale and Lacorte, in press; Cristale et al., 2013). For water samples, a volume of 500 mL of unfiltered water was spiked with labeled surrogate standards (100 ng of TPhP-D15, TBP-D27 and MBDE 209; 25 ng of MHBB and MBDE 77) and was extracted using OASIS HLB 200 mg cartridges (WATERS, USA). The cartridges were conditioned with 15 mL of hexane followed by 15 mL of dichloromethane, 15 mL of methanol and