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Tracing organophosphorus and brominated flame retardants and plasticizers in an estuarine food web

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HIGHLIGHTS

- Nine PFRs were detected in the Dutch estuarine food webs of the Western Scheldt.
- Concentrations of several PFRs were an order of magnitude higher than those of PBDEs.
- Trophic magnification was observed for all PBDEs with the exception of BDE209.
- Tentative TMFs >1 were observed in the benthic food web for TBOEP, TCIPP and TCEP.

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ABSTRACT

Nine organophosphorus flame retardants (PFRs) were detected in a pelagic and benthic food web of the Western Scheldt estuary, The Netherlands. Concentrations of several PFRs were an order of magnitude higher than those of the brominated flame retardants (BFRs). However, the detection frequency of the PFRs (6–56%) was lower than that of the BFRs (50–97%). Tris(2-butoxyethyl) phosphate (TBOEP), tris(isobutyl) phosphate (TIBP) and tris(2-chloroisopropyl) phosphate (TCIPP) were the dominant PFRs in sediment with median concentrations of 7.0, 8.1 and 1.8 ng/g dry weight (dw), respectively. PFR levels in the suspended particular matter (SPM) were 2–12 times higher than that in sediment.

TBOEP, TCIPP, TIBP, tris(2-chloroethyl) phosphate (TCEP) and tris(phenyl) phosphate (TPHP) were found in organisms higher in the estuarine food web. The highest PFR concentrations in the benthic food web were found in sculpin, goby and lugworm with median concentrations of 17, 7.4, 4.6 and 2.0 ng/g wet weight (ww) for TBOEP, TIBP, TCIPP and TPHP, respectively. Comparable levels were observed in the pelagic food web, BDE209 was the predominant PBDE in sediment and SPM with median concentrations up to 9.7 and 385 ng/g dw, respectively. BDE47 was predominant in the biotic compartment of the food web with highest median levels observed in sculpin and common tern eggs of 79 ng/g lipid weight (lw) (2.5 ng/g ww) and 80 ng/g lw (11 ng/g ww), respectively. Trophic magnification was observed for all PBDEs with the exception of BDE209. Indications of trophic magnification of PFRs were observed in the benthic food web for TBOEP, TCIPP and TCEP with tentative trophic magnification factors of 3.5, 2.2 and 2.6, respectively ($p < 0.05$). Most of the other PFRs showed trophic dilution in both food webs. The relative high PFR levels in several fish species suggest high emissions and substantial exposure of organisms to PFRs in the Western Scheldt.

1. Introduction

During the last decades many studies have reported the presence of brominated flame retardants (BFRs) like polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) in the environment (De Wit, 2002; R.J. Law et al., 2006; De Boer et al., 1998). Some of these BFRs are considered to be toxic, persistent and accumulate in the food chain. New legislation led to a ban of the commercial BFR mixtures, Penta-BDE and Octa-BDE and restrictions on Deca-BDE. Modern fire safety standards still require the presence of FRs in many products. The ban and restriction on the commercial BDE mixtures have led to an increase in the production and use of alternative flame retardants (FRs). Many of these alternative FRs contain bromine, e.g. decabromodiphenylethane (DBDPE) and 1,2-bis-(2,4,6-tribromophenoxy)ethane (BTBPE) as alternatives for Deca-BDE and Octa-BDE, respectively. Also, Firemaster 550 which contains a mixture of bis(2-ethylhexyl) 2,3,4,5-tetrabromophthalate (BEH-TEBP) and 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB) is used as alternative for the replacement of Penta-BDE in polyurethane foam (PUF) (Stapleton et al., 2009). Another group of alternative FRs is the organophosphorus flame retardants (PFRs) (Van der Veen and De Boer, 2012). In 2012 the global consumption of FRs was 1.8 million tonnes, which is

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expected to grow 5% each year for the coming 5 years with the highest growth for the PFRs (BCC research, 2013). The total consumption of FRs in Europe in 2006 was 565,000 tonnes, of which 20% were PFRs and 10% BFRs (Van der Veen and De Boer, 2012). Organophosphorus compounds that are used as FRs are also used as plasticizers, and anti-foaming agents in various products such as upholstered furniture, plastics, textile, electronics, lacquers, floor finishing products, construction and isolation materials (Marklund et al., 2003; Van der Veen and De Boer, 2012). PFRs are ubiquitously detected in house dust with concentrations in the μg/g ranges (Brandsma et al., 2014). This indicates that PFRs leach from various products into the environment. PFRs have been detected in surface-water, influents, effluents, sewage sludge, sediment and soil (Reemstra et al., 2008; Fries and Püttmann, 2001; Mihajlović et al., 2011; Martínez-Carballo et al., 2007; Meyer and Bester, 2004; Marklund et al., 2005). The structural differences among PFRs lead to a variety of chemical and physical properties within this class. The log K_{ow} ranges from 1.44 for tris(2-chloroethyl) phosphate (TCEP) to 9.49 for tris(2-ethylhexyl) phosphate (TEHP) (Reemstra et al., 2008). Some PFRs are volatile and dominate in the air phase, while others are water soluble or sorb strongly to particulate matter (Reemstra et al., 2008). The structural differences also influence the persistence of the various PFRs in the environment. Chlorinated PFRs are more resistant to biodegradation than the alkyl and aryl phosphates (WHO, 1998, 2000; Reemstra et al., 2008). The chlorinated PFRs TCEP, tris(2-chloroisopropyl) phosphate (TCIPP) and tris(1,3-dichloroisopropyl) phosphate (TDCIPP) are particularly poorly removed by waste water treatment plants (WWTPs) (Martínez-Carballo et al., 2007; Meyer and Bester, 2004; Marklund et al., 2005).

Toxicity data on PFRs is still limited. The chlorinated PFRs like TCEP and TDCIPP were proven to be neurotoxic and carcinogenic (Van der Veen and De Boer, 2012). TCIPP is suspected to be carcinogenic (Van der Veen and De Boer, 2012; WHO, 1998, 2000). The non-chlorinated tris(2-butoxyethyl) phosphate (TBOEP) is possibly carcinogenic and ortho-tris(methylphenyl) phosphate (TMPP) (or ortho-TCP) is neurotoxic (WHO, 2000; Van der Veen and De Boer, 2012). Tris(phenyl) phosphate (TPHP) is acutely toxic to water organisms and tris(butyl) phosphate (TNBP) was associated with the sick-building-syndrome (Van der Veen and de Boer, 2012; Kanazawa et al., 2010). Recently, effects on the neurodevelopment in PC12 cell studies were observed for TCEP, TCIPP and TDCIPP (Dishaw et al., 2011). In in vitro tests using human nuclear receptors, Kojima et al. (2013) observed that several PFRs may have potential endocrine disrupting effects. Consequently, the EU Directive (2014/81/EU) introduced specific limit values (5 mg/kg) for TCEP, TCIPP and TDCIPP in certain toys, which shall be applied on 21 December 2015 (Directive 2014/81/EU).

Very limited information is available on the occurrence of PFRs in biota. Total PFR concentrations of >1000 ng/g lipid weight (lw) have been observed in marine and freshwater biota from Swedish lakes and in different fish species from Manila Bay (Philippines) (Sundkvist et al., 2010; Kim et al., 2011). Lower amounts of PFRs were detected in herring gull eggs from the Great Lakes (Chen et al., 2012), an order of magnitude lower than in fish from the Swedish lakes and from the Philippines.

The objective of the present study was to investigate the trophic magnification of a number of PFRs and BFRs (PBDEs and HBCDs) in a pelagic and a benthic food web in the Western Scheldt estuary in the Netherlands. To facilitate this study, a fast analytical method was developed to analyze ten PFRs with LC–MS/MS in biota and sediment samples.

2. Materials and methods

2.1. Materials

The solvents and chemicals used were all pro-analysis quality or HPLC grade, unless otherwise stated. Hexane, isooctane, HPLC water, acetone, dichloromethane (DCM), methanol and acetonitrile (ACN) used for the extraction and cleanup were from Promochem (Wesel, Germany). Formic acid (98%) was obtained from Merck (Darmstadt, Germany). TCEP, TDCIPP, TPHP, TMPP, TNBP, EHDPP, TEHP and TBOEP were supplied by Sigma-Aldrich Chemie B.V. (Zwijndrecht, the Netherlands). TIBP was supplied by Merck (Darmstadt, Germany) and TCIPP from Ehrenstorfer (Augsburg, Germany). The internal standards TPHP-$_{d15}$ and TNBP-$_{d27}$ were supplied by Sigma-Aldrich Chemie B.V. (Zwijndrecht, the Netherlands) and Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). Native and mass labeled ($^{13}C_{12}$) α-, β-, and γ-HBCDs, ($^{13}C_{12}$) decabromodiphenyl ether (^{13}C-BDE209) and the PDBE congeners were purchased as a mixture (BDE–MXE) from Wellington Laboratories (Guelph, Ontario, Canada).

2.2. Sample collection

The Western Scheldt estuary, situated in the south of the Netherlands was selected as the sampling location (Fig. S1). The Western Scheldt is well-studied in terms of national water monitoring programs and surveys (Holierhoek et al., 2008) and many industries (e.g. textiles, BFR manufacturing) are located in this estuary as well as further upstream on the Scheldt River in Belgium. The Western Scheldt is also an important shipping lane to Antwerp Harbor in Belgium. While many different chemicals including BFRs have been reported in different compartments of the Western Scheldt ecosystem (De Boer et al., 2003; Covaci et al., 2005; Lopez et al., 2011), PFRs have not yet been studied in this area. Samples were collected in September 2008 in cooperation with colleagues from Deltares (Delft, the Netherlands), Grontmij (the Netherlands) and local fishermen. Sample information including lipid and total organic carbon (TOC) contents, dry weights and trophic levels is given in the Supporting information Table S1. Samples were collected both from the pelagic and benthic food webs, ensuring that the food chains are as long as possible (Table S1). The samples collected were the main species present in this area, which has been studied for many years. More detailed information on the food chains and relationships between the organisms can be found in Veltman et al. (2005). For the benthic aquatic food web macro-invertebrates (lug worms, rag worms) were collected from the mudflat. With nets various invertebrate species were collected: cockles, shore crabs and common shrimp (also called brown or sand shrimp). Benthic fish species included sculpin, plaice, goby, and sole. Mysis (zooplankton) were sampled and these organisms are a key link between the benthic and pelagic food chains. For the pelagic food web suspended matter/algae, jellyfish, and planktivorous fish (European sprat, herring, sandeel) were collected. In addition, a terrestrial piscivorous bird species (common tern), mainly feeding on herring and sprat, was sampled to provide information on the bioaccumulation from the aquatic to the terrestrial environment. The link with the terrestrial food chain is provided by the tern eggs from the colony feeding in the study area (n = 5). Samples were combined on board, directly frozen with dry ice and transported to the laboratory and finally stored at −20 °C. Samples were pooled on size and length. For some fish species different length classes were made. The organisms were not depurated because in trophic magnification studies it is a general practice not to depurate as the aim is to investigate the transfer of contaminates along the food chain (K. Law et al., 2006; Wu et al., 2009; Yu et al., 2009; Losada et al., 2009; Van Ael et al., 2012; Ma et al., 2013). In that case the intake is the whole organism including sediment particles, which are also a source of contaminants. The use of whole organisms without depuration could lead to elevated levels. However, we investigated the levels of PBDEs in lugworm which were depurated and not depurated (data not shown). These results showed similar levels of PBDEs between the two groups, except for BDE209, which was 3 times higher in the lugworm that was not depurated.