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# Regional variations of organophosphorus flame retardants - Fingerprint of large river basin estuaries/deltas in Europe compared with China<sup>☆</sup>

Hendrik Wolschke<sup>a, b, \*</sup>, Roxana Sühring<sup>c</sup>, Riccardo Massei<sup>d, e</sup>, Jianhui Tang<sup>f</sup>, Ralf Ebinghaus<sup>a</sup>

<sup>a</sup> Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, Germany

<sup>b</sup> Leuphana Universität Lüneburg, Germany

<sup>c</sup> The Centre for Environment, Fisheries & Aquaculture Science (Cefas), UK

<sup>d</sup> Helmholtz Center for Environmental Research, Germany

<sup>e</sup> RWTH Aachen University, Germany

<sup>f</sup> Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, CAS, Yantai 264003, China

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## ABSTRACT

This study reports the occurrence and distribution of organophosphorus flame retardants and plasticizer (OPEs) in sediments of eight large river basin estuaries and deltas across Europe. A robust and sensitive OPE analysis method was developed through the application of an in-cell clean-up in an accelerated solvent extraction and the use of an GC-MSMS System for instrumental analyses. OPEs were detected in all sediment samples with sum concentrations of up to 181 ng g<sup>-1</sup> dw. A fingerprinting method was used to identify river specific pattern to compare river systems. The estuaries and deltas were chosen to have a conglomerate print of the whole river. The results are showing very similar OPE patterns across Europe with minor differences driven by local industrial input. The European estuary concentrations and patterns were compared with OPEs detected in the Xiaoqing River in China, as an example for a region with other production, usage and legislative regulations. The Chinese fingerprint differed significant from the overall European pattern.

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## 1. Introduction

Sediments provide important services in the estuarine ecosystem. They are habitats for a variety of species that form the basis for local food-webs (Kennish, 1992). Due to this importance and their place at the “start” of the food-web, sediments have often been discussed as starting point of bioaccumulation and magnification of lipophilic contaminants (Ernst et al., 1988; Kennish, 1992). Mid-to non-polar compounds adsorb to particles and are deposited on the sea floor (Ernst et al., 1988) where they can be immobilized and stored or enter the food-web. Therefore, sediments can be function as sink but also as a secondary source for contaminants

(Laane et al., 2013).

Organophosphate esters (OPEs) are widely used as flame retardant and plasticizers in a variety of products such as electronic equipment, furniture, textiles, isolation material and wires (Muir, 1984). Additionally, they are used in up to 15% (by weight) as additives in hydraulic fluids, lubricants and antifoaming agents (Hartmann et al., 2004). With the restriction of polybrominated diphenylethers (PBDEs), organophosphate based flame retardants have become a focus for the polymer industry (van der Veen and Boer, 2012). A result of that is a strong increasing of the production and consumption of OPEs as flame retardants on the global market (van der Veen and Boer, 2012; Wang et al., 2010).

OPEs are primarily used additively in products, which mean they are not chemical bound to the product, which aids the leach-out into the environment (Staaf and Östman, 2005). Risk assessments of several, especially chlorinated, OPEs have shown a potential for carcinogenic effects, acute toxicity as well as high environmental persistence (Reemtsma et al., 2008; Waaijers and

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\* Corresponding author. Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, Germany.

E-mail address: [hendrik.wolschke@hzg.de](mailto:hendrik.wolschke@hzg.de) (H. Wolschke).

Parsons, 2016; Wang et al., 2015). OPEs primarily enter the aquatic environment through atmospheric deposition and leaching from waste water treatment, from where they can be transported into marine areas (Bollmann et al., 2012; Wolschke et al., 2015). Some OPEs travel in part attached to particles (Wolschke et al., 2016; Sührling et al., 2016b) which allows for sinking and accumulating in sediments (Giulivo et al., 2017). Based on their physical-chemical properties, especially the longer chained and the chlorinated OPEs have the potential to accumulate in sediments (Zhang et al., 2016; Sührling et al., 2016b). However, the occurrence and distribution of organophosphate flame retardants in sediments is still not sufficiently understood. The presented study focused on the accumulation of OPE sediments from seven major European estuaries. Estuaries were chosen as study areas because they represent a conglomeration over the whole river and allow fingerprinting of the river contamination profile. At the same time estuaries are very specific unique ecosystems which have to handle the fluctuating salinity gradients with moving turbidity and nutrient conditions (Martin and Brun-Cottan, 1988).

In this study, we compared eight European river basins to identify contamination levels and river specific patterns across Europe. Europe has relatively limited production of OPEs and has strict environmental legislations that prevent the production or use of particularly hazardous OPEs (European Commission, 2014). To compare the contamination with a different catchment area and legislative regulation, sediments samples from an estuary in north east China were analyzed.

## 2. Materials and methods

### 2.1. Sample collection

29 surface sediment samples were collected from eight large estuaries and delta in Europe. The samples were collected from 2013 to 2015 by stainless steel grab sampler from ship or from shore at low tide. The sediment samples were stored at  $-20^{\circ}\text{C}$  prior to analysis. Sampling sites are shown in Fig. 1. From the Xiaoking River in China 5 samples were collected in 2014.

A full list of the sampling sites is presented in the Supplementary Information (Si) Table S1.

### 2.2. Sample preparation

The extraction and clean-up were adapted from a method

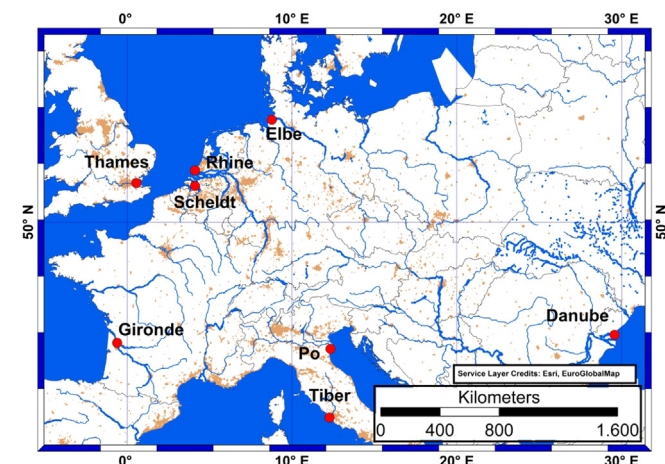


Fig. 1. European sampling sites.

presented by Sührling et al. (2016a). Larger pieces ( $>2\text{ mm}$ ) were removed by hand from the sediment samples. The samples were homogenized with anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) using an agate mortar. The samples were extracted using accelerated solvent extraction (Thermo Fisher ASE-350) with an in-cell clean-up (Sührling et al., 2016a). 22 mL stainless steel ASE cells were filled with 7 g 10% deactivated silica gel, 2 g activated Copper and 5–15 g dried sediment. All samples were spiked with mass labelled surrogate standards TCEP-d12, TBP-d27, TPHP-d15.

The cells were extracted sequentially in two fractions. The first fraction was extraction with following parameters: 2 cycles, hexane as solvent, pressure (nitrogen): 9 bar, temperature:  $100^{\circ}\text{C}$ , pressure: 120 bar, heat: 5 min, static (2x): 8 min, flush: 100%, purge: 60 s. The second fraction was extracted using the same conditions with 90:10 Dichloromethane:Acetone as solvent. This second fraction (containing the OPEs), was reduced in volume and subjected to a further clean-up by a 2.5 g 10% water deactivated silica gel column. For elution 20 mL of acetone/DCM (1:1 v/v) were used and the sample reduced to a volume of  $150\ \mu\text{L}$  under a gentle stream of heated nitrogen ( $40^{\circ}\text{C}$ ). Finally, 500 pg (absolute)  $^{13}\text{C}$ -PCB-141 and  $^{13}\text{C}$ -PCB-208 were added as injection standards to each sample. Recoveries of deuterated standards, extraction efficiency, blanks and reproducibility were tested with and without matrix, during method validation. All samples were analyzed in duplicates.

Separate sample aliquots were dried to constant weight (at  $105^{\circ}\text{C}$ ) for the gravimetric determination of water content as well as the subsequent analysis of total organic carbon (TOC). TOC was measured using a LECO RC612 multiphase carbon/hydrogen/moisture determinator combustion method at  $400^{\circ}\text{C}$ .

### 2.3. Instrumental analysis

The samples were analyzed on a GC-MS/MS system (Agilent 7010) in electron impact ionization mode (EI) equipped with two DB-35MS columns ( $15\text{ m} \times 0.25\text{ mm i.d.} \times 0.25\ \mu\text{m}$  film thickness, J&W Scientific) connected to a purge unit for backflush after each run. The injector was operated in pulsed-splitless mode (injection pulse 20 psi for 2 min) with an inlet temperature program as follows:  $60^{\circ}\text{C}$  for 0.1 min and  $300^{\circ}\text{C min}^{-1}$  until  $300^{\circ}\text{C}$  and held for a final 20 min. The GC oven program was as follows: initial  $60^{\circ}\text{C}$  for 4 min,  $25^{\circ}\text{C min}^{-1}$  until  $100^{\circ}\text{C}$ ,  $7^{\circ}\text{C min}^{-1}$  until  $310^{\circ}\text{C}$  and held for 1 min. The backflush was performed at 310 min with a flow of  $1.5\text{ mL min}^{-1}$  at the first column for 5 min. The temperature of the MS transfer line was held at  $280^{\circ}\text{C}$ . The ion source and quadrupole temperatures were  $150^{\circ}\text{C}$ .

A list of the mass transitions used for quantitative analysis are provided in Table S2.

### 2.4. Quality assurance and quality control (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 was cleaned prior to use by a laboratory dishwasher, baked at  $250^{\circ}\text{C}$  and rinsed with acetone.  $\text{Na}_2\text{SO}_4$  was cleaned by Soxhlet extraction with DCM for 12 h and baked at  $450^{\circ}\text{C}$ . Blank samples were analyzed with every batch of 10 samples. Detected blanks were at least one order of magnitude below the measured concentrations for all of the target compounds. Absolute blank values ranged from  $0.1 \pm 0.02\text{ ng}$  for TiBP to  $0.5 \pm 0.15\text{ ng}$  for TCPP for the whole method. Method detection limits (MDLs) were derived from either the mean blank values plus three times the standard deviation or at a signal-to-noise ratio of 3 ( $S/N = 3$ ), whichever approach yielded the higher

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