



Organophosphorus flame retardants and plasticizers in the aquatic environment: A case study of the Elbe River, Germany



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ABSTRACT

This study reports the occurrence and distribution of organophosphorus flame retardants and plasticizers (OPEs) in the Elbe and Rhine rivers. A special focus of this investigation concerns the potential impacts of a major flood event in 2013 on the OPE patterns and levels in the Elbe River. In this river, 6 of 13 OPEs were detected, with tris-ethyl-phosphate (TEP, 168 ± 44 ng/L), tris-1,3-dichloro-2-propyl-phosphate (TDCPP, 155 ± 14 ng/L) and tris-1-chloro-2-propyl phosphate (TCPP, 126 ± 14 ng/L) identified as the dominant compounds. Relative to previous studies, an increase in the concentrations and relative contributions of TDCPP to the total level of OPEs was observed, which was likely caused by its increased use as a replacement for the technical pentaBDE formulation. During the flood event, the concentrations of OPEs were similar to the normal situation, but the mass fluxes increased by a factor of approximately ten (~ 16 kg/d normal versus ~ 160 kg/d flood peak). No input hotspots were identified along the transects of the Elbe and Rhine rivers, and the mass flux of OPEs appeared to be driven by water discharge.

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1. Introduction

Organic flame retardants have been used for decades to reduce the flammability of polymer-based industrial and consumer products. In addition to classic brominated flame retardants such as polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCDD) and organophosphorus esters (OPEs) have been used. The restrictions and phasing out of PBDEs since the early 2000s (viz. the Stockholm convention of 2009) have led to an increase in the production and use of OPEs over the past few years (Reemtsma et al., 2008). Because of their historical use and their growing economic importance since the ban of PBDEs, OPEs are often described as re-emerging chemicals (Reemtsma et al., 2008). OPEs are high production chemicals, with a global annual production in 2004 of 207,200 t (EFRA - Cefic, 2007). In general, these chemicals are applied as additives; yet, their specific application varies widely between the different OPE classes. Chlorinated OPEs are mainly used as flame retardants, whereas non-chlorinated OPEs are also applied as plasticizers, antifoaming agents and additives in hydraulic fluids (Marklund et al., 2003). OPEs are applied in textiles, plastics and furniture.

Similar to other additives, OPEs are not chemically bound to the material and can therefore easily migrate to the environment via diffusion and leaching processes. As a result, OPEs have been frequently detected in the environment and are ubiquitously present in all environmental compartments.

Halogenated OPEs have been shown to be persistent towards biodegradation (Kawagoshi et al., 2002; Meyer and Bester, 2004), whereas the persistence of non-halogenated OPEs has been shown to increase with alkyl chain length (Saeger et al., 1979). Laboratory studies have shown that the majority of OPEs are moderately persistent in the environment. However, because of their considerable application and subsequent environmental input, especially into aquatic environments, OPEs are often considered to be pseudo persistent contaminants (EPA, 2014; Waaijers et al., 2013). Additionally, increasing amounts of OPEs have been detected in remote areas (Möller et al., 2012; Salamova et al., 2014) such as the Arctic and Antarctic, which makes the task of gathering the necessary data to evaluate their persistence in these environments challenging.

High loads of dissolved OPEs have been reported in water. The concentrations of OPEs were the highest in rivers (up to several hundred ng/L) (Bacaloni et al., 2007; Bollmann et al., 2012; Fries and Püttmann, 2003; Rodil et al., 2009), followed by groundwater (up to 4 ng/L) (Fries and Püttmann, 2003) and seawater (below the

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ng/L range) (Andresen et al., 2007; Bollmann et al., 2012). The retention capacity in waste water treatment plants for OPEs has been shown to be insufficient, which has resulted in high loads of OPEs to be present in discharges and rivers (Cristale et al., 2013).

Several OPEs have known or suspected adverse health effects including skin irritation, carcinogenicity, dermatitis and neurotoxicity (Camarasa and Serra-Baldrich, 1992; Matthews, 1993; Nakamura, 1991a, 1991b; Sato et al., 1997; World Health Organization, 1998). As a result, the carcinogen TCEP (tris(2-chloroethyl)phosphate) was largely removed from use and replaced by TCPP (tris(1-chloro-2-propyl) phosphate) and TDCPP (tris(1,3-dichloro-2-propyl) phosphate). However, the production of TCEP is not prohibited (European Commission - Scientific Committee on Health and Environmental Risks, 2012).

This study focused on the patterns and behavior of OPEs in the Elbe River and its tributaries Havel, Mulde and Saale. The aim was to investigate the occurrence and distribution of OPEs along the German part of the river and to identify the major sources of contamination. The results were compared with the results from samples taken during a historically severe flood event in the summer of 2013 at the barrage in Geesthacht. In this case the aim was to assess the possible impacts on the surrounding areas caused by this extreme event and to trace their sources. Questions we considered include, for example, whether it is possible to identify unique signals from overloaded waste water treatment plants, flooded cities or agricultural areas.

Finally, the OPE contamination of the Elbe River was compared with the levels of contamination in the Rhine and Ems rivers to investigate the regional differences of OPE concentrations and patterns.

2. Material and methods

2.1. Chemicals

Information on CAS-No., abbreviations, producers, and purity of the used OPE standards are listed in [Table S1 of the Supplementary Material](#). SERDOLITH PAD 2 and 3 (analytical grade) were purchased from Serva (Germany) and deionized water was supplied from a Milli-Q Integral 5 System (Germany). All solvents were of the highest purity (picograde) and were obtained from Promochem (Germany). Sodium sulfate (granular, anhydrous for organic trace analysis) was purchased from Merck (Germany).

2.2. Sampling

Surface water samples (at a water depth of >0.5 m to avoid the surface microlayer) were obtained with a stainless steel bucket and stored in pre-cleaned 1 L glass bottles. A total of 15 samples were taken from the Elbe River and its tributaries Havel, Mulde and Saale during a three-day ship-based sampling campaign in August 2013. During a parallel campaign (over 4 days), a total of 22 samples and 3 samples were taken along the riverbanks of the Rhine River and Ems River, respectively. For the ship-based campaign, a sampling route against the flow direction was chosen to avoid duplicate sampling of the same water masses. In addition, 25 samples were taken at the barrage in Geesthacht during the flood of the Elbe River in June 2013. The sampling points along the Elbe River during the flood event are shown in [Fig. 1](#). For comparison, the positions from Ems and Rhine rivers are presented in [S2 of the Supplementary Material](#).

2.3. Sample preparation

The extraction procedure was adapted from [Bollmann et al.](#),

2012. The analytical process was performed in a Varipro cleanroom (class 10,000, Daldropf, Dr. Ing. Huber, Neckartaltingen, Germany). All lab equipment was cleaned with acetone prior to use and/or baked for 12 h at 250°/450 °C. Sodium sulfate was cleaned by Soxhlet extraction with dichloromethane (DCM).

The use of OPE containing materials was avoided throughout the analytical process. To separate the particulate and dissolved phases, water samples were filtered with GF/C (Whatman) glass fiber filters. A volume of 500 mL of the filtrates was spiked with 20 ng of deuterated surrogate standards (TEP-d15, TPrP-d21, TCEP-d12, TBP-d27, TPhP-d15) and enriched on self-packed SPE cartridges with 0.5 g of SERDOLITH PAD III (particle size 0.1–0.2 mm) as the adsorption material. Before loading, the cartridges were cleaned and conditioned with 10 mL of DCM, 10 mL of methanol and 10 mL of pre-cleaned deionized water. After loading, the cartridges were washed with 5 mL of pre-cleaned deionized water and centrifuged to dryness (3000 rpm, 5 min). Target analytes were eluted with 5 × 10 mL of DCM. The extracts were then reduced in volume to 5–10 mL by rotary evaporation.

The dissolved phase from the samples from the Rhine and Ems rivers were extracted by liquid–liquid extraction (LLE) using 2 × 50 mL of DCM.

Filters were ultrasonic extracted (2 × 15 min) with 20 mL of DCM. The extracts were combined and reduced in volume to 5–10 mL by rotary evaporator.

For all samples, water was removed from the extracts by subsequent elution over a Na₂SO₄-column using DCM. Extracts were further reduced in volume to 150 µL under a gentle stream of nitrogen and the solvent was exchanged to n-hexane. Finally, 500 pg of ¹³C-PCB 141 and ¹³C-PCB 208 was added as the injection standard.

2.4. Instrumental analysis

Analysis was performed on an Agilent 7890 gas chromatograph coupled with an Agilent 7000B tandem mass spectrometer (GC-QQQ-MS/MS) using the electron ionization (EI) mode. The injection was performed using a PTV injector in the pulsed splitless mode. The initial temperature of the injector was held at 60 °C for 0.1 min and then increased at 500 °C/min to 300 °C. The injection volume was 2 µL and the helium carrier gas flow was 2.1 mL/min. The GC was fitted with an HP-5MS column (30 m, 0.25 mm i.d., 0.25 µm film thickness, J&W Scientific). The temperature program started at 40 °C for 4 min, increased at 5 °C/min to 170 °C (5 min), 10 °C/min to 230 °C (5 min), 5 °C/min to 250 °C and finally 10 °C/min to 300 °C. The MS transfer line and the ion source were held at 280 °C and 230 °C, respectively. The MS was operated in multiple reactions monitoring (MRM) mode. Mass transitions for all target analytes and surrogates are presented in [S3 of the Supplementary Material](#).

2.5. QA/QC

Because of the widespread presence of OPEs in a variety of laboratory equipment, the use of rubber and plastic materials was avoided to minimize blank contamination during the transport, storage and treatment of the samples. All glassware were cleaned prior to use by a laboratory dishwasher, baked at 250 °C and rinsed with acetone. Na₂SO₄ was cleaned by Soxhlet extraction with DCM for 12 h and baked at 450 °C. Glass columns were used as SPE cartridges and self-packed with pre-cleaned adsorbents. GFFs were baked for 12 h at 450 °C. Blank samples were analyzed with every batch of 5 samples. Detected blanks were at least one order of magnitude below the measured concentrations for all of the target compounds, except for TPhP. Absolute blank values ranged from 0.7 ± 0.2 ng for TEP to 12.4 ± 5.8 ng for TPhP for both the LLE and

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