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Occurrence and distribution of organophosphorus flame retardants and plasticisers in the coastal environment

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Abstract

Organophosphorus flame retardants and plasticizers (OPEs) have been utilized for decades as plasticizers and, to a lesser extent, as flame retardants in various consumer products to improve their material properties. With the restriction and ban of the widely used brominated diphenyl ethers (PBDEs) by, ultimately, the Stockholm Convention due to their adverse effects on humans and the environment, the use of OPEs as replacements has increased rapidly. However, the potential adverse properties, environmental distribution and fate of OPEs are insufficiently understood.

The research presented in this thesis investigated the occurrence, distribution and transport of OPEs with a focus on the coastal and estuarine environment. Due to the wide range of physico-chemical properties of OPEs, the environmental fate and behaviour of OPEs was investigated over a range of compartments, starting from the atmospheric occurrence to the aquatic phase and the behaviour in sediments. The aim was to gather information on the OPE contamination situation in the coastal and estuarine environments, to identify specific contamination patterns for source assessment and to investigate the distribution behaviour of OPEs between gas- and particle-phases to evaluate their environmental transport mechanism. To achieve these scientific goals, sensitive and robust chemical analytical methods for the detection and quantification of OPEs in a variety of environmental samples using gas-chromatography coupled with tandem mass spectrometry were developed.

Water samples were removed along the Elbe and Rhine Rivers to test the hypothesis of whether specific point sources, such as wastewater treatment plants, are the major input pathways for OPE contamination in rivers. A total of 65 water samples, including an intensive measurement campaign during the flood event in 2013 at the Elbe, was taken and analysed for OPEs. No obvious point sources were identified along either of the rivers analysed. No significant increase or decrease in the OPE concentrations or a change in patterns were observed over a transect of over 300 km at the Elbe, with an increase in water discharge of 2.5. This finding suggested that the OPE input in large rivers is primarily driven by diffuse sources, such as surface runoff, or by minor point sources rather than local point sources.

To examine the specific pattern of OPE contamination in individual rivers and estuaries, 37 sediment samples from 8 rivers in Europe and China were analysed. With this analytical data, a fingerprint analysis of the OPE patterns identified could be conducted. All the rivers investigated in Europe displayed a very similar fingerprint, which can be explained by the common European market with consistent legislative regulations. In contrast, the fingerprint from China differed

significantly from the one in Europe. For example, in China, the OPE restricted in Europe, Tris(2-chloroethly)phosphate, was found to be one of the major OPE components, while Tris(2-butoxyethyl) phosphate, a major compound in Europe, was negligible in China. The investigation showed that the fingerprinting analysis is a useful tool to identify different regions or characterize specific rivers regarding their OPE contamination. In addition, it could be shown that legislative restriction and processes have an impact on local or even EU-wide contamination patterns.

At a coastal site next to the German city of Büsum, 58 air samples were taken over one year. Using the newly developed analytical method, it was possible to analyse the gas, as well as the particle phase, of the samples collected with very low detection limits for OPEs. In contrast to expectations, no annual trend in OPE concentrations, phase distributions or patterns was observed, but the investigation of the phase distribution challenged the previous scientific consensus that OPEs occur as primarily bound to particles in the atmosphere. Several compounds were detected in significant amounts in the gas phase. To validate these novel results, a model analysis based on the chemical properties of OPEs was conducted using three different phase distribution models. The results from the environmental data were strongly supported by the simulations, and the formal knowledge could be refuted. Consequently, the atmospheric transport assumptions and estimations about the long-range transport of OPEs have to be reassessed because compounds in the gas phase undergo other types of transport degradation and elimination mechanisms than particle-bound ones.

The novel findings presented in this thesis challenged an important aspect regarding the perceived scientific knowledge about the behaviour of OPEs in the environment and call on the scientific community to reassess the environmental behaviour of OPEs. The insights presented on the patterns highlight the impact of environmental policies and regulatory mechanisms to work towards the final goal of a good environmental status and the avoidance of adverse effects of discarded chemicals on humans and the environment.

Zusammenfassung

Organophosphor Flammschutzmittel und Weichmacher (OPEs) wurden seit Dekaden als Weichmacher und in einem geringeren Maß auch als Flammschutzmittel in diversen Produkten eingesetzt um die Eigenschaften von Kunstoffen zu verbessern. Durch die Restriktionen und schlussendlich das Verbot durch die Stockholm Konvention der bromierten Diphenlyethern stieg der Einsatz von OPEs als Ersatzprodukt rasant an. Jedoch sind mögliche negative Umwelteigenschaften, das Verteilungs- und Depositionsverhalten bis heute nicht ausreichend erforscht und evaluiert.

Die in dieser Doktorarbeit präsentierten Ergebnisse untersuchen das Auftreten, Verhalten und den Transport von OPEs in der Umwelt, mit einem Fokus auf den Ästuarien- und Küstenbereich. Aufgrund der sehr unterschiedlichen physiko-chemischen Eigenschaften und der daraus resultierenden Möglichkeit in allen Umweltkompartimenten aufzutreten, wurde ein transversaler Schnitt von der Atmosphäre über die aquatische Umwelt bis hin zu den Sedimenten um Mündungsbereich untersucht. Ziel ist es, Informationen über die Kontaminationssituation zu sammeln, Verteilungsmuster für eine Quellenidentifikation zu spezifizieren und das Verteilungsverhalten zwischen Gas- und Partikelphase in der Atmosphäre für eine Evaluation des Transportverhaltens zu untersuchen. Um diese wissenschaftlichen Ziele zu erreichen, wurden mehrere sensitive und robuste chemisch analytische Methoden für Umweltproben entwickelt. Alle Methoden basieren auf deiner chemischen Aufarbeitung, sowie einer Instrumentellen Analyse mit einem Gas-Chromatographen gekoppelt mit einem Tandemassen-Spektrometer.

Um die Hypothese zu überprüfen, dass spezifische Punktquellen wie Kläranlagen, die Hauptquellen für die Kontamination von OPEs in Flusssystemen sind, wurden Längsprofile der Flüsse Elbe und Rhein aufgenommen. Insgesamt wurden hierfür 65 Wasserproben auf OPEs analysiert. Die Ergebnisse konnten keine Hauptquellen identifizieren. Auf dem 300 km langen untersuchten Abschnitt der Elbe steigt die Wasserfracht um das 2,5-fach an, jedoch bleiben sowohl die Konzentrationen als auch das Substanzmuster weitestgehend konstant. Hieraus lässt sich ableiten, dass nicht einzelne Hauptquellen für den Input verantwortlich sind sondern die Einträge eher durch kleinere Punktquellen und durch direkten Oberflächenabfluss erfolgt.

Um die Substanzmuster in Hinblick auf verschiedene Regionen zu untersuchen, wurden insgesamt 37 Sedimentproben aus 8 Ästuarien und Deltas aus Europa und China analysiert und anhand einer Fingerprint Analyse charakterisiert. Die Flüsse in Europa zeigen einen sehr ähnlichen Fingerprint mit Pearson Korrelationen von bis zu >0.99, die durch den harmonisierten europäischen Markt der EU mit einer abgestimmten Chemikalienregulierung erklärt werden können. Dagegen zeigt sich

bei dem Fingerprint aus China ein deutlicher Unterschied zu Europa. Unter anderem ist in China das Tri(2-chlor)ethylphosphat, welches in Europa nur noch eingeschränkt nutzbar ist, eine Hauptkomponente. Im Kontrast dazu ist das Tris(2-butoxyethyl)phosphat, in Europa stark präsent und in China zu vernachlässigen. Insgesamt zeigen die Untersuchungen, dass die Fingerprintanalyse für Schadstoffe wie OPEs ein geeignetes Mittel ist um Regionen zu unterscheiden und Charakteristika herauszuarbeiten. Des Weiteren zeigt sich, dass eine abgestimmte Chemikalienregulierung zu einer übergreifenden Wirkung im Kontaminationsmuster in der Umwelt führt.

Für die atmosphärischen Untersuchungen wurden in der Nähe von Büsum über ein Jahr lang 58 Luftproben genommen. Mit der neu entwickelten Analysemethode war es möglich, die Partikel- und Gasphasenproben mit sehr geringen Nachweisgrenzen zu untersuchen. Entgegen den Erwartungen konnte weder im Konzentrations- noch im Substanzmuster ein Jahresgang identifiziert werden. Jedoch haben die Untersuchungen des Verteilungsverhaltens zwischen Partikel- und Gasphase, mit einem signifikanten Anteil in der Gasphase, Fragen aufgeworfen. In der bestehenden Literatur wurde dieser Anteil als nebensächlich betrachtet. Um die neuen Resultate zu bestätigen wurde eine modellierende Analyse basierend auf den physiko-chemischen Eigenschaften mit 3 verschiedenen Verteilungsmodellen durchgeführt. Die Modelle bestätigen das chemisch analytisch gefundene Verteilungsverhalten und stellen damit die bisherigen Studien in Frage. Das Verteilungsverhalten bestimmt atmosphärische Transport-, Abbau- und Eliminationsmechanismen, daher müssen die Annahmen und Berechnungen zum Langstreckentransport von OPEs in der Atmosphäre überprüft werden.

Die neuen Erkenntnisse, welche in dieser Doktorarbeit präsentiert werden, stellen einige wissenschaftliche Annahmen zum Umweltverhalten von OPEs infrage und fordern die Wissenschaftsgemeinschaft dazu auf, das Umweltverhalten von OPEs neu einzuschätzen. Die Erkenntnisse zum Substanzmuster zeigen die Wirksamkeit der Umweltregulation hinsichtlich des übergeordneten Ziels des guten Umweltzustands und der Vermeidung von negativen Effekten von Chemikalien auf Mensch und Umwelt.

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Preface

The research for this cumulative dissertation was conducted at the Department for Environmental Chemistry, Institute of Coastal Research, at the Helmholtz-Zentrum Geesthacht. The thesis consists of two primary parts. First is an extended summary, including an introduction (Chapter 1), background information on organophosphorus flame retardants and plasticizers in the environment (Chapter 2), the point of departure and objectives of this thesis (Chapters 3+4) and the applied methodology (Chapter 5). The Results and Discussion of the studies conducted are provided in Chapter 6. The overall conclusion and future perspectives are presented in Chapter 7.

The second part is the cumulative thesis, consisting of five scientific papers on the occurrence, distribution and behaviour of halogenated flame retardants in the atmosphere, aquatic environment and sediments. All the papers were published in or submitted to international peer-review journals and are reprinted in their latest version.

Erklärung zur Dissertationsschrift

Hiermit erkläre ich,

1. dass ich anderweitig weder eine Dissertation eingereicht, einen Dissertationsentwurf vorgelegt noch einen Antrag auf Zulassung zur Promotion gestellt.

2. dass die eingereichte Dissertation in der gegenwärtigen oder einer anderen Fassung noch keiner anderen Fakultät oder Hochschule vorgelegt.

3. dass ich die eingereichte Dissertation mit dem Titel „Occurrence and distribution of organophosphorus flame retardants and plasticisers in the coastal environment“ selbstständig und ohne unerlaubte Hilfe verfasst habe. Anderer als der von mir angegebenen Hilfsmittel und Schriften habe ich mich nicht bedient. Alle wörtlich oder sinngemäß den Schriften anderer Autorinnen oder Autoren entnommenen Stellen habe ich kenntlich gemacht.

Hendrik Wolschke

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List of abbreviations

φ_{Aer}	Volume fraction of aerosol particles in the air
ASE	Accelerated solved extraction
BCF	Bioconcentration factor
DCM	Dichloromethane
EFRA	European Flame Retardants Association
EI	Electron impact chemical ionization
EPA	United States Environmental Protection Agency
EU	European Union
$f_{partJ\text{-}P}$	Partitioning particle phase of the “Junge-Pankow model”
$f_{part,H\text{-}B}$	Partitioning particle phase of the “Harner-Bidleman model”
$f_{part,T}$	Partitioning particle phase of “the Tool”
f_{partL}	Partitioning particle phase of Möller et. al. (2011)
f_{partM}	Partitioning particle phase of PAPER III
GC	Gas chromatograph
GFF	Glass fibre filter
IDLs	Instrumental detection limits
K_P	Particle-Gas partition coefficient
log K_{aw}	Air-Water-Distribution coefficient
log K_{oc}	Soil-Adsorption-Coefficient for organic carbon
log K_{ow}	Octanol-Water-Distribution coefficient
LRAT	Long range atmospheric transport
MDL	Method detection limits
MRM	Multiple reactions monitoring
MS	Mass spectrometer
MS/MS	Tandem mass spectrometer
Na_2SO_4	Sodium sulfate
OECD	Organization for Economic Co-operation and Development
OPEs	Organophosphorus flame retardants and plasticizers
PBDEs	Polybrominated diphenylethers

PCBs	Polychlorinated biphenyls
PET	Terephthalate
P_L	Vapour pressure
PM 2.5	Particulate matter <2.5 µm
POPs	Persistent Organic Pollutants
PTV	Temperature Vapourising Injector
PUFs	Polyurethane forms
SPE	Solid-Phase-Extraction
TBEP	Tris(2-butoxyethyl) phosphate
TCEP	Tris(2-chloroethly)phosphate
TCEP-d12	Tris(2-chloroethly)phosphate (12-fold deuterated)
TCP	Tricresyl phosphate
TCPP	Tris(chloropropyl)phosphate
TEHP	Tris(2-ethly-hexyl)phosphate
TEP	Triethlyphosphate
TiBP	Tributyl-iso-phosphate
TnBP	Tributyl-n-phosphate
TnBP-d27	Tributyl-n-phosphate (27-fold deuterated)
TOC	Total organic carbon
TPhP	Triphenyl phosphate
TPhP-d15	Triphenyl phosphate (15-fold deuterated)
TSP	Total suspended particulates

Part I

Extended Summary

1. Introduction

The focus of environmental sciences on emerging or re-emerging pollutants, such as flame retardants, plasticizers, personal care products, pesticides or pharmaceuticals, has increased in recent years. These contaminates have been continuously released into the environment during production and usage processes as a result of anthropogenic activities (*1*). Many of these pollutants are used in high production volumes with global applications in a variety of products (*2*). With the restriction of widely used compounds, such as the flame retardants polybrominated diphenylethers (PBDEs), due to their persistence, bioaccumulation potential and toxic properties in the 1990s and later by the Stockholm Convention, a second generation of compounds has emerged as replacements for the banned or restricted compounds (*3*). Often, these replacements are substances that were developed many years ago and have been in use for many years but, until now, in smaller amounts than, e.g., PBDEs. With the ban of the classic compounds, such as polychlorinated biphenyls (PCBs), chlorinated pesticides and PBDEs, the production volumes of the replacement compounds are rapidly increasing (*4*). There is a lack of information on the biodegradability, ecotoxicology potential and environmental fate for most of these chemicals, but since it is almost impossible to recapture them once they have been emitted into the environment, their potential risks to human health and the environment are growing research fields (*2*). The research presented in this thesis investigated the occurrence and distribution of organophosphorus flame retardants and plasticizers, a chemical group of concern with increasing production and consumption over the last decades (*4*) in the coastal environment.

2. Background information

2.1. Organophosphorus flame retardants and plasticizers

Organophosphorus flame retardants and plasticizers (OPEs) are one group of these so called re-emerging pollutants in the environment for which significant data gaps regarding the environmental fate and potential adverse effects on ecosystems and human health have been identified (*5*).

OPEs are triesters of phosphor acid and can be grouped into 3 categories: the halogenated alkyl phosphates, the non-alkyl phosphates and the aryl-phosphates (*2*). The major compounds for the halogenated OPEs are tris(2-chloroethly)phosphate (TCEP) and the three isomers of the tris(chloropropyl)phosphate (TCPP). The most reported non-chlorinated OPE compounds in the environment are the tributylphosphates in the form of n-(TnBP), as well as in the iso-configuration (TiBP) (*4*). The third group is the aryl-phosphates with triphenylphosphates (TPhP) as the leading compounds (*5*).

An overview of the individual compounds discussed in this thesis is presented in Table 1. Chemical structures are presented in the Appendix of PART I. The selection is limited to the analysed and detected substances and do not provide a completely thorough listing of the existing phosphor-based flame retardants and plasticizers.

The physico-chemical properties differ considerably between the different groups of OPEs (*6, 7*). The molecular weight, vapour pressure, water solubility, octanol-water-distribution coefficient (log K_{ow}), octanol-air-distribution coefficient (log K_{oa}), air-water-distribution coefficient (log K_{aw}), soil-adsorption-coefficient for organic carbon (log K_{oc}) and the bioconcentration factor (BCF) are listed in Table 1. The vapour pressure is a criterion for the volatility of the compound, which is an important factor in estimating the potential of a compound to be transported away from the emission source via the atmosphere (*8*). The log K_{OW} describes the distribution between the particles and the dissolved phases of a compound in the aquatic environment. Compounds with an increasing log K_{ow} are more attached to solid and lipophilic media, leading to a higher bioaccumulation potential with increasing log K_{ow} (*9*).

Overall, the triesters are following the general trend that larger molecules (in this case longer chain length) have a higher log K_{ow}, a lower water solubility and a lower vapour pressure, which leads to their varied behaviours and fates in the environment (*4, 7*). For example, the short chain triethlyphosphate (TEP) with a high vapor pressure (52.4 pa) is highly water soluble (500 g L^{-1}) and has a low bioaccumulation potential. In contrast, the larger tris(2-ethly-hexyl)phosphate (TEHP) is not volatile (V_P= 1.1 E-03), is poorly water soluble (6.0 E-04 g L^{-1}) and has a high bioaccumulation potential (log K_{ow} 9.49) (*7*). An exemption to the rule is the chlorinated compounds, which are all water soluble even at a larger carbon chain length due to the presence of the polar chlorinated ester (TCPP: 1.2 g L^{-1}, TCEP: 7 g^{-1} L).

Chemical Name	Abbreviation	CAS Number	Molecular Weight [g mol $^{-1}$]	Solubility [log mg L^{-1}]	Vapour Pressure [log Pa]	log Kaw [atm m^{-3}]	log Kow	log Koa	Log Koc	BCF	Application
Triethyl phosphate	TEP	78-40-0	182	4.0	1.7	-4.6	0.90	5.50	1.68	4	Plasticizer, polyvinylchloride, polyester resins, polyurethane foam
Tri-n-butyl phosphate	TnBP	126-73-8	266	0.9	-0.8	-3.9	3.80	7.70	3.28	1030	Plasticizer, hydraulic fluids, floor finish, wax, lacquer, paint, glue, anti-foam agent, industrial processes
Tri-iso-butyl phosphate	TiBP	126-71-6	266	1.0	-1.0	-4.1	3.90	7.20	3.28	--	Plasticizer, hydraulic fluids, floor finish, wax, lacquer, paint, glue, anti-foam agent, industrial processes
Tris(2-butoxyethyl) phosphate	TBEP	78-51-3	398	0.3	-3.8	-9.3	3.00	12.30	4.38	1080	Flame retardant, plasticizer, floor finish, wax, lacquer, paint, glue, anti-foam agent
Triphenyl phosphate	TPhP	115-86-6	326	0.0	-2.1	-5.8	4.70	10.50	3.72	113	Flame retardant, plasticizer, hydraulic fluids, lacquer, paint, glue
Tris(2-ethylhexyl) phosphate	TEHP	78-42-2	435	-4.8	-5.0	-2.4	9.50	11.90	6.87	100000	Flame retardant, plasticizer, fungal resistance
Tricresyl phosphate	TCP	1330-78-5	368	-0.7	-4.1	-5.7	6.30	12.00	4.35	8560	Plasticizer, polyvinylchloride, hydraulic fluids, cellulose, cutting oils, transmission fluids
Tris(2-chloroethyl) phosphate	TCEP	115-96-8	285	2.9	0.9	-6.0	1.60	7.60	2.48	1	Flame retardant, plasticizer, lacquer, paint, glue, industrial processes
Tris(2-chloropropyl) phosphate	TCPP	13674-84-5	328	1.7	-2.1	-5.6	2.90	8.50	2.71	42	Flame retardant, plasticizer
Tris(1,3-dichloro-2-propyl) phosphate	TDCPP	13674-87-8	431	0.2	-3.9	-7.0	3.70	10.60	2.30	14	Flame retardant, plasticizer, lacquer, paint, glue

Table 1: Chemical Names, Abbreviations, CAS-Numbers and physico-chemical properties of the OPEs investigated (Data summarized from Zhang and Sühring et. al. (2016) and Wei et. al. (2015)

2.2. Production and use

Organic flame retardants have been used for decades to reduce the flammability of polymer-based industrial and consumer products (*10*). In addition to classic brominated flame retardants, such as polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A, hexabromo-cyclododecane and OPEs have been used (*10*).

The flame retardant mechanism of OPEs is the suppression of flaming and glowing during the combustion of polymers due to the formation of phosphoric acids (*11*). The phosphoric acids formed act as a coating, which protects the polymer against oxidative degradation (*12*). In addition, the chloride in the halogenated compounds can reduce the combustion reaction by trapping free oxygen radicals. The fire resistance and thermal stability of OPEs is also important for their use as hydraulic fluids and lubricants (*12*). However, by replacing brominated flame retardant with OPEs, more flame retardant has to be applied for a comparable protection (*12*).

Because of the restrictions in the production and use of brominated flame retardants (viz. the Stockholm Convention), the annual worldwide production of their replacements -OPEs- (*13*) has increased in the last decades (*5*). Approximately 20-25% of the annual amount of organic chemicals used as flame retardants are OPEs (2, *10*), making many of them high production chemicals (>1000 tons/a) (*14*). In Europe, the use of OPEs has grown from 58,000 tons in 1998 to up to 91,000 tons in 2006 (*4*, *10*). In Japan, the production and shipment quantities were estimated at 45,500 tons in 2005 with an increase to 85,700 tons in 2010 (*15*). The European Flame Retardants Association (EFRA) market statistic from 2007 calculated a worldwide annual production of OPEs used as flame retardants of 207,200 tons a^{-1} in 2007 (*10*). Ou et al. 2011 estimated a global production of 500,000 tons a^{-1} for 2011 and predicted an increase to 680 000 t a^{-1} by 2015. For China, they estimated an annual production of 100,000 t a^{-1} with a growth of 15% per year. Because of their historical use and their growing economic importance, since the ban of PBDEs, OPEs are often described as re-emerging chemicals (*5*).

2.3. Environmental occurrence

OPEs are frequently used as additives rather than being chemically bound to the final products and therefore, could easily be released into the environment via volatilization, abrasion and/or leaching during production, use, disposal and recycling processes (*4*). Typical amounts of OPEs in the products are in the mg g^{-1} range. Ingerowski et al. (2001) reported 68 mg g^{-1} TCEP in acoustic ceiling coatings and 19.8 mg g^{-1} in polyurethane forms (PUFs). In addition, these authors found 180 mg g^{-1} TCPP in PUF fillers and 1.5 mg g^{-1} in polyurethane mattresses. Based on a risk assessment by the EU, approximately 40% of the TCPP in the finished product is available for release into the environment (*13*).

OPEs are reported in indoor and outdoor environments, including house dust (*11*), wastewater treatment plants (*16, 17*), surface waters (*18*), sediments (*19*), the atmosphere (*20*), and remote areas (*21, 22*). A very detailed overview of the environmental occurrence of the OPEs was presented in the reviews of van der Veen et al. (2012) and Wei et al. (2015). In the following section, selected studies are presented to give an overview of the environmental concentrations and knowledge about OPEs in the environment.

The highest emission potential of OPEs for commercial products is the release from materials and vehicles, as well as from e-waste recycling. Consequently, these sources are the dominant sources for OPE contamination in indoor and outdoor environments (*4*). Discharges from treated and untreated wastewater are presumed to be the primary source for surface water and subsequent groundwater infiltration (*23–25*). In wastewater treatment plants, OPEs can easily pass classic treatment steps and are released into the receiving freshwater streams (*5*).

In surface waters, OPEs are mostly present in the dissolved phase (*18*). Typical large river sum concentrations are in the hundreds of ng L^{-1}. Bollmann et al reported sum concentrations of OPEs of up to 350 ng L^{-1} in the Elbe River with TCPP as the primary contributor. In Hessen, Germany OPE concentrations of up to 1100 ng L^{-1} were reported (*23*). In the Pearl River in China, concentrations reached up to 2300 ng L^{-1} with TCEP as the major component (*26*).

Data on sediment and soil contamination is limited. There are reports on considerable sewage sludge OPE concentrations in Norway, Sweden, Spain and Germany with 0.62 to 21 µg g^{-1}, dominated by TCPP, TBEP and TBP (*16, 19, 25*). Representative data for the sediments have become available in the recent years. In Greece, sediment concentrations between 10.5 – 248 ng g^{-1} were reported in the Evrotas River (*27*). In the Adige River, Italy, OPE concentrations in the sediments ranged from 11.5 – 549 ng g^{-1} and in Slovenia in the Sava River basin they ranged from 0.31-310 ng g^{-1} (*27*). In Spanish rivers, the sum of the concentrations of 3.8 to 824 ng g^{-1} were detected (*28*). Brandsma et al. (2015) reported lower OPE concentrations compared to other rivers in the Scheldt River, a heavily industrialized river, with <0.1 – 19.6 ng g^{-1}. However, despite these first important investigations, the behaviour and fate of OPEs in sediments is still not well understood. Sink and source mechanisms, ecotoxicology risks and degradation processes have yet to be investigated.

Outdoor atmospheric studies are limited as well because of the necessary high-volume sampling in conjunction with the problematic blank situation. In the air, OPEs have been almost exclusively investigated and detected in the particle phase. In urban atmospheric samples, concentrations of up to 30 ng m^{-3} were reported (*29*). In more remote areas, such as the North Sea, concentrations of approximately 500 pg m^{-3} were measured (*20*). Comparable concentrations were reported by Salamova et al. (2014) at Svalbard (a Norwegian Arctic site). Over the northern Pacific Ocean, Arctic Ocean and Indian Ocean, Möller et al. (2012) detected mean concentrations of approximately 500 pg m^{-3} with a major contribution from chlorinated compounds. Near the Antarctic continent, the atmospheric concentrations of OPEs on marine aerosols of 20 pg m^{-3} were measured (*30*). Because of the increasing contribution of chlorinated compounds from urban regions to remote areas, it is reasonable to conclude that chlorinated OPEs have a longer environmental lifetime and higher potential for long-range atmospheric transport (LRAT) than non-chlorinated ones (*4*).

OPEs have been reported to be resistant to biodegradation (*31, 17*) and photo-degradation (*32*). In addition, hydrolysis in neutral or acidic waters (pH 5-7) is negligible (*32*). However, laboratory studies have shown that the majority of the OPEs are moderately persistent in the environment. Because of their considerable application and subsequent environmental input, especially into the aquatic environment, the OPEs are often considered to be pseudo-persistent contaminants (*33, 34*). In addition, increasing amounts of the OPEs have been detected in remote areas such as the Arctic and Antarctic (*21, 22, 35*), which indicates an environmental persistence.

The toxicity data on OPEs is still limited (*36*). The non-chlorinated TBEP has been shown to be carcinogenic and TCP, as ortho isomer, tested positive as a neurotoxin (*37*). TPhP is acutely toxic to aquatic organisms (*2*). The chlorinated TCEP and TDCPP were proven to be neurotoxic and carcinogenic (*38*). TDCPP, TCPP and TCEP have been shown to have negative effects on neurodevelopment in cell studies (*39*). Several *in vitro* tests have indicated that many OPEs have the potential to induce endocrine disrupting effects (*40*). Therefore, the EU Directive (2014/79/EU) has prescribed specific limits (5 mg g^{-1}) for TCEP, TCPP, and TDCPP in toys, starting in December 2015 (*41*) and, in the EU, TCEP is recommended to be phased out from consumer products (*42*).

3. Point of departure of this thesis

The situation on the chemical marked at the starting point of the thesis was that traditional brominated flame retardants have been largely banned or phased-out for several years. Several alternatives have been established, including various brominated and chlorinated alternatives, as well as the organophosphorus flame retardants. Minor amounts of OPEs were already in use before the ban of classic brominated flame retardants, but the restrictions and subsequent need for alternatives have led to a strong increase in the demand for OPEs. In addition, OPEs are being used as plasticizers rather than just as flame retardants. Several environmental studies have shown the occurrence of OPEs in the environment, as well potential toxicological effects. However, at the start of the research presented in this thesis, there was still little information available on sources, distribution and behaviour, including partitioning, and their storage and remobilization mechanism in sediments, especially the in river-sea continuum and the coastal areas. These scientific knowledge gaps as key questions for further research and the requirement for the assessment of OPEs were the point of departure of this thesis.

4. Research objectives

The objective of this thesis was to assess the distribution and behaviour of organophosphorus flame retardants and plasticizers in the coastal environment and to identify driving factors for the patterns observed. Due to the broad range of physico-chemical properties of this chemical group, the aquatic environment with sediment, as well as the water phase, was chosen to evaluate the river systems. The atmospheric environment was chosen to investigate potential large-scale transportation mechanisms.

The specific aims of the individual papers included in this thesis were:

Paper I: to investigate the pattern and behaviour of OPEs in the Elbe River and its tributaries to identify major sources of contamination. The second aim of this paper was to evaluate the impact of a historically severe flood event regarding OPE contamination and specific flood representative effects.

Paper II: to investigate the occurrence and pattern of OPEs in the industrial zone around the Bohai Sea, China by analysing the contamination pattern in all the tributary rivers. In addition, to calculate the individual riverine input into the sea to identify major sources.

Paper III: to investigate the occurrence and pattern of OPEs in the atmosphere in a coastal area with the aim of distinguishing spatially separated air masses by air- mass back-trajectory analyses and to investigate the particle-gas phase partitioning.

Paper IV: to investigate the particle-gas phase partitioning of OPEs using a model-based approach to verify the findings from Paper III and to provide more precise data for long-range atmospheric transport (LRAT) potential calculations where the partitioning is an important factor.

Paper V: to investigate the contamination levels and river specific patterns of OPEs across Europe. For analyses of a long-term conglomerated signal, sediments from estuaries and deltas were chosen as an investigation matrix. Through the comparison of European OPE concentrations with the situation in an estuary in China, the effects of different regulations and industrial behaviour were analysed.

5. Material and methods

Details on sampling, sample preparation, extraction, clean up and instrumental analyses are presented in the respective papers and supplement information.

5.1. Sampling

Sample	Type	Region	n	Paper
River Water	Longitudinal profile - 1L	North Germany - Elbe	15	I
River Water	Longitudinal profile - 1L	Netherland/Germany - Rhine	25	I
River Water	Flood Profile	North Germany - Elbe	25	I
River Water	Single spot samples	Various rivers around the Bohai Sea, China	40	II
Atmospheric Sample	Gas phase	North Germany – Büsum	58	III
Atmospheric Sample	Particle phase	North Germany – Büsum	58	III
Sediment	Estuary /delta	Across Europe	32	V
Sediment	Estuary	China - Xiaoquing River	5	V

Table 2: Summary of the samples analysed for this thesis

The longitudinal profile river water samples were taken during a ship-based campaign with the research vessel Storch in 2013. The samples during the flood from the Rhine and various rivers around the Bohai Sea were taken from shore in 2013. The surface water samples were taken by a stainless steel bucked or water scoop at a water depth > 0.5 m to avoid sampling the surface microlayer. The water samples were stored in glass or contamination-free terephthalate (PET) bottles at 4 °C until extraction.

Air samples were taken via a high-volume air sampler placed at the "Research and Technology Centre, West Coast" next to a weather station at the sea-side town Büsum, Germany in 2011-2012. Air samples were taken for one week (~2000 m^3) per sample. Airborne particles were trapped on a glass-fibre filter (GFF, Macharey Nagel GF/F), and the gaseous phase was trapped on a self-packed glass cartridge filled with polyurethane foam and Amerlite XAD-2. Cartridges and filters were stored at -20 °C until extraction.

Sediment samples were taken by stainless steel sediment grab sampler or shovel during ship-based campaigns or from the shore at low tide in 2013-2015. Only the first five centimetres of largely undisturbed sample cores or surface layers were used for analysis. The samples were stored in metal containers at -20 °C until extraction.

5.2. Sample preparation

5.2.1. Water samples

The water samples were filtrated using GF/C (Whatman) glass-fibre filters to separate the particulate and dissolved phases. Two existing methods were re-validated and used to extract the water samples (*18, 24*). Briefly, a Solid-Phase-Extraction (SPE) with self-packed cartridges with 0.5 g of SERDOLITH PAD III (particle size 0.1-0.2 mm) as an adsorption material was used to enrich the samples. Deuterium-labelled internal standards were added prior to extraction. The samples were eluted using dichloromethane (DCM). The second method deployed was liquid-liquid-extraction with DCM as the organic phase. For both methods, a drying step was included using a sodium sulfate column, and afterwards the sample volumes were reduced under a gentle stream of nitrogen to 150 µL for analysis.

5.2.2. Air samples

The method used was refined from the method described by Möller et al. (2011). Prior to extraction, a PUF/XAD-2 cartridge and GFFs were spiked with 20 ng of mass-labelled internal standards. PUF/XAD-2 was extracted with a modified Soxhlet extractor for 16 h using DCM. Particle samples on GFF were extracted with a standard Soxhlet extractor using DCM for 16 h. The extracts were concentrated to approximately 2 mL using hexane as a keeper and passed over 3 g sodium sulfate (Na_2SO_4) to remove residual water. A total of 2.5 g 10% water deactivated silica gel columns were used to clean up the samples. Two fractions were eluted: F1 for non-polar compounds, such as polychlorinated biphenyl, using 15 mL of hexane and F2 for semi-polar compounds using 20 mL of acetone/DCM (1:1, v/v). The F2 fraction contained the OPEs and was used for instrumental analysis. Both fractions were concentrated to 150 µL under a gentle stream of nitrogen for analysis. The F1 fraction was not investigated in this thesis but could be used for other purposes.

5.2.3. Sediments

To investigate the occurrence and distribution of OPEs in sediments and establish representative fingerprints, the analysis of a large sample set with varying total organic carbon (TOC) and water contents was necessary. To be able to process such a set under reasonable time and cost, the first challenge was to develop a fast and efficient extraction and clean up method, which is robust, precise and not vulnerable for blank contamination. A sieving to a <63 µm fraction was attempted by wet sieving in a closed water cycle, but the blank contamination was too high to apply it to the environmental samples. For that reason, a sensitive full sample method using accelerated solved extraction (Thermo Fisher ASE-350) with a new in-cell clean up as described by Sühring et al. (2016) was adopted to include a second extract fraction for the analysis of the OPEs. A chemical drying step was performed by homogenization with sodium sulfate. The two-fraction extraction method used 10% deactivated silica gel and activated copper as in-cell clean up agents. The first fraction was used to determine the PCBs and brominated flame retardants (*43*), and the second fraction after another silica gel clean up was used for the OPE analysis. Separate sample aliquots were dried to a constant weight (at 105 °C) for the gravimetrical determination of the water content, as well as the subsequent analysis of total organic carbon (TOC). The TOC was measured using a LECO RC612 multiphase carbon/hydrogen/moisture determinator combustion method at 400 °C.

5.3. Instrumental analysis

Two systems were used for the instrumental analysis. For Paper II, a classic gas chromatography mass spectrum (GC-MS) with a 30 m column as described by Bollmann et al. was applied. For Papers I, III, and V, a new method with a gas chromatography - tandem mass spectrometer system was developed. The methodology varies slightly from study to study, and therefore, the details are described in the Material and Method chapters of the individual papers. Briefly, the analysis was performed on an Agilent 7010 gas chromatograph - tandem mass spectrometer (GC-MS/MS), fitted with a Programmed Temperature Vapourising Injector (PTV) in pulsed split-less mode. The sample injection volume was 1-2 μL. Helium was used as the carrier gas at a flow of 1.3 mL min^{-1}. The GC was equipped with an HP-5MS or HP-35MS column from J&W Scientific applied in different length and configurations. The column configuration for the MS/MS system included a mid-column backflush. The MS transfer line and the ion source (electron impact chemical ionization, EI) were held at 280 °C and 230 °C, respectively. The MS was operated in multiple reactions monitoring (MRM) mode.

5.4. Quality assurance and quality control

Because of the widespread presence of OPEs in various 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 °C and rinsed with acetone. Na_2SO_4 was cleaned using Soxhlet extraction with DCM for 12 h and baked at 450 °C. Blank samples were analysed with every batch of samples. 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), choosing the approach that yielded the higher value. Detected blanks were minimized by modification of the methods used and considered in the calculations of the concentrations and detection limits. The recoveries of the target compounds were controlled and corrected using mass-labelled internal OPEs (TCEP-d12, TnBP-d27, and TPhP-d15). Recoveries from the internal standards were controlled by injection standards. All reported concentrations were corrected for the blanks and recoveries.

5.5. Fingerprint analyses

For the Fingerprint analyses of the different estuaries and deltas in PAPER V and the comprehensive analysis of the aquatic data of PAPER I and PAPER II, a method for the "Fingerprint Analysis of Contaminant Data" by the United States Environmental Protection Agency (EPA) (*44*) was used. The average concentrations [pg g^{-1} dw, ng L^{-1}] of each river were used to determine the contribution to the sum contamination in the investigation area (i.e., specific estuary) was calculated with:

$$con_{xi}[\%] = \frac{c_{xi}[pg\ g^{-1}\ dw]}{\sum_{i=1}^{n} c_{xi}\ [pg\ g^{-1}\ dw]}$$

with

$con_x[\%]$: Contribution in % of the compound $X_{i=1-n}$ to the sum concentration in the investigation area

$c_{xi}[pg\ g^{-1}\ dw]$: Concentration of the compound $X_{i=1-n}$ in pg g^{-1} dw

$d\sum_{x=1}^{n} c_x\ [pg\ g^{-1}\ dw]$: Sum concentration of all compounds X in the investigation area in pg g^{-1} dw

5.6. Prediction models

For Paper IV, the gas-particle partitioning of OPEs was investigated by comparing model predictions from the commonly used OECD P_{OV} and LRTP Screening Tool ("the Tool") (45), and the distribution models by Junge-Pankow (46) and Harner-Bidleman (8). The Model approaches are briefly described below; a detailed description is given in Paper IV and in more detail in the corresponding publication of the first applications (*8, 45, 46*).

5.6.1. OECD Tool

The OECD P_{OV} and LRTP Screening Tool ("the Tool") (Version 2.2 (*45*)) calculates the partitioning into the particle-phase ($f_{\text{part,T}}$) based on the octanol-air (K_{OA}) partition coefficient. This approach assumes that absorption into the organic film coating of the atmospheric particles is the driving factor for the gas-particle partitioning of the contaminants (*47*). Using generalized parameters for the global environment, $f_{\text{part,T}}$ is represented in the Tool by the following equation:

$$f_{\text{part,T}} = \frac{\varphi_{\text{Aer}} * K_{OA} * 0.42}{\varphi_{\text{Aer}} * K_{OA} * 0.42 + 1}$$

The volume fraction of the aerosol particles in the air (φ_{Aer}) in the Tool is set by default to $2 * 10^{-11} \frac{m^3}{m^3}$. The default settings in the Tool use coarse particles with an aerosol deposition velocity of 10.8 m h^{-1}, usually attributed to a particle diameter of 2.5–10 μm (*48*). Assuming an average density of aerosol particles of 1.5 g cm^{-3}, this value reflects a particle concentration of 30 μg m^{-3} in the air, which is the target value for PM 2.5 in the Canada-wide Standard for Particulate Matter and Ozone (*49*). K_{OA} in the Tool is calculated as the ratio of the octanol-water partition coefficient (K_{OW}) and the air-water partition coefficient (K_{AW}), with $K_{OA} = \frac{K_{OW}}{K_{AW}}$. The gas constant (R) is defined as $8.314 \frac{m^3 Pa}{K\, mol}$, and the temperature (TK) is set to 298.15 K.

5.6.2. Junge-Pankow ($f_{\text{part,J-P}}$)

The Junge-Pankow model (*46*) assumes adsorption to the active sites of an aerosol particle based on the subcooled liquid vapour pressure (P_L, Pa) of the compound, and the surface area of the adsorbing aerosol particle per volume air (θ, cm^2 aerosol cm^{-3} air) (*46*). $f_{part(J\text{-}P)}$ is calculated with:

$$f_{part,J-P} = \frac{c\theta}{P_L + c\theta}$$

where $f_{part,J\text{-}P}$ is the fraction of chemical adsorbed to air particles, and c is a constant. The constant (c) depends on the desorption temperature from the particle surface, the volatilization temperature of the compound and the active sites of the aerosol. We used default values of c = 0.172 Pa cm^{-1} and $\theta = 1.1 * 10^{-5} \frac{cm^2}{cm^3}$ for urban air (*47*). The P_L data were obtained using EPI Suite's MPBPVP v1.43 (*50*), SPARC (*51*) as well as data measured (*6*) and from the literature (*5, 2*).

5.6.3. Harner-Bidleman ($f_{\text{part,H-B}}$) predictions and evaluation

The third model, the Harner-Bidleman model (*52*), is very similar to the tool. The estimations of f_{part}, is based on the K_{OA} and assumes primary absorption into the organic layers of the aerosols. $f_{part,H\text{-}B}$ is calculated as:

$$f_{part,H-B} = \frac{K_p * TSP}{(K_p * TSP + 1)}$$

with
$$\log K_p = \log K_{OA} + \log f_{OM} - 11.91$$

where $f_{part,H\text{-}B}$ is the fraction of chemical adsorbed to the air particles; K_P (m^3 μg^{-1}) is the particle-gas partition coefficient; TSP is the total suspended particulates concentration (μg m^{-3}); K_{OA} is the octanol-air partitioning coefficient, and f_{OM} is the fraction of organic matter (OM) on the aerosol particles ($g_{OM}\, g_{TSP}^{-1}$). For the calculations, a default value for urban air was used with the TSP set to 55 μg m^{-3} and $f_{OM} = 0.40\ g_{OM}\, g_{TSP}^{-1}$ (*47*).

6. Results and discussion

The research presented in this thesis has contributed substantially to the scientific knowledge on the occurrence, fate and transport of OPEs in the environment, especially the costal environment and rivers-sea continuum. Since the study covered a broad field of environmental behaviour of OPEs, the discussion in this thesis had to be limited to the primary achievements and findings. However, detailed discussions on several other aspects of the fate and behaviour of OPEs in the environment are presented in the individual papers. The results of this thesis are summarized and discussed in the following chapters addressing:

- Improvements in the analytical methods to detect and quantify OPEs in the environment
- Occurrence of OPEs in European rivers – point sources versus diffuse input.
- Fingerprint of OPEs in the environment – regional differences
- Partitioning of OPEs between the gas- and particle-phases
- Annual variability in the atmospheric occurrence of OPEs

6.1. Improvements in the analytical methods to detect and quantify OPEs in the environment

For the research presented in this thesis, methods for sampling, sample preparation and analysis of 4 different types of environmental compartments (water, gas-phase, particle-phase and sediment) were used. The methods were based on a newly developed GC-MS/MS method with a (mid-column) backflush system. The backflush system, compared to classical GC configurations, provided a strong increase in condition stability, while reducing the matrix accumulation on the column. After each run, the first half part of the column was flushed backwards with high temperature carrier gas to eliminate matrix debris on the column. The second advantage was the MS/MS configuration. Due to the wide range of physico-chemical properties, the instability of the compounds and the blank contamination of OPEs have made it challenging to develop an efficient and simple sample extraction and clean up method for complex samples using a classic GC-MS. With the higher selectivity of the GC-MS/MS for matrix-loaded samples, it was possible to reduce the time and effort in sample preparation with a strong improvement in the detection limits. In the past, the atmospheric samples for the gas-phase were particularly difficult to analyse, because of a high matrix leach-out from the adsorbents into the extracts during the sample preparation and clean up process. In PAPER III, the same sample and extraction method but different instrumental analyses was compared for instrumental detection limits using environmental samples. The results are shown in Figure 1. The GC-MS/MS System archived a significant reduction of instrumental detection limits of up to a factor 50 compared to the "old method" using a GC-MS. The highest improvements were achieved for TCPP, TDCPP and TBEP in the gas-phase samples.

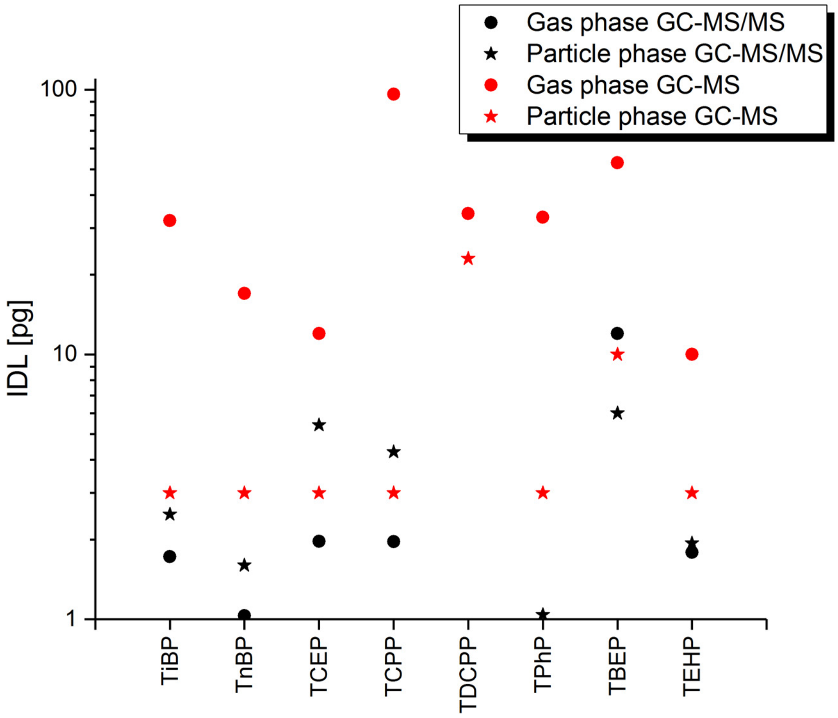


Figure 1: Comparison of the instrumental detection limits (IDL) from GC-EI-MS and GC-EI-MS/MS of the air samples (Paper III)

6.2. Occurrence of OPEs in European rivers – Point sources versus diffuse input

The occurrence of OPEs in river systems has been studied repeatedly. Most studies have reported high concentrations in the water phase compared to other organic contaminants, such as pesticides, poly-fluorinated compounds or classic Persistent Organic Pollutants (POPs) (*18, 53*). The OPE concentrations reached the threshold of 100 ng L^{-1} for "Acceptable concentrations in surface waters" proposed by the Federal Environmental Agency of Germany (*38*). Bollmann et. al. (2012) concluded that the input through the rivers is the largest source for the OPEs in the marine environment. Several studies have shown an input of OPEs into the aquatic environment via wastewater treatment plants, as well as through atmospheric deposition (*54*). However, the observed local OPE concentrations and patterns seemed to be variable (*18, 55*), indicating that the pathways of OPEs into the rivers are still not sufficiently understood (*4*). To gather further insight in the specific local OPE sources at the Elbe and Rhine Rivers, longitudinal profiles were sampled along the rivers and major tributaries. The results for the Elbe River are shown in Figure 2.

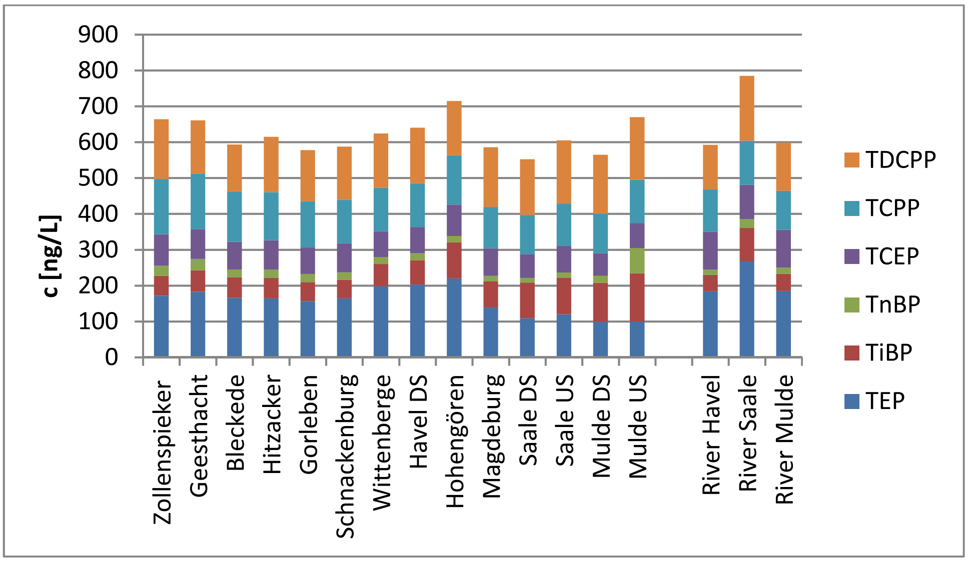


Figure 2: Concentration along the Elbe River, including the tributary for the Havel, Saale and Mulde Rivers in ng/L. DS = downstream, US = upstream.

Over a 300 km long transect of the Elbe River, the water discharge increased by 2.5-fold, while the OPE concentrations showed no clear trend and minimal variability (approximately 15%). This finding indicated that there are no major local point sources, larger point sources, or dilution effects along this part of the river. Therefore, the OPE concentrations observed are likely to be the result of a constant diffuse input or minor point source along the entire distance, rather than major point sources, such as large wastewater treatment plants, manufacturing sites or waste disposal sites. Similar observations were made for the major tributary rivers the Havel, Saale and Mulde, which support the assumption of diffuse sources with similar pattern. The transect along the Rhine River displayed similar characteristics with comparable concentrations (see also PAPER I). As in the other rivers, no specific point sources were observed. A slight increase of the OPE concentrations downstream of the city of Magdeburg at the Elbe and the Ruhr area at the Rhine indicated an influence of population density on the OPE concentrations. Interestingly, the third data set investigated, an assessment of occurrence during the strong flood event in 2014 at the Elbe (Figure 3), with increasing water masses of up to five times of the normal water discharge, the concentrations were decreased/diluted to 2/3 of the normal concentration level. This resulted in a doubling of the OPE mass flux.

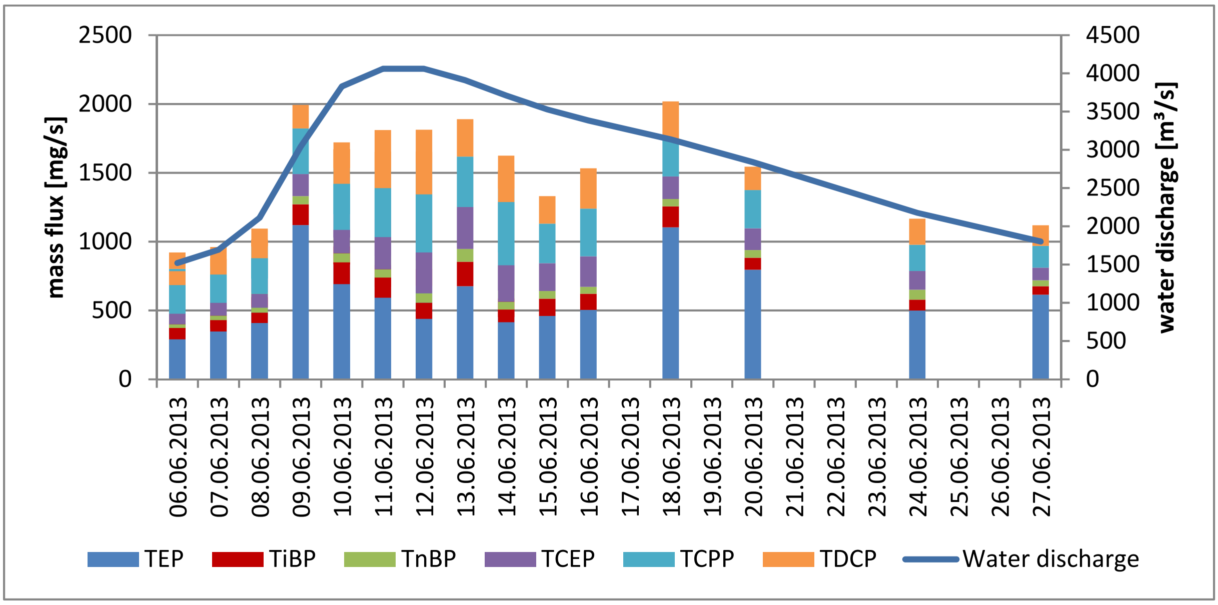


Figure 3: OPE mass flux during the flood event 2013, including the water discharge

Two explanations could explain this observation. First, it is possible that the flooded urban areas discharged a high OPE load into the Elbe during the flood. Several villages and towns in the catchment area were flooded or reported overflowing wastewater treatments plants during the flood. However, direct input from the overflowing wastewater treatment plants would be expected to affect the observed OPE patterns due to the differences in the retained functions of normal and overloaded treatment plants (*25*). No significant pattern change between the flood event and normal flow conditions was observed to support this explanation. Another explanation, which supports the diffuse source theory, is that with precipitation and overland discharges, stored OPEs in the terrestrial ecosystem are remobilized as a "secondary source" for the river, but based on terrestrial investigation (*56*), a change in the pattern would be expected. However, a clear explanation for this interesting phenomenon is not possible with a dataset from just one flood event, calling for further research on the OPE concentrations and patterns during flood conditions. In general, the study indicated several effects related to the input of the OPEs into the river system that should be investigated further. A high-density sampling campaign, including the investigation of possible input pathways and input fluxes, such as surface runoff, precipitation, dry deposition, soil remobilization, combined with a hydrological transport model, could present an interesting approach to understand the sources.

6.3. Fingerprint of OPEs in the environment – differences of regions

6.3.1. Sediments

To test the hypothesis that regions with different production, use and disposal characteristics - based on developmental status, legislative policies and regulations or geographic/climatic differences - have different OPE contamination patterns, sediment data from estuaries and deltas distributed over Europe and China were investigated using a fingerprinting method based on the "Fingerprint Analysis of Contaminant Data" from the EPA (*44*). The results are shown in Figure 4 and Table 3.

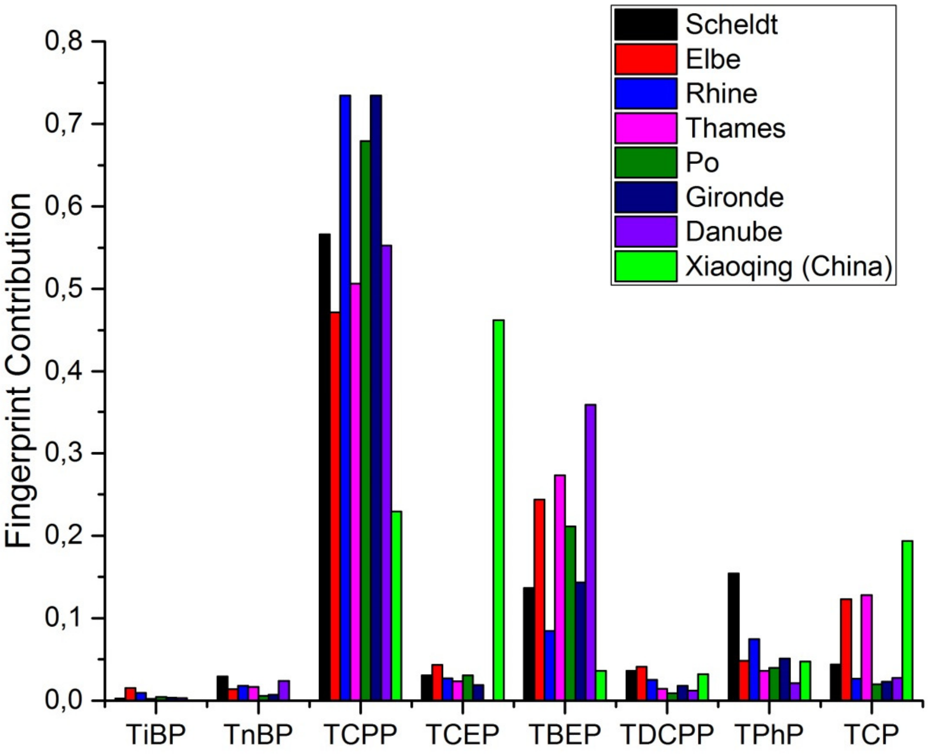


Figure 4: Fingerprint of the sediments in different estuaries/deltas

The results showed a general conformity over all river systems in Europe (Pearson r between 0.86 and > 0.99), consistent with the common market and legislative regulations within the EU (Table 3, Figure 4). Slight clusters could be identified between different European rivers. As expected, the Scheldt and Rhine with nearby catchment areas had highly correlated OPE patterns (r = 0.99). In addition, their fingerprint was very similar to that of the Gironde River in France (> 0.99) and the Po River in Italy (> 0.98) (Table 3). The second cluster consisted of the Elbe River in Germany, the Thames in England and (to a lesser extent) the Danube in Rumania with high inter-correlated patterns (Elbe-Thames > 0.99, Elbe/Thames- Danube >0.97). These two clusters were still highly correlated but showed less correlation than the pattern among the rivers within one cluster (<0.97). The OPE pattern in the Chinese Xiaoqing River was significantly ($p < 0.01$) different from all the European rivers investigated with correlation coefficients ranging from 0.08 (Danube) to 0.27 (Scheldt) (Table 3). The driving factor for the differences between the Chinese river and the European rivers was the high amount of the TCEP in the Chinese Xiaoqing River, which was phased-out in Europe. Alternatively, the European rivers had a higher contribution of the TCEP replacements TCPP and TCP compared to the Chinese river. The difference in the OPE profiles highlighted the differences between contamination situations in production and use areas, as well as the differences in legislation between China and the EU.

		Elbe	**Rhine**	**Thames**	**Po**	**Gironde**	**Danube**	**Xiaoqing (China)**
Scheldt	Pearson r	**0.91**	**0.99**	**0.89**	**0.98**	**0.99**	**0.86**	**0.27**
	Sig.	1.7E-03	1.1E-08	2.7E-03	3.3E-05	6.4E-07	0.0060	0.52
Elbe	Pearson r	**1**	**0.91**	**0.99**	**0.967**	**0.94**	**0.97**	**0.22**
	Sig.		1.8E-03	2.4E-08	8.8E-05	4.8E-04	6.7E-05	0.60
Rhine	Pearson r		**1**	**0.89**	**0.98**	**0.99**	**0.86**	**0.24**
	Sig.			2.8E-03	3.4E-05	3.0E-07	0.0062	0.56
Thames	Pearson r			**1**	**0.96**	**0.93**	**0.98**	**0.19**
	Sig.				1.7E-04	8.5E-04	4.0E-05	0.65
Po	Pearson r				**1**	**0.99**	**0.95**	**0.22**
	Sig.					1.03E-06	3.3E-04	0.60
Gironde	Pearson r					**1**	**0.91**	**0.23**
	Sig.						0.0020	0.59
Danube	Pearson r						**1**	**0.09**
	Sig.							0.83

Table 3: Pearson correlations of fingerprint analyses of sediments in the different estuaries/ deltas

6.3.2. River water

To verify the findings of the sediment investigations, the river water data from the Elbe, Rhine and Ems Rivers from PAPER I and the 4 major rivers from PAPER 2 along the rivers that discharge into the Bohai Sea (Yalu, Daliao, Luanhe and Yellow Rivers) were reanalysed with the fingerprinting tool. The results are displayed in Figure 5. The Chinese rivers had highly correlated OPE patterns with Pearson r between 0.96 and > 0.99. Interestingly, the correlation decreased with the distance of the catchments, indicating that regional differences occur even in the relatively small area around the Bohai Sea. A possible explanation is the difference in industrial production and wastewater cleaning (*57*). The European rivers were less correlated for this dataset with 0.91 (Ems-Rhine), 0.73 (Rhine- Elbe) and 0.87 (Elbe and Ems). However, the intra-correlation of the continents was still significantly higher than the inter-correlation between continents with an average $r = 0.81$ for Europe, 0.99 for China and 0.64 for the Europe-China comparison, respectively. The differences were driven by two primary factors. In Europe, the non-chlorinated

OPEs were detected more frequently than in China, and the PBDE and TCEP replacement TDCPP contributed to approximately 25% of the OPE fingerprint in Europe compared to a mere 2% in China. Unexpectedly, the phased-out TCEP had similar contributions to the OPE fingerprint in the water phase in Europe and China, whereas its replacement TCPP was lower in Europe. This contradicts the hypothesis of an environmental effect of the phase-out, a result that cannot be explained through the currently available data and knowledge and should be investigated further. An explanation for the occurrence of TDCPP in Europe compared to China could be the fact that both TDCPP and TCPP are replacements for penta-BDEs, as well as TCEP, but following the pressure on TCEP and TCPP in Europe, the more expensive TDCPP (*13*) is used to a larger extent than in China.

Overall, the fingerprint analysis was proven to be a useful tool to compare different sets of environmental contamination data and to distinguish sources or specific regions. The results indicated that a common market and harmonized regulations generate a comparable OPE fingerprint and can at least be supported by the sediment data and reduce environmental contamination from hazardous compounds on a continental scale.

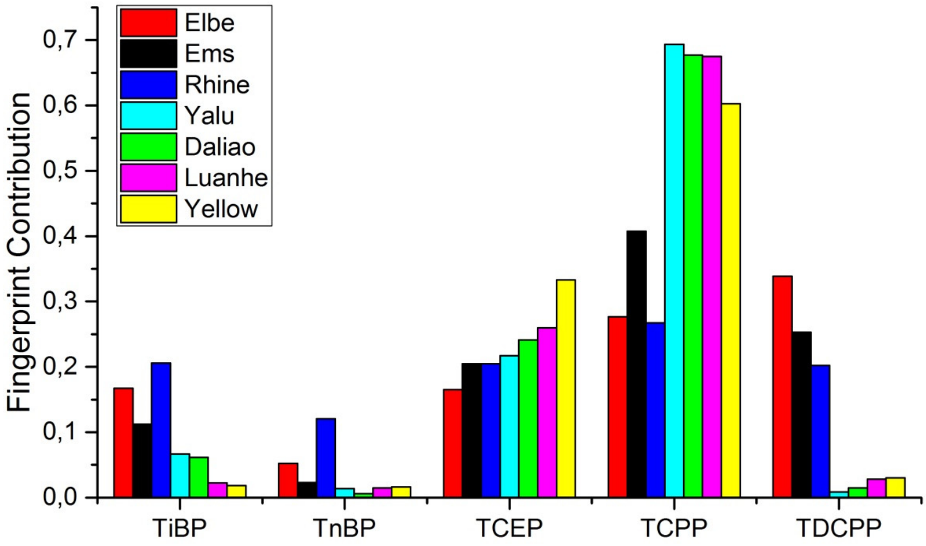


Figure 5: Fingerprint of the water phase of rivers from Europe and China collected from PAPER I and PAPER II

6.4. Partitioning of OPEs between gas- and particle-phases

The partitioning of OPEs in the atmosphere is a key factor to assess their atmospheric lifetimes and LRAT potential, because both degradation processes and elimination processes depend on the partitioning behaviour. Using classic GC-MS analyses, previous studies reported that OPEs predominantly adsorb to the particle-phase in the atmospheric samples (>95%) (*20, 35, 58*). However, in Paper III, an annual observation of OPEs in the atmosphere with weekly samples using the novel GC-MSMS technique, six of the nine analysed OPEs were detected at over 20% or even predominantly in the gas-phase (Figure 6). In the following chapter, it will be discussed whether these novel finding can be attributed to a sampling or analytical error or describe a genuine, previously unobserved, environmental behaviour of OPEs.

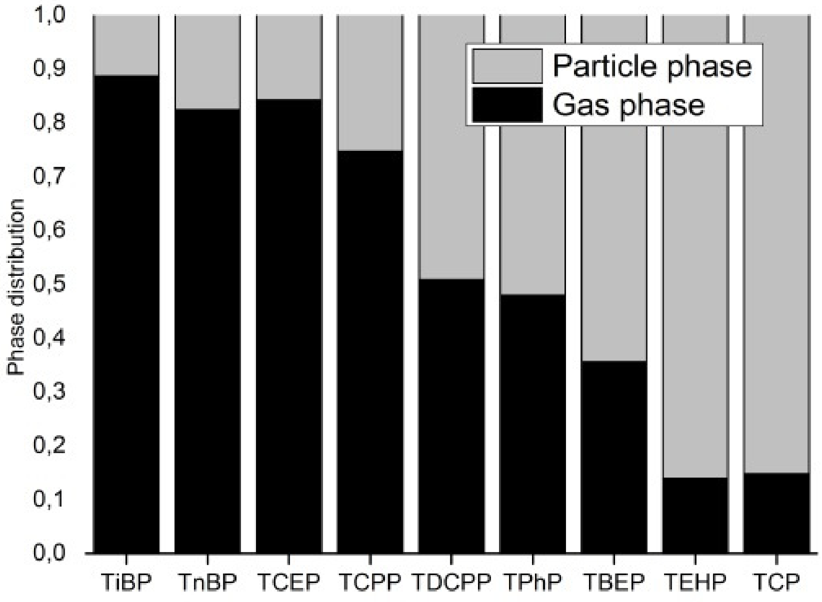


Figure 6: Average phase distribution of OPEs in the atmosphere of Büsum (PAPER III)

A potential sampling error for the distinction of the gas-phase and particle-phase has generally to be taken into consideration when sampling OPEs. In the typically used sampling setup, the gas-phase has to cross a filter before being adsorbed on the PUF-foam/XAD-2 adsorbents. This might lead to the adsorption of gas-phase OPEs on the filter due to polar interactions with the GF/F filter. Alternatively, small particles could penetrate the filter and be trapped on the PUF-foam, leading to a potential overestimation of the gas-phase OPEs. This is particularly a risk for long sampling times when a breakthrough of the filter or a changeover into the gas-phase is conceivable.

However, the sampling technique used has been successfully validated and is applied in numerous studies with a clear separation between the gas- and particle-phases for pesticides, brominated flame retardants and fluorinated compounds (*59-62*).

To evaluate the accuracy of the novel findings on OPE partitioning, a correlation analysis of the observed partitioning behaviour of the individual analytes with the theoretical partitioning coefficient between the non-polar octanol phase (e.g., particle) and the air (K_{OA}) was conducted (PAPER III). The results showed strong correlations between the K_{OA} and the observed partitioning behaviour (Pearson R: 0.96), indicating that the observed partitioning into the gas-phase could be genuine.

The differences in observed partitioning compared to a previous study by Möller et al. (2011) with a very similar method could be explained through a detailed comparison of the analytical approaches. The sampling technique, equipment and sample preparation were the same for the two studies with the only difference being the overall sampling time, which supports the hypothesis that particle breakthrough might be an explanation for the differences observed. A major difference in the analytical methodology was the instrumental analytical part. In the previous study, a GC-MS system was used with higher instrumental detection limits (IDLs) for gas-phase samples compared to the particle-phase samples (Figure 1). The improved selectivity of the novel GC-MSMS method removed these differences in the IDLs between the gas- and particle-phases, leading to an improvement representation of the OPE partitioning behaviour.

Because the OPE partitioning results were in contrast to those of all previous studies, the analytical results were compared with model predictions to verify the results and support the assessments of long range atmospheric transport (LRAT) (PAPER IV).

In this study, the partitioning behaviour of 32 OPEs (more than in the chemical analytical studies) was analysed using the OECD P_{ov} and LRTP Screening Tool ("the tool") (46), the Junge-Pankow (J-P) (45) and the Harner-Bidleman (H-B) (8) partitioning models. Literature data from over 50 publications from between 1979 and 2015 was used as the input data for the models (details on the criteria are presented in PAPER IV). To test the variations in the input data and subsequent impacts on model result uncertainty, three groups were defined, "INPUT ALL" (the whole data set), "OUTLIER REMOVED" (whole data set excluding outliers) and "MODELED INPUT DATA" (Data collection of the EPISuite, SPARC and Absolv). In general, the estimations indicated, with some exceptions, that the variability in the K_{AW} and K_{OW} input data have a minor impact on the predicted partitioning. As in the second step, the different models were compared. For the "INPUT ALL" and the OUTLIER REMOVED data set, the prediction for f_{part} was indistinguishable for “the tool” and the H-B model, which are both based on the $K_{OA.}$ The J-P prediction for 27 of the 32 compounds also suggested similar partitioning behaviour. An explanation for the differences of the six remaining compounds could be the K_{OA} between 10 -12, which is in a sensitive range for the partitioning. Compounds with higher/lower values are almost exclusively predicted in the particle/gas phase. In this range, compounds are present in both phases. Therefore, in this range variability in input data and models was found to be crucial.

Unexpectedly, predictions using the modelled input data varied significantly between the different models. Only 17 compounds showed similar partitioning behaviour, while 15 compounds were significantly different (t test at $p < 0.05$) between the J-P model and the K_{OA}-models. The different estimations for f_{part} from the J-P model compared to “the Tool” and H-B model were lower, meaning that the J-P model seemed to underestimate the f_{part}, in contrast to previous studies showing overestimations compared to the measurements for several classes of semi-volatile organic compounds (*8, 65, 66*).

As the third step, the prediction from “the Tool” the H-B model and the J-P model were compared with the analytical partitioning results from PAPER III (f_{partM}) and a previous study from Möller et al. (2011) (f_{partL}). In Figure 7, the model results for the particle phase ($F_{part)}$ were plotted against the measurements. The brown dots are the results of the “MODELED INPUT DATA”, the orange dots the ”INPUT ALL” and the green triangles the “OUTLIER REMOVED”. The data from PAPER III agreed very well with the modelled data (Figure 7). All correlations between the measured data by Möller et. al. (f_{partL}) and the model results were negative (Figure 7), indicating that the reported data did not fit the predictions of any of the models. These results supported strongly the novel findings of the partitioning behaviour presented in PAPER III. In addition, these results could have a high impact on the knowledge of the behaviour of OPEs in the atmosphere. With the higher amount of OPEs in the gas-phase, the assumptions regarding physico-chemical processes, such as transport, elimination and degradation have to be revised.

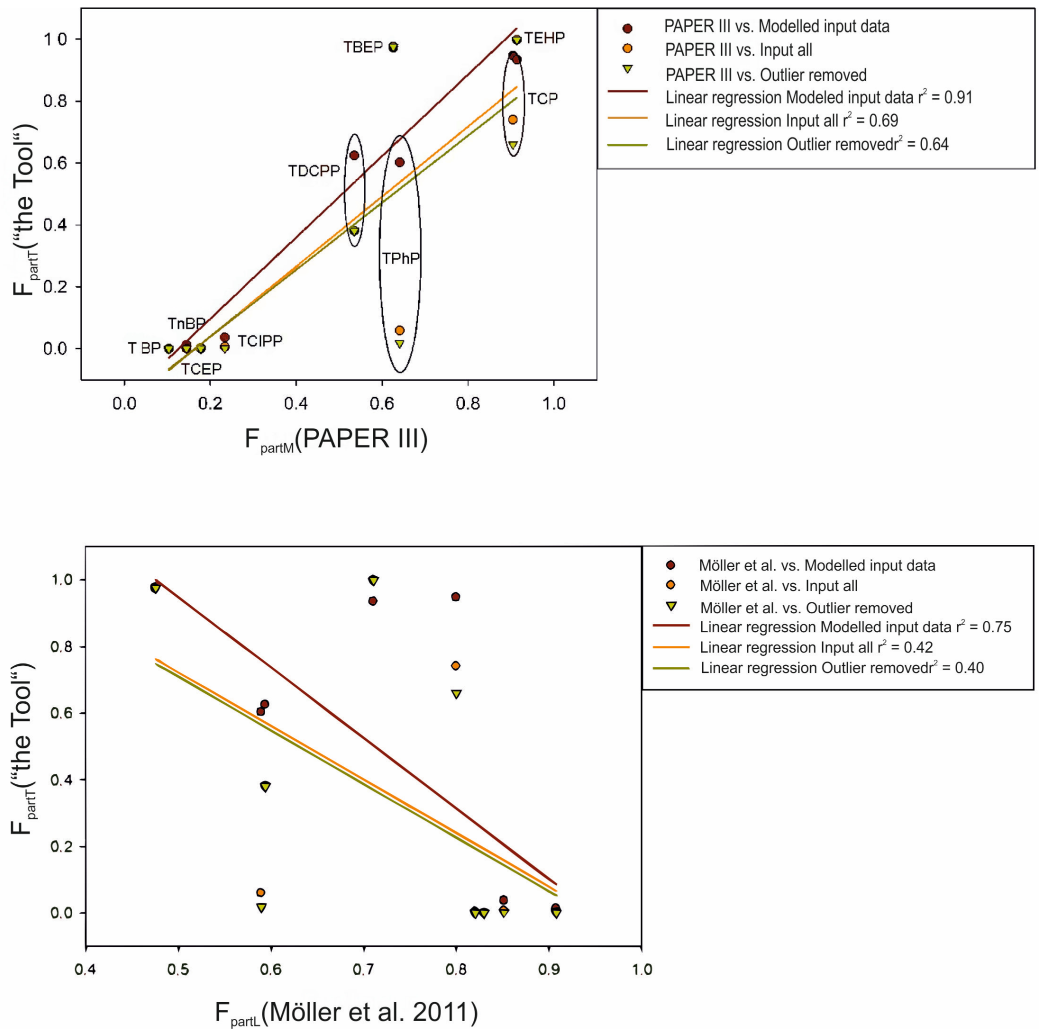


Figure 7: Correlation of fpart predicted by the Tool for the different input datasets vs. fpart PAPER III (top) and Möller et. al. (2011) (bottom) (modified PAPER IV)

6.5. Annual variability in atmospheric occurrence

In the literature, a temperature dependent behaviour of OPEs in the atmosphere is being discussed. Higher temperatures are expected to lead to higher OPE concentrations due to a higher rate of volatilization (*21*). In addition, temperature is expected to drive the partitioning between the gas- and particle-phases, as well as pattern contribution. The data set recorded in PAPER III (annual atmospheric data) was analysed to test this hypothesis. The results did not support or refute the hypothesis. The highest concentrations were detected in the relative cold month of November, and a temperature dependent correlation of concentrations was not detected. However, from the analysis of wind directions and air mass origin, it was not possible to define a stable source region for each sample or the data set as a whole. The partitioning between the gas-phase and the particle-phase should not be source dependent, because, in theory, the partitioning will reach an equilibration over time and is dependent on the particle concentration and temperature rather than a specific source. The particle concentration observed at the sampling site was consistent with an average of 16 µg g^{-1} (PAPER IV), but no correlation between temperature and the partitioning was observed (Pearson correlation of 0.09 - 0.23 ($p < 0.05$)). An explanation could be the low temperature amplitude of this marine-influenced position, which was on average a temperature variation of 11° K (except for the three samples). In addition, the short travelling times from local sources and precipitation washout effects could overlay a potential correlation. To investigate the hypotheses described, a dataset with a higher time resolution would be necessary. Such sampling is challenging to set up at a low concentration background site, such as Büsum, due to the high sampling volumes required to sample detectable concentrations, while ensuring that the flow rates are kept low enough to prevent filter breakthrough.

7. Conclusions and future perspectives

The studies underlying this thesis contribute substantially to the knowledge and understanding of the occurrence, distribution and behaviour of OPEs in the coastal environment. The developed analytical method enables a robust and precise measurement of OPEs at environmental concentration levels for gaseous, dissolved and particle-bound samples, enabling a gain in environmental data for the OPE occurrence, distribution and behaviour in water, atmosphere and sediments in the coastal zone. Using this novel method, several open questions regarding the transport and distribution of OPEs in the costal/estuarine environment could be investigated, providing unprecedented insight into the environmental fate of these contaminants. The overall conclusions of this thesis are:

Organophosphorus flame retardants and plasticizers are ubiquitously present in the coastal environment. A troubling level of contamination is observed, but the processes are still not fully understood. The outcomes of this thesis challenge the conclusions regarding the input pathways, partitioning and transport behaviour of OPEs in the environment presented in previous studies. Fingerprinting analysis has shown that regional differences occur in contamination patterns, which implicate that legislative policy and regulations and/or geographic variation have a significant impact on the environmental levels of the OPEs.

More specifically, the target compounds were detected in all the environmental compartments investigated, suggesting that the OPEs are released from production processes, that they are used in and are disposed into the environment and that they can be transported into coastal areas. In addition, indications were found that the assumed primary input pathway through wastewater treatment plants is not the only significant input pathway into the large river basins. Surface run-off and precipitation were found to probably have a substantial contribution to the OPE concentrations in rivers as well. The question of input pathways has to be further investigated because only with a comprehensive understanding of these pathways will it be possible to develop strategies to reduce the OPE concentrations in the European rivers and meet the target for "Acceptable concentrations in surface waters" proposed by the Federal Environmental Agency of Germany (*38*). The importance of the different input pathways of OPEs into the aquatic environment should be investigated in detailed multimedia fate studies to enable overall input estimations as the basis for risk assessments and prevention or remediation strategies.

The observed atmospheric partitioning between the gas- and particle-phases verified by physico-chemical distribution models challenged the conclusions from previous studies. With the new insights, the assessment of the atmospheric half-lives and long-range atmospheric transport of OPEs has to be re-evaluated. With the presence of OPEs in the gas-phase, previously neglected transport and degradation processes could become relevant. In addition, sensitive methods for the analysis of OPEs in the gas-phase should be developed and applied in further studies. To reassess previous long-term datasets, where only the particle-phase was investigated, the model approach can be used to estimate gaseous concentrations in the sensitive K_{oa} range of 10-12 with OPEs partition between the particle- and the gas-phase.

Using the fingerprinting analyses for different regions made it possible to distinguish areas from each other based on their specific OPE contamination patterns. Fingerprinting was found to be a powerful tool to identify different sources in a region, to specify contamination changes over time or to analyse regional differences. In this study, several interesting effects were observed. The increasing presence of TDCPP in Europe can be interpreted as a movement from the restricted TCEP and TCPP to the third-most prominent chlorinated OPE. The higher contribution of the non-chlorinated TiBP and TnBP in Europe compared to China, which are primarily used as plasticizers, implicate that different plasticizers are used on these two continents. In addition to these differences, regional commonalities were identified for both China and Europe, indicating that common markets produce similar OPE contamination fingerprints. This implies that different legislative regulations have an impact on the contamination pattern, or vice versa, showing that the use of OPEs or, in general, flame retardants and plasticisers is governed by a flexible market that allows for the regulation of harmful chemicals through targeted policies.

Overall, the occurrence of OPEs seems to coincide with the restriction of brominated flame retardants, such as penta-BDE, and the production volumes of the OPEs have obviously increased. In particular, the chlorinated OPE replacements have been detected in increasing amounts because of the lower efficiency compared to PBDEs and consequential higher application doses. With the detection of OPEs in all environmental compartments, which attests to an at least moderate persistence in the environment, and the rising reports on toxicological effects paired with first restrictions and limit values, the question has to be raised regarding the advantage of these introduced replacements. All of the discussed chemicals, the "old" and "new" compounds, were developed to contribute to human safety and prosperity. However, since their application, risk assessments and retrospective studies have proven or at least raised concerns regarding their environmental and human safety. The results of the studies presented have shown that legislative regulations and policy processes have an impact on the contamination situation and pattern. This knowledge should be used to evaluate the risks and benefits of possible alternatives before they are introduced into the market to prevent an environmental/human exposure through "regrettable substitutes". With the release of hazardous and persistent chemicals into the environment, substantial overhead costs have been caused for the human population and the ecosystems of our entire planet. However, the collaboration of science and policy makers clearly has the chance to assess the potential negative impacts before they occur and ensure that chemical products are only used where they are truly needed and with as minimal negative effects on human health and the environment as possible.

8. References

(1) Reemtsma, T.; Weiss, S.; Mueller, J.; Petrovic, M.; González, S.; Barcelo, D.; Ventura, F.; Knepper, T. P. Polar Pollutants Entry into the Water Cycle by Municipal Wastewater: A European Perspective. *Environ. Sci. Technol.* **2006,** *40* (17), 5451–5458; DOI 10.1021/es060908a.

(2) van der Veen, I.; Boer, J. de. Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere* **2012,** *88* (10), 1119–1153; DOI 10.1016/j.chemosphere.2012.03.067.

(3) Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. Polybrominated diphenyl ethers (PBDEs) and alternative brominated flame retardants in air and seawater of the European Arctic. *Environmental Pollution* **2011,** *159* (6), 1577–1583; DOI 10.1016/j.envpol.2011.02.054.

(4) Wei, G.-L.; Li, D.-Q.; Zhuo, M.-N.; Liao, Y.-S.; Xie, Z.-Y.; Guo, T.-L.; Li, J.-J.; Zhang, S.-Y.; Liang, Z.-Q. Organophosphorus flame retardants and plasticizers: Sources, occurrence, toxicity and human exposure. *Environmental Pollution* **2015,** *196*, 29–46; DOI 10.1016/j.envpol.2014.09.012.

(5) Reemtsma, T.; Quintana, J. B.; Rodil, R.; Garcı´a-López, M.; Rodrı´guez, I. Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. *TrAC Trends in Analytical Chemistry* **2008,** *27* (9), 727–737; DOI 10.1016/j.trac.2008.07.002.

(6) Brommer, S.; Jantunen, L. M.; Bidleman, T. F.; Harrad, S.; Diamond, M. L. Determination of Vapor Pressures for Organophosphate Esters. *J. Chem. Eng. Data* **2014,** *59* (5), 1441–1447; DOI 10.1021/je401026a.

(7) Zhang, X.; Sühring, R.; Serodio, D.; Bonnell, M.; Sundin, N.; Diamond, M. L. Novel flame retardants: Estimating the physical–chemical properties and environmental fate of 94 halogenated and organophosphate PBDE replacements. *Chemosphere* **2016,** *144*, 2401–2407; DOI 10.1016/j.chemosphere.2015.11.017.

(8) Harner, T.; Bidleman, T. F. Octanol−Air Partition Coefficient for Describing Particle/Gas Partitioning of Aromatic Compounds in Urban Air. *Environ. Sci. Technol.* **1998,** *32* (10), 1494–1502; DOI 10.1021/es970890r.

(9) Brandsma, S. H.; Boer, J. de; Leonards, P. E.; Cofino, W. P.; Covaci, A. Organophosphorus flame-retardant and plasticizer analysis, including recommendations from the first worldwide interlaboratory study. *TrAC Trends in Analytical Chemistry* **2013,** *43*, 217–228; DOI 10.1016/j.trac.2012.12.004.

(10) EFRA - Cefic. EFRA Marktstatistik No.31. http://www.flameretardants.eu/Content/Default.asp?PageName=openfile&Doc (accessed November 20, 2010).

(11) Marklund, A.; Andersson, B.; Haglund, P. Screening of organophosphorus compounds and their distribution in various indoor environments. *Chemosphere* **2003,** *53* (9), 1137–1146; DOI 10.1016/S0045-6535(03)00666-0.

(12) Wensing, M.; Uhde, E.; Salthammer, T. Plastics additives in the indoor environment—flame retardants and plasticizers. *Science of The Total Environment* **2005,** *339* (1-3), 19–40; DOI 10.1016/j.scitotenv.2004.10.028.

(13) Scientific Committee on Health and Environmental Risks (SCHER). *Scientific opinion on the risk assessment report on tris [2-chloro-1- (chloromethyl)ethyl]phosphate (CAS 13674-87-8), Environmental Part,*

(14) OECD. List of High Production Volume Chemicals. http://webnet.oecd.org/HPV/UI/Default.aspx.

(15) Research and Statistics Department, M. o. E. J. *Yearbook of Chemical Industry Statistics 2009*, 2010.

(16) Marklund, A.; Andersson, B.; Haglund, P. Organophosphorus Flame Retardants and Plasticizers in Swedish Sewage Treatment Plants. *Environ. Sci. Technol.* **2005,** *39* (19), 7423–7429; DOI 10.1021/es051013l.

(17) Meyer, J.; Bester, K. Organophosphate flame retardants and plasticisers in wastewater treatment plants. *J. Environ. Monitor.* **2004,** *6* (7), 599; DOI 10.1039/B403206C.

(18) Bollmann, U. E.; Möller, A.; Xie, Z.; Ebinghaus, R.; Einax, J. W. Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. *Water Research* **2012,** *46* (2), 531–538; DOI 10.1016/j.watres.2011.11.028.

(19) Cristale, J.; Lacorte, S. Development and validation of a multiresidue method for the analysis of polybrominated diphenyl ethers, new brominated and organophosphorus flame retardants in sediment, sludge and dust. *Journal of Chromatography A* **2013,** *1305*, 267–275; DOI 10.1016/j.chroma.2013.07.028.

(20) Möller, A.; Xie, Z.; Caba, A.; Sturm, R.; Ebinghaus, R. Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea. *Environmental Pollution* **2011,** *159* (12), 3660–3665; DOI 10.1016/j.envpol.2011.07.022.

(21) Salamova, A.; Hermanson, M. H.; Hites, R. A. Organophosphate and Halogenated Flame Retardants in Atmospheric Particles from a European Arctic Site. *Environ. Sci. Technol.* **2014,** *48* (11), 6133–6140; DOI 10.1021/es500911d.

(22) Sühring, R.; Diamond, M. L.; Scheringer, M.; Wong, F.; Pućko, M.; Stern, G.; Burt, A.; Hung, H.; Fellin, P.; Li, H.; Jantunen, L. M. Organophosphate Esters in Canadian Arctic Air: Occurrence, Levels and Trends. *Environ. Sci. Technol.* **2016,** *50* (14), 7409–7415; DOI 10.1021/acs.est.6b00365.

(23) Fries, E.; Püttmann, W. Occurrence of organophosphate esters in surface water and groundwater in Germany. *J. Environ. Monitor.* **2001,** *3* (6), 621–626; DOI 10.1039/b105072a.

(24) Martínez-Carballo, E.; González-Barreiro, C.; Sitka, A.; Scharf, S.; Gans, O. Determination of selected organophosphate esters in the aquatic environment of Austria. *Science of The Total Environment* **2007,** *388* (1-3), 290–299; DOI 10.1016/j.scitotenv.2007.08.005.

(25) Bester, K. Comparison of TCPP concentrations in sludge and wastewater in a typical German sewage treatment plant—comparison of sewage sludge from 20 plants. *J. Environ. Monit.* **2005,** *7* (5), 509; DOI 10.1039/b502318a.

(26) Wang, X.; He, Y.; Lin, L.; Zeng, F.; Luan, T. Application of fully automatic hollow fiber liquid phase microextraction to assess the distribution of organophosphate esters in the Pearl River Estuaries. *Science of The Total Environment* **2014,** *470-471*, 263–269; DOI 10.1016/j.scitotenv.2013.09.069.

(27) Giulivo, M.; Capri, E.; Kalogianni, E.; Milacic, R.; Majone, B.; Ferrari, F.; Eljarrat, E.; Barceló, D. Occurrence of halogenated and organophosphate flame retardants in sediment and fish samples from three European river basins. *Science of The Total Environment* **2017,** *586*, 782–791; DOI 10.1016/j.scitotenv.2017.02.056.

(28) Cristale, J.; García Vázquez, A.; Barata, C.; Lacorte, S. Priority and emerging flame retardants in rivers: Occurrence in water and sediment, Daphnia magna toxicity and risk assessment. *Environment International* **2013,** *59*, 232–243; DOI 10.1016/j.envint.2013.06.011.

(29) Ohura, T.; Amagai, T.; Senga, Y.; Fusaya, M. Organic air pollutants inside and outside residences in Shimizu, Japan: Levels, sources and risks. *Science of The Total Environment* **2006,** *366* (2-3), 485–499; DOI 10.1016/j.scitotenv.2005.10.005.

(30) Cheng, W.; Xie, Z.; Blais, J. M.; Zhang, P.; Li, M.; Yang, C.; Huang, W.; Ding, R.; Sun, L. Organophosphorus esters in the oceans and possible relation with ocean gyres. *Environmental Pollution* **2013,** *180*, 159–164; DOI 10.1016/j.envpol.2013.05.032.

(31) Kawagoshi, Y.; Nakamura, S.; Fukunaga, I. Degradation of organophosphoric esters in leachate from a sea-based solid waste disposal site. *Chemosphere* **2002,** *48* (2), 219–225; DOI 10.1016/S0045-6535(02)00051-6.

(32) WATTS, M.; LINDEN, K. Photooxidation and subsequent biodegradability of recalcitrant tri-alkyl phosphates TCEP and TBP in water. *Water Research* **2008,** *42* (20), 4949–4954; DOI 10.1016/j.watres.2008.09.020.

(33) U. S. EPA. *Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update*; EPA 744-R-15-002, 2015.

(34) Waaijers, S. L.; Kong, D.; Hendriks, H. S.; Wit, C. A. de; Cousins, I. T.; Westerink, R. H. S.; Leonards, P. E. G.; Kraak, M. H. S.; Admiraal, W.; Voogt, P. de; Parsons, J. R. Persistence, bioaccumulation, and toxicity of halogen-free flame retardants. *Rev Environ Contam Toxicol* **2013,** *222*, 1–71; DOI 10.1007/978-1-4614-4717-7_1.

(35) Möller, A.; Sturm, R.; Xie, Z.; Cai, M.; He, J.; Ebinghaus, R. Organophosphorus Flame Retardants and Plasticizers in Airborne Particles over the Northern Pacific and Indian Ocean toward the Polar Regions: Evidence for Global Occurrence. *Environ. Sci. Technol.* **2012,** *46* (6), 3127–3134; DOI 10.1021/es204272v.

(36) Brandsma, S. H.; Leonards, P. E.; Leslie, H. A.; Boer, J. de. Tracing organophosphorus and brominated flame retardants and plasticizers in an estuarine food web. *Science of The Total Environment* **2015,** *505*, 22–31; DOI 10.1016/j.scitotenv.2014.08.072.

(37) Esch, G. J. v. *Flame retardants. Tris(2-butoxyethyl) phosphate, tris(2-ethylhexyl) phosphate and tetrakis(hydroxymethyl) phosphonium salts*; Environmental health criteria 218; World Health Organization: Geneva, 2000.

(38) Leisewitz, Kruse, Schramm. *Erarbeitung von Bewertungsgrundlagen zur Substitution umweltrelevanter Flammschutzmittel Umweltforschungsplan des. Band I: Ergebnisse und zusammenfassende Übersicht*; Forschungsbericht 297 44 542, 2000.

(39) Dishaw, L. V.; Powers, C. M.; Ryde, I. T.; Roberts, S. C.; Seidler, F. J.; Slotkin, T. A.; Stapleton, H. M. Is the PentaBDE replacement, tris (1,3-dichloro-2-propyl) phosphate (TDCPP), a developmental neurotoxicant? Studies in PC12 cells. *Toxicology and Applied Pharmacology* **2011,** *256* (3), 281–289; DOI 10.1016/j.taap.2011.01.005.

(40) Kojima, H.; Takeuchi, S.; Itoh, T.; Iida, M.; Kobayashi, S.; Yoshida, T. In vitro endocrine disruption potential of organophosphate flame retardants via human nuclear receptors. *Toxicology* **2013,** *314* (1), 76–83; DOI 10.1016/j.tox.2013.09.004.

(41) European Commission. *COMMISSION DIRECTIVE 2014/79/EU*, 2014.

(42) World Health Organization. *Flame retardants. Tris(chloropropyl) phosphate and tris(2-chloroethyl) phosphate*; Environmental health criteria 209; World Health Organization: Geneva, 1998.

(43) Sühring, R.; Busch, F.; Fricke, N.; Kötke, D.; Wolschke, H.; Ebinghaus, R. Distribution of brominated flame retardants and dechloranes between sediments and benthic fish — A comparison of a freshwater and marine habitat. *Science of The Total Environment* **2016,** *542*, 578–585; DOI 10.1016/j.scitotenv.2015.10.085.

(44) Russell H. Plumb. *Fingerprint analysis of contaminant data. A forensic tool for evaluating environmental .;* Bibliogov: [Place of publication not identified], 2013.

(45) Wegmann, F.; Cavin, L.; MacLeod, M.; Scheringer, M.; Hungerbühler, K. The OECD software tool for screening chemicals for persistence and long-range transport potential. *Environmental Modelling & Software* **2009,** *24* (2), 228–237; DOI 10.1016/j.envsoft.2008.06.014.

(46) Pankow, J. F. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmospheric Environment* **1994,** *28* (2), 185–188; DOI 10.1016/1352-2310(94)90093-0.

(47) Lohmann, R.; Lammel, G. Adsorptive and Absorptive Contributions to the Gas-Particle Partitioning of Polycyclic Aromatic Hydrocarbons: State of Knowledge and Recommended Parametrization for Modeling. *Environ. Sci. Technol.* **2004,** *38* (14), 3793–3803; DOI 10.1021/es035337q.

(48) Götz, C. W.; Scheringer, M.; MacLeod, M.; Wegmann, F.; Hungerbühler, K. Regional differences in gas–particle partitioning and deposition of semivolatile organic compounds on a global scale. *Atmospheric Environment* **2008,** *42* (3), 554–567; DOI 10.1016/j.atmosenv.2007.08.033.

(49) Canadian Council of Ministers of the Environment. *CANADA-WIDE STANDARDS for PARTICULATE MATTER (PM) and OZONE;* Endorsed by CCME Council of Ministers, June 5-6, 2000, Quebec City, 2000.

(50) United States Environmental Protection Agency (USEPA). *EPI Suite- Estimation Programs Interface Suite*, 2013.

(51) Hilal, S. H.; Saravanaraj, A. N.; Whiteside, T.; Carreira, L. A. Calculating physical properties of organic compounds for environmental modeling from molecular structure. *Journal of Computer-Aided Molecular Design* **2007,** *21* (12), 693–708; DOI 10.1007/s10822-007-9134-y.

(52) Bidleman, T. F. Atmospheric processes. *Environ. Sci. Technol.* **1988,** *22* (4), 361–367; DOI 10.1021/es00169a002.

(53) Andresen, J.; Grundmann, A.; Bester, K. Organophosphorus flame retardants and plasticisers in surface waters. *Science of The Total Environment* **2004,** *332* (1-3), 155–166; DOI 10.1016/j.scitotenv.2004.04.021.

(54) Regnery, J.; Püttmann, W. Organophosphorus Flame Retardants and Plasticizers in Rain and Snow from Middle Germany. *Clean Soil Air Water* **2009,** *37* (4-5), 334–342; DOI 10.1002/clen.200900050.

(55) Regnery, J.; Püttmann, W. Occurrence and fate of organophosphorus flame retardants and plasticizers in urban and remote surface waters in Germany. *Water Research* **2010,** *44* (14), 4097–4104; DOI 10.1016/j.watres.2010.05.024.

(56) Mihajlović, I.; Miloradov, M. V.; Fries, E. Application of Twisselmann Extraction, SPME, and GC-MS To Assess Input Sources for Organophosphate Esters into Soil. *Environ. Sci. Technol.* **2011,** *45* (6), 2264–2269; DOI 10.1021/es103870f.

(57) Men, B.; He, M.; Tan, L.; Lin, C. Distributions of polychlorinated biphenyls in the Daliao River estuary of Liaodong Bay, Bohai Sea (China). *Marine Pollution Bulletin* **2014,** *78* (1-2), 77–84; DOI 10.1016/j.marpolbul.2013.11.005.

(58) Lai, S.; Xie, Z.; Song, T.; Tang, J.; Zhang, Y.; Mi, W.; Peng, J.; Zhao, Y.; Zou, S.; Ebinghaus, R. Occurrence and dry deposition of organophosphate esters in atmospheric particles over the northern South China Sea. *Chemosphere* **2015,** *127*, 195–200; DOI 10.1016/j.chemosphere.2015.02.015.

(59) Möller, A.; Xie, Z.; Sturm, R.; Ebinghaus, R. Large-Scale Distribution of Dechlorane Plus in Air and Seawater from the Arctic to Antarctica. *Environ. Sci. Technol.* **2010,** *44* (23), 8977–8982; DOI 10.1021/es103047n.

(60) Xie, Z.; Möller, A.; Ahrens, L.; Sturm, R.; Ebinghaus, R. Brominated Flame Retardants in Seawater and Atmosphere of the Atlantic and the Southern Ocean. *Environ. Sci. Technol.* **2011,** *45* (5), 1820–1826; DOI 10.1021/es103803t.

(61) Dreyer, A.; Weinberg, I.; Temme, C.; Ebinghaus, R. Polyfluorinated Compounds in the Atmosphere of the Atlantic and Southern Oceans: Evidence for a Global Distribution. *Environ. Sci. Technol.* **2009,** *43* (17), 6507–6514; DOI 10.1021/es9010465.

(62) Zhong, G.; Tang, J.; Xie, Z.; Mi, W.; Chen, Y.; Möller, A.; Sturm, R.; Zhang, G.; Ebinghaus, R. Selected current-use pesticides (CUPs) in coastal and offshore sediments of Bohai and Yellow seas. *Environ Sci Pollut Res* **2014; DOI** 10.1007/s11356-014-2648-7.

(63) Automated Reasoning in Chemistry. SPARC Performs Automated Reasoning in Chemistry.

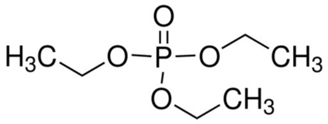
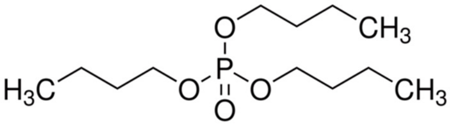
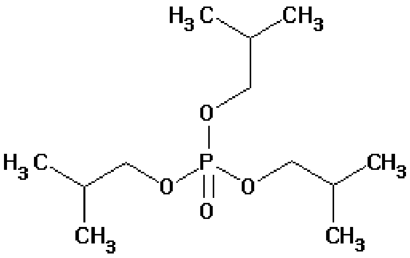
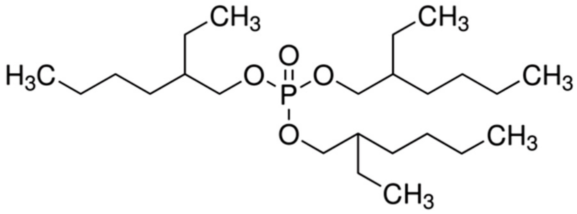
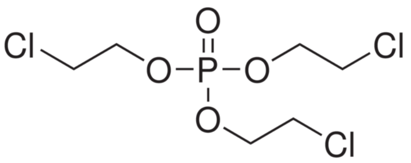
(64) ADC LABS. ACD/Absolv. Advanced Chemistry Development. http://www.acdlabs.com/.

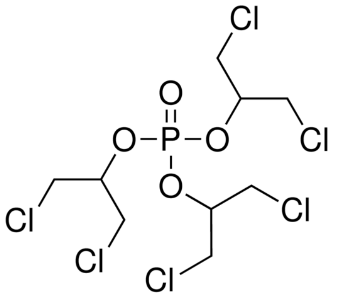
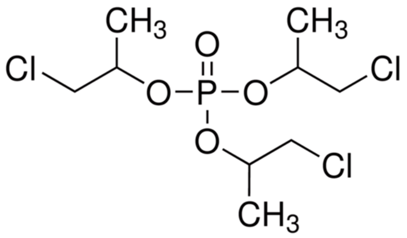
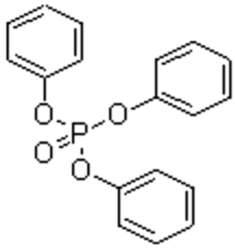
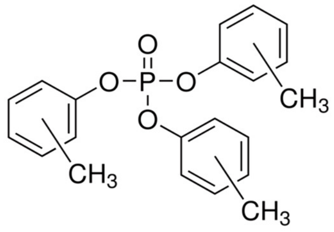
(65) Chen, L.; Mai, B.; Xu, Z.; Peng, X.; Han, J.; Ran, Y.; Sheng, G.; Fu, J. In- and outdoor sources of polybrominated diphenyl ethers and their human inhalation exposure in Guangzhou, China. *Atmospheric Environment* **2008,** *42* (1), 78–86; DOI 10.1016/j.atmosenv.2007.09.010.

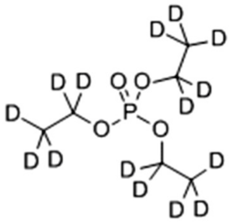
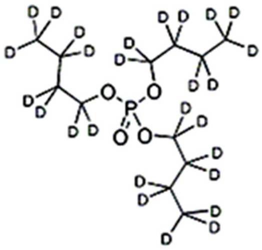
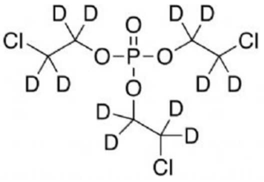
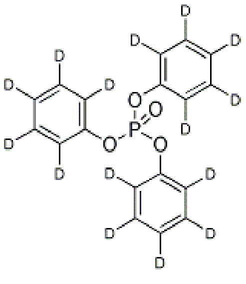
(66) Cotham, W. E.; Bidleman, T. F. Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls in Air at an Urban and a Rural Site Near Lake Michigan. *Environ. Sci. Technol.* **1995,** *29* (11), 2782–2789; DOI 10.1021/es00011a013.

9. Appendix Part I

Chemical structures of OPEs

Triethyl phosphate CAS-No.: 78-40-0	 $(C_2H_5O)_3PO$ $C_6H_{15}O_4P$ Mol. Wt.: 182.15 Exact mass: 182.07	**TEP**
Tributyl phosphate CAS-No.: 126-73-8	 $(CH_3(CH_2)_3O)_3PO$ $C_{12}H_{27}O_4P$ Mol. Wt.: 266.31 Exact mass: 266.16	**TnBP**
Triisobutylphosphat CAS-No.: 126-71-6	 $((CH_3)_2CHCH_2)_3PO$ $C_{12}H_{27}O_4P$ Mol. Wt.: 266.31 Exact mass: 266.16	**TiBP**
Tris(2-ethylhexyl) phosphate CAS-No.: 78-42-2	 $[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_3P(O)$ $C_{24}H_{51}O_4P$ Mol. Wt.: 434.63 Exact mass: 434.35	**TEHP**
Tris(2-chloroethyl) phosphate CAS-No.: 115-96-8	 $(ClCH_2CH_2O)_3P(O)$ $C_6H_{12}Cl_3O_4P$ Mol. Wt.: 285.49 Exact mass: 283.95	**TCEP**

Tris(1,3-dichloro-2-propyl) phosphate CAS-No.: 13674-87-8	 $C_9H_{15}Cl_6O_4P$ Mol. Wt.: 430.90 Exact mass: 427.88	**TDCPP**
Tris(1-chloro-2-propyl) phosphate CAS-No.: 13674-84-5	 $C_9H_{18}Cl_3O_4P$ Mol. Wt.: 327.57 Exact mass: 326,0	**TCPP**
Triphenyl phosphate CAS-No.: 115-86-6	 $(C_6H_5O)_3PO$ $C_{18}H_{15}O_4P$ l. Wt.: 326.28 Exact mass: 326.07	**TPhP**
Tricresyl phosphate **Tritolyl phosphate** CAS-No.: 1330-78-5	 $(CH_3C_6H_4O)_3PO$ $C_{21}H_{21}O_4P$ Mol. Wt.: 368.36 Exact mass: 368.12	**TCP**

Triethyl-D15 phosphate CAS-No.: 135942-11-9	 $(C_2D_5O)_3PO$ $C_6D_{15}O_4P$ Mol. Wt.: 197.25 Exact mass: 197.16	**TEP-D15**
Tributyl-D27 phosphate CAS-No.:	 $(CD_3(CD_2)_3O)_3PO$ $C_{12}D_{27}O_4P$ l. Wt.: 293.48 Exact mass: 293.33	**TnBP-D27**
Tris(2-chloroethyl)-D12 phosphate CAS-No.: -	 $(ClCD_2CD_2O)_3P(O)$ $C_6D_{12}Cl_3O_4P$ Mol. Wt.: 297.56 Exact mass: 296.03	**TCEP-D12**
Triphenyl-D15 phosphate CAS-No.:	 $(C_6D_5O)_3PO$ $C_{18}D_{15}O_4P$ Mol. Wt.: 341.37 Exact mass: 341.16	**TPhP-D15**

PART II

Cumulative Thesis

Declaration of the individual papers

This cumulative thesis is based on five scientific papers, all are published in international peer-reviewed journals. In the following, declarations to the contribution of the authors to the papers and quality of the publication are given in accordance with the guideline for cumulative dissertations in Sustainability Science, January 2012.

Papers included:

PAPER I: **Wolschke, H.**, Sühring, R., Xie, Z., Ebinghaus, R., 2015. Organophosphorus flame retardants and plasticizers in the aquatic environment: A case study of the Elbe River, Germany. Environmental Pollution 206, 488–493.

PAPER II: Wang, R., Tang, J., Xie, Z., Mi, W., Chen, Y., **Wolschke, H.**, Tian, C., Pan, X., Luo, Y., Ebinghaus, R., 2015. Occurrence and spatial distribution of organophosphate ester flame retardants and plasticizers in 40 rivers draining into the Bohai Sea, north China. Environmental Pollution 198, 172–178.

PAPER III: **Wolschke, H.**, Sühring, R., Mi, W., Möller, A., Xie, Z., Ebinghaus, R., 2016. Atmospheric occurrence and fate of organophosphorus flame retardants and plasticizer at the German coast. Atmospheric Environment 137, 1–5.

PAPER IV: Sühring, R., **Wolschke, H.**, Diamond, M.L., Jantunen, L.M., Scheringer, M., 2016. Distribution of Organophosphate Esters between the Gas and Particle Phase–Model Predictions vs Measured Data. Environ. Sci. Technol. 50 (13), 6644–6651.

PAPER V: **Wolschke, H.**, Sühring, R., Massei, R., Tang, J., Ebinghaus, R. Regional variations of organophosphorus flame retardants - Fingerprint of large river basin estuaries/deltas in Europe compared with China. Environmental Pollution (2018) 236, 391-395.

Authors’ contributions to the articles & their publication status (according to §12b, §14 and §16 of the guideline).

Article #	Title	Specific contributions of all authors	Author status	Weighting factor	Publication status	Conference contributions
[1]	Organophosphorus flame retardants and plasticizers in the aquatic environment: A case study of the Elbe River, Germany.	Hendrik Wolschke (70%):concept, labratory work, data evaluation and anaysis, discussion, manusript preparation Roxana Sühring (20%): concept, comments on the manuscript Zhiyong Xie (5%): comments on the mausript Ralf Ebinghaus (5%): concept, comments on the manuscript	Co-author with predominant contribution	1.0	Published in: Environmental Pollution (2015) 206, 488–493 (IF: 5.099)	34nd DIOXIN Symposium, 31st of August – 5th of September 2014, Madrid, Spain www.dioxin20xx.org (poster presentation)
[2]	Occurrence and spatial distribution of organophosphate ester flame retardants and plasticizers in 40 rivers draining into the Bohai Sea, north China	Runmei Wang (35%):concept, data evaluation and analysis, discussion, manusript preparation Jianhui Tang (15%): concept, discussion comments on the manuscript Zhiyong Xie (15%): concept, data evaluation and analysis, discussion comments on the manuscript Wenying Mi (5%): labratory work, data evaluation Yingjun Chen (5%): concept, comments on the manuscript Hendrik Wolschke (5%) comments on the manuscript Chongguo Tian (5%) comments on the manuscript Xiaohui Pan (5%) comments on the manuscript Yongming Luo (5%) concept, comments on the manuscript Ralf Ebinghaus (5%) concept, comments on the manuscript	Co-authorship: minor contribution	0.0	Published in: Environmental Pollution (2015) 198, 172-178 (IF: 5.099)	

[3]	Atmospheric occurrence and fate of organophosphorus flame retardants and plasticizer at the German coast	Hendrik Wolschke (65%):concept, laboratory work, data evaluation and analysis, discussion, manuscript preparation Roxana Sühring (15%): concept, discussion, comments on the manuscript Wenying Mi (4%): laboratory work Axel Möller (4%) sampling concept Zhiyong Xie (8%): concept, comments on the manuscript Ralf Ebinghaus (4%): concept	Co-author with predominant contribution	1.0	Published in: Atmospheric Environment (2016) 137, 1–5 (IF: 3.629)	34nd DIOXIN Symposium, 31st of August – 5th of September 2014, Madrid, Spain www.dioxin20xx.org (poster presentation)
[4]	Distribution of Organophosphate Esters between the Gas and Particle Phase–Model Predictions vs Measured Data	Roxana Sühring (55%): concept, data evaluation and analysis, discussion, manuscript preparation Hendrik Wolschke (30%): concept, discussion, comments on the manuscript Miriam L. Diamond (5%): comments on the manuscript Liisa M. Jantunen (5%): comments on the manuscript Martin Scheringer (5%): concept, comments on the manuscript	important contribution	0.5	Published in: Environmental Science & Technology (2016) 50 (13), 6644-6651 (IF: 6.198)	
[5]	Regional variations of organophosphorus flame retardants - Fingerprint of large river basin estuaries/deltas in Europe compared with China	Hendrik Wolschke (70%):concept, laboratory work, data evaluation and analysis, discussion, manuscript preparation Roxana Sühring (15%): concept, discussion, comments on the manuscript Riccardo Massei (5%): sampling concept Jianhui Tang (5%): sampling concept Ralf Ebinghaus (5%): concept	Co-author with predominant contribution	1.0	Published om: Environmental Pollution (2018) 236, 391-395 (IF: 5.099)	
			Sum:	3.5		

Author status and Weighting factor (WF)

According to §12b and §14 of the guideline:

Single author [Allein-Autorenschaft] = Own contribution amounts to 100%. (WF = 1.0)

Co-author with predominant contribution [Überwiegender Anteil] = Own contribution is greater than the individual share of all other co-authors and is at least 35%. (WF = 1.0)

Co-author with equal contribution [Gleicher Anteil] = (1) own contribution is as high as the share of other co-authors, (2) no other co-author has a contribution higher than the own contribution, and (3) the own contribution is at least 25%. (WF = 1.0)

Co-author with important contribution [Wichtiger Anteil] = own contribution is at least 25%, but is insufficient to qualify as single authorship, predominant or equal contribution. (WF = 0.5)

Co-author with small contribution [Geringer Anteil] = own contribution is less than 20%. (WF = 0)

Impact factors (IF): Thomson Reuters Journal Citation Reports; impact factors 2016

Declaration (according to §16 of the guideline)

I avouch that all information given in this PART is true in each instance and overall.

Hendrik Wolschke

Presentations in framework of the PhD-Thesis

Conferences

- SETAC Europe 23rd annual meeting 12th – 16th of May 2013, Glasgow, Scotland, http://glasgow.setac.eu/ (Poster presentation)
- 7th Annual POPs Network Conference April 24-25 2013 at University of Birmingham, England, (Poster presentation)
- 34nd DIOXIN Symposium, 31st of August – 5th of September 2014, Madrid, Spain, http://www.dioxin20xx.org/ (2 poster presentations)

Presentations outside of Conferences

- Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, China, 30th Septemer 2014 “Organophosphorus Flame Retardants and Plasticisers in the marine environment” (oral presentation)
- Nankai University, Collage of Environmental Science and Engineering, Tianjin, China, 20th October 2014 “Organophosphorus Flame Retardants and Plasticisers in the marine environment” (oral presentation)
- Helmholtz Centre for Environmental Research, closing Workshop PhD-Twining project UFZ-HZG, 18th January 2016, Leipzig, Germany “Emerging Contaminants in Aquatic Sediments” (oral presentation)

Paper I

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

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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.

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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0269-7491/

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 in 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, Daldropþ, Dr. Ing. Huber, Neckartalfingen, 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 filtrated 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 Na_2SO_4-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 ^{13}C-PCB 141 and ^{13}C-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. Na_2SO_4 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

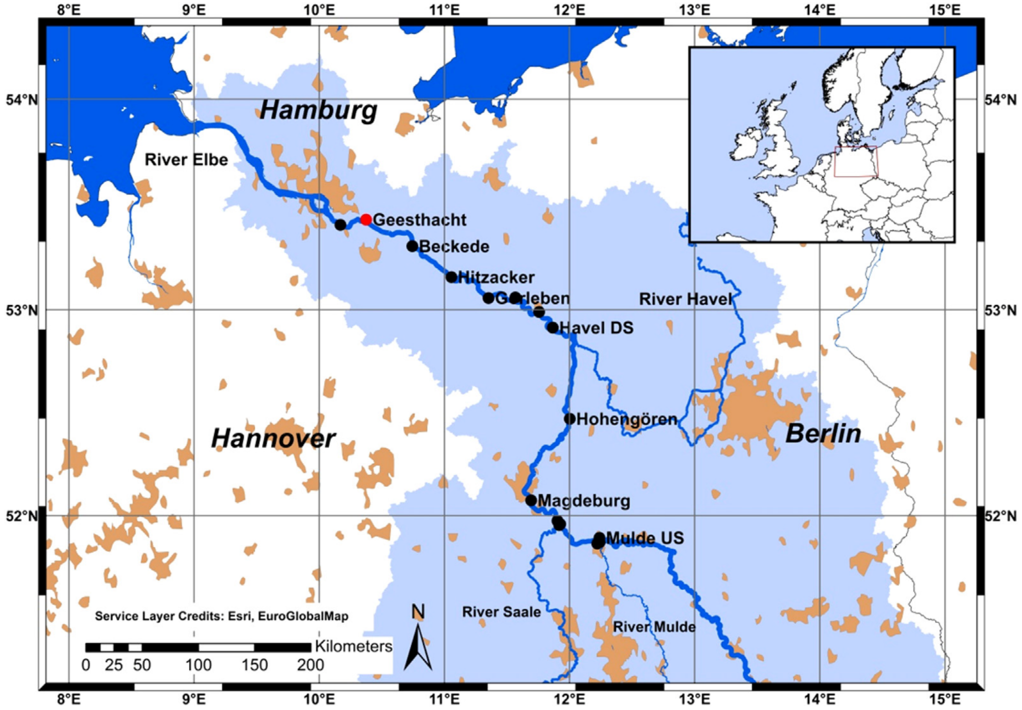


Fig. 1. Sampling map for the Elbe River, black dots: sampling spots longitudinal profile, red dot: sampling spot flood event, light blue area: drainage area Elbe River. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

SPE methods. Method detection limits (MDLs) were derived from either the mean blank values plus three times the standard deviation or the signal-to-noise ratio (S/N = 3), whichever approach yielded the higher value. Based on a volume of 500 mL, MDLs ranged from 2.7 ng/L for TEP to 26.6 ng/L for TPhP (see S4 of the Supplementary Material for further details). Recoveries of the surrogates were 61 ± 23% for TEP-d15, 43 ± 25% for TCEP-d12, 70 ± 20% for TBP-d27, and 78 ± 11% for TPhP-d15 for the SPE method. The liquid–liquid extraction (LLE) method recoveries were 45 ± 22% for TEP-d15, 45 ± 27% for TCEP-d12, 60 ± 18% for TBP-d27, and 77 ± 12% for TPhP-d15. All reported concentrations were corrected for recoveries. Both of the applied extraction techniques (i.e., SPE and LLE) proved useful for the analysis of OPEs and provided comparable results.

3. Results and discussion

3.1. Transect along the Elbe River

In all dissolved phase samples, 6 of the 13 investigated OPEs were detected along the Elbe River and its tributaries Havel, Mulde and Saale. In the particulate phase, all of the OPEs were below the MDLs. The average sum concentration was 627 ± 57 ng/L, with the following average compound distribution: TEP, 168 ± 44 ng/L; TDCPP, 155 ± 14 ng/L; TCPP, 126 ± 14 ng/L; TCEP, 81 ± 12 ng/L; TiBP, 73 ± 24 ng/L; and TnBP, 23 ± 12 ng/L. TDCPP was detected in suspiciously high concentrations compared to the earlier studies of Bollmann et al. (2012). An explanation for the observed differences could be the increased application of TDCPP as a replacement for the technical PentaBDE formulation as the flame retardant in PUF forms (Shaw et al., 2010). Another indication for the increasing application of OPEs as replacements for PentaBDE was the high concentrations of TCPP, which is another common PentaBDE replacement. Throughout the Elbe River, TCPP concentrations exceeded the "acceptable concentration in surface waters" of 100 ng/L proposed by the Federal Environmental Agency of Germany (Leisewitz et al., 2000). Variations in OPE concentrations over the 300 km transect were generally low (Fig. 2), despite a 2.5-fold increase of water discharge from the first to the last sampling point along the transect. No specific local inputs or dilution effects were visible. This result indicates a constant diffuse input along the entire distance, rather than via point source inputs such as wastewater treatment plants. Similar concentrations to those measured in the Elbe River were found in the three investigated major tributary rivers Havel, Saale and Mulde. Notably, a slowly increasing concentration of TnBP towards the river mouth was observed in the Elbe River, whereas its isomer TiBP displayed a decreasing trend. A transformation of the TiBP isomers has not been reported in the literature. Additionally, their estimated life times in aquatic environments according to the EPI Suite (US EPA, 2014) is 208 h for

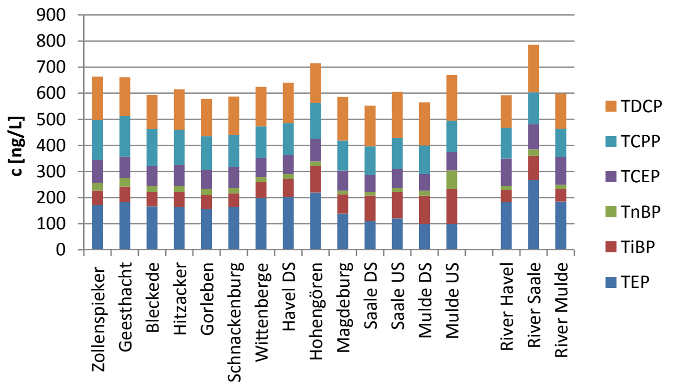


Fig. 2. Concentration along the Elbe River including the tributary Rivers Havel, Saale and Mulde in ng/L. DS = downstream, US = upstream.

TnBP and 360 h for TiBP. Thus, these data would suggest an opposite trend; that is, an increase of TiBP contributions towards the river mouth would be expected. With a log K_{OW} of 4.0, a sorption to sediment of the TiBP isomers could be a possible removal pathway from the water phase, which would offer a potential explanation for the observed pattern changes. However, the observations could also be attributed to temporal variations.

OPE mass fluxes were calculated using daily mean water discharge data from the BfG (German Federal Institute of Hydrology (2014)). Detailed results are presented in the Supplementary Material. Mass flux calculations showed a OPE discharge in the upstream sampling areas of 135 mg/s (Station Wittenberg), which increased to 304 mg/s at the river mouth (Station Bleckede). This increase appears to be exclusively driven by the higher water discharge because the concentrations remained constant.

A comparison of concentration levels measured in this study with a previous study (Bollmann et al., 2012) could provide information on changes in OPE concentrations in the Elbe River over the last three years. Bollmann et al. reported average concentrations of 240 ng/L in 2010 at a station 30 km downstream from the last sampling station of this study; which is approximately a factor of 2.5 lower than the 660 ng/L observed at the Zollenspieker sampling station in this study (Fig. 2). However, the observed mass fluxes were comparable, with an average OPE discharge estimated to be 220 mg/s in 2010 and 330 mg/s in this study.

It has previously been discussed that OPEs could play a role as a phosphorus source in the aquatic phosphorus cycle (Castro-Jiménez et al., 2014). In this study we found that OPEs are only a minor contributor to the total phosphorus level in the Elbe River. The phosphorus load related to OPEs was calculated to be approximately 60 ng/L, whereas the total phosphorus load in the Elbe River is approximately 0.1 mg/L (RBC Elbe) during the same time frame, which is more than 4 orders of magnitude higher.

3.2. *Flood event of the Elbe River*

The flood of the Elbe River occurred in June 2013 in Middle and Northern Germany and has been described as a century flood event. Because of strong rain in May and June 2013 the water levels of the Elbe River rose to levels not witnessed for a century. The highest water level was 7 m (3 m over the mean) at the sampling station, with a water discharge of 4060 m^3/s, which is 5.5 times higher than the mean water discharge under “normal” conditions. Some cities along the upper river were flooded and several waste water treatment plants overflowed. The samples were taken from the platform at the barrage in Geesthacht. The barrage separates the lower river, which is influenced by the North Sea tides, and the middle reach. The sampling point was in a rural area upstream of the city of Hamburg.

OPEs were detected throughout the investigation period in the dissolved phase. All levels of the OPEs were below the MDLs in the particulate phase. The lowest sum concentrations were 392 ng/L, and thus 1/3 lower than the highest observed concentration in the Elbe River (612 ng/L). The contamination pattern did not change significantly over a three-week sampling period. Compared to the “regular” contamination situation (i.e., no flooding), no unexpected compounds from special inputs as, for example, the flooding of sewage treatment plants or higher inputs of the present compounds, were observed. High fluctuations were observed for the very volatile TEP, with a strong increase directly after the highest water levels. This result is consistent with previous reports (Bollmann et al., 2012) that also reported high TEP fluctuations.

In general, the highest concentrations were observed before the maximum water level with a decreasing trend during the flood wave and a slight increase afterwards. These trends were expected and corresponded with previous observations of metals during the flood event of the Elbe River in 2002 (Baborowski et al., 2005). In this study, the authors observed a “clean out” with higher concentrations in front of the water level, followed by a dilution period and an increase after the water level returned back to its normal level.

The daily mean water discharge data from the Neu Dachau station (German Federal Institute of Hydrology (2014)) was used for OPE mass flux calculations during the flood event. The highest mass flux was observed simultaneously with the highest water discharge at the June 12, 2013 with 4060 m^3/s and 1850 mg/s of sum OPEs. This result indicates a four-fold increase relative to the observed mass flux at normal conditions for the Elbe transect. The change in mass flux appeared to be mostly driven by changes in the water discharge (relative SD of 30.1%) rather than change in the concentration (relative SD of 16%).

The total mass flux over the three week measurement period during the flood event was 2.8 t, which is approximately 50% of the annual OPE discharge of the Elbe River in 2010 (Bollmann et al., 2012). However, the possibility of higher risks for negative effects of OPEs for organisms within the Elbe River caused by the flood event can be excluded because of the overall similar concentrations. However, for the estuaries and the North Sea, temporary effects caused by OPEs cannot be ruled out, as the OPE input increased ten-fold (~16 kg/d normal; ~160 kg/d flood peak) during the flood event.

3.3. *Rhine and Ems Rivers*

The samples from the Rhine and Ems rivers were extracted via a liquid–liquid extraction technique. TEP was not analyzed in these samples. Compared to the Elbe River, the concentration trends were limited along the Rhine River transect from the Ruhr River in Germany to the Delta in the Netherlands. Detailed concentrations and sampling points are presented in the Supplementary Material (S6). The average concentration over the transect was 385 ± 46 ng/L, which is comparable to the data measured for the Elbe River (without TEP). In the German part of the Rhine River, slightly higher concentrations of OPEs were observed than in the Dutch part of the river, with the highest concentrations at the Neuss station. No specific local inputs or dilution effects were observed, including the industrial area around the Ruhr River or in the harbor of Rotterdam, which are two very intensively industrialized areas. Consistent with the results obtained for the Elbe River, TDCPP concentrations were highest in the Rhine River (Fig. 3).

The concentrations of OPEs in the Ems River, which is a relatively small river close to the German/Dutch border (~80 m^3/s), were, on average, 277 ± 46 ng/L. These concentrations are comparable to the OPE concentrations measured in the Elbe and Rhine rivers, even though the Ems River is less influenced by industry, except for the Meyer dockyard in Papenburg. Relative to the more stable chlorinated TCEP, TCPP and TDCPP compounds, the contribution of individual OPEs (Fig. 4) to the average concentrations showed that the levels of the non-chlorinated compounds TnBP and TiBP increased as the density of the industrialized areas increased (Ems - > Elbe - > Rhine). The contribution of TDCPP, which is one recommended replacement for PentaBDEs, was highest in the Elbe River, followed by the Ems and Rhine rivers. This result is notable because, in the past, new contaminates such as PFC replacements were usually first detected in areas highly influenced by industry (Möller et al., 2010), which would suggest high concentrations in the Rhine River.

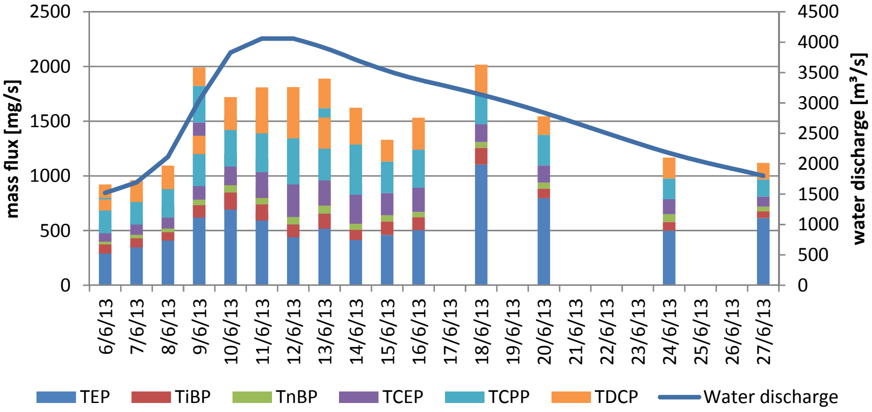


Fig. 3. SUM OPE mass flux during the flood event 2013 including the water discharge.

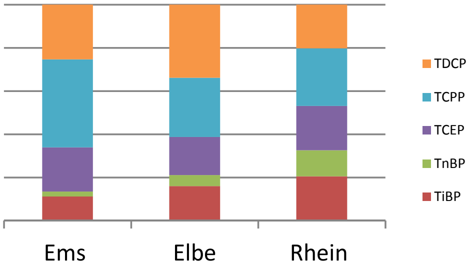


Fig. 4. Comparison of OPE contribution in different rivers.

3.4. *Comparison of the different river systems with other studies*

There is little data available of OPEs in sediment or air. However, several data sets have been published that concern the presence of OPEs in water. A comparison of different rivers is presented in Table 1. The focus of this compilation was to compare the different data sets from the Elbe River to construct a timeline and to give an overview of the other regions.

The following trends were observed for the Elbe River. First, a decrease of TCEP was observed, which supports the observed trend reported by Quednow and Püttmann (2008). Second, constant levels of TCPP have been measured over the last 20 years in the larger river systems of Europe (Bollmann et al., 2012; Knepper et al., 1999; this study). Third, a decrease of TnBP over the last few years is evident, indicating changes in the production and use of OPEs. Fourth, the increasing concentrations of TDCPP suggest that this compound may pose a risk to the aquatic environment.

In an international comparison, the highest concentrations were detected in industrial areas of Spain (Barcelona), China (Peal River) and the UK. Cristale et al. (2013b) reported a clear increasing trend from the spring to the mouth in Spanish rivers, which was not observed in the present study. It is likely that this difference is the result of the present study being focused only on the larger water basin of the river, which is influenced by urban areas. Additionally, the Spanish studies included the spring of the river in the

Table 1
Overview of OPEs in different rivers around the world. Concentrations are given in [ng/L] (*annual average, ** median).

Country	River	Location	Year	TCPP	TCEP	TDCPP	TiBP	TBP	TBEP	TPhP	TEP	Reference
Germany	Elbe	Dessau-Hamburg	2013	126	81	155	73	23			168	This study
Germany	Elbe	Hamburg-Cuxhaven	2010	40–250	5–20	8–25	10–50	2–7.5	LOD-80	0.3–0.4		(Bollmann et al., 2012)
Germany	Elbe	Dommitzsch	2007				27	102				(RBC Elbe)*
Germany	Elbe	Dommitzsch	2008				22	155				(RBC Elbe)*
Germany	Elbe	Dommitzsch	2009				48	123				(RBC Elbe)*
Germany	Elbe	Dommitzsch	2010				72	70				(RBC Elbe)*
Germany	Elbe	Dommitzsch	2011					65				(RBC Elbe)*
Germany	Elbe	Brunsbüttel	2012	257	<40	<100						(RBC Elbe)
Netherlands	Rhine	Delta	2010	75–160	12–25		17–84	6–28	28–54	1–2		(Bollmann et al., 2012)
Germany		Rüsselsheim	2000		24			318	321			(Fries and Püttmann, 2001)
Germany		Colone	1995	30–150	50–500							(Knepper et al., 1999)
Spain	Mero, Anllons	Galicia	2008	47	5			37			3	(Rodil et al., 2012)**
Spain	Nalon, Arga, Besos	North Spain	2012	LOD-1800	LOD-330	LOD-200	LOD-1200	LOD-370	LOD-4600	LOD-35		(Cristale et al., 2013b)
UK	Aire			113–26,050	119–316	62–149	n.a.	n.a	n.a.	6–22		(Cristale et al., 2013)
Germany	Several creeks	Hessen		502	118			276	183			(Quednow and Püttmann, 2008)
China	40 Rivers China	Boahai Sea	2013	5–921	1–268	<LOD-44	<LOD-218	<LOD-81	<LOD-47	<LOD-16	<LOD-350	(Wang et al., 2015)
China	Pearl River			150–1150	220–1166							(Wang et al., 2014)
Austria	Danube	Vienna		33–43	13–23			20–110	24–52	<LOQ-6		(Martínez-Carballo et al., 2007)

mountains where the water is not strongly influenced by human activity.

4. Conclusion

The results of this study show the presence of OPEs in sum concentrations of hundreds of ng/L in all of the investigated rivers. The concentration ratio and the compound pattern over the transects along the rivers display only minor variations. Point sources were not identified. These results imply that the sources of OPEs to the rivers are mainly diffuse or ubiquitous distributed sources such as household discharge or atmospheric deposition.

During the Elbe flood event of 2013 the local concentrations were similar to the normal situation, but the mass flux increased significantly. Within the estuarine part of the river the OPE concentrations caused by the flood wave increased beyond the expected increase caused by the change of salinity in this section of the river. The increasing concentration of TDCPP may be a potential cause for concern. Indeed, in addition to its reported mutagenic effects, the use of TDCPP is currently recommended and is increasingly applied as a replacement for the technical PentaBDE formulation.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2015.08.002.

References

Andresen, J.A., Muir, D., Ueno, D., Darling, C., Theobald, N., Bester, K., 2007. Emerging pollutants in the North sea in comparison to Lake Ontario, Canada, data. Environ. Toxicol. Chem. 26 (6), 1081–1089.

Baborowski, M., Claus, E., Friese, K., Kammer, F., von der Kasimir, P., Pelzer, J., Heininger, P., 2005. Comparison of different monitoring programs of the 2002 summer flood in the river elbe. Acta hydrochim. hydrobiol. 33 (5), 404–417.

Bacaloni, A., Cavaliere, C., Foglia, P., Nazzari, M., Samperi, R., Laganà, A., 2007. Liquid chromatography/tandem mass spectrometry determination of organophosphorus flame retardants and plasticizers in drinking and surface waters. Rapid Commun. Mass Spectrom. 21 (7), 1123–1130.

Bollmann, U.E., Möller, A., Xie, Z., Ebinghaus, R., Einax, J.W., 2012. Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. Water Res. 46 (2), 531–538.

Camarasa, J.G., Serra-Baldrich, E., 1992. Allergic contact dermatitis from triphenyl phosphate. Contact Derm. 26 (4), 264–265.

Castro-Jiménez, J., Berrojalbiz, N., Pizarro, M., Dachs, J., 2014. Organophosphate ester (OPE) flame retardants and plasticizers in the open mediterranean and black seas atmosphere. Environ. Sci. Technol. 48 (6), 3203–3209.

Cristale, J., Garcia Vazquez, A., Barata, C., Lacorte, S., 2013b. Priority and emerging flame retardants in rivers: occurrence in water and sediment, Daphnia magna toxicity and risk. Environ. Int. 59, 232–243.

Cristale, J., Katsoyiannis, A., Sweetman, A.J., Jones, K.C., Lacorte, S., 2013. Occurrence and risk assessment of organophosphorus and brominated flame retardants in the River Aire (UK). Environ. Pollut. 179, 194–200.

EFRA – Cefic, 2007. EFRA Marktstatistik No.31. http://www.flameretardants.eu/Content/Default.asp?PageName=openfile&Doc [accessed 20.11.10].

EPA, U.S., 2014. Flame Retardants Used in Flexible Polyurethane Foam: an Alternatives Assessment Update [accessed 06.02.15].

European Commission – Scientific Committee on Health and Environmental Risks, 2012. Opinion on Tris(2-chloroethyl)phosphate (TCEP) in Toys [accessed 18.02.15].

Fries, E., Püttmann, W., 2001. Occurrence of organophosphate esters in surface water and groundwater in Germany. J. Environ. Monit. 3 (6), 621–626.

Fries, E., Püttmann, W., 2003. Monitoring of the three organophosphate esters TBP, TCEP and TBEP in river water and ground water (Oder, Germany). J. Environ. Monit. 5 (2), 346–352.

German Federal Institute of Hydrology, 2014. German Federal Waterways and Shipping Administration (WSV), Distributed by German Federal Institute of Hydrology. www.bafg.de.

Kawagoshi, Y., Nakamura, S., Fukunaga, I., 2002. Degradation of organophosphoric esters in leachate from a sea-based solid waste disposal site. Chemosphere 48 (2), 219–225.

Knepper, T., Sacher, F., Lange, F., Brauch, H., Karrenbrock, F., Roerden, O., Lindner, K., 1999. Detection of polar organic substances relevant for drinking water. Waste Manag. 19 (2), 77–99.

Leisewitz, Kruse, Schramm, 2000. Erarbeitung von Bewertungsgrundlagen zur Substitution umweltrelevanter Flammschutzmittel Umweltforschungsplan des. In: Band I: Ergebnisse und zusammenfassende Übersicht, p. 209 [accessed 21.01.14].

Marklund, A., Andersson, B., Haglund, P., 2003. Screening of organophosphorus compounds and their distribution in various indoor environments. Chemosphere 53 (9), 1137–1146.

Martínez-Carballo, E., González-Barreiro, C., Sitka, A., Scharf, S., Gans, O., 2007. Determination of selected organophosphate esters in the aquatic environment of Austria. Sci. Total Environ. 388 (1–3), 290–299.

Matthews, H., 1993. Toxicity and carcinogenicity of chronic exposure to Tris(2-chloroethyl)phosphate. Fundam. Appl. Toxicol. 20 (4), 477–485.

Meyer, J., Bester, K., 2004. Organophosphate flame retardants and plasticisers in wastewater treatment plants. J. Environ. Monit. 6 (7), 599.

Möller, A., Ahrens, L., Surm, R., Westerveld, J., van der Wielen, F., Ebinghaus, R., Voogt de, P., 2010. Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. Environ. Pollut. 158 (10), 3243–3250.

Möller, A., Sturm, R., Xie, Z., Cai, M., He, J., Ebinghaus, R., 2012. Organophosphorus flame retardants and plasticizers in airborne particles over the northern Pacific and Indian ocean toward the polar regions: evidence for global occurrence. Environ. Sci. Technol. 46 (6), 3127–3134.

Nakamura, A., 1991a. Tri-n-butyl Phosphate. Environmental Health Criteria 112. World Health Organization, Geneva, p. 80.

Nakamura, A., 1991b. Triphenyl Phosphate. Environmental Health Criteria 111. World Health Organization, Geneva, p. 80.

Quednow, K., Püttmann, W., 2008. Organophosphates and synthetic Musk fragrances in freshwater streams in Hessen/Germany. Clean. Soil Air Water 36 (1), 70–77.

RBC Elbe, RBC data information system (FIS). www.fgg-elbe.de. [accessed 10.02.15].

Reemtsma, T., Quintana, J.B., Rodil, R., García-López, M., Rodríguez, I., 2008. Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. TrAC Trends Anal. Chem. 27 (9), 727–737.

Rodil, R., Quintana, J.B., López-Mahía, P., Muniategui-Lorenzo, S., Prada-Rodríguez, D., 2009. Multi-residue analytical method for the determination of emerging pollutants in water by solid-phase extraction and liquid chromatography–tandem mass spectrometry. J. Chromatogr. A 1216 (14), 2958–2969.

Rodil, R., Quintana, J.B., Concha-Garna, E., Lopez-Mahia, P., Muniategui-Lorenzo, S., Prada-Rodriguez, D., 2012. Emerging pollutants in sewage, surface and drinking water in Galicia (NW Spain). Chemosphere 86 (10), 1040–1049.

Saeger, V.W., Hicks, O., Kaley, R.G., Michael, P.R., Mieure, J.P., Tucker, E.S., 1979. Environmental fate of selected phosphate esters. Environ. Sci. Technol. 13 (7), 840–844.

Salamova, A., Hermanson, M.H., Hites, R.A., 2014. Organophosphate and halogenated flame retardants in atmospheric particles from a european arctic site. Environ. Sci. Technol. 48 (11), 6133–6140.

Sato, T., Watanabe, K., Nagase, H., Kito, H., Niikawa, M., Yoshioka, Y., 1997. Investigation of the hemolytic effects of various organophosphoric acid triesters (OPEs) and their structure-activity relationship. Toxicol. Environ. Chem. 59 (1–4), 305–313.

Shaw, S.D., Blum, A., Weber, R., Kannan, K., Rich, D., Lucas, D., Koshland, C.P., Dobraca, D., Hanson, S., Birnbaum, L.S., 2010. Halogenated flame retardants: do the fire safety benefits justify the risks? Rev. Environ. Health 25 (4), 261–305.

US EPA, 2014. Estimation Programs Interface Suite™ for Microsoft® Windows, 411. http://www.epa.gov/opptintr/exposure/pubs/episuite.htm.

Waaijers, S.L., Kong, D., Hendriks, H.S., Wit, C.A., de Cousins, I.T., Westerink, R.H.S., Leonards, P.E.G., Kraak, M.H.S., Admiraal, W., Voogt de, P., Parsons, J.R., 2013. Persistence, Bioaccumulation, and Toxicity of Halogen-free Flame Retardants [accessed 29.09.14].

Wang, R., Tang, J., Xie, Z., Mi, W., Chen, Y., Wolschke, H., Tian, C., Pan, X., Luo, Y., Ebinghaus, R., 2015. Occurrence and spatial distribution of organophosphate ester flame retardants and plasticizers in 40 rivers draining into the Bohai Sea, north China. Environ. Pollut. 198, 172–178.

Wang, X., He, Y., Lin, L., Zeng, F., Luan, T., 2014. Application of fully automatic hollow fiber liquid phase microextraction to assess the distribution of organophosphate esters in the Pearl River Estuaries. Sci. Total Environ. 470–471, 263–269.

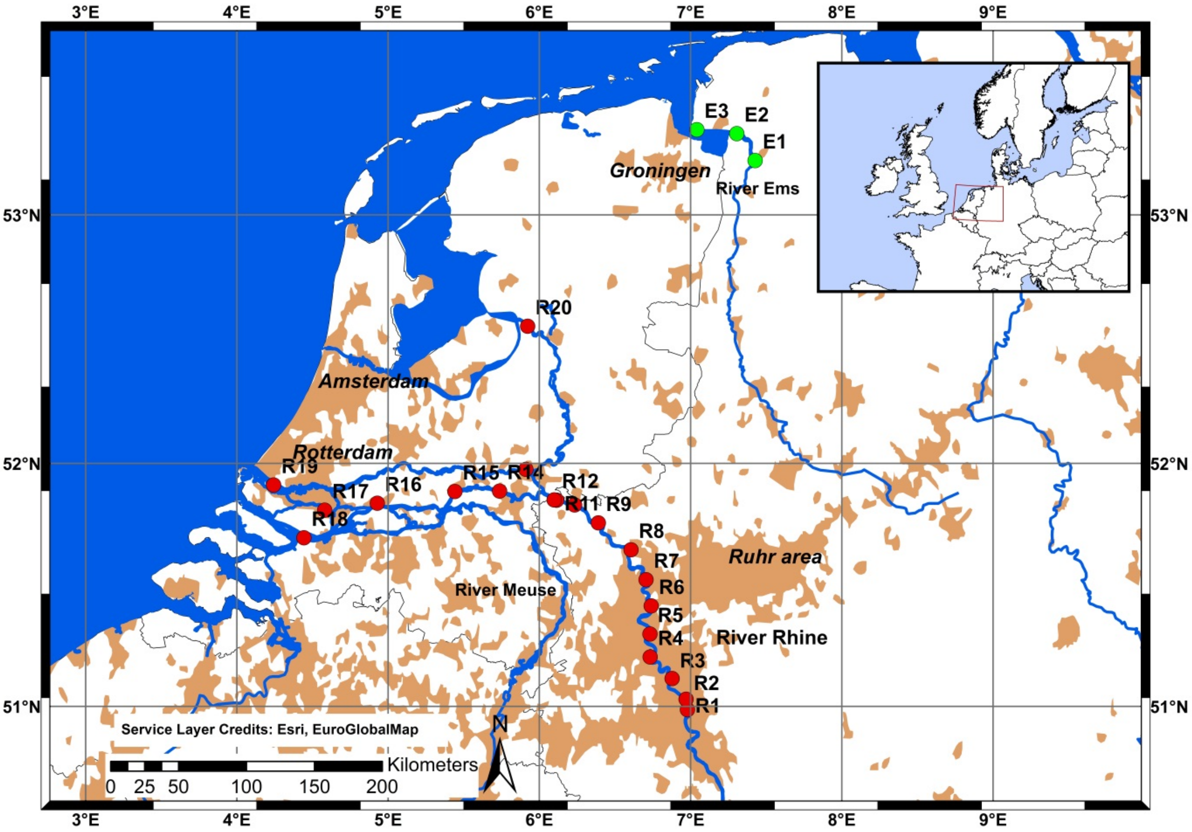
World Health Organization, 1998. Flame Retardants: Tris(chloropropyl) Phosphate and Tris(2-chloroethyl) Phosphate. In: Environmental Health Criteria 209, xix. World Health Organization, Geneva, p. 106.

Supplementary Material

S1

Name		Molecular formula	CAS-No.	Purity %	Producer
d15-Triethylphosphat	D15-TEP	$C_6D_{15}O_4P$		99,2	Dr. Ehrenstorfer
d15-Triphenylphosphat	D15-TPhP	$C_{18}D_{15}O_4P$		98	Sigma Aldrich
d21-Tri-*n*-propylphosphat	D21-TPrP	$C_9D_{21}O_4P$		98,2	Dr. Ehrenstorfer
d27-Tri-*n*-butylphosphat	D27-TnBP	$C_{12}D_{27}O_4P$	61196-26-7	99,7	Dr. Ehrenstorfer
Tris(2-butoxyethyl)phosphat	TBEP	$C_{18}H_{39}O_7P$	78-51-3	94	Sigma Aldrich
Tri-*n*-butylphosphat	TnBP	$C_{12}H_{27}O_4P$	126-73-8	≥ 99	Sigma Aldrich
Tris(2-chloroethyl)phosphat	TCEP	$C_6H_{12}Cl_3O_4P$	115-96-8	97	Sigma Aldrich
Tricresylphosphat	TCP	$C_{21}H_{21}O_4P$	1330-78-5	90 (Isomere)	Sigma Aldrich
Tris(1-chloro-2-propyl)phosphat	TCPP	$C_9H_{18}Cl_3O_4P$	13674-84-5	Anal.Std. (Isomere)	Sigma Aldrich
Tris(dichlorisopropyl)phosphat	TDCPP	$C_9H_{15}Cl_6O_4P$	13674-87-8	95,8	Sigma Aldrich
Tris(2-ethylhexyl)phosphat	TEHP	$C_{24}H_{51}O_4P$	78-42-2	≥ 99	Sigma Aldrich
Triethylphosphat	TEP	$C_6H_{15}O_4P$	78-40-0	≥ 99,8	Sigma Aldrich
Tri-*iso*-butylphosphat	TiBP	$C_{12}H_{27}O_4P$	126-71-6	≥ 99	Merck
Tri-*iso*-propylphosphat	TiPrP	$C_9H_{21}O_4P$	513-02-0	97	Sigma Aldrich
Tripentylphosphat	TPeP	$C_{15}H_{33}O_4P$	2528-38-3	≥ 98	TCI Europe
Triphenylphosphat	TPhP	$C_{18}H_{15}O_4P$	115-86-6	≥ 99	Sigma Aldrich
Tri-*n*-propylphosphat	TPrP	$C_9H_{21}O_4P$	513-08-6	99	Sigma Aldrich

S2 Samplingmap for the rivers Rhine and Ems.



S3

		Quantifier			Qualifier		
Compound	Retention time	Precurser Ion	Product Ion	CE (V)	Precurser Ion	Product Ion	CE (V)
dTEP	*12.1*	*135*	*99*	*15*	*167*	*103*	*15*
dTPrP	*22.8*	*151*	*103*	*10*	*199*	*103*	*10*
dTnBP	*29.1*	*103*	*83*	*15*	*167*	*103*	*15*
dTCEP	*32.4*	*261*	*196*	*5*	*261*	*103*	*25*
dTPhP	*44.6*	*341*	*223*	*35*	*341*	*178*	*35*
INJ-PCB141	*43.5*	*372*	*302*	*40*			
INJ-PCB208	*50.2*	*476*	*406*	*40*			
TEP	12.3	155	99	15	127	99	15
TiPrP	17.8	141	99	5	99	81	20
TPrP	23.1	183	99	10	141	99	10
TiBP	26.4	99	81	25	155	99	5
TnBP	29.4	99	81	35	155	99	5
TCEP	32.6	249	187	5	249	99	35
TCPP	33.46	277	125	5	157	117	5
TPeP	37.3	99	81	20	239	99	20
TDCPP	43.7	381	159	15	191	75	5
TPhP	44.8	326	215	25	326	170	25
TBEP	45.1	299	199	5	227	101	5
TEHP	46.3	99	81	25			
TCP	50.1	368	198	30	368	165	30

S4: Limit of detection combined for both methods [ng/L] based on an extraction volume of 500 mL.

Limit of detection	
TEP	2.7
TiBP	17.7
TnBP	6.4
TCEP	5.3
TCPP	7.9
TDCP	9.0
TPhP	26.6

S5: Mass flux along the river Elbe with Feeder Rivers

	Discharge [m³/s]	TEP [mg/s]	TiBP [mg/s]	TnBP [mg/s]	TCEP [mg/s]	TCPP [mg/s]	TDCP [mg/s]	SUM [mg/s]
Zollenspieker	514	88.2	28.6	14.3	45.2	79.0	85.8	341.2
Bleckede	514	85.6	28.7	11.5	39.7	72.3	67.2	305.0
Wittenberge	439	87.2	26.9	8.8	31.4	53.5	66.4	274.1
Hohengören	324	71.2	32.7	5.8	28.3	44.5	49.2	231.6
Magdeburg	325	45.1	24.0	4.7	25.0	37.4	54.3	190.5
Saale DS	308	33.6	30.5	4.1	20.4	33.6	48.0	170.2
Saale US	227	27.2	23.1	3.3	16.8	26.8	40.0	137.3
Mulde US	202	20.2	27.1	14.2	14.1	24.4	35.3	135.3
River Havel	37.4	6.9	1.7	0.6	3.9	4.4	4.6	22.2
River Saale	67	17.9	6.3	1.6	6.4	8.2	12.2	52.6
River Mulde	29	5.4	1.4	0.5	3.1	3.1	3.9	17.4

S6: Concentration along the river Rhine (R) and Ems (E) [ng/L]

		TiBP	TnBP	TCEP	TCPP	TDCP
R01	Stammheim	63.8	34.1	67.3	94.8	71.9
R02	Wiesdorf	88.3	41.0	91.6	104.5	83.4
R03	Monheim	83.0	44.1	80.4	108.1	76.8
R04	Neuss	94.1	107.9	94.4	110.7	78.1
R05	Düsseldorf	76.5	60.8	103.7	106.7	75.2
R06	Duisburg	80.6	37.5	82.2	105.0	110.5
R07	Walsum	87.6	69.2	73.8	103.0	80.4
R08	Wesel	91.3	83.6	97.9	109.1	85.7
R09	Rees	78.0	66.5	80.4	101.4	78.1
R10	Emmerich	101.4	50.1	94.8	111.6	77.7
R11	Lobith	83.0	34.1	67.4	89.9	69.2
R12	Tolkamer	87.7	37.8	83.2	105.5	73.8
R13	Arnhem	69.4	30.0	72.8	94.2	72.8
R14	Ewijk	76.6	29.5	68.4	101.6	72.2
R15	Tiel	74.5	26.1	58.2	90.6	64.6
R16	Gorinchem	52.2	18.9	85.2	122.0	79.0
R17	Zwijndrecht	71.1	37.0	78.1	94.3	78.6
R18	Willemstad	82.3	54.3	68.4	97.4	77.7
R19	Rozenburg	70.9	37.8	65.6	113.6	74.5
R20	Kampen	67.6	24.0	60.5	91.1	72.0
E1	Leer	34.9	8.2	74.9	120.5	81.5
E2	Gandersum	31.8	5.2	61.9	127.8	77.8
E3	Wybelsum	26.7	5.6	33.8	91.6	51.8

Paper II

Occurrence and spatial distribution of organophosphate ester flame retardants and plasticizers in 40 rivers draining into the Bohai Sea, north China

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ABSTRACT

Organophosphate esters (OPEs) are alternatives to polybrominated diphenyl ethers, often used as flame-retardants and plasticizers. There are few reports of OPEs in river water. This study focused on the occurrence and spatial distribution of 11 OPE congeners and one synthetic intermediate triphenylphosphine oxide (TPPO) in 40 major rivers entering into the Bohai Sea. Total OPEs ranged from 9.6 to 1549 ng L^{-1}, with an average of 300 ng L^{-1}. Tris(1-chloro-2-propyl) phosphate (TCPP) (4.6–921 ng L^{-1}, mean: 186 ng L^{-1}) and tris(2-choroethyl) phosphate (TCEP) (1.3–268 ng L^{-1}, mean: 80.2 ng L^{-1}) were the most abundant OPEs and their distribution patterns are similar, indicating the same source ($r = 0.61$, $P < 0.05$) and the influence of large production and consumption of chlorinated OPEs in the region. Priority should be given to TCPP, PCEP and TPPO due to their high concentrations in the rivers and potential threat to aquatic organisms.

1. Introduction

Organophosphate esters (OPEs) have been used as organophosphorus flame-retardants (OPFRs) and plasticizers for decades due to their excellent physicochemical properties and low cost. Since brominated flame-retardants (BFRs) such as polybrominated diphenyl ethers (PBDEs) have gradually been restricted worldwide due to environmental concerns, OPEs, have increasingly been used as alternatives to BFRs in many industrial applications and household products. Halogenated (chlorinated) OPEs are predominantly used as flame-retardants in furniture, textiles, mattresses, electronics (e.g., televisions, cell phones) and even child-related products such as strollers, sleepwear and baby clothing (Stapleton et al., 2009; Regnery and Puttmann, 2010a; Bollmann et al., 2012; CTIF, 2014; Salamova et al., 2014). Non-halogenated OPEs are mostly applied as plasticizers, antifoaming agents and additives (Regnery and Puttmann, 2010a; Bollmann et al., 2012). Another organophosphorus compound, triphenylphosphine oxide (TPPO), is extensively employed as a synthetic intermediate in pharmaceutical products and as ligand for many transitional metals (Hu et al., 2009).

Organophosphorus flame-retardants are listed in the High Production Volume Chemicals (HPVC) program. The global consumption of OPEs amounted to 500,000 t in 2011 and is expected to reach 680,000 t in 2015 (Ou, 2011; Veen and Boer, 2012). In China, the production of PFRs (phosphorus flame retardants) was estimated to be 100,000 t in 2011 and the demand for PFRs is expected to increase every year by 15% (Ou, 2011). Similar to PBDEs, OPEs are not chemically bonded to polymeric materials, and are typically water soluble, they can easily leach out into the environment via volatilization, abrasion and dissolution (Wang et al., 2014). Large production and consumption of OPEs has resulted in high frequency of detection in both domestic (air and dust) and natural (water, air and sediment) environments over the past decade (Reemtsma et al., 2008; Wang et al., 2014).

Chlorinated OPEs have been proven persistent in the

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environment and resistant to hydrolysis at neutral pH (Reemtsma et al., 2008). Risk assessment with respect to human health for OPEs is in progress (Reemtsma et al., 2008; Waaijers et al., 2013). Nevertheless, even the draft risk assessment of tris(2-chloroethyl) phosphate (TCEP) recognized its carcinogenicity, high toxicity and environmental persistence (EC, 2006). Furthermore, tri(dichloropropyl) phosphate (TDCPP) is a proven carcinogen and tris(1-chloro-2-propyl) phosphate (TCPP) and tributoxyethyl phosphate (TBEP) are suspected carcinogens (WHO, 1998, 2000). New York prohibited the use of TCEP in products for children under the age of three, as of 1 December, 2013 (N.Y., 2011). After the action by New York City, Washington prohibited the use of TCEP and TDCPP in child products and home furniture from 1 July, 2014 (ESHB1294, 2013).

Considering the toxic effects of these compounds, together with the limited reports on the occurrence of OPEs in the environment, especially in China, it is worthwhile to collect more information on these contaminants to fill our knowledge gaps of the fate of OPEs in the natural environment.

The Bohai Sea is a semi-enclosed Chinese water body, with a huge amount of domestic sewage and industrial waste water pouring into it every day. Rivers are one of the major sources/pathways for terrestrial pollutants to the sea. According to a recent report about the water quality in the rivers emptying into Chinese coastal seas, all 11 of the routinely monitored rivers emptying into the Bohai Sea, were equal to or lower than Level IV Environmental Quality Standards for Surface Water (GB3838-2002). Five of the 11 rivers exceeded Level V standards (SOA, 2013). In detail, according to Environmental Quality Standards for Surface Water (GB3838-2002) published by State Environmental Protection Administration of China, and the General Administration for Quality Supervision, Inspection and Quarantine, the five levels of environmental quality standards are defined based on the environmental functions of surface-water and on specific objectives of protection. Level IV applies to ordinary industrial water areas and recreation areas without direct human contact, and level V applies to agricultural water areas and ordinary scenery water areas.

The river basins in the study area have been subjected to heavy anthropogenic influences owing to the high-speed development of the agriculture, industry and overall economy during the past ca. 50 years (Men et al., 2014). This is one of the most important heavy industrial complexes in Northeast Asia, including chemical (flame-retardant production), petrochemical, pharmaceutical, steel-iron, and machinery industries (Men et al., 2014). Nearly 100 billion tons of river water per year brings a variety of organic pollutants, including OPEs, into the Bohai Sea.

In the present study, OPEs were analyzed to determine their occurrence in aqueous phase and their spatial distribution in different rivers. In addition, the riverine input of OPEs into the Bohai Sea was estimated. To the best of our knowledge, this is the first study of organophosphate esters (OPEs) in the aqueous environment around Bohai Sea and the first report on the environmental distribution of TPPO in China.

2. Experimental section

2.1. Study area and sample collection

Water samples were collected in 40 major rivers around the Bohai Sea and the north Yellow Sea in August 2013, to investigate the distribution characteristics and flux of emerging organic compounds in the rivers. The rivers were chosen based on their length, water loading volume, and pollution status according to previous studies. The total water volume of these 40 rivers accounted for about 96% of all the rivers emptying into the Bohai Sea and northern Yellow Sea, for detailed information, see Table S1. The total watershed area is up to 1,412,581 km^2, nearly 15% of the Chinese total (Table S1, Cui, 2008).

The locations of sampling stations are illustrated in Fig. 1a and b. Sampling sites were chosen as close as possible to the river mouth while avoiding the influence of salt water. In most of the rivers in this study, there are floodgates/dams near the river mouth to prevent sea-water intrusion during high tides, and also to keep the fresh water level high. Water samples were collected across the floodgates/dams and in some cases across the bridges. The water sampling procedure conformed to the Chinese National Standard—Technical Specifications Requirements for Monitoring of Surface Water and Waste Water (HJ/T91 2012), with small modifications. In brief, one transect with three to five stations according to the river width, was set and a 10 L stainless steel bucket was used to collect the surface water. Three to five 10-L water samples were mixed together in one 60 L stainless steel bucket and then 1 L mixed water was kept frozen in polyethylene terephthalate (PET) bottles prior to extraction. All the sampling buckets and PET bottles were rinsed with acetone in a clean lab and then rinsed with river water three times on station.

2.2. Analysis

The extraction, purification, concentrate and analysis followed the method presented in Quintana et al. and Andresen et al. (Andresen et al., 2004; Quintana et al., 2008) Briefly, 800 mL water sample was spiked with 20 ng surrogates (D_{27} TBP and D_{15} TPP) after filtrated by glass fiber filters (GFF, diameter: 47 mm, pore size: 0.7 μm) and then extracted 30 min with 50 mL dichloromethane for three times. The extracts were combined together and residual water was removed by freezing and Na_2SO_4. Finally, the extract was evaporated and blown down to 150 μL and 500 pg $^{13}C_6$-PCB 208 was added as injection standard. The samples were analyzed by Agilent 6890 gas chromatograph coupled to an Agilent 5975 mass spectrometer (GC-MS) equipped with a programmed temperature vaporizer (PTV) injector. The GC separation was performed with an HP-5MS column (30 m × 0.25 mm i.d.; 0.25 μm film thickness, J&W Scientific). The PTV (2 μL injection volume with a pulse pressure of 20 psi for 2 min and inlet temperature of 280 °C) was operated in PTV pulse split-less mode 50 °C (2 min) → 5 °C/min → 170 °C (5 min) → 10 °C/min → 230 °C (5 min) → 5 °C/min → 270 °C → 30 °C/min → 300 °C (10 min). The quadrupole was maintained at 150 °C and the ion source of the mass spectrometer was operated at 230 °C and 70 eV electron impact (EI). Selected masses of fragmental ions for quantification and quantitation are listed in Table S2. The response factors were derived from the calibration curves (8-points) made to determine the response ratio between target compounds and surrogate standards (0–5000 ng mL^{-1}).

This study covered 12 organophosphorus compounds: three halogenated (chlorinated) alkyl phosphates, tris(1-chloro-2-propyl) phosphate (TCPP), tris(2-choroethyl) phosphate (TCEP), and tri(dichloroisopropyl) phosphate (TDCPP); eight non-halogenated alkyl phosphates, tri-*iso*-butyl phosphate (TiBP), tri-*n*-butyl phosphate (TBP), tris(2-butoxyethyl) phosphate (TBEP), trihexyl phosphate (THP), tripentyl phosphate (TPeP), and tris(2-ethylhexyl) phosphate (TEHP); two aryl phosphates, triphenyl phosphate (TPP) and tricresyl phosphate (TCP), and also the synthetic intermediate triphenylphosphine oxide (TPPO). Their acronyms, chemical structures, applications, toxicity and CAS numbers are given in Table S3.

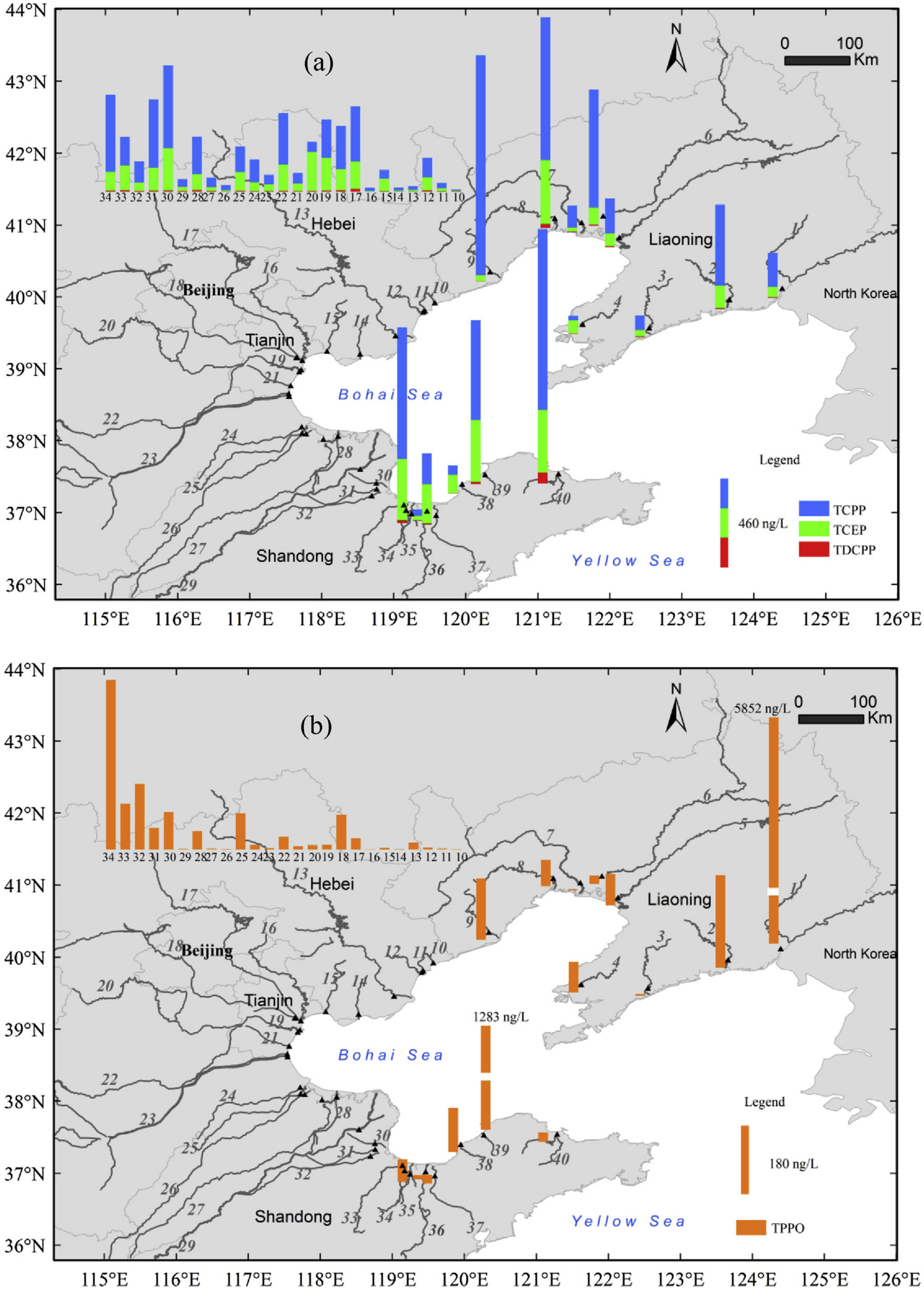

Fig. 1. The figures showing the study area and sampling stations of 40 rivers (▲). a showing the spatial distributions of TCPP, TCEP and TDCPP. b showing the spatial distributions of TPPO.

2.3. Quality assurance/quality control (QA/QC)

The recoveries of spiked experiments were from 67 ± 2% (TPPO) to 95 ± 8% (TCEP) for 12 target organophosphorus compounds with a mean recovery of 81% (n = 5). A method blank with each sample batch (six samples) was included. The mean of blanks was between

7 ± 3 (TPPO) to 235 ± 102 (TCPP) pg/L. The instrumental limit of detection (LOD) was defined as three times the signal-to-noise ($S/N = 3$) and ranged from 0.1 ng (TBP) to 6 ng (TBEP). The method detection limit (MDL) was defined as the mean field blank concentration plus three times the standard deviation (3σ) of the field blanks, and ranged from 0.02 (TPPO) to 0.54 (TCPP) ng/L. Detailed information on recoveries, means of blanks and MDL are listed in Table S2. None of the concentrations of organophosphorus compounds in this paper was corrected for recovery.

3. Results and discussion

3.1. Concentration and distribution characteristics

OPEs were detected in all samples with water phase concentrations and the concentrations varied largely. The concentrations of total OPEs ($\sum$OPEs) ranged from 9.6 to 1549 ng L^{-1}, with an average value of 300 ng L^{-1}. Three chlorinated alkyl phosphates (TCPP, TCEP and TDCPP) accounted for 69%–99% of $\sum$OPEs in concentration, with an average of 91%. All three were detected in all 40 rivers, with the following concentrations in decreasing order: TCPP (4.6–921 ng L^{-1}, mean: 186 ng L^{-1}), TCEP (1.3–268 ng L^{-1}, mean: 80.2 ng L^{-1}), TDCPP (0.2–44.5 ng L^{-1}, mean: 4.3 ng L^{-1}), see Fig. 1a. Although TCPP, TCEP and TDCPP were three of the most common products of organophosphate esters, the concentration of TDCPP was an order of magnitude lower than those of TCPP and TCEP. The distribution patterns of TCPP and TCEP were similar, which may indicate that they came from the same source ($r = 0.61$, $P < 0.05$).

As traditional brominated flame retardants (BFRs), polybrominated diphenyl ethers (PBDEs) tend to absorb onto fine particles due to their lipophilic and hydrophobic characteristics and $\sum_7$PBDEs (BDE28, 47, 99, 100, 153, 154 and 183) and BDE209 ranged from 0.01 to 53 ng g^{-1} dw and from 0.74 to 285 ng g^{-1} dw, with an average of 4.5 ng g^{-1} dw and 54 ng g^{-1} dw in riverine sediments in Laizhou Bay area (Pan et al., 2011). In contrast, contamination levels of OPEs are comparable to PBDEs or even worse.

Notably, the synthetic intermediate TPPO in this study ranged from 0.7 to 5852 ng L^{-1}, with an average value of 224 ng L^{-1}. This is far higher than in Elbe (Germany, 10–40 ng L^{-1}) and in three Volcanic Lakes (Italy, 2 ± 1 ng L^{-1}) (Bacaloni et al., 2008; Bollmann et al., 2012). There are very limited reports about TPPO in river water, only these two studies are available. The spatial distribution of TPPO concentration is showed in Fig. 1b. Although the concentration of TPPO in the Elbe was much lower than in this study, it was assessed as one of the major organophosphorus compounds. According to the results of this study, there is no correlation between TPPO and other OPEs concentrations. We may draw the conclusion that OPEs are not potential sources of this chemical. However, TPPO is extensively employed as a synthetic intermediate in organic synthesis and pharmaceutical products, and as ligand for many transitional metals (Hu et al., 2009). Our study area is one of the most important heavy industrial complexes in China, including chemical, petrochemical, pharmaceutical, steel-iron, and machinery industries (Men et al., 2014). TPPO may directly come from the production pollutions. Moreover, TPPO is in R50/53, that is to say, TPPO is harmful to aquatic organisms and may cause long-term adverse effects in the aquatic environment. In consequence, priority attention should be given to TPPO contamination in rivers around the Bohai Sea, especially in the Yalu (5852 ng L^{-1}) and Jiehe (1283 ng L^{-1}) Rivers.

Concentrations of eight non-halogenated alkyl phosphates are shown in a box plot in Fig. 2.

The concentrations of TiBP, TBP, TBEP and THP were at the same level. TiBP and TBP were detected in all samples, with concentrations of 0.2–217 ng L^{-1}, average: 13.4 ng L^{-1} and 0.1–80.9 ng L^{-1}, average: 6.3 ng L^{-1}, respectively. TBEP and THP were detected in 70% and 18% of samples, respectively, at concentrations of <MOD–47.2 ng L^{-1}, average: 4.2 ng L^{-1} and <MOD–105 ng L^{-1}, average: 3.5 ng L^{-1}. Concentrations of TPeP, TEHP, TPP and TCP were at the same level. TPeP and TEHP were detected in 45% and 78% of samples, respectively, at concentrations of <MOD–3.1 ng L^{-1}, average: 0.2 ng L^{-1} and <MOD–3.3 ng L^{-1}, average: 0.4 ng L^{-1}. TPP and TCP were detected in 95% and 5% of samples, respectively, at concentrations of <MOD–15.7 ng L^{-1}, average: 1.0 ng L^{-1} and <MOD–15.0 ng L^{-1}, average: 0.4 ng L^{-1}.

In terms of rivers, the Jiahe, Liugu, Xiaoling, Yuhe, and Jiehe Rivers were the most contaminated by OPEs, with $\sum$OPEs concentrations in 1549, 953, 938, 870, 808 ng L^{-1}. The Liugu River was the most contaminated by TCPP, and the Xiaoling River most

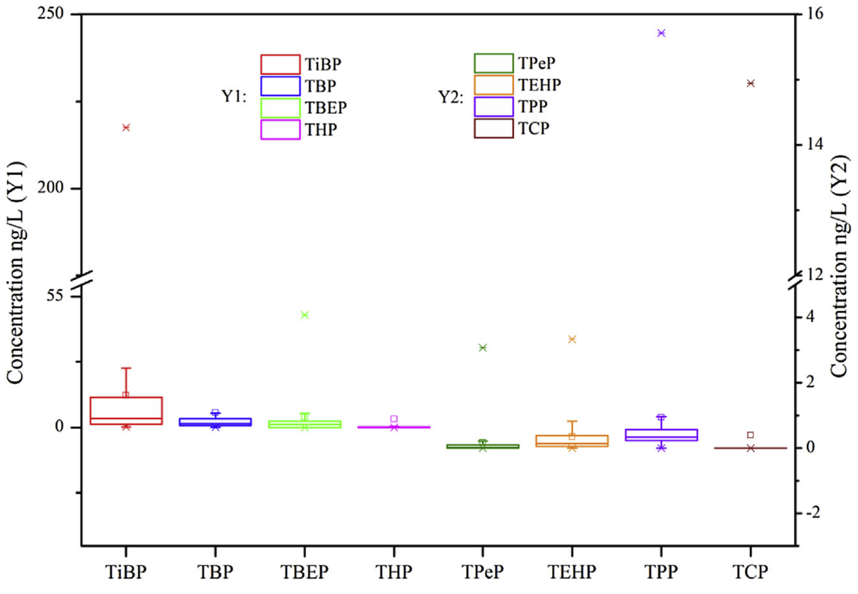

Fig. 2. Concentrations of eight non-halogenated alkyl phosphates in a box plot.

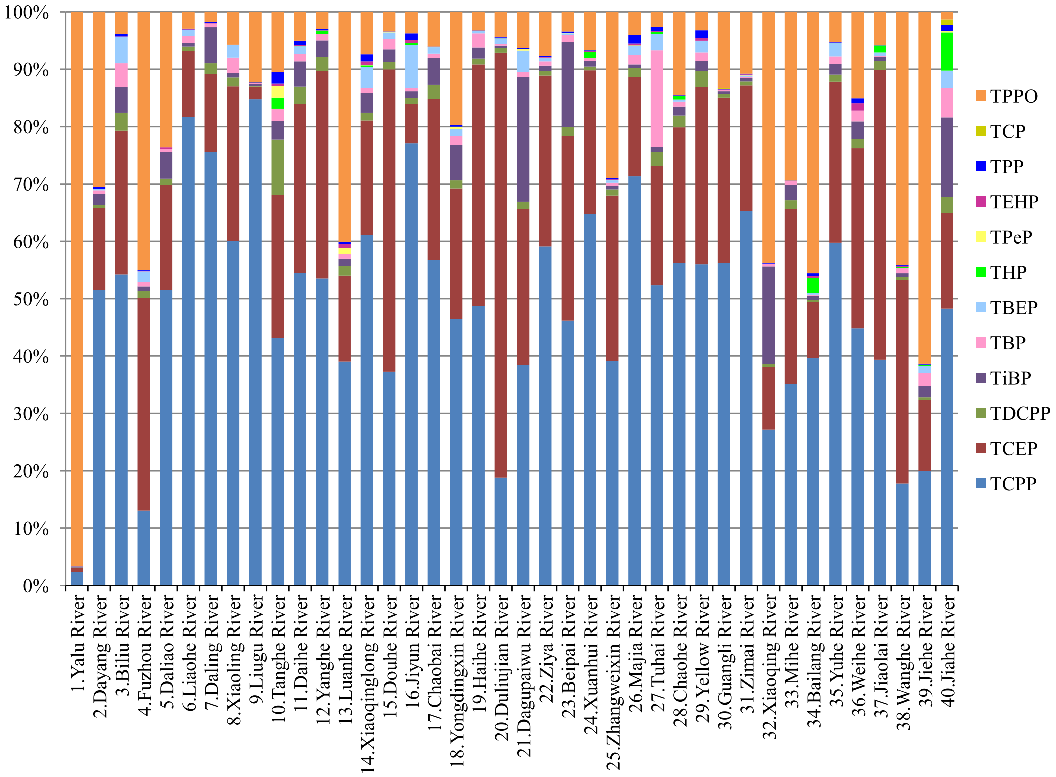

Fig. 3. Concentration-percent composition of 12 OPFRs in the river water.

contaminated by TCEP. The Jiahe River was the most contaminated by TDCPP, TiBP, TBP, TBEP, THP, TPeP, TPP and TCP. As for TPPO, the Yalu and Jiehe Rivers were most contaminated, as discussed above.

Fig. 3 shows the concentration-percent composition of 12 organophosphorus compounds in this study in the river water. TCPP, TCEP and TPPO were the most abundant organophosphorus compounds and their concentration-percent composition ([TCPP] + [TCEP] + [TDCPP]) accounted for 66.2%–99.7% of the total, with an average of 91.1%. When only OPEs were considered, TCPP and TCEP were the most abundant in all the rivers, and the sum of their concentration-percent composition ([TCPP] + [TCEP]) ranged from 65.8% to 99.2%, with an average of 89.3%. This behavior is in agreement with studies in Pearl River (Wang et al., 2014). It may be attributed to that TCPP and TCEP were two of the most common products of halogenated phosphate esters, and that they appeared to be the most recalcitrant in water (Reemtsma et al., 2008). The intermediate concentrations of TDCPP, TiBP, TBP, TBEP, and THP may reflect the widespread distribution of this family of contaminants in rivers influenced by anthropogenic pressures, as reported for other sites previously (Wang et al., 2014, 2011; Bollmann et al., 2012; Bollmann et al., 2012). In contrast, TPeP, TEHP TPP, and TCP were detected at the lowest concentrations or not detected in most of the rivers. The different patterns of these OPEs may be attributed to their differences in physicochemical

Table 1
Concentrations of selected OPEs and TPPO in different studies in river water in the world (ng L^{-1}).

River	Location	TCPP	TCEP	TDCPP	TiBP	TBP	TBEP	TPP	TPPO	Ref.
40 rivers	North China	5-921	1-268	<LOD-44	<LOD-218	<LOD -81	<LOD-47	<LOD-16	<LOD -5852	This study
Pearl River Estuaries	South China	150-1150	220-1160	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Wang et al. (2014)
Songhua River	Northeast China	5-190	38-3700	2-46	n.a.	87-960	5-310	5-65	n.a.	Wang et al. (2011)
Elbe	Germany	40-250	5-20	n.a.	10-50	2-8	<LOD-80	<LOD-4	10-40	Bollmann et al. (2012)
Rhine	Germany	75-160	12-25	n.a.	17-84	6-28	28-54	1-2	n.a.	Bollmann et al. (2012)
Four streams	Germany	<LOD-2914	<LOD-557	<LOD-1284	n.a.	<LOD-3889	<LOD-1773	n.a.	n.a.	Quednow and Püttmann (2008)
Aire	UK	113-26,050	119-316	62-149	n.a.	n.a.	n.a.	6-22	n.a.	Cristale et al. (2013c)
Aire	UK	4821	181	49	n.a.	n.a.	n.a.	17	n.a.	(Cristale et al., 2013b)
Navarra, Asturias, Catalonia	Spain	<LOD-1800	<LOD-330	<LOD-200	<LOD-1200	<LOD-370	<LOD-4600	<LOD-18	n.a.	Cristale et al. (2013a)
Three rivers	Austria	33-170	13-130	<LOD-19	n.a.	20-110	24-500	<LOD-10	n.a.	Martinez-Carballo et al. (2007)
Three major rivers	South Korea.	n.a.	42	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	Kim et al. (2007)
Arkansas streams	USA	n.a.	48-700	n.a.	n.a.	31-560	n.a.	n.a.	n.a.	Haggard et al. (2006)

<LOD: below limit of detection; n.a.: not available.

properties and consequent differences that affect accumulation features and degradability, as well as differences in production and employment.

In addition, 37 of the rivers sampled flow into embayment of the Bohai Sea, namely, the Liaodong, Bohai, and Laizhou Bays. It could be shown that the average concentrations of OPEs in rivers flowing into Laizhou Bay (415 ng L^{-1}) were at the same level as in rivers flowing into Liaodong Bay (395 ng L^{-1}), but higher than in rivers flowing into Bohai Bay (148 ng L^{-1}). Many manufacturing bases for flame-retardants are scattered around Laizhou Bay, so it may be suggested that rivers flowing through OPE production areas contributed to the higher values (Pan et al., 2011).

3.2. *Comparison with other studies*

To our knowledge, limited reports about the occurrence of OPEs in river water are available throughout the world. The concentrations of selected OPEs and TPPO in other studies of river water are listed in Table 1. In contrast to findings published previously, organophosphorus compound contamination in China remains at high levels, but not higher than reported for UK. As we discussed in 3.1, TCPP and TCEP were the most abundant OPEs in Chinese rivers. However, TCEP was not among the most abundant OPEs in German rivers, for instance, the Elbe, Rhine and four river systems in Hessen (Quednow and Püttmann, 2008; Wang et al., 2011). The difference could be explained by the industrial replacement of TCEP by TCPP in Europe in the 1990s (Quednow and Puttmann, 2009). In this study, there was no reflection of the shift in usage from TCEP to TCPP in China. What's more, priority attention should be given to TPPO contamination, as we discussed before.

3.3. *Riverine input into the Bohai Sea*

Runoff into riverine systems is generally considered to play an important role in the transport of anthropogenic pollutants from terrestrial sources to the ocean (Regnery and Puttmann, 2010b). According to the sample concentrations and annual runoff, the total riverine input of OPEs was estimated to be 16 ± 3.2 t yr^{-1} and the total riverine input of TPPO was estimated to be 113 ± 22.6 t yr^{-1}(Table S4). Liaodong Bay received relatively high riverine input of 12 organophosphorus compounds (7.0 ± 1.4 t yr^{-1}) in comparison to Bohai Bay (3.4 ± 0.7 t yr^{-1}) and Laizhou Bay (1.5 ± 0.3 t yr^{-1}).

4. Conclusions

This study focused on the occurrence and spatial distribution of OPEs and TPPO in rivers draining into the Bohai Sea. This study area is located in one of the most important heavy industrial complexes in Northeast Asia, with heavy anthropogenic influence owing to the high speed development of the agriculture, industry and economy there during the past 50 years. Contamination levels of OPEs are comparable to PBDEs or even worse. Chlorinated OPE, TCPP and TCEP were the most abundant OPEs in the river water of north China, indicating the influence of large production and consumption of chlorinated OPE in the study area. Priority should be given to TPPO due to its relatively high concentrations in river water, and to its great potential for harm to aquatic organisms.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2014.12.037.

References

Andresen, J.A., Grundmann, A., Bester, K., 2004. Organophosphorus flame retardants and plasticisers in surface waters. Sci. Total Environ. 332, 155–166.
Bacaloni, A., Cucci, F., Guarino, C., Nazzari, M., Samperi, R., Lagana, A., 2008. Occurrence of organophosphorus flame retardant and plasticizers in three volcanic lakes of Central Italy. Environ. Sci. Technol. 42, 1898–1903.
Bollmann, U.E., Moller, A., Xie, Z., Ebinghaus, R., Einax, J.W., 2012. Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. Water Res. 46, 531–538.
Cristale, J., Garcia Vazquez, A., Barata, C., Lacorte, S., 2013a. Priority and emerging flame retardants in rivers: occurrence in water and sediment, Daphnia magna toxicity and risk assessment. Environ. Int. 59, 232–243.
Cristale, J., Katsoyiannis, A., Chen, C., Jones, K.C., Lacorte, S., 2013b. Assessment of flame retardants in river water using a ceramic dosimeter passive sampler. Environ. Pollut. 172, 163–169.
Cristale, J., Katsoyiannis, A., Sweetman, A.J., Jones, K.C., Lacorte, S., 2013c. Occurrence and risk assessment of organophosphorus and brominated flame retardants in the River Aire (UK). Environ. Pollut. 179, 194–200.
CTIF, 2014. http://www.cefic-efra.com/index.php/furniture-a-textile/introduction.
Cui, Z., 2008. Study on Scheme of Total Emission Control of Main Chemical Pollutants in 13 Cities Around Bohai Sea. Ocean University of China, p. 154.
EC, 2006. European Commission, EU Risk Assessment Report, Tris (2-chloroethyl) Phosphate, TCEP, Draft. http://ecb.jrc.it/esis/index.php?PGM=ora.
ESHB1294, 2013. Toxic-free Kids and Families Act: an Act Relating to Flame Retardants. ESHB 1294.
Hu, F., Wang, L., Cai, S., 2009. Solubilities of triphenylphosphine oxide in selected solvents. J. Chem. Eng. Data 54, 1382–1384.
Haggard, B.E., Galloway, J.M., Green, W.R., Meyer, M.T., 2006. Pharmaceuticals and other organic chemicals in selected north-central and northwestern Arkansas streams. J. Environ. Qual. 35, 1078–1087.
Kim, S.D., Cho, J., Kim, I.S., Vanderford, B.J., Snyder, S.A., 2007. Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. Water Res. 41, 1013–1021.
Martinez-Carballo, E., Gonzalez-Barreiro, C., Sitka, A., Scharf, S., Gans, O., 2007. Determination of selected organophosphate esters in the aquatic environment of Austria. Sci. Total Environ. 388, 290–299.
Men, B., He, M., Tan, L., Lin, C., 2014. Distributions of polychlorinated biphenyls in the Daliao River estuary of Liaodong Bay, Bohai Sea (China). Mar. Pollut. Bull. 78, 77–84.
N.Y., 2011. Prohibits the Manufacture, Distribution, and Sale of Child Care Products Containing TRIS. NY A06195.
Ou, Y.X., 2011. Developments of organic phosphorus flame retardant industry in China. Chem. Indust. Eng. Prog. 30, 210–215.
Pan, X.H., Tang, J.H., Li, J., Zhong, G.C., Chen, Y.J., Zhang, G., 2011. Polybrominated diphenyl ethers (PBDEs) in the riverine and marine sediments of the Laizhou Bay area, North China. J. Environ. Monit. 13, 886–893.
Quednow, K., Puttmann, W., 2009. Temporal concentration changes of DEET, TCEP, terbutryn, and nonylphenols in freshwater streams of Hesse, Germany: possible influence of mandatory regulations and voluntary environmental agreements. Environ. Sci. Pollut. Res. 16, 630–640.
Quednow, K., Püttmann, W., 2008. Organophosphates and synthetic musk fragrances in freshwater streams in Hessen/Germany. Clean Soil Air Water 36, 70–77.
Quintana, J.B., Rodil, R., Reemtsma, T., García-López, M., Rodríguez, I., 2008. Organophosphorus flame retardants and plasticizers in water and air II. Analytical methodology. Trends Anal. Chem. 27, 904–915.
Reemtsma, T., Quintana, J.B., Rodil, R., García-López, M., Rodríguez, I., 2008. Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. Trends Anal. Chem. 27, 727–737.
Regnery, J., Puttmann, W., 2010a. Occurrence and fate of organophosphorus flame retardants and plasticizers in urban and remote surface waters in Germany. Water Res. 44, 4097–4104.
Regnery, J., Puttmann, W., 2010b. Seasonal fluctuations of organophosphate concentrations in precipitation and storm water runoff. Chemosphere 78, 958–964.
Salamova, A., Ma, Y., Venier, M., Hites, R.A., 2014. High levels of organophosphate flame retardants in the Great Lakes Atmosphere. Environ. Sci. Technol. Lett. 1, 8–14.
SOA, 2013. Marine Environmental Information, Section 8 (Total 21). State Oceanic Administration, People's Republic of China.
Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A., Webster, T.F., 2009. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. Environ. Sci. Technol. 43, 7490–7495.
Veen, I.v.d., Boer, J.d., 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere 88, 1119–1153.
Waaijers, S.L., Hartmann, J., Soeter, A.M., Helmus, R., Kools, S.A., de Voogt, P., Admiraal, W., Parsons, J.R., Kraak, M.H., 2013. Toxicity of new generation flame retardants to Daphnia magna. Sci. Total Environ. 463–464, 1042–1048.

Wang, X., He, Y., Lin, L., Zeng, F., Luan, T., 2014. Application of fully automatic hollow fiber liquid phase microextraction to assess the distribution of organophosphate esters in the Pearl River Estuaries. Sci. Total Environ. 470–471, 263–269.

Wang, X.W., Liu, J.F., Yin, Y.G., 2011. Development of an ultra-high-performance liquid chromatography-tandem mass spectrometry method for high throughput determination of organophosphorus flame retardants in environmental water. J. Chromatogr. A 1218, 6705–6711.

WHO, 1998. Environmental Health Criteria 209. Flame Retardants: Tris(-chloropropyl) Phosphate and Tris(2-chloroethyl) Phosphate. Geneva, Switzerland.

WHO, 2000. Environmental Health Criteria 209. Flame Retardants: Tris(2-butoxyethyl) Phosphate, Tris(2-ethylhexyl) Phosphate and Tetrakis (Hydroxymethyl) Phosphonium Salts. Geneva, Switzerland.

Supporting Information

Occurrence and spatial distribution of organophosphate ester flame retardants and plasticizers in 40 rivers draining into the Bohai Sea, north China

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Table S1

Hydrologic information and water quality standards of the 40 rivers.

No.	River	Estuary	annual runoff 10^8m^3 (2012a; 2012b; Cui, 2008)	Lenth Km (Cui, 2008)	Basin area Km^2 (Cui, 2008)	Water quality standards a(SOA, 2013)	Hydrologic characteristics (Cui, 2008)
1	Yalu River	North Yellow Sea	190.59	795	32500^b	level Ⅳ	seasonal river，70％ precipitation in June to September
2	Dayang River	North Yellow Sea	9.80	180	6504	level Ⅲ	seasonal river，60％ precipitation in July to September
3	Biliu River	North Yellow Sea	9.00	156	2814	level Ⅳ	seasonal river，52％ precipitation in July to September
4	Fuzhou River	Liaodong Bay	2.37	137	1638	level Ⅳ	seasonal river，76％ precipitation in June to September
5	Daliao River	Liaodong Bay	46.60	94	1926	level Ⅴ	the same as Liaohe River
6	Liaohe River	Liaodong Bay	70.97	1430	229000	lower than level Ⅴ	seasonal river，60%～70% precipitation in June to September
7	Daling River	Liaodong Bay	19.63	397	23500	n.a.	seasonal river，precipitation mainly in July and August
8	Xiaoling River	Liaodong Bay	4.03	206	5475	lower than level Ⅴ	mountain river，78% precipitation in June to September
9	Liugu River	Liaodong Bay	6.02	149	3080	level Ⅳ	seasonal river，80％ precipitation in June to September
10	Tanghe River	Liaodong Bay	0.34	110	1253	n.a.	seasonal river，80％ precipitation in June to September
11	Daihe River	Bohai Bay	0.51	35	2909	n.a.	seasonal river，80％ precipitation in June to September
12	Yanghe River	Bohai Bay	0.28	n.a.	1029	n.a.	seasonal river，80％ precipitation in June to September
13	Luanhe River	Bohai Bay	29.04	877	318000^c	lower than level Ⅴ	75～85％ precipitation in June to September（Haihe river system）www.hydroinfo.gov.cn/swqbyb/lygk/200309/t20030925_49015.html
14	Xiaoqinglong River	Bohai Bay	0.07	79		level Ⅳ	
15	Douhe River	Bohai Bay	13.18	122		lower than level Ⅴ	
16	Jiyun River	Bohai Bay	15.85	145		lower than level Ⅴ	
17	Chaobai River	Bohai Bay	15.00	458		lower than level Ⅴ	
18	Yongdingxin River	Bohai Bay	0.71	66		lower than level Ⅴ	
19	Haihe River	Bohai Bay	2.85	76		lower than level Ⅴ	
20	Duliujian River	Bohai Bay	9.77	67		level Ⅳ	
21	Dagupaiwu River	Bohai Bay	4.76	82		n.a.	
22	Ziya River	Bohai Bay	3.09	144		lower than level Ⅴ	
23	Beipai River	Bohai Bay	10.03	162		lower than level Ⅴ	
24	Xuanhui River	Bohai Bay	0.44	165		lower than level Ⅴ	
25	Zhangweixin River	Bohai Bay	7.55	257		lower than level Ⅴ	
26	Majia River	Bohai Bay	2.93	521		n.a.	
27	Tuhai River	Bohai Bay	8.97	436		n.a.	
28	Chaohe River	Bohai Bay	0.89	55	452	lower than level Ⅴ	70％ precipitation in June to August

29	Yellow River	Bohai Bay	282.50	5464	752443	level Ⅳ	70％ precipitation in June to September
30	Guangli River	Laizhou Bay	2.30	48	510	n.a.	n.a.
31	Zimai River	Laizhou Bay	2.58	n.a.	n.a.	n.a.	n.a.
32	Xiaoqing River	Laizhou Bay	8.78	237	10572	lower than level Ⅴ	the source is Ji'nan spring groups,the annual runoff distribution relatively uniform
33	Mihe River	Laizhou Bay	4.23	206	3848	n.a.	the flow of large seasonal variations
34	Bailang River	Laizhou Bay	1.22	127	1237	lower than level Ⅴ	seasonal river
35	Yuhe River	Laizhou Bay	0.05	80	890	n.a.	more than 70％ precipitation in June to September
36	Weihe River	Laizhou Bay	14.46	246	6376	n.a.	n.a.
37	Jiaolai River	Laizhou Bay	2.33	130	5479	n.a.	precipitation mainly in June to September
38	Wanghe River	Laizhou Bay	0.98	50	327	n.a.	n.a.
39	Jiehe River	Laizhou Bay	2.46	45	590	lower than level Ⅴ	seasonal river
40	Jiahe River	North Yellow Sea	6.15	75	230	lower than level Ⅴ	monsoon rain source type River

n.a.: not available;

[a]: Water Quality Standards means National Environmental Quality Standards for Surface Water; It refers to the river water quality standards in August 2013, i.e. the river water quality standards when we collected the samples.

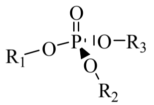
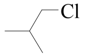
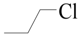
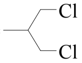
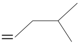
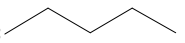
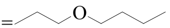
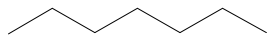
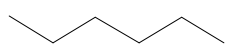
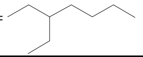
[b]: Basin area of Yalu River within China；

[c]: Here the basin area refers to the basin area of the whole Haihe River system, including the Luanhe River to Tuhai River.

Table S2. Selected masses of fragment ions for quantification and quantitation using GC-MS-EI, the recovery rates for LLE and the method detect limits**.**

Compound	Q1	Q2	Recovery (%)	Blank (ng L^{-1})	MDL (ng L^{-1})
TCPP	125	99	82 ± 4	235 ± 102	0.54
TCEP	249	143	95 ± 8	54 ± 32	0.15
TDCPP	75	381	84 ± 3	32 ± 12	0.07
T*i*BP	99	155	78 ± 3	41 ± 20	0.10
TBP	99	155	80 ± 3	21 ± 11	0.05
TBEP	85	199	76 ± 7	82 ± 41	0.20
THP	99	183	95 ± 5	125 ± 87	0.39
TPeP	99	169	81 ± 3	12 ± 4	0.03
TEHP	99	113	81 ± 5	15 ± 11	0.05
TPP	326	215	82 ± 2	14 ± 4	0.03
TCP	368	165	76 ± 1	42 ± 20	0.10
TPPO	277	183	67 ± 2	7 ± 3	0.02

Table S3. The chemical structures, applications, toxicity, CAS No. and physicochemical. properties (log K_{OW}: n-octanol-water partition coefficient, W_S: water solubility, V_P: vapor pressure) of the OPEs and TPPO in this study. R_1, R_2, R_3 are functional groups listed in Chemical structure.

Acronym	**Chemical structure** 	**Applications** (Bollmann et al., 2012; Etter and Baures, 1987; Fuheng et al., 2009)	**Toxicity** (WHO, 1998, 2000)' (Yan et al., 2012)' (Cristale et al., 2013b; Salamova et al., 2014)	**phys.-chem. properties**(Bollmann et al., 2012)	**CAS no.** (Bollmann et al., 2012)
TCPP	R_1=R_2=R_3= 	flame retardant, plasticizer	suspected carcinogenicity ; bioaccumulation; suspected toxicity;	log K_{OW} =2.59 W_S = 1.2 g L^{-1} $V_P = 2.7 \cdot 10^{-3}$ Pa	13674-84-5
TCEP	R_1=R_2=R_3= 	flame retardant, plasticizer, lacquer/paint/glue, industrial processes	carcinogenicity ; neurotoxicity; suspected toxicity;	log K_{OW} =1.44 W_S = 7.0 g L^{-1} V_P = 8.2 Pa	115-96-8
TDCPP	R_1=R_2=R_3= 	flame retardant, plasticizer, lacquer/paint/glue	carcinogenicity; neurotoxicity; higher acute toxicity than TCEP and TCPP	log K_{OW} = 3.65 $W_S = 7.0 \cdot 10^{-3}$ g L^{-1} $V_P = 9.8 \cdot 10^{-6}$ Pa	13674-87-8
T*i*BP	R_1=R_2=R_3= 	lacquer/paint/glue, anti-foaming agent, industrial processes	n.a.	log K_{OW} = 3.6 $W_S = 1.6 \cdot 10^{-2}$ g L^{-1} V_P = 1.71 Pa	126-71-6
TBP (TnBP)	R_1=R_2=R_3= 	plasticizer, hydraulic fluid, floor covering, lacquer/paint/glue, anti-foaming agent, industrial processes	suspected neurotoxicity	log K_{OW} = 4.0 W_S = 0.28 g L^{-1} V_P = 0.15 Pa	126-73-8
TBEP	R_1=R_2=R_3= 	flame retardant, plasticizer, fungus resistance, lacquer/paint/glue, anti-foaming agent	suspected carcinogenicity	log K_{OW} = 3.75 W_S = 1.1 g L^{-1} $V_P = 3.3 \cdot 10^{-6}$ Pa	78-51-3
THP	R_1=R_2=R_3= 	n.a.	n.a.	n.a.	2528-39-4
TPeP	R_1=R_2=R_3= 	n.a.	n.a.	log K_{OW} = 5.29 $W_S = 3.3 \cdot 10^{-4}$ g L^{-1} $V_P = 2.2 \cdot 10^{-3}$ Pa	2528-38-3
TEHP	R_1=R_2=R_3= 	flame retardant, plasticizer, fungus resistance	n.a.	log K_{OW} = 9.49	78-42-2

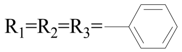
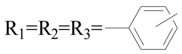
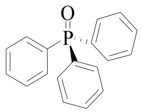
				$W_S = 6.0 \cdot 10^{-4}$ g L^{-1} $V_P = 1.1 \cdot 10^{-5}$ Pa	
TPP (TPhP)		flame retardant, plasticizer, hydraulic fluid, lacquer/paint/glue	suspected neurotoxicity；high toxicity；bioaccumulation	log $K_{OW} = 4.59$ $W_S = 1.9 \cdot 10^{-3}$ g L^{-1} $V_P = 8.4 \cdot 10^{-4}$ Pa	115-86-6
TCP		flame retardant, hydraulic fluid, lacquer/paint/glue, industrial processes	n.a.	log $K_{OW} = 5.11$ $W_S = 3.6 \cdot 10^{-4}$ g L^{-1} $V_P = 8.0 \cdot 10^{-5}$ Pa	1330-78-5
TPPO		flame-retardant; ligand for many metals; solvent extraction; synthetic intermediate Crystallization Aid	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment	log $K_{OW} = 2.83$ $W_S = 6.3 \cdot 10^{-2}$ g L^{-1} $V_P = 3.47 \cdot 10^{-7}$ Pa	791-28-6

Table S4. Total concentration and total riverine of Σ_{11}OPEs and TPPO input in kg yr^{-1}in the surveyed 40 rivers around the Bohai Sea.

River	Annual runoff(10^8m^3) (2012a; 2012b; Cui, 2008)	Σ_{11}OPEs (ng L^{-1})	Σ_{11}OPEs-input (kg yr^{-1})	TPPO (ng L^{-1})	TPPO-input (Kg yr^{-1})
Yalu River	190,59	206,61	3937,82	5852,42	111541,36
Dayang River	9,80	457,28	448,14	201,34	197,32
Biliu River	9,00	106,97	96,27	4,26	3,84
Fuzhou River (L)	2,37	81,12	19,23	66,24	15,70
Daliao River (L)	46,6	219,80	1024,29	67,94	316,58
Liaohe River (L)	70,97	588,03	4173,23	17,80	126,31
Daling River (L)	19,63	118,74	233,08	2,09	4,10
Xiaoling River (L)	4,03	937,64	377,87	56,76	22,88
Liugu River (L)	6,02	953,35	573,91	133,46	80,34
Tanghe River (L)	0,34	9,55	0,32	1,11	0,04
Daihe River (B)	0,51	39,21	2,00	2,07	0,11
Yanghe River (B)	0,28	148,04	4,11	4,59	0,13
Luanhe River (B)	29,04	23,63	68,63	15,81	45,91
Xiaoqinglong River (B)	0,07	18,36	0,13	1,47	0,01
Douhe River (B)	13,10	95,07	124,55	3,36	4,40
Jiyun River (B)	15,85	18,05	28,62	0,70	1,11
Chaobai River (B)	15,00	382,90	574,36	24,61	36,91
Yongdingxin River (B)	0,7119	310,41	22,10	76,35	5,44
Haihe River (B)	2,85	315,90	90,09	10,40	2,97
Duliujian River (B)	9,77	211,50	206,64	9,61	9,39
Dagupaiwu River (B)	4,76	107,36	51,10	7,23	3,44
Ziya River (B)	3,09	337,01	104,13	28,04	8,66
Beipai River (B)	10,03	83,28	83,53	2,95	2,96
Xuanhui River (B)	0,44	138,00	6,07	9,95	0,44
Zhangweixin River (B)	7,55	193,60	146,17	79,06	59,69
Majia River (B)	2,93	28,47	8,34	1,20	0,35
Tuhai River (B)	8,97	74,06	66,43	2,00	1,80
Chaohe River (B)	0,89	238,48	21,28	40,42	3,61
Yellow River (B)	282,50	55,58	1570,02	1,84	52,05
Guangli River (LZ)	2,30	533,42	122,69	81,67	18,78
Zimai River (LZ)	2,58	390,22	100,68	47,17	12,17
Xiaoqing River (LZ)	8,78	183,18	160,84	142,94	125,50
Mihe River (LZ)	4,23	239,54	101,32	99,80	42,21
Bailang River (LZ)	1,22	441,48	53,86	369,75	45,11
Yuhe River (LZ)	0,05	870,31	4,35	48,57	0,24
Weihe River (LZ)	14,46	50,46	72,96	8,95	12,93
Jiaolai River (LZ)	2,33	307,07	71,55	18,70	4,36
Wanghe River (LZ)	0,98	121,63	11,92	96,34	9,44
Jiehe River (LZ)	2,46	808,08	198,79	1283,12	315,65
Jiahe River	6,15	1548,64	952,41	20,88	12,84
Annual input		15913,84			113147,07

L stands for Liaodong Bay, B stands for Bohai Bay, LZ stands for Laizhou Bay.

References

2012a. Ministry of Water Resources of the People's Republic of China, Chinese river sediment Bulletin.

2012b. The Songliao water Resources Commission Ministry of water conservancy, Songliao Basin Sediment Bulletin.

Bollmann, U.E., Moller, A., Xie, Z., Ebinghaus, R., Einax, J.W., 2012. Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. Water Res 46, 531-538.

Cristale, J., Garcia Vazquez, A., Barata, C., Lacorte, S., 2013a. Priority and emerging flame retardants in rivers: occurrence in water and sediment, Daphnia magna toxicity and risk assessment. Environ Int 59, 232-243.

Cristale, J., Katsoyiannis, A., Sweetman, A.J., Jones, K.C., Lacorte, S., 2013b. Occurrence and risk assessment of organophosphorus and brominated flame retardants in the River Aire (UK). Environ Pollut 179, 194-200.

Cui, Z., 2008. Study on Scheme of Total Emission Control of Main Chemical Pollutants in 13 Cities around Bohai Sea. Ocean University of China, p. 154.

EPA, 2014. ECOTOX Database.

Etter, M.C., Baures, P.W., 1987. Triphenylphosphine Oxide as a Crystallization Aid. J. Am. Chem. SOC 110, 639-640.

Fuheng, H., Wang, L., Shuangfei, C., 2009. Solubilities of Triphenylphosphine Oxide in Selected Solvents. J. Chem. Eng. 54, 1382-1394.

Salamova, A., Ma, Y., Venier, M., Hites, R.A., 2014. High Levels of Organophosphate Flame Retardants in the Great Lakes Atmosphere. Environmental Science & Technology Letters 1, 8-14.

SOA, 2013. Marine Environmental Information, section 8 (total 21),State Oceanic Administration People's Republic of China.

WHO, 1998. Environmental Health Criteria 209, Flame Retardants: Tris(chloropropyl) phosphate and Tris(2-chloroethyl) phosphate, Geneva,Switzerland.

WHO, 2000. Environmental Health Criteria 209, Flame Retardants: Tris(2-butoxyethyl) phosphate, Tris(2-ethylhexyl) phosphateand Tetrakis (hydroxymethyl) phosphonium salts, Geneva,Switzerland.

Yan, X., He, H., Peng, Y., Wang, X., Gao, Z., Yang, S., Sun, C., 2012. Determination of Organophosphorus Flame Retardants in Surface Water by Solid Phase Extraction Coupled with Gas Chromatography-Mass Spectrometry. Chinese Journal of Analytical Chemistry 40, 1693-1697.

Paper III

Atmospheric occurrence and fate of organophosphorus flame retardants and plasticizer at the German coast

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Atmospheric occurrence and fate of organophosphorus flame retardants and plasticizer at the German coast

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HIGHLIGHTS

- Yearlong investigations of OPEs in the atmosphere.
- Gas/particle phase partitioning of OPEs.
- Advantage of GC-MS/MS method.

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ABSTRACT

This study reports the occurrence and distribution of organophosphor esters (OPEs), used as flame retardants and plasticizer, in the marine atmosphere of the German Coast. From August 2011 to October 2012, 58 high volume air samples (gas/particle phase separately) were collected at the German North Sea coast town Büsum. With the use of a GC-MS/MS System for instrumental analysis, detection limits for OPEs in air samples could be significantly improved compared to the previously used single GC-MS method. The concentration (gas + particle phase) of total OPEs was on average 5 pg/m^3, with eight of the nine investigated compounds detectable in over 50% of the samples. A focus of this investigation concerned the partioning of OPEs between the particle and the gas phase. The observed partitioning of OPEs in this study was distinguished from previous studies. While previous studies reported OPEs exclusively in the particle phase, a significant part of the sum OPE concentration (55%) was detected in the gas phase. The contribution of the gas phase even reached up to as high as 88% for individual compounds such as tri-iso-butyl phosphate.

1. Introduction

Organophosphorus compounds (OPEs) are high production volume industrial chemicals which are widely used as plasticizers and flame retardants in various household and industrial products (Marklund et al., 2003). Varying alkyl- and aryl-ester groups, some of them halogenated, lead to a large variation in the physico-chemical properties. Octanol-water (KOW) and air-water (KAW) partitioning coefficients range from log K_{OW} of −1 (trimethyl phosphate) to 11 (Tetrakis(2,6-*dimethylphenyl*)-*m*-phenylene biphosphate) and log K_{AW} of −12 (Tetrakis(2-*chloroethyl*)dichloroisopentyldiphosphate) to −3 (Triisobutyl phosphate) (Zhang et al., 2016). Halogenated OPEs are mainly used as flame retardant, whereas non-halogenated OPEs are predominantly used as plasticizers and for other applications (Marklund et al., 2003). In the last decades OPEs have already been extensively used, yet they have recently, additionally, been recommending as substitutes for the banned polybrominated diphenylethers (PBDE) (Shaw et al., 2010). An increase in the OPE production and emission can therefore be expected and has started to become apparent. Even though first reports of OPEs in the environment date back to the 1970s environmental research and monitoring has only recently started focusing on these compounds (Reemtsma et al., 2008). Due to their long term use and recent increase of environmental relevance OPEs

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are often referred to as "re-emerging" compounds (Reemtsma et al., 2008). OPEs are mostly used additively, which means that they are not chemically bound to the polymers they are used in, but merely blended into the product. Therefore, they have a high potential to leach out from the material by volatilization, abrasion and dissolution and enter the environment (Rodríguez et al., 2006).

Since the start of the newly increased scientific interest in OPEs, numerous studies have reported OPEs in indoor air (Björklund et al., 2004; Chung and Ding, 2009; Fromme et al., 2014), human blood, house dust (Fromme et al., 2014; Takeuchi et al., 2014), river water (Bollmann et al., 2012; Wang et al., 2015; Wolschke et al., 2015) and sediments (Chung and Ding, 2009), the great lakes (Venier et al., 2014), the marine water phase (Bollmann et al., 2012), as well as fish and biota (Campone et al., 2010; Sundkvist et al., 2010). However, studies reporting OPEs in ambient air are still limited. The few respective studies reported OPEs in in the atmosphere of the great lakes (up to 2.1 ng/m^3) (Salamova et al., 2014b), over the North Sea (Möller et al., 2011) and in the Arctic (Salamova et al., 2014a). As early as in 1994, OPEs were reported in aerosols from Antarctica with up to 1 ng/m^3, indicating a potential for long range transport. They were, furthermore, reported in Finnish air from a remote sampling site with up to 13 ng/m^3 (Marklund et al., 2005), in air masses from Longyearbyen, Svalbard at 1.45 ng/L and in the water phase of closed volcanic lakes in central Italy (up to 951 ng/L) (Bacaloni et al., 2008). Möller et al. (2011) reported data on OPE concentrations in airborne particles along transects in the pacific and Indian Ocean to the Arctic and South Pacific Ocean with OPEs concentrations up to 3 ng/m^3 in these remote marine areas.

In this study we present the results of continuous weekly sampling over one year in 2011–2012. Samples were collected over one week each at the sea side village Büsum at the shore of the North Sea. The occurrence of 9 OPEs was investigated separately for gas and particle phase. With this study we hope to contribute to the understanding of the complex problem of OPEs in the atmospheric environment and provide new insights into their environmental fate and behavior.

2. Material methods

2.1. Air sampling

Sampling was conducted weekly from August 3, 2011 to October 2, 2012 at the seaside village Büsum (54.13°N, 8.88°E), Germany (Fig. S1). A total of 58 air samples (about 2800 m^3 over 7 day periods) were collected using a high-volume air sampler. A glass fiber filter (GFF, pore size: 0.7 μm) and a self-packed polyurethane foam (PUF)/XAD-2 cartridge (PUF: ϕ5.0 cm × 2.5 cm; 35 g XAD-2, particle size: 0.3–1.0 mm) were employed simultaneously to collect particle and gas phase separately. Field blanks of GFFs and PUF/XAD-2 cartridge were collected by exposing them for 1 min at the sampling site and subsequently treating them in the same way as real samples. Both PUF/XAD-2 cartridge and filters were stored at −20 °C in darkness until analysis. Detailed information on the sampling dates and air volume and are presented in Table S2.

2.2. Sample preparation and analysis

The presented method was refined from the method presented in Möller et al. (2011). Prior to extraction, PUF/XAD-2 cartridge and GFFs were spiked with 20 ng of mass-labeled surrogate standards ([d12]-TCEP, [d27]-TnBP, [d15]-TPhP). PUF/XAD-2 was extracted with a modified Soxhlet extractor for 16 h using dichloromethane (DCM). Particle samples (GFF) were extracted using a standard Soxhlet extractor using DCM for 16 h. Extracts were concentrated to approximately 2 mL using hexane as keeper and passed over 3 g Na_2SO_4 to remove residual water. For clean-up 2.5 g 10% water deactivated silica gel columns were used. Two fractions were eluted: F1 for non-polar compounds, using 15 mL of hexane and F2 for semi-polar compounds, using 20 mL of acetone/DCM (1:1 v/v). The F2 fraction contained the OPEs and was used for instrumental analysis. Both fractions were concentrated to 150 μL under a gentle stream of nitrogen and 500 pg of 13C-labeled PCB141 as injection standard were added prior to analysis.

2.3. Instrumental analysis

Analysis was performed on an Agilent 7010 gas chromatograph - tandem mass spectrometer (GC-MS/MS), fitted with a PTV injector in pulsed split-less 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 sample injection volume was 1 μL. Helium was as carrier gas at a flow of 1.3 mL min$^{-1.}$ The GC was equipped with an HP-5MS column (30 m 0.25 mm i.d. 0.25 mm film thickness, J&W Scientific). The temperature program started at 40 °C held for 4 min, afterward increased by 5 °C min^{-1} to 170 °C, held for 5 min, 10 °C min^{-1} to 230 °C, held for 5 min, 5 °C min^{-1} to 250 °C and finally 10 °C min^{-1} to 300 °C. The MS transfer line and the ion source (electron impact chemical ionization, EI) were held at 280 °C and 230 °C, respectively. The MS was operated in multiple reactions monitoring (MRM) mode. Details on monitored mass transitions for the detection of OPEs and surrogates are presented in Table S3. Samples were analyzed for the following 9 OPEs: Tris(2-*chloroethyl*) phosphate (TCEP), Tris(dichloroisopropyl) phosphate (TDCP), Tris(1-*chloro*-2-*propyl*)phosphate (TCPP mix of isomers), tri-iso-butyl phosphate (TiBP), tri-*n*-buthyl phosphate (TnBP), triphenyl phosphate (TPhP), Tris(2-butoxyethyl) phosphate (TBEP), tri(2-ethylhexyl) phosphate (TEHP) and tricresyl phosphate (TCrP, mix of isomers). [d15]-Triphenylphosphate ([d15]-TPhP), [d27]-Tri-*n*-butylphosphate ([d27]-TnBP), [d12]-Tris(2-chloroethyl) phosphate ([d12]-TCEP) were used as surrogate standards. Information on CAS-No., producers, and purities of the used OPE standards are listed in Table S4 in the supplement material.

2.4. QA/QC

Since OPEs are widely used and therefore are also likely to be present in various lab equipment, the use of any plastic and rubber material was avoided to minimize possible contamination of the samples during sampling, storage, transport, and extraction. The sampling equipment used to trap airborne particles was exclusively made of stainless steel. Before use, GFFs were baked at 450 °C for 12 h and wrapped in aluminum foil prior and after use. Glass cartridges were extracted with acetone and DCM by Soxhlet before use. All used glass ware was baked at 250 °C for 12 h and rinsed with acetone. Silica gel was Soxhlet extracted with DCM for 12 h and baked at 450 °C for 12 h prior to use. 10 field blanks were taken during sampling and treated similar to the real samples, but with only 1 m^3 air being pumped through the collecting system. TiBP, TnBP, TEHP, TCEP, TCPP, TDCPP, TPhP, TEHP and TCP were detected in the blanks. Absolute blank values ranged from 50 ± 9 pg (TCP) to 814 ± 330 pg (TECP) and were similar between the blank replicates. Method detection limits (MDLs) were derived from mean blank values plus three times the standard deviation or, for those compounds with no detected blanks, from the instrumental detection limits at signal–to–noise (S/N) ratios of three. Based on a nominal sampling volume of 2000 m^{-3}, MDLs ranged from 0.1 pg m^{-3} (TDCPP) to 1 pg m^{-3} (TBEP). Note that values below the detection limits were determined based on absolute MDL values (in pg OPEs absolute) due to the variation of the sampling volume. The recoveries of the surrogate standards were 95± 34% [D27]–TnBP, 54 ± 30% [D12]—TCEP and 95± 27% for [D15]—TPhP for the particle phase. For the gas phase surrogate recoveries were 218± 34% [D27]—TnBP, 83 ± 46% [D12]—TCEP and 218± 70% for [D15]—TPhP, respectively. All concentrations were recovery corrected by the surrogates.

3. Results and discussion

3.1. Method

The measurement of OPEs in remote environmental systems is challenging. There are two major factors that have to be taken into consideration. On the one hand site there are possible contaminations during the sampling and sample treatment. OPEs are present in various sampling and lab equipment that contain plastic parts, rubbers, oils or greases and can be emitted from these materials into the atmosphere. Especially in remote areas, with expected low concentrations, it has to be ensured that detected OPE concentrations are not an artifact of contaminated equipment.

The second factor is the sample treatment. Because of the medium stability, midrange polarity and volatility, only very gentle cleanups are suitable. In order not to destroy analytes the purification is therefore often only partially satisfactory. In this case instrumental detection limits rise and might reach levels of the same magnitude or even higher than the expected OPE concentrations in remote environments.

Using the GC-MS/MS System we achieved a significant reduction of instrumental detection limits of up to a factor 50 compared to our old instrumental method using a GC-MS (Möller et al., 2011). This reduction was achieved by the higher selectivity of the MS/MS system for analytes and consequently reduced signal-to-noise range, especially, for samples with high (sampling-)matrix interference. The comparisons of the MS/MS and MS MDLs in air samples are presented in Fig. 1.

3.2. Phase distribution

A potential sampling error for the distinction of gas phase and particle phase should generally be taken into consideration for all sampling setups. In this setup the gas phase has to cross the filter before being adsorbed on the PUF-XAD2-cardrige. This might lead to adsorption of gas phase OPEs on the filter due to polar interactions as well as a potential for small particles to penetrate the GF/F filter (average pore size 0.7 μm).

Previous studies have reported that OPEs predominantly adsorb to the particle phase in the atmosphere (>95%) (Möller et al., 2011, 2012; Salamova et al., 2014b). However, in this study we detected six of the nine analyzed OPEs with more than 20% or even predominantly in the gas phase. To evaluate the accuracy of these novel findings we correlated the observed partioning behavior of the individual analytes with the theoretical partitioning coefficient between non-polar octanol phase (e.g. particle) and air (K_{OA}) (Fig. 2). The results were in very good agreement (Pearson R: 0.96) indicating that the observed partitioning into the gas phase could be genuine (Fig. 2).

An explanation for the difference in observed partitioning compared to our previous study from 2011 (Möller et al., 2011) could be the difference in applied method and resulting instrumental detection limits (Fig. 1). In our previous study MDLs differed significantly between the gas phase and the particle phase due to the sensitivity of single mass spectrometer to matrix effects and the blank contamination. The improved selectivity of the novel MS/MS method removed the resulting differences in MDLs for the different phases, leading to an improved representation of OPE partitioning behavior.

Further factors that could lead to differences in the actual partitioning of OPEs could be environmental and sampling conditions such as e.g. temperature. High contributions of OPEs in the particle phase in samples from polar latitudes could be explained by the low temperatures in these arias, potentially leading to reduced volatilization and cold condensation (Mackay and Wania, 1995). Further factors impacting the partitioning could include humidity and particle concentration in air. Further research should be conducted to investigate these factors and their potential implications on behavior and sampling of OPEs in air.

Interestingly, no seasonal trends, temperature dependence or other specific patterns were apparent in the gas-particle partitioning observed in this study. This could be an indication that temperature is not the main driver for OPE partitioning and atmospheric behavior in locations with temperate, marine climate and i.e. relatively low temperature variability.

Due to this lack of temperature dependence and trendsas well as the overall low concentrations, sum gas and particle phase concentrations were used for further discussion of the detected OPEs. The summarized OPE concentrations are presented in Fig. 3.

3.3. Concentration

Eight compounds were detected in the majority of samples with average concentrations of 11.4 ± 13.1 pg m^{-3} for TEHP, 9.8 ± 6.1 pg m^{-3} for TCPP, 8.6 ± 5.8 pg m^{-3} for TiBP, 6.3 ± 10.8 pg m^{-3} for TnBP, 3.4 ± 2.1 pg m^{-3} for TCEP, 3.5 ± 4.6 pg m^{-3} for TCP, 3.2 ± 3.2 pg m^{-3} for TPhP and 0.95 ± 0.76 pg m^{-3} for TDCPP. TBEP was detected with up to 9.2 pg m-3 but in only in 50% of the samples, likely caused by its higher detection limits compared to the other analytes.

The observed concentrations in this study were significantly lower than results reported in previous studies (Castro-Jiménez et al., 2014; Möller et al., 2011; Salamova et al., 2014a, Salamova et al., 2014b). A good overview of published atmospheric OPE data can be found elsewhere (Castro-Jiménez et al., 2014; Lai et al., 2015). Detected concentrations were ten times lower than OPE concentrations reported in a previous study from the same area (Möller et al., 2011) that was performed with similar sampling technique but MS as detector. Other studies from comparably remote environments also reported higher concentrations (Castro-Jiménez et al., 2014; Möller et al., 2011). In contrast, some recently published studies reported comparable low concentrations in air samples from the South China Sea (Lai et al., 2015), raising the

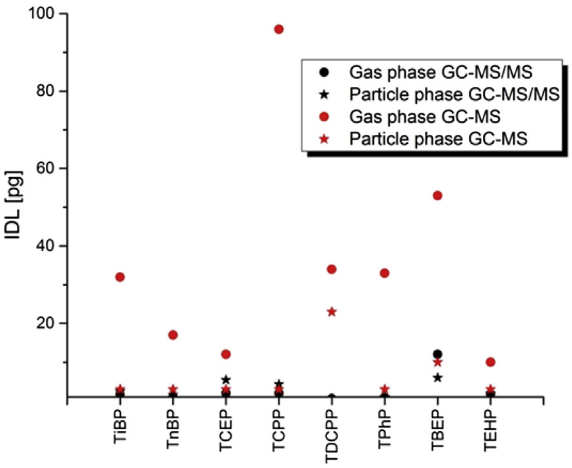

Fig. 1. Comparison of Instrumental detection limits (IDL) from GC-EI-MS and GC-EI-MS/MS.

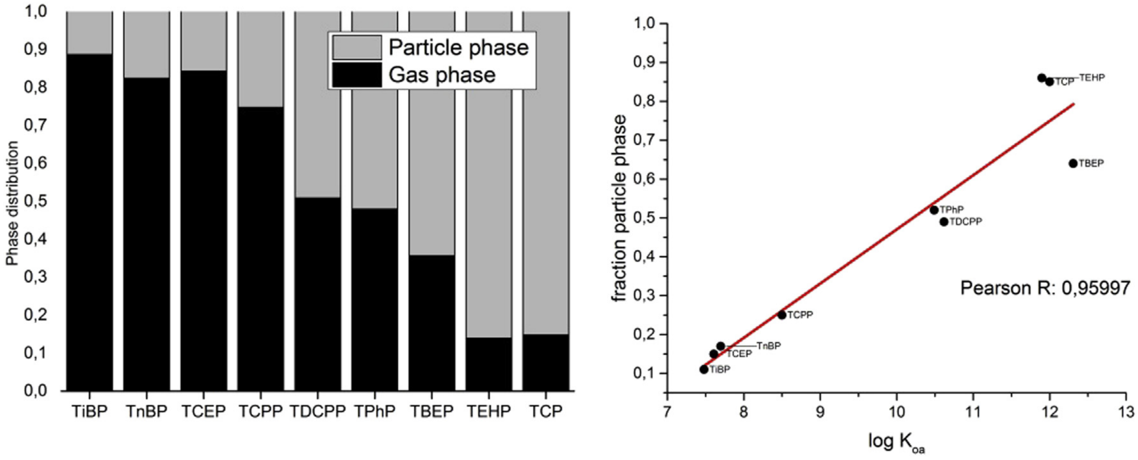

Fig. 2. Average phase distribution of OPEs.

question, whether the difference in concentrations indicate an environmental decreasing trend or are an indication for strong analytical variability.

Similar to the particle-gas phase partitioning, no significant seasonal trend was apparent for general OPE concentrations. However, a different ratio of chlorinated compounds (ClOPEs = TCEP, TCPP, TDCPP) to short chained non-halogenated compounds (sc-nhOPEs = TnBP, TiBP) between summer and winter was observed. In summer the contribution of ClOPEs to the sum concentration of ClOPEs and sc-nhOPEs was 0.60 while it decreased to 0.43 in winter. This could be an indication for a higher photolytic degradation of non-halogenated OPEs compared to ClOPEs in summer, congruent with the overall higher persistence of ClOPEs. Interestingly, TEHP concentrations peaked in October and May, contrary to the lack of general seasonal trends in OPE concentrations. The source of these increases remain unknown, because the main use of TEHP is in PVCs, paint, coatings and PUF (Esch, 2000; van Esch, 1997), which should have no specific seasonal applications in spring and fall.

To gather further information on potential sources of the detected OPEs, the air masses of the different samples were characterized. To this end, an analysis of the predominant wind directions was performed with two defined sectors. The first sector represented the contribution of land based air masses 0°–180°. The second sector covered the sea based air masses 180°–360°. The results are presented in Fig. 3. In general, the magnitude of detected OPE concentrations correlated best with the contribution of land base wind direction (R = 0.57 (Pearson)). However, correlations between wind direction and OPE concentrations varied strongly between short-chain and long-chain OPEs. The sc-nhOPEs had comparably low correlations with land-based wind directions of 0.38 (TiBP) and 0.25 (TnBP). Similar results were also observed for short-chain chlorinated OPEs, with Pearson correlation of 0.30 (TDCPP), 0.18 (TCPP) and 0.11 (TCEP). The long chain OPEs, on the other hand, correlated well with the land-based wind direction, with 0.64 (TPhP), 0.60 (TBEP), 0.57 (TEHP) and 0.67 (TCP). Several factors could explain these observations. The long chain OPEs were primarily detected in the particle phase, which could induce higher

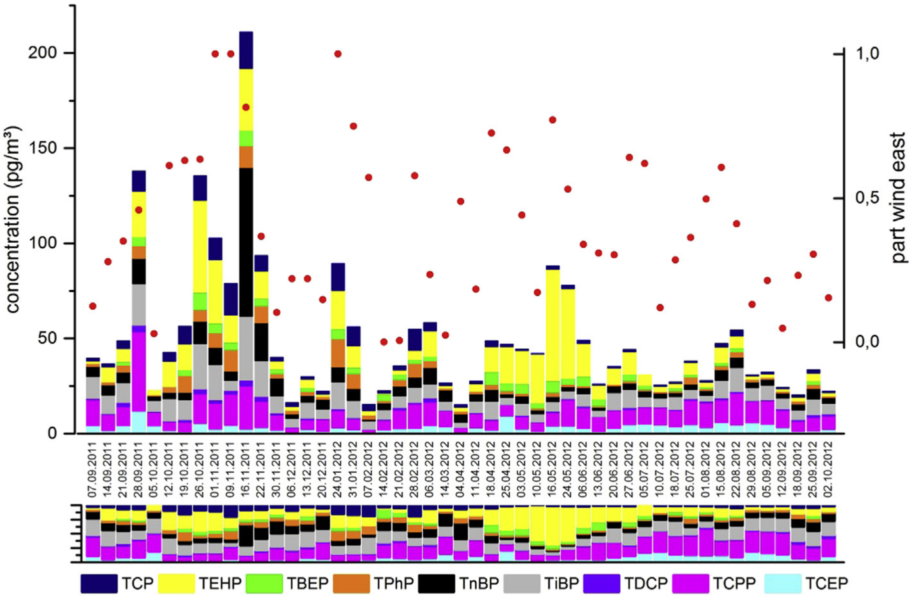

Fig. 3. The upper bars represent the sum concentration (gas and particle phase) of detected OPEs; the red dots indicate the probabilities of easterly winds (land based); the lower bars show the contribution of detected OPEs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

removal by dry and wet deposition compared to gas phase OPEs. The photolytic degradation on the other hand is reduced for particle bound OPEs compared to those in the gas phase (Liu et al., 2014). This combination could explain a relative accumulation of long chain OPEs in air masses related to local source regions compared to ClOPEs and sc-OPEs.

4. Conclusion

This study has shown that the advances in new GC-MS/MS systems are powerful instruments for an increase in accuracy of OPE analysis compared to single MS systems. The new findings of the phase distribution in the atmosphere should be further investigated and discussed in respect to transport and degradation of OPEs. Furthermore, the low observed concentrations are an interesting result, raising questions regarding possible contamination pathways during sampling from ambient equipment or buildings.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.04.028.

References

Bacaloni, A., Cucci, F., Guarino, C., Nazzari, M., Samperi, R., Laganà, A., 2008. Occurrence of organophosphorus flame retardant and plasticizers in three volcanic lakes of Central Italy. Environ. Sci. Technol. 42 (6), 1898–1903.

Björklund, J., Isetun, S., Nilsson, U., 2004. Selective determination of organophosphate flame retardants and plasticizers in indoor air by gas chromatography, positive-ion chemical ionization and collision-induced dissociation mass spectrometry. Rapid Commun. Mass Spectrom. 18 (24), 3079–3083.

Bollmann, U.E., Möller, A., Xie, Z., Ebinghaus, R., Einax, J.W., 2012. Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. Water Res. 46 (2), 531–538.

Campone, L., Piccinelli, A.L., Östman, C., Rastrelli, L., 2010. Determination of organophosphorous flame retardants in fish tissues by matrix solid-phase dispersion and gas chromatography. Anal. Bioanal. Chem. 397 (2), 799–806.

Castro-Jiménez, J., Berrojalbiz, N., Pizarro, M., Dachs, J., 2014. Organophosphate ester (OPE) flame retardants and plasticizers in the open Mediterranean and Black seas atmosphere. Environ. Sci. Technol. 48 (6), 3203–3209.

Chung, H.-W., Ding, W.-H., 2009. Determination of organophosphate flame retardants in sediments by microwave-assisted extraction and gas chromatography–mass spectrometry with electron impact and chemical ionization. Anal. Bioanal. Chem. 395 (7), 2325–2334.

Esch, G.J.v., 2000. Flame Retardants: Tris(2-butoxyethyl) Phosphate, Tris(2-ethylhexyl) Phosphate and Tetrakis(hydroxymethyl) Phosphonium Salts. In: Environmental Health Criteria 218. World Health Organization, Geneva, p. 130 xix.

Fromme, H., Lahrz, T., Kraft, M., Fembacher, L., Mach, C., Dietrich, S., Burkardt, R., Völkel, W., Göen, T., 2014. Organophosphate flame retardants and plasticizers in the air and dust in German daycare centers and human biomonitoring in visiting children (LUPE 3). Environ. Int. 71, 158–163.

Lai, S., Xie, Z., Song, T., Tang, J., Zhang, Y., Mi, W., Peng, J., Zhao, Y., Zou, S., Ebinghaus, R., 2015. Occurrence and dry deposition of organophosphate esters in atmospheric particles over the northern South China Sea. Chemosphere 127, 195–200.

Liu, Y., Liggio, J., Harner, T., Jantunen, L., Shoeib, M., Li, S.-M., 2014. Heterogeneous OH initiated oxidation: a possible explanation for the persistence of organophosphate flame retardants in air. Environ. Sci. Technol. 48 (2), 1041–1048. http://dx.doi.org/10.1021/es404515k.

Mackay, D., Wania, F., 1995. Transport of contaminants to the Arctic: partitioning, processes and models. Sci. Total Environ. 160/161 (1995), 25–38.

Marklund, A., Andersson, B., Haglund, P., 2003. Screening of organophosphorus compounds and their distribution in various indoor environments. Chemosphere 53 (9), 1137–1146.

Marklund, A., Andersson, B., Haglund, P., 2005. Traffic as a source of organophosphorus flame retardants and plasticizers in snow. Environ. Sci. Technol. 39 (10), 3555–3562.

Möller, A., Xie, Z., Caba, A., Sturm, R., Ebinghaus, R., 2011. Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea. Environ. Pollut. 159 (12), 3660–3665.

Möller, A., Sturm, R., Xie, Z., Cai, M., He, J., Ebinghaus, R., 2012. Organophosphorus flame retardants and plasticizers in airborne particles over the northern pacific and Indian Ocean toward the polar regions: evidence for global occurrence. Environ. Sci. Technol. 46 (6), 3127–3134.

Reemtsma, T., Quintana, J.B., Rodil, R., García-López, M., Rodríguez, I., 2008. Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. TrAC Trends Anal. Chem. 27 (9), 727–737.

Rodríguez, I., Calvo, F., Quintana, J.B., Rubí, E., Rodil, R., Cela, R., 2006. Suitability of solid-phase microextraction for the determination of organophosphate flame retardants and plasticizers in water samples. J. Chromatogr. A 1108 (2), 158–165.

Salamova, A., Hermanson, M.H., Hites, R.A., 2014a. Organophosphate and halogenated flame retardants in atmospheric particles from a european arctic site. Environ. Sci. Technol. 48 (11), 6133–6140.

Salamova, A., Ma, Y., Venier, M., Hites, R.A., 2014b. High levels of organophosphate flame retardants in the great lakes atmosphere. Environ. Sci. Technol. Lett. 1 (1), 8–14.

Shaw, S.D., Blum, A., Weber, R., Kannan, K., Rich, D., Lucas, D., Koshland, C.P., Dobraca, D., Hanson, S., Birnbaum, L.S., 2010. Halogenated flame retardants: do the fire safety benefits justify the risks? Rev. Environ. Health 25 (4), 261–305.

Sundkvist, A.M., Olofsson, U., Haglund, P., 2010. Organophosphorus flame retardants and plasticizers in marine and fresh water biota and in human milk. J. Environ. Monit. 12 (4), 943.

Takeuchi, S., Kojima, H., Saito, I., Jin, K., Kobayashi, S., Tanaka-Kagawa, T., Jinno, H., 2014. Detection of 34 plasticizers and 25 flame retardants in indoor air from houses in Sapporo, Japan. Sci. Total Environ. 491–492, 28–33.

van Esch, G., 1997. Environmental Health Criteria 192. World Health Organization.

Venier, M., Dove, A., Romanak, K., Backus, S., Hites, R., 2014. Flame retardants and legacy chemicals in great lakes' water. Environ. Sci. Technol. 48 (16), 9563–9572.

Wang, R., Tang, J., Xie, Z., Mi, W., Chen, Y., Wolschke, H., Tian, C., Pan, X., Luo, Y., Ebinghaus, R., 2015. Occurrence and spatial distribution of organophosphate ester flame retardants and plasticizers in 40 rivers draining into the Bohai Sea, north China. Environ. Pollut. 198, 172–178.

Wolschke, H., Sühring, R., Xie, Z., Ebinghaus, R., 2015. Organophosphorus flame retardants and plasticizers in the aquatic environment: a case study of the Elbe River, Germany. Environ. Pollut. 206, 488–493.

Zhang, X., Sühring, R., Serodio, D., Bonnell, M., Sundin, N., Diamond, M.L., 2016. Novel flame retardants: estimating the physical-chemical properties and environmental fate of 94 halogenated and organophosphate PBDE replacements. Chemosphere 144, 2401–2407. http://dx.doi.org/10.1016/j.chemosphere.2015.11.017.

Atmospheric occurrence and fate of organophosphorus flame retardants and plasticizer at the German coast

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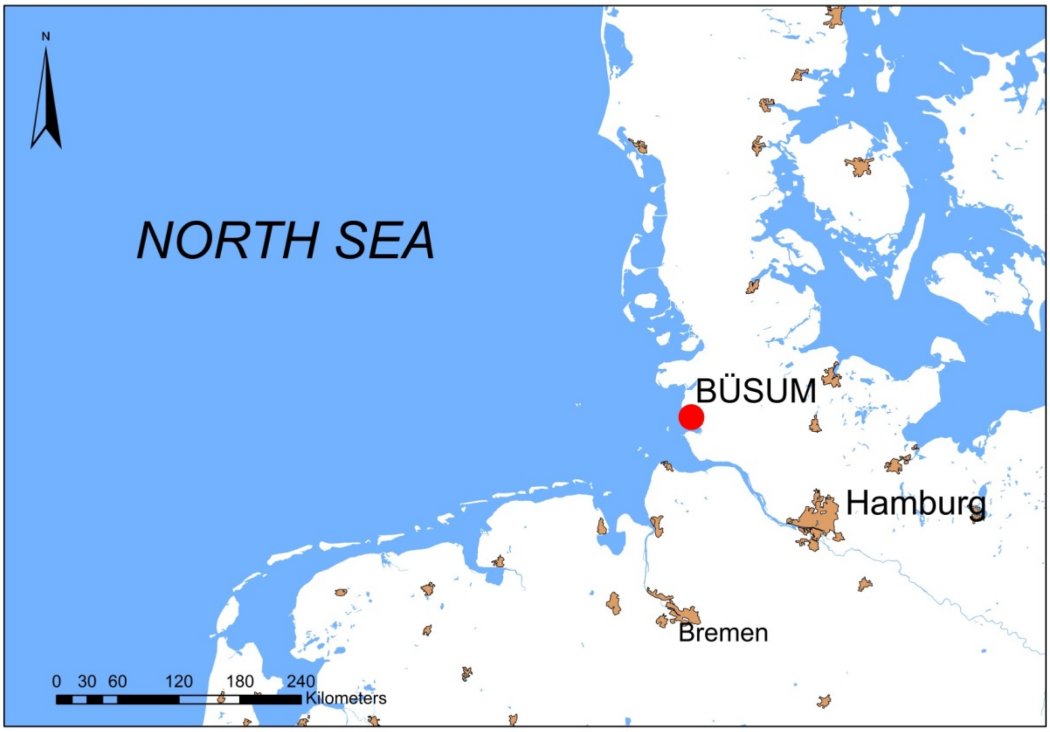
Supplementary data

S1: Map of the sampling station



S2: Detailed information on the sampling dates, air volume, and average temperature

start date	stop date	sample volume (m^3)	Temperature (ºC)
2011/09/14	2011/9/21	2740	13.9
2011/09/21	2011/9/28	2948	14.4
2011/09/28	2011/10/5	2846	16.2
2011/10/05	2011/10/12	2559	12.1
2011/10/12	2011/10/19	2495	9.0
2011/10/19	2011/10/26	2038	7.9
2011/10/26	2011/11/1	2491	10.2
2011/11/01	2011/11/9	3407	9.6
2011/11/09	2011/11/16	2720	3.3
2011/11/16	2011/11/22	2034	3.4
2011/11/22	2011/11/30	2349	6.4
2011/11/30	2011/12/6	1755	6.2
2011/12/06	2011/12/13	2136	4.3
2011/12/13	2011/12/20	2270	4.3
2011/12/20	2012/01/03	4198	5.7
2012/01/03	2012/01/10	2180	5.7
2012/01/10	2012/01/18	2328	4.7
2012/01/18	2012/01/24	1647	3.8
2012/01/24	2012/01/31	2370	-1.1
2012/01/31	2012/02/07	2715	-7.5
2012/02/07	2012/02/14	2453	-3.4
2012/02/14	2012/02/21	2155	2.4
2012/02/21	2012/02/28	2231	4.6
2012/02/28	2012/03/06	2219	5.0
2012/03/06	2012/03/14	2680	5.6
2012/03/14	2012/03/20	2828	6.7
2012/03/20	2012/03/27	2898	6.6
2012/03/27	2012/04/04	2416	6.5
2012/04/04	2012/04/11	2221	4.7
2012/04/11	2012/04/18	2755	6.7
2012/04/18	2012/04/25	2760	8.8
2012/04/25	2012/05/03	2920	11.9
2012/05/03	2012/05/10	2350	9.8
2012/05/10	2012/05/16	2128	11.0
2012/05/16	2012/05/24	3049	14.7
2012/05/24	2012/05/30	2272	17.1
2012/06/06	2012/06/13	2134	13.8
2012/06/13	2012/06/20	2725	14.1
2012/06/20	2012/06/27	2568	15.0
2012/06/27	2012/07/5	2811	17.4
2012/07/05	2012/07/10	2230	18.0
2012/07/10	2012/07/18	2907	15.6
2012/07/18	2012/07/25	2639	16.6
2012/07/25	2012/08/1	2888	17.7
2012/08/01	2012/08/15	4971	17.3
2012/08/15	2012/08/22	2633	20.3
2012/08/22	2012/08/29	2746	17.2
2012/08/29	2012/09/05	2980	16.6
2012/09/05	2012/09/12	2981	16.8
2012/09/12	2012/09/18	2606	14.6
2012/09/18	2012/09/25	2606	11.8
2012/09/25	2012/10/02	2620	12.5
2012/10/02	2012/10/10	3197	11.4

S3: GC-MS/MS Transitions

Compound	Trasition 1	Transition 2	Retention time
d27-TnBP	***103.0 -> 83.0***	***167.0 -> 103.0***	***29.00***
d12-TCEP	***261.0 -> 196.0***	***261.0 -> 103.0***	***31.90***
d15-TPhP	***341.0 -> 223.0***	***341.0 -> 178.0***	***44.50***
C13-PCB141	***372.0 -> 302.0***		***43,50***
TiBP	99.0 -> 81.0	155.0 -> 99.0	26.40
TnBP	99.0 -> 81.0	155.0 -> 99.0	29.40
TCEP	249.0 -> 187.0	249.0 -> 99.0	32.20
TCPP I1	277.0 -> 125.0	157.0 -> 117.0	33.30
TCPP I2	277.0 -> 125.1	157.0 -> 117.1	33.80
TCPP I3	277.0 -> 125.2	157.0 -> 117.2	34.20
TDCPP	381.0 -> 159.0	191.0 -> 75.0	43.50
TPhP	326.0 -> 215.0	326.0 -> 170.0	44.60
TBEP	299.0 -> 199.0	227.0 -> 101.0	45.10
TEHP	99.0 -> 81.0		46.35
TCP I1	368.0 -> 198.1	368.0 -> 165.1	49.90
TCP I2	368.0 -> 198.0	368.0 -> 165.0	50.40
TCP I3	368.0 -> 198.1	368.0 -> 165.1	50.90

S4: Chemicals

Name		**Molecular formula**	**CAS-No.**	**Purity %**	**Producer**
D12-Tris(2-chloroethyl)phosphate	D15-TECP	C12D12Cl$_3$O$_4$P		99.2	Dr. Ehrenstorfer
d15-Triphenylphosphate	D15-TPhP	$C_{18}D_{15}O_4P$		98	Sigma Aldrich
d21-Tri-*n*-propylphosphate	D21-TPrP	$C_9D_{21}O_4P$		98.2	Dr. Ehrenstorfer
d27-Tri-*n*-butylphosphate	D27-TnBP	$C_{12}D_{27}O_4P$	61196-26-7	99.7	Dr. Ehrenstorfer
Tris(2-butoxyethyl)phosphate	TBEP	$C_{18}H_{39}O_7P$	78-51-3	94	Sigma Aldrich
Tri-*n*-butylphosphate	TnBP	$C_{12}H_{27}O_4P$	126-73-8	≥ 99	Sigma Aldrich
Tris(2-chloroethyl)phosphate	TCEP	$C_6H_{12}Cl_3O_4P$	115-96-8	97	Sigma Aldrich
Tricresylphosphate	TCP	$C_{21}H_{21}O_4P$	1330-78-5	90 (Isomere)	Sigma Aldrich
Tris(1-chloro-2-propyl)phosphate	TCPP	$C_9H_{18}Cl_3O_4P$	13674-84-5	Anal.Std. (Isomere)	Sigma Aldrich
Tris(dichlorisopropyl)phosphate	TDCPP	$C_9H_{15}Cl_6O_4P$	13674-87-8	95,8	Sigma Aldrich
Tris(2-ethylhexyl)phosphate	TEHP	$C_{24}H_{51}O_4P$	78-42-2	≥ 99	Sigma Aldrich
Tri-*iso*-butylphosphate	TiBP	$C_{12}H_{27}O_4P$	126-71-6	≥ 99	Merck
Triphenylphosphate	TPhP	$C_{18}H_{15}O_4P$	115-86-6	≥ 99	Sigma Aldrich

Paper IV

Distribution of Organophosphate Esters between the Gas and Particle Phase–Model Predictions vs Measured Data

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Distribution of Organophosphate Esters between the Gas and Particle Phase—Model Predictions vs Measured Data

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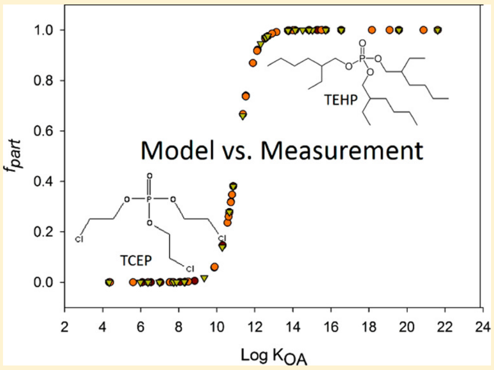
S *Supporting Information*

ABSTRACT: Gas-particle partitioning is one of the key factors that affect the environmental fate of semivolatile organic chemicals. Many organophosphate esters (OPEs) have been reported to primarily partition to particles in the atmosphere. However, because of the wide range of their physicochemical properties, it is unlikely that OPEs are mainly in the particle phase "as a class". We compared gas-particle partitioning predictions for 32 OPEs made by the commonly used OECD P_{OV} and LRTP Screening Tool ("the Tool") with the partitioning models of Junge-Pankow (J-P) and Harner-Bidleman (H-B), as well as recently measured data on OPE gas-particle partitioning. The results indicate that half of the tested OPEs partition into the gas phase. Partitioning into the gas phase seems to be determined by an octanol-air partition coefficient ($\log K_{OA}$) < 10 and a subcooled liquid vapor pressure ($\log P_L$) > −5 (P_L in Pa), as well as the total suspended particle concentration (TSP) in the sampling area. The uncertainty of the physicochemical property data of the OPEs did not change this estimate. Furthermore, the predictions by the Tool, J-P- and H-B-models agreed with recently measured OPE gas-particle partitioning.



1. INTRODUCTION

Organic flame retardants (FRs) have been used in increasing amounts since the 1950s in a variety of polymer-based industrial and consumer products to comply with flammability standards. Some FRs, such as penta- and octa- polybrominated diphenyl ethers (PBDEs) have been restricted from new production and application under the Stockholm Convention due to their hazardous properties, including high persistence and bioaccumulation potential.[1,2] Other brominated FRs (BFRs) such as deca-PBDE are partially restricted or voluntarily phased-out by industry.[3] However, the overall demand and production of FRs is still increasing.[4] Therefore, the restrictions and phasing-out of PBDEs since the early 2000s have led to the introduction of a variety of halogenated and nonhalogenated alternatives.[5,6]

One group of substitutes are organophosphate esters (OPEs), which comprise a diverse set of compounds varying widely in physicochemical properties. Their production and use have been increasing, in part, as a result of restrictions on PBDE use.[7] In 2004 the global annual use was 207 200 tonnes,[8] which makes OPEs high-production volume chemicals. OPE uses extend beyond application as FRs. Whereas chlorinated OPEs are mainly used as flame retardants, nonchlorinated OPEs are also used as plasticizers, antifoaming agents and additives in hydraulic fluids.[9]

Whether or not OPEs are suitable replacements for hazardous FRs, such as PBDEs with known carcinogenic or endocrine disrupting properties, is controversial. OPEs are, in general, regarded as less persistent in the environment—one of

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the key criteria for evaluating the potential environmental hazard of a chemical. However, our recent study suggested that many OPEs have medium to high persistence (>1700 h) and that tetrakis(2-chloroethyl)dichloroisopentyldiphosphate, ethylhexyldiphenyl phosphate, isodecyl diphenyl phosphate, 2,2-bis(bromomethyl)-3-chloropropyl bis[2-chloro-1-(chloromethyl)ethyl] phosphate, tricresyl phosphate, triphenyl phosphate, tris(tribromo-neopentyl) phosphate, and potentially tris(2-butoxyethyl) phosphate and tris(2,3-dichloropropyl) phosphate (BCMP-BCEP, EHDPP, IDDPP, MC984, TCP, TPhP, TTBNPP, TBEP, TDCPP) have a persistence similar to that of PBDEs they are replacing.[10] Furthermore, increasing amounts of OPEs have been detected in remote areas[11−13] such as the Arctic and Antarctic, which indicates their persistence (P_{OV}) and long-range transport potential (LRTP).

To assess potential risks posed by OPEs, it is essential to establish suitable measurement and estimation methods that provide information on where and how OPEs are distributed. Most studies of OPEs have focused on the particle phase,[12,14,15] because many OPEs have been reported to mostly partition to particles in the atmosphere.[14,15] Sorption to particles has, furthermore, been hypothesized as one potential explanation for reduced degradation and thereby increased P_{OV} and LRTP of OPEs in the environment.[16] However, considering the range of physicochemical properties of OPEs, notably the vapor pressure (P_L) and octanol-air partition coefficient (K_{OA}), from which gas-particle partitioning of semivolatile chemicals can be estimated,[17,18] it seems unlikely that all OPEs are particle-sorbed.

Revisiting the literature that has reported that OPEs are primarily in the particle phase, we found that these studies either investigated selected OPEs with similar properties (e.g., only halogenated OPEs), screened selected samples for OPEs in the gas phase, or that the detection limits were significantly higher for the gas phase than for the particle phase.[12,14,15] Furthermore, studies using the OECD P_{OV} and LRTP screening tool ("the Tool") for the estimation of the environmental behavior of OPEs predicted that about half of the tested OPEs should be primarily in the gas phase.[10,19] This could, of course, be an error of the model or an error in the physicochemical properties used as input parameters.

Considering the importance of an accurate and reliable assessment of LRTP and persistence for the risk assessment of OPEs, we assessed the hypothesis that OPEs primarily partition to the particle phase. Due to the importance of the OECD P_{OV} and LRTP screening tool as a tool for assessing P_{OV} and LRTP in chemical risk assessment[20] we decided to use this model, which derives gas-particle partitioning from K_{OA} to predict the fraction of OPEs in the particle phase (f_{part}). Here, f_{part} is defined as the ratio of the concentration of a chemical in the particle phase (c_{part}, ng m^{-3}) to its total concentration in particle and gas-phases (c_{part} + c_{gas}, ng m^{-3}), with $f_{part} = \frac{c_{part}}{(c_{part} + c_{gas})}$.

Our aim was to investigate the hypothesis that all OPEs are predominantly present in the particle phase. We first assessed the impact of uncertainty of various model input parameters on predicted values of f_{part}, identified the factors determining f_{part}, and then evaluated and compared these predictions to other gas-particle partitioning models (Harner-Bidleman[17]) (Junge-Pankow[18]), as well as measured values of f_{part} from previous studies.

2. MATERIALS AND METHODS

2.1. Compounds Evaluated. The 32 compounds evaluated for gas-particle partitioning (Table 1, S1) were taken from those assessed by Zhang and Sühring et al. (2016),[10] Liagkouridis et al. (2015),[19] measured in the atmosphere by Möller et al. (2011),[15] and measured during a one-year weekly stationary sampling at Büsum, Northern Germany.[21] We included OPEs with a wide range of physicochemical properties: log P_L (P_L in Pa) ranged from −5.6 for BCMP-BCEP, resorcinol bis(diphenyl phosphate) (PBDPP) and TTBNPP to 1.7 for trimethyl phosphate (TMP) and log K_{OA} ranged from 4.3 for TMP to 22 for tetrakis(2,6-dimethylphenyl)-*m*-phenylene biphosphate (PBDMPP) (see Supporting Information Tables S2−S7 for a detailed description of all input data).

2.2. Log K_{OA}-Based f_{part} Estimated with the OECD Tool. The OECD P_{OV} and LRTP screening tool ("the Tool") (Version 2.2[22]) calculates $f_{part,T}$ based on the octanol-air partition coefficient (K_{OA}). This approach assumes that absorption into the organic film coating of atmospheric particles is the driving factor for the gas-particle partitioning of chemicals,[23] rather than the adsorption to active sites hypothesized by Junge and Pankow.[24,25] The particle-bound fraction, $f_{part,T}$, is calculated in the Tool by the following equation:

$$f_{part,T} = \frac{\varphi_{aer} \cdot 0.42 \cdot K_{OA}}{\varphi_{aer} \cdot 0.42 \cdot K_{OA} + 1} \qquad (1)$$

The volume fraction of aerosol particles in air (φ_{aer}) in the Tool is set by default to $2 \times 10^{-11} \frac{m^3}{m^3}$. The default settings in the Tool assume coarse particles with an aerosol deposition velocity of 10.8 m h^{-1}, usually attributed to a particle diameter of 2.5−10 μm.[26] Assuming an average density of aerosol particles of 1.5 g cm^{-3} this value reflects a particle concentration in air of 30 μg m^{-3}, which is the target value for $PM_{2.5}$ in the Canada-wide Standard for particulate matter and ozone.[27] K_{OA} in the Tool is calculated as the ratio of the octanol−water partition coefficient (K_{OW}) and the air−water partition coefficient (K_{AW}), with $K_{OA} = \frac{K_{OW}}{K_{AW}}$. In the Tool, all partition coefficients are used with their values for 298 K.

Data for the Tool input parameters were extracted from a total of 50 publications (1979−2015) and sorted into three data sets for the evaluation of the Tool (see Supporting Information Tables S2−S7 for a detailed list of data used and sources). To test the hypothesis that uncertainty of input data is responsible for the discrepancy between modeled and measured partitioning behavior of OPEs, we collected input data with high variability. We explicitly included data published by industry and government authorities, as well as data from sources dating back more than 30 years. The aim of this approach was to "simulate" data sets that would be used by different stakeholder groups such as regulators, industry, the scientific community and NGOs and to test whether the use of different data sets and sources would have a significant effect on the predicted f_{part}.

Input all. Values of K_{OW}, K_{AW}, and P_L were obtained from modeled and measured data from all 50 publications (1979−2015) and data provided for registration under the European chemicals regulation, REACH. The median values of the combined data set were used as input data for the Tool (a full list of the data used and their sources is presented in Tables S1–S4). Log K_{OA} was calculated as

$$\log K_{OA} = \log K_{OW} - \log K_{AW} \tag{2}$$

Modeled Data. Values of K_{OW}, K_{AW}, and P_L estimated by EPI Suite, SPARC and Absolv were taken from the studies by Zhang and Sühring et al. (2016)[10] and Liagkouridis et al. (2015).[19] This data set was used to specifically assess the uncertainty of estimated physicochemical properties. Log K_{OA} was calculated from log K_{OW} and log K_{AW} (2).

Outlier Removed. These are the partition coefficients, K_{OW}, K_{AW}, from the "input-all" data set with outliers removed. Outliers were defined as data points with a value below $Q_1 - 1.5$ IQR or above $Q_3 + 1.5$ IQR, respectively, with Q_1 as the first quartile or 25th percentile, Q_3 as the third quartile or 75th percentile, and IQR as the interquartile range, $Q_3 - Q_1$. Log K_{OA} was calculated as noted above.

Predictions by the Tool ($f_{\text{part,T}}$) were compared with those calculated from the Junge-Pankow model ($f_{\text{part,J-P}}$) and the Harner-Bidleman model ($f_{\text{part,H-B}}$). Input data to these models were obtained from the three most commonly used estimation methods for physicochemical properties, EPISuite, SPARC and Absolv, as well as from measured data.

2.3. Data Evaluation for the Tool. To evaluate the impact of uncertain input parameters on the prediction of $f_{\text{part,T}}$, a sensitivity analysis was performed for the "Outlier Removed" data set, as well as a Monte Carlo uncertainty analysis for compounds of the "Outlier Removed" data set with low or intermediate $f_{\text{part,T}}$ ($f_{\text{part,T}} < 0.9$).

The sensitivity analysis was performed as described by Morgan and Henrion (1992).[28] The sensitivity of $f_{\text{part,T}}$ to a specific input parameter was tested by changing the input parameters one-by-one and evaluating the impact on $f_{\text{part,T}}$. A factor of 1.1 was chosen for the change of parameter values. The sensitivity (S) of f_{part} to an individual parameter was quantified as

$$S = \frac{\Delta f_{\text{part,T}}}{f_{\text{part,T}}} \frac{I}{\Delta I} \tag{3}$$

with S defined as sensitivity, $\Delta f_{\text{part,T}}$ defined as the change in $f_{\text{part,T}}$; I as the initial input parameter value, and ΔI as the change in input parameter value.

A Monte Carlo uncertainty analysis was performed on all compounds with partitioning behavior contrary to the hypothesis of partitioning into the particle phase, that is, with $f_{\text{part,T}} < 0.9$. The Monte Carlo calculation assumed that the values of all chemical properties are distributed log-normally around their true value. Dispersion factors describe the width of the log-normal distribution. In the default Monte Carlo analysis implemented in the Tool, this width is estimated by multiplying or dividing the median by a factor of 5 for the partition coefficients.[22] The Monte Carlo uncertainty analysis then generates random values from the distribution of each input parameter, using the defined dispersion factors and assuming uncertainties in chemical input parameters were uncorrelated. The model was run for a set number, N, of combinations of the dispersed input parameters.[22] For this study the Q1 and Q3 determined in the "Outlier Removed" data set were used as dispersion factors, as well as the (higher) default Tool dispersion factors and N was set to 200 (Tables S9 and S10 for calculated dispersion factors, initial and median f_{part} from Monte Carlo analysis for default and calculated dispersion factors).

2.4. Junge-Pankow ($f_{\text{part,J-P}}$) and Harner-Bidleman ($f_{\text{part,H-B}}$) Predictions and Evaluation. Predictions of $f_{\text{part,T}}$ from the Tool were compared to those from the Junge-Pankow (J-P) and Harner-Bidleman (H-B) models. The J-P model[18] assumes adsorption to the active sites of an aerosol particle according to the subcooled liquid vapor pressure (P_L, Pa) of the compound, and the surface area of the adsorbing aerosol particle per volume air (θ, cm^2 aerosol cm^{-3} air).[18] $f_{\text{part(J-P)}}$ is then calculated as

$$f_{\text{part,J-P}} = \frac{c\theta}{P_L + c\theta} \tag{4}$$

where $f_{\text{part,J-P}}$ is the fraction of chemical adsorbed to particles and c is a constant. The constant (c) depends on the surface concentration for monolayer coverage, sorbate molecular weight, and the difference between the the heat of vaporization of the liquid-phase sorbate and the heat of desorption from the particle surface.[17] We used default values of $c = 0.172$ Pa cm^{-1} and $\theta = 1.1 \times 10^{-5} \frac{\text{cm}^2}{\text{cm}^3}$ for urban air.[23] P_L data were obtained using EPI Suite's MPBPWIN v1.43,[29] SPARC,[30] as well as measured data[31] and literature data[7,32] (Tables S6, S7).

The Harner-Bidleman model[17] estimates f_{part}, similarly to the Tool, based on K_{OA} and assuming primary absorption into the organic layer of aerosols. $f_{\text{part,H-B}}$ is calculated as

$$f_{\text{part,H-B}} = \frac{K_p \times \text{TSP}}{(K_p \times \text{TSP} + 1)} \tag{5}$$

with

$$\log K_p = \log K_{OA} + \log f_{OM} - 11.91 \tag{6}$$

where $f_{\text{part,H-B}}$ is the fraction of chemical adsorbed to particles, K_P (m^3 μg^{-1}) is the particle-gas partition coefficient, TSP is the total suspended particulates concentration (μg m^{-3}), and f_{OM} is the fraction of organic matter (OM) on the aerosol particles (g_{OM} $g_{TSP}{}^{-1}$). We used default values for urban air of TSP of 55 μg m^{-3} and f_{OM} of 0.40 g_{OM} $g_{TSP}{}^{-1}$.[23]

2.5. Measured $f_{\text{part,M}}$. Finally, $f_{\text{part,T}}$, $f_{\text{part,H-B}}$, and $f_{\text{part,J-P}}$ were compared to measured $f_{\text{part,M}}$ values obtained by Wolschke et al.,[21] who measured weekly OPE air concentrations over one year at the sea-side town of Büsum in northern Germany. The temperature varied between −7 °C and 20 °C over the course of the sampling period and TSP varied from 2 μg m^{-3} to 65 μg m^{-3} (median 16 μg m^{-3}) (a summary of the sampling and analysis techniques is presented in the SI).

The set of compounds for comparison of $f_{\text{part,T}}$, $f_{\text{part,H-B}}$, $f_{\text{part,J-P}}$, and $f_{\text{part,M}}$ included nine compounds: TBEP, TCEP, TCP, TCPP, TDCPP, TEHP, TIBP, TnBP, and TPhP. This reduced dataset covers a wide range of physicochemical properties with log P_L between −4.5 for TDCPP and 0.9 for TCEP, and log K_{OA} between 7 for TIBP and 14 for TEHP.

3. RESULTS AND DISCUSSION

3.1. f_{part} Predictions by the Tool. The Tool calculates K_{OA} based on the partition coefficients K_{AW} and K_{OW}. Data for log K_{AW} and log K_{OW} for each compound were on average within two log units but deviated by up to eight and nine log units, respectively, for log K_{AW} (TDBPP) and log K_{OW} (MC984) (Tables S1, S2). Data sets from estimation methods

(EPISuite, SPARC and Absolv) were on average lower for log K_{AW} and higher for log K_{OW} than data from literature sources (Table S5).

The approximation of K_{OA} derived from other partition coefficients in itself introduces uncertainty. Furthermore, scatter of K_{AW} and K_{OW} data can add additional uncertainty and could, therefore, impact the uncertainty of $f_{part,T}$.

For most chemicals, values of $f_{part,T}$ obtained from the three data sets were consistent (Table 1, Figure 1): All input data sets led to $f_{part,T} > 0.9$ for 13 compounds and $f_{part,T} < 0.1$ for 9 compounds (Table 1). The results were more diverse for only for seven OPEs; $f_{part,T}$ estimated from the "Modelled Data" set for isomers of TCP (TmCP, ToCP, and TpCP) as well as BEHP, EHDPP, IDDPP, and TEHP were considerably lower (0.35, 0.70, 0.24, 0.67, and 0.87) than the results of the "Input all" and "Outlier Removed" data sets (1.00, 0.94, 0.97, 0.98, and 1.0) (Table 1).

Table 1. Predictions of $f_{part,T}$ for 32 OPEs Obtained From the OECD Tool

compound	input all	outlier removed	modeled input data
BCMP-BCEP	1.00	1.00	1.00
BDCPP	0.48	0.48	0.32
BEHP	0.92	0.94	0.74
BPA-BDPP (BADP)	0.97	0.97	1.00
DCP	0.15	0.14	0.28
DOPO	1.8×10^{-3}	1.8×10^{-3}	2.8×10^{-4}
EHDPP	0.97	0.97	0.24
IDDPP	0.98	0.98	0.67
MC 984	1.00	1.00	0.99
PBDMPP	1.00	1.00	1.00
PBDPP (RDP)	1.00	1.00	1.00
TBEP	0.98	0.98	0.92
TCEP	4.5×10^{-4}	4.5×10^{-4}	3.4×10^{-4}
TCIPP	5.8×10^{-3}	1.6×10^{-3}	2.7×10^{-3}
TCP	0.74	0.66	0.54
TDBPP	1.00	1.00	1.00
TDCIPP	0.28	0.28	0.26
TDCPP	0.38	0.38	0.31
TDMPP	1.00	1.00	0.97
TEHP	1.00	1.00	0.87
TEP	1.0×10^{-5}	8.0×10^{-6}	3.3×10^{-6}
TIBP	9.1×10^{-5}	8.1×10^{-5}	2.9×10^{-4}
TiPP	2.9×10^{-5}	2.0×10^{-5}	2.1×10^{-5}
TmCP	1.00	1.00	0.35
TMP	1.8×10^{-7}	1.8×10^{-7}	2.1×10^{-7}
TnBP	1.0×10^{-3}	6.0×10^{-4}	4.2×10^{-4}
ToCP	1.00	1.00	0.35
TpCP	1.00	1.00	0.35
TPhP	0.059	0.018	0.061
TPPP	1.00	1.00	0.98
TTBNPP	1.00	1.00	1.00
TTBPP	1.00	1.00	1.00

These results do not support the contention that OPEs partition only to the particle phase. Specifically, compounds with a log K_{OA} between 10 and 12 were partially in the gas and partially in the particle phase: $f_{part,T}$ for BDCPP was 0.32−0.48, for DCP was 0.14−0.28, for TDCIPP was 0.27, and for TDCPP was 0.31−0.38. BEHP, EHDPP, IDDPP and the TCP isomers in the "Modelled Data" set were also predicted to have appreciable fractions in both phases (as described above) (Figure 1, Table 1).

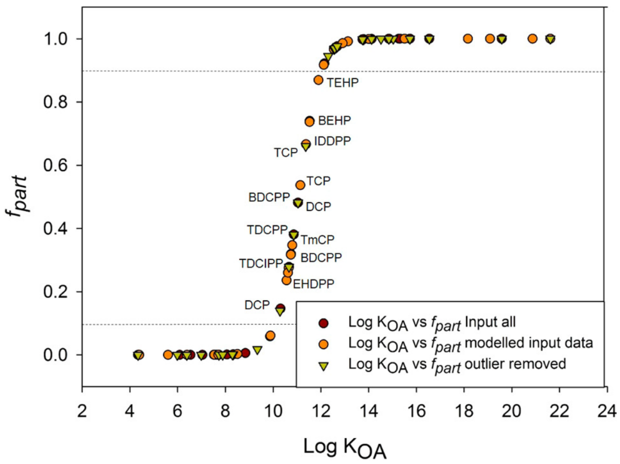

Figure 1. $f_{part,T}$ predicted by the Tool plotted against log K_{OA} obtained from the three input data sets (Input all, Modeled Data, and Outlier Removed). The dotted lines mark the areas with compounds predominantly in the particle phase ($f_{part,T} > 0.9$) and compounds predominantly in the gas phase ($f_{part,T} < 0.1$). Compounds with more than 10% in both phases are labeled individually.

3.2. Evaluation of the Impact of Uncertainty of Input Data on the Prediction of OPE Environmental Behavior with the Tool.

To evaluate the sensitivity of the tested compounds to individual changes of log K_{OW} and log K_{AW} as well as the uncertainty of $f_{part,T}$, sensitivity and Monte Carlo uncertainty analyses were performed. For the sensitivity analysis log K_{OW} and log K_{AW} data from the "Outlier Removed" data set were used. The Monte Carlo uncertainty analysis was performed for all compounds of the "Outlier Removed" data set with $f_{part,T} < 0.9$.

f_{part} values of 22% of the 32 OPEs (seven compounds) displayed sensitivities from less than 5% (absolute) to as high as 10^8% to individual changes of log K_{AW} and log K_{OW} by a factor of 1.1 (±10%). Within this group of seven compounds, sensitivity was greatest for changes in log K_{AW}. Very high sensitivities were observed for compounds with predicted $f_{part,T} \leq 10^{-3}$, while compounds with predicted f_{part} close to 1 displayed the lowest sensitivities to log K_{OW} and log K_{AW}. However, high absolute sensitivity values for compounds with $f_{part,T} \leq 10^{-3}$ did not change their general partitioning behavior of $f_{part,T} < 0.1$. Effects of changing log K_{OW} and log K_{AW} on the partitioning behavior were only observed for compounds with $f_{part,T}$ between 0.1 and 0.9 (Table S8).

The Monte Carlo analysis revealed that uncertainties in values of log K_{OW} and log K_{AW} did not alter the general partitioning tendency of the tested compounds using either the 25th−75th percentile or the default dispersion factors (Table S9 and S10). Interestingly, even OPEs with intermediate f_{part} values (between 0.1 and 0.9) such as BDCPP were not greatly affected by the variation: the predicted value for f_{part} was 0.46 and the Monte Carlo analysis returned 0.4 and 0.52 for the 25th and 75th percentile.

In summary the results of the sensitivity as well as the uncertainty analysis indicated that the Tool's prediction of OPE partitioning between gas and particle phases did not significantly change with input data uncertainty. Compounds with initial low or nondistinct gas-particle partitioning properties (f_{part} between 0.1 and 0.9) were found to be more affected by changes in input data than compounds with f_{part} close to 1. However, this sensitivity did not cause any significant changes in the f_{part} prediction.

3.3. Comparison of Tool ($f_{\mathrm{part,T}}$), J-P Model ($f_{\mathrm{part,J\text{-}P}}$) and H-B Model ($f_{\mathrm{part,H\text{-}B}}$) Predictions. Using the "Input all" or "Outlier Removed" data set, f_{part} predictions were statistically indistinguishable for the two K_{OA}-based models, the Tool and the H-B model (Table S11). The J-P model, in general, predicted similar partitioning behavior to the Tool and H-B model for 27 out of 32 compounds (81%). For the remaining six compounds (DCP, TMP, TnBP, ToCP, PBDMPP, and TDBPP) the Tool/H-B model and J-P model predictions differed considerably (Table S11).

An explanation for the considerable differences could be that all of these compounds had either a log K_{OA} between 10 and 12 (Figure 1) or a log P_{L} between −5 and −2 and were therefore predicted to partition between gas and particle phases, which means that f_{part} is relatively sensitive to differences in input data or estimation method (Figure 1).

Unexpectedly, f_{part} predictions from the J-P model changed significantly when physicochemical input data estimated by SPARC or EPISuite were used (t test at $p < 0.05$). Furthermore, J-P results based on EPISuite input data indicated significantly different partitioning behavior (t test at $p < 0.05$) for 15 OPEs (47%) compared to the Tool and H-B model (Table S11).

Interestingly, most of the $f_{\mathrm{part,J\text{-}P}}$ predictions with significant differences compared to the other prediction methods were lower than the Tool and H-B model. Previous studies reported that the J-P model tended to overestimate f_{part} compared to measurements for several classes of semivolatile organic compounds.[33−36]

3.4. Comparison of Modeled Partitioning with Measured Partitioning of OPEs ($f_{\mathrm{part,M}}$). Neither the sensitivity nor the uncertainty analysis provided compelling evidence that the uncertainty of chemical property data is responsible for the observed discrepancy between the f_{part} values from the Tool and the prevalent hypothesis in the literature that OPEs partition primarily to the particle phase. We therefore reassessed the initial hypothesis. To this end, we compared the $f_{\mathrm{part,T}}$, $f_{\mathrm{part,H\text{-}B}}$ and $f_{\mathrm{part,J\text{-}P}}$ values with measured $f_{\mathrm{part,M}}$ data. We used the data set of Wolschke et al.,[21] who reported a year of weekly OPE air concentrations for 13 OPEs. The median TSP for the Wolschke et al.[21] data set was 16 μg m^{-3}. For comparison we calculated all f_{part} based on this value.

Plotting f_{part} results of calculated vs measured data sets yielded unexpected results. Calculated values of $f_{\mathrm{part,T}}$, $f_{\mathrm{part,H\text{-}B}}$ and $f_{\mathrm{part,J\text{-}P}}$ correlated well with $f_{\mathrm{part,M}}$ values,[21] which reported a significant fraction of OPEs in the gas phase (Figure S1, Table 2), whereas they did not agree with the hypothesis that OPEs primarily partition into the particle-phase (Figure S1, S2).

Furthermore, $f_{\mathrm{part,T}}$, $f_{\mathrm{part,H\text{-}B}}$, $f_{\mathrm{part,J\text{-}P}}$ and $f_{\mathrm{part,M}}$ all showed strong positive correlations with log K_{OA} and negative correlations with log P_{L} (Table 2, Figures S3 and S4). The weakest correlation resulted from the H-B model for log P_{L} and the J-P model for log K_{OA} with Pearson correlation coefficients, r, of −0.40 for log P_{L} vs $f_{\mathrm{part,H\text{-}B}}$ and r of 0.65 for log K_{OA} vs $f_{\mathrm{part,J\text{-}P}}$ (Table 2). The resulting plots of f_{part} vs log K_{OA} show the S-shape that is typical for the relationship between log K_{OA} and particle partitioning with 0% partitioning to particles at log K_{OA} < 10 and 100% partitioning into the particle phase at log K_{OA} > 12 (Figure 1).

Table 2. Pearson Correlation Coefficient, r, for f_{part} Results of Measured and Modelled Datasets As Well As with the Partition Coefficients Log K_{OW} and Log K_{OA} and Subcooled Liquid Vapour Pressure Log P_{L}

		OECD P_{OV} and LRTP Screening Tool				
	$f_{\mathrm{part,M}}$	f_{part} modeled data	f_{part} input all	f_{part} outlier removed	f_{part} H-B model	f_{part} J-P model
log P_{L}	−0.90	−0.70	−0.76	−0.75	−0.40	−0.91
log K_{OA}	0.89	0.84	0.85	0.86	0.83	0.65
$f_{\mathrm{part,M}}$	1	0.95	0.83	0.80	0.87	0.90

The strong correlations between predicted and measured f_{part} for the nine compared OPEs (presented in Figure S1) are primarily related to the agreement of predictions and measurements of f_{part} for OPEs with distinct predicted partitioning (f_{part} below 0.1 or above 0.9). OPEs with predicted f_{part} between 0.1 and 0.9 displayed high variability in measured as well as modeled f_{part}. To identify the driving factors for the variation in observed f_{part} for these compounds, namely TDCPP, TPhP and TCP, we assessed the impact of various factors on their partitioning.

EPISuite, SPARC and Absolv are commonly used to estimate physicochemical properties. In our recent paper (Zhang and Suhring et al. 2016)[10] we found that predictions for physicochemical properties may vary significantly between EPISuite and SPARC, whereas Absolv and EPISuite yielded similar results. We therefore assessed the correlations of f_{part} estimates from the Tool, the H-B model and the J-P model with measured $f_{\mathrm{part,M}}$ data using only measured physicochemical properties and those estimated by EPISuite and SPARC as model inputs.

For all three models input data estimated with SPARC led to highest correlations with $f_{\mathrm{part,M}}$ (Figure 2). The Tool had the overall best agreement with $f_{\mathrm{part,M}}$ followed by the H-B model predictions (Figure 2). Unexpectedly, $f_{\mathrm{part,J\text{-}P}}$ correlated poorly with the measured results ($f_{\mathrm{part,M}}$) when either EPISuite or SPARC input data were used (Figure 2). This was unexpected because, with median values from SPARC, EPISuite and literature, $f_{\mathrm{part,J\text{-}P}}$ was in good agreement with $f_{\mathrm{part,M}}$ (Table 2). Furthermore, using measured P_{L} as input also gave good agreement of $f_{\mathrm{part,J\text{-}P}}$ and $f_{\mathrm{part,M}}$ (Table 2, Figure 2).

Contrary to the Tool predictions, the J-P model predictions seemed to be strongly affected by the variability in input data, specifically P_{L}. These strong differences in J-P model predictions based on different input data sets emphasize the need for reliable and evaluated physicochemical property data in order to obtain consistent and reproducible results that can be used in chemical risk assessment.

3.5. Driving Factors for Partitioning Behavior of OPEs. All tests assessing potential errors and sources of uncertainty in the Tool and H-B model—the evaluation of the impact of input data uncertainty, the comparison of model results with measured $f_{\mathrm{part,M}}$ and correlation with physicochemical properties—led to the same conclusion: OPEs with a log K_{OA} < 10 partition into the gas phase. This is in contrast to previous reports on OPE behavior in the environment.[12−15,37]

To some extent, this discrepancy may be explained by the choice of analytes in the literature, e.g. primarily halogenated OPEs with high log K_{OA}. However, that does not explain the frequent reports of, for example, TCEP in the particle phase of atmospheric samples around the world,[12,13,15,37,38] because

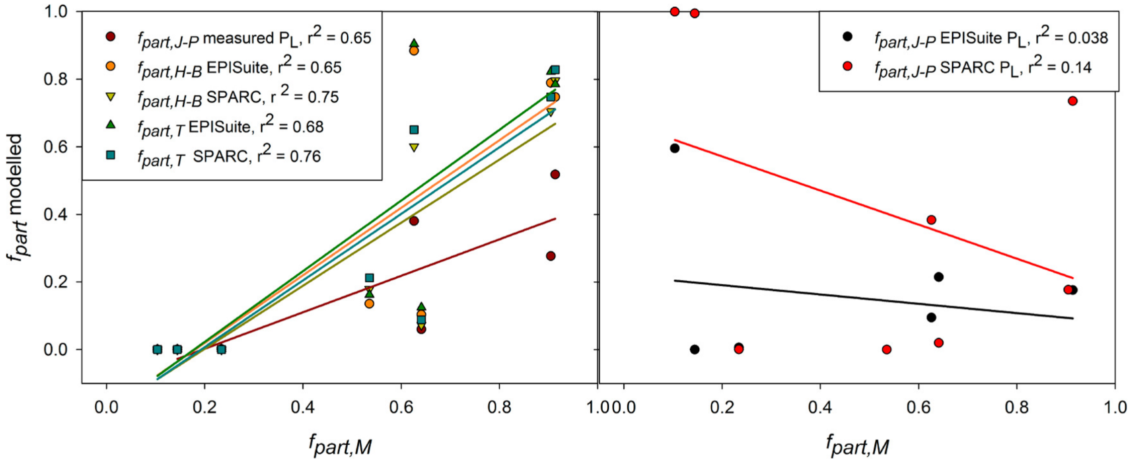

Figure 2. $f_{\text{part,M}}$ vs $f_{\text{part,H-B}}$ and $f_{\text{part,J-P}}$ (measured P_L) (left) and $f_{\text{part,M}}$ vs $f_{\text{part,J-P}}$ (right) using physicochemical properties estimated by EPISuite and SPARC as well as measured P_L.

according to the Tool, H-B and J-P model TCEP should primarily partition into the gas phase.

Our results indicate that uncertainty (Monte Carlo analysis) of physicochemical properties such as log K_{AW}, log K_{OW}, and log P_L was not responsible for significant differences in the predicted partitioning behavior between gas and particle phases in the Tool and H-B model. Therefore, our next step was to identify and evaluate potential external drivers. External factors could be meteorological factors such as temperature.

The temperature in the Tool is set to 298 K by default. However, the partitioning behavior, as calculated by the Tool, does not capture the effects of changes in temperature (Table S12). This lack of temperature dependence in the Tool could be a source of error for f_{part} predictions. Both log K_{OA} as well as P_L are highly temperature dependent.[39] The derived partition coefficient log K_{OA} in the Tool should represent this temperature dependence. Otherwise, f_{part} could be systematically underpredicted in regions with temperatures consistently below 25 °C (298 K) such as the Arctic. A correlation of the f_{part} values reported by Wolschke et al.[21] with temperatures at the time of sampling yielded, however, a correlation coefficient, r, (Pearson) below 0.30, perhaps because of the narrow temperature range between 3 and 17 °C (Table S13). The parameter with the highest correlation with $f_{\text{part,M}}$ was the particle concentration in air, with r up to 0.45 for compounds with measured (and predicted) $f_{\text{part}} > 0.8$ (Table S13).

Thus, we next assessed the impact of particle concentration (coarse, ø 2.5−10 μm) in the atmosphere ($\text{TSP}_{\text{coarse}}$) on $f_{\text{part,T}}$. $\text{TSP}_{\text{coarse}}$ varies by several orders of magnitude between different countries or regions; with annual mean values between 2 μg m^{-3} in Powell River, Canada, to 153 μg m^{-3} in Delhi, India.[40] Daily concentrations have even been reported to reach up to 1000 μg m^{-3} in Beijing, China.[41] Locally, $\text{TSP}_{\text{coarse}}$ concentrations can be increased at low temperatures or decreased by rain/snow events.[26]

In the Tool $\text{TSP}_{\text{coarse}}$ is expressed as a volume fraction. The default value is 2×10^{-11}, which represents an average background particle concentration, equal to 30 μg m^{-3}. However, OPEs are usually produced and emitted in urban or industrial areas, with $\text{TSP}_{\text{coarse}}$ in the 10^{-10} range or higher, whereas deposition in the Arctic would suggest $\text{TSP}_{\text{coarse}}$ volume fractions of 10^{-12}. The default $\text{TSP}_{\text{coarse}}$ used in the Tool is therefore likely not representative for the conditions in these environments.

To assess the impact of varying particle concentrations in the atmosphere on $f_{\text{part,T}}$ we used $\text{TSP}_{\text{coarse}}$ volume fractions between 10^{-12} and 10^{-9} on the "Outlier Removed" data set as well as the "Modelled Data" set. This caused major changes in the partitioning behavior of OPEs with log K_{OA} between 7 and 12, whereas the partitioning of compounds with log K_{OA} below 7 or higher than 12 was not affected (Figure 3).

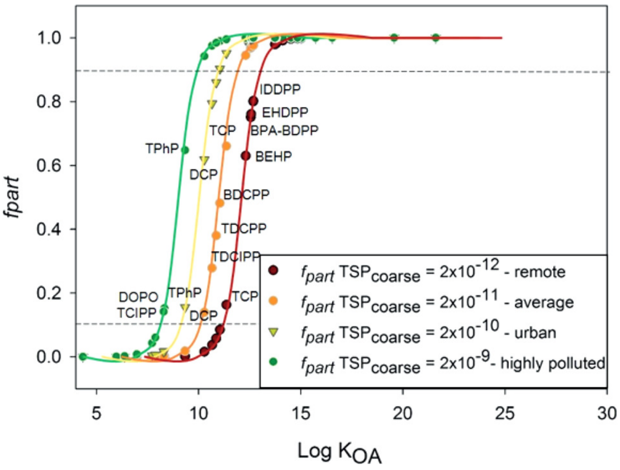

Figure 3. Log K_{OA} vs $f_{\text{part,T}}$ for the "Outlier Removed" data set for different values of $\text{TSP}_{\text{coarse}}$; the dotted lines mark the areas of distinct partitioning behavior for all scenarios (above $f_{\text{part,T}} = 0.9$/below $f_{\text{part,T}} = 0.1$). Compounds with major $f_{\text{part,T}}$ changes depending on $\text{TSP}_{\text{coarse}}$ are labeled individually.

Interestingly, differences in the general predicted partitioning behavior between the "Outlier Removed" and "Modeled Data" sets (Table 1) disappeared at $\text{TSP}_{\text{coarse}}$ above 10^{-11} (Tables S14, S15). For $\text{TSP}_{\text{coarse}}$ of 10^{-12} in the "Outlier Removed" and "Modeled" data sets, the fraction of OPEs partitioning into the gas phase was 44% and 66%, respectively. At $\text{TSP}_{\text{coarse}}$ of 10^{-11}, this fraction was reduced to 41% and 53%. At $\text{TSP}_{\text{coarse}}$ of 10^{-10} and 10^{-9} the data sets produced the same predictions for the number of OPEs in the gas phase with 28% and 25%, respectively (see Tables S14 and S15 for detailed information).

Our results indicate that roughly half of the OPEs partition into the gas phase regardless of whether predictions are made with the Tool, the H-B model, or J-P model, and are consistent with measurements of f_{part} by Wolschke et al.[21] However, the lack of temperature dependence of $f_{\mathrm{part,T}}$ estimated by the Tool is a potential source of error and could lead to a systematic underestimation of f_{part} in cold regions.

Of the commonly used models for estimating partition coefficients, SPARC led to f_{part} estimates closer to the measured data than EPISuite. The unexpected discrepancy between $f_{\mathrm{part,J\text{-}P}}$ estimates from modeled P_L and measured $f_{\mathrm{part,M}}$ should be further investigated, especially considering that J-P predictions using measured P_L showed strong correlations with $f_{\mathrm{part,M}}$.

Changes in $f_{\mathrm{part,T}}$ based on differences in TSP emphasize the importance of sampling location in addition to time (e.g., before or after rain events) on f_{part}. In conclusion, our results show that OPEs with log K_{OA} values below 10 or a log P_L above −5 (P_L in Pa), such as BDCPP, DCP, DOPO, TCEP, TCIPP, TDCIPP, TDCPP, TEP, TIBP, TIPP, TMP, TnBP, and TPhP, should not be limited to the particle phase.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00199.

Additional information as noted in the text (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Darnerud, P. Toxic effects of brominated flame retardants in man and in wildlife. *Environ. Int.* **2003**, *29* (6), 841−853.

(2) Stockholm Conference of Parties. Report of the Conference of the Parties of the Stockholm Convention on Persistent Organic Pollutants on the Work of Its Fourth Meeting: Stockholm Convention on Persistent Organic Pollutants: Geneva, **2009**.

(3) United States Environmental Protection Agency (USEPA). DecaBDE phase-out initiative. Announcement on the EPA website.

(4) China Market Research Reports. Global and China Flame Retardant Industry Report, 2014−2016 by Research In China at China Market Research Reports. http://www.chinamarketresearchreports.com/114859.html (accessed January 8, 2016).

(5) Bergman, A.; Rydén, A.; Law, R. J.; Boer, J. de; Covaci, A.; Alaee, M.; Birnbaum, L.; Petreas, M.; Rose, M.; Sakai, S.; van den Eede, N.; van der Veen, I. A novel abbreviation standard for organobromine, organochlorine and organophosphorus flame retardants and some characteristics of the chemicals. *Environ. Int.* **2012**, *49*, 57−82.

(6) Stapleton, H. M.; Klosterhaus, S.; Keller, A.; Ferguson, P. L.; van Bergen, S.; Cooper, E.; Webster, T. F.; Blum, A. Identification of flame retardants in polyurethane foam collected from baby products. *Environ. Sci. Technol.* **2011**, *45* (12), 5323−5331.

(7) Reemtsma, T.; Quintana, J. B.; Rodil, R.; García-López, M.; Rodríguez, I. Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. *Trends Anal. Chem.* **2008**, *27* (9), 727−737.

(8) China Market Research Reports: *Global and China Flame Retardant Industry Report, 2014−2016*. http://www.chinamarketresearchreports.com/114859.html (accessed May 19, 2016).

(9) Marklund, A.; Andersson, B.; Haglund, P. Screening of organophosphorus compounds and their distribution in various indoor environments. *Chemosphere* **2003**, *53* (9), 1137−1146.

(10) Zhang, X.; Sühring, R.; Serodio, D.; Bonnell, M.; Sundin, N.; Diamond, M. L. Novel flame retardants: Estimating the physical-chemical properties and environmental fate of 94 halogenated and organophosphate PBDE replacements. *Chemosphere* **2016**, *144*, 2401−2407.

(11) Möller, A.; Sturm, R.; Xie, Z.; Cai, M.; He, J.; Ebinghaus, R. Organophosphorus flame retardants and plasticizers in airborne particles over the Northern Pacific and Indian Ocean toward the Polar Regions: evidence for global occurrence. *Environ. Sci. Technol.* **2012**, *46* (6), 3127−3134.

(12) Salamova, A.; Hermanson, M. H.; Hites, R. A. Organophosphate and halogenated flame retardants in atmospheric particles from a European Arctic site. *Environ. Sci. Technol.* **2014**, *48* (11), 6133−6140.

(13) Jantunen, L. M., Gawor, A., Wong, F., Bidleman, T., Wania, F., Stern, G. A., Pucko, M., Hung, H. *Organophosphate Ester Flame Retardants and Plasticizers in the Canadian Arctic*; Workshop on Brominate & Other Flame Retardants, Indianapolis, USA, 2014.

(14) Bergman, A.; Östman, C.; Nybom, R.; Sjödin, A.; Carlsson, H.; Nilsoson, U.; Wachtmeister, C. A. Flame Retardants and Plasticisers on Particulate−in the Modern Computerized Indoor Environment. *Organohalogen Compd.* **1997**, 33, 414−419.

(15) Möller, A.; Xie, Z.; Caba, A.; Sturm, R.; Ebinghaus, R. Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea. *Environ. Pollut.* **2011**, *159* (12), 3660−3665.

(16) Liu, Y.; Liggio, J.; Harner, T.; Jantunen, L.; Shoeib, M.; Li, S.-M. Heterogeneous OH initiated oxidation: a possible explanation for the persistence of organophosphate flame retardants in air. *Environ. Sci. Technol.* **2014**, *48* (2), 1041−1048.

(17) Bidleman, T. F. Atmospheric processes. *Environ. Sci. Technol.* **1988**, *22* (4), 361−367.

(18) Pankow, J. F. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmos. Environ.* **1994**, *28* (2), 185−188.

(19) Liagkouridis, I.; Cousins, A. P.; Cousins, I. T. Physical-chemical properties and evaluative fate modelling of 'emerging' and 'novel' brominated and organophosphorus flame retardants in the indoor and outdoor environment. *Sci. Total Environ.* **2015**, *524−525*, 416−426.

(20) UNEP. *Stockholm Convention on Persistent Organic Pollutants − Report on the Assessment of Chemical Alternatives to Endosulfan*, UNEP/POPS/POPRC.8/INF/28, 2012.

(21) Wolschke, H.; Sühring, R.; Mi, W.; Möller, A.; Xie, Z.; Ebinghaus, R. Atmospheric occurrence and fate of organophosphorus flame retardants and plasticizers at the German coast. *Atmos. Environ.* **2016**, *137*, 1−5.

(22) Wegmann, F.; Cavin, L.; MacLeod, M.; Scheringer, M.; Hungerbühler, K. The OECD software tool for screening chemicals for persistence and long-range transport potential. *Environ. Model. Softw.* **2009**, *24* (2), 228−237.

(23) Lohmann, R.; Lammel, G. Adsorptive and Absorptive Contributions to the Gas-Particle Partitioning of Polycyclic Aromatic Hydrocarbons: State of Knowledge and Recommended Parametrization for Modeling. *Environ. Sci. Technol.* **2004**, *38* (14), 3793−3803.

(24) Schnoor, J. L. *Environmental Modeling. Fate and Transport of Pollutants in Water, Air, And Soil*. Wiley: New York, 1996.

(25) Pankow, J. F. Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmos. Environ.* **1987**, *21* (11), 2275−2283.

(26) Götz, C. W.; Scheringer, M.; MacLeod, M.; Wegmann, F.; Hungerbühler, K. Regional differences in gas−particle partitioning and

deposition of semivolatile organic compounds on a global scale. *Atmos. Environ.* **2008**, *42* (3), 554−567.

(27) Canadian Council of Ministers of the Environment (CCME). *Canada-Wide Standards for Particulate Matter (PM) And Ozone*; Endorsed by CCME Council of Ministers, June 5−6, 2000, Quebec City. 2000.

(28) Morgan, M. G.; Henrion, M.; Small, M. *Uncertainty. A Guide to Dealing with Uncertainty in Quantitative Risk and Policy Analysis*; Cambridge University Press: Cambridge, NY, 1992.

(29) United States Environmental Protection Agency (USEPA). *EPI Suite- Estimation Programs Interface Suite*, 2013. http://www.epa.gov/oppt/exposure/pubs/episuite.htm.

(30) Hilal, S. H.; Saravanaraj, A. N.; Whiteside, T.; Carreira, L. A. Calculating physical properties of organic compounds for environmental modeling from molecular structure. *J. Comput.-Aided Mol. Des.* **2007**, *21* (12), 693−708.

(31) Brommer, S.; Jantunen, L. M.; Bidleman, T. F.; Harrad, S.; Diamond, M. L. Determination of Vapor Pressures for Organophosphate Esters. *J. Chem. Eng. Data* **2014**, *59* (5), 1441−1447.

(32) van der Veen, I.; Boer, J. de. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. *Chemosphere* **2012**, *88* (10), 1119−1153.

(33) Cotham, W. E.; Bidleman, T. F. Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in air at an urban and a rural site near Lake Michigan. *Environ. Sci. Technol.* **1995**, *29* (11), 2782−2789.

(34) Harner, T.; Bidleman, T. F. Octanol−Air Partition Coefficient for Describing Particle/Gas Partitioning of Aromatic Compounds in Urban Air. *Environ. Sci. Technol.* **1998**, *32* (10), 1494−1502.

(35) Chen, L.; Mai, B.; Xu, Z.; Peng, X.; Han, J.; Ran, Y.; Sheng, G.; Fu, J. In- and outdoor sources of polybrominated diphenyl ethers and their human inhalation exposure in Guangzhou, China. *Atmos. Environ.* **2008**, *42* (1), 78−86.

(36) Cincinelli, A. Atmospheric Occurrence and Gas-Particle Partitioning of PBDEs in an Industrialised and Urban Area of Florence, Italy. *Aerosol Air Qual. Res.* **2014**, DOI: 10.4209/aaqr.2013.01.0021.

(37) Salamova, A.; Ma, Y.; Venier, M.; Hites, R. A. High Levels of Organophosphate Flame Retardants in the Great Lakes Atmosphere. *Environ. Sci. Technol. Lett.* **2014**, *1* (1), 8−14.

(38) Ciccioli, P.; Cecinato, A.; Brancaleoni, E.; Montagnoli, M.; Allegrini, I. Chemical Composition of Particulate Organic Matter (POM) Collected at Terra Nova Bay in Antarctica. *Int. J. Environ. Anal. Chem.* **1994**, *55* (1−4), 47−59.

(39) Wania, F.; Mackay, D. Tracking the Distribution of Persistent Organic Pollutants. *Environ. Sci. Technol.* **1996**, *30* (9), 390A−396A.

(40) World Health Organization. Ambient Air Pollution Database, WHO, May 2014. http://www.who.int/phe/health_topics/outdoorair/databases/cities/en/ (accessed August 28, 2015).

(41) Clean Air Alliance of China (CAAC). Air Pollution Episode Planning Gains Momentum in China - - Clean Air Alliance of China. http://en.cleanairchina.org/product/6185.html (accessed January 8, 2016).

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Distribution of organophosphate esters between the gas and particle phase – model predictions vs. measured data

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Gas-particle partitioning is one of the key factors that affect the environmental fate of semivolatile organic chemicals. Many organophosphate esters (OPEs) have been reported to primarily partition to particles in the atmosphere. However, because of the wide range of their physicochemical properties, it is unlikely that OPEs are mainly in the particle phase “as a class”.

We compared gas-particle partitioning predictions for 32 OPEs made by the commonly used OECD POV and LRTP Screening Tool (“the Tool”) with the partitioning models of Junge-Pankow (J-P) and Harner-Bidleman (H-B), as well as recently measured data on OPE gas-particle partitioning.

The results indicate that half of the tested OPEs partition into the gas phase. Partitioning into the gas phase seems to be determined by an octanol-air partition coefficient (log K_{OA}) < 10 and a subcooled-liquid vapour pressure (log P_L) > –5 (P_L in Pa), as well as the total suspended particle concentration (TSP) in the sampling area. The uncertainty of the physicochemical property data of the OPEs did not change this estimate. Furthermore, the predictions by the Tool, J-P- and H-B-models agreed with recently measured OPE gas-particle partitioning.*

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Table S1: OPEs evaluated in this study, including acronym, full name, CAS number and molecular weight (MW) in g mol^{-1}.*

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BCMP-BCEP	Tetrakis(2-chloroethyl)dichloroisopentyl diphosphate	38051-10-4	583
BDCPP	Bis(1,3-dichloro-2-propyl) phosphate	72236-72-7	320
BEHP	Bis(2-ethylhexyl) phosphate	298-07-7	322
BPA-BDPP	Bisphenol A bis(diphenyl phosphate)	5945-33-5	693
DCP	Diphenyl cresyl phosphate	26444-49-5	340
DOPO	9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide	35948-25-5	216
EHDPP	Ethylhexyldiphenyl phosphate	1241-94-7	362
IDDPP	Isodecyl diphenyl phosphate	29761-21-5	390
MC 984	2,2-bis(bromomethyl)-3-chloropropyl bis[2-chloro-1-(chloromethyl)ethyl] phosphate	66108-37-0	582
PBDMPP	Tetrakis(2,6-dimethylphenyl)-*m*-phenylene biphosphate	139189-30-3	687
PBDPP (RDP)	Resorcinol bis(diphenyl phosphate)	57583-54-7, 125997-21-9	574
TBEP	Tris(2-butoxyethyl) phosphate	78-51-3	398
TCEP	Tris(2-chloroethyl) phosphate	115-96-8	285
TCIPP	Tris(1-chloro-2-propyl)phosphate	13674-84-5	328
TCP	Tricresyl phosphate	1330-78-5	368
TDBPP	Tris(2,3-dibromopropyl) phosphate	126-72-7	698
TDCIPP	Tris(1,3-dichloro-2-propyl) phosphate	13674-87-8	431
TDCPP	Tris(2,3-dichloropropyl) phosphate	78-43-3	431
TDMPP	Tris(3,5-dimethyl phenyl) phosphate	9006-37-5	410
TEHP	Tris(2-ethylhexyl) phosphate	78-42-2	435
TEP	Triethyl phosphate	78-40-0	182
TIBP	Triisobutyl phosphate	126-71-6	266
TiPP	Triisopropyl phosphate	513-02-0	224
TmCP	Tris-o-cresyl phosphate	78-30-8	368
TMP	Trimethyl phosphate	512-56-1	140
TnBP	Tri *n*-butyl phosphate	126-73-8	266
ToCP	Tris-m-cresyl phosphate	563-04-2	368
TpCP	Tri-p-cresyl phosphate	78-32-0	368
TPhP	Triphenyl phosphate	115-86-6	326
TPPP	Tris(2-isopropyl phenyl) phosphate	64532-95-2	453
TTBNPP	Tris(tribromo-neopentyl) phosphate	19186-97-1	1018
TTBPP	Tris(4-tert-butylphenyl) phosphate	78-33-1	495

The Tool requires degradation half-lives for soil, ocean water and air as well as two partition coefficients, the octanol-water partition coefficient (log K_{OW}) and the Henry's law constant (log K_{AW}), as substance-specific inputs. The predicted gas/ particle phase partitioning is, however, only affected by log K_{OW} and log K_{AW}. Therefore, only these input values are presented here.

Table S2: Data sets for log K_{AW} values; references are presented in[].

Acronym	[50] (EPISuite, Absolv, SPARC)	[26]	[14]	[6]	[7]	[19]	[10-13]	Median
BCMP-BCEP	-12.20, -13.96, -5.35	-12.2					-8.58 [10]	-12.20
BDCPP	-8.82, -9.16, -6.00							-8.82
BEHP	-5.77, -7.02, -3.70							-5.77
BPA-BDPP		-11.72	-4.76, -5.41					-5.41
DCP		-5.75		-5.49		-5.76		-5.75
DOPO		-5.65						-5.65
EHDPP	-4.99, -8.56, -1.79							-4.99
IDDPP	-4.75, -8.39, -1.82							-4.75
MC 984	-8.15, -8.10, -5.49							-8.10
PBDMPP*		-10.58						-10.58
PBDPP*		-10.92		-5.53				-8.23
TBEP	-9.31, -8.93, -5.65	-9.31	-8.43		-7.92			-8.68
TCEP	-5.98, -2.69, -6.86	-5.98			-6.1		-7.78 [13]	-6.04
TCIPP	-5.61, -1.53, -6.71	-5.61	-6.77		-5.37		-6.81 [11]	-5.61
TCP	-5.66, -3.16, -9.92	-5.66			-5.99			-5.66

*less than 3 data points available

Table S2 continued: Data sets for log K_{AW}; references are presented in[].

Acronym	[50] (EpiSuite, Absolv, SPARC)	[26]	[14]	[7]	[19]	[10-13]	Median
TDBPP	-9.88, -10.98, -5.78	-9.78			-3.05		-9.78
TDCIPP	-6.97, -7.58, --4.29	-6.97		-5.4		-7.30 [12]	-6.97
TDCPP	-6.97, -9.11, -4.49	-6.97					-6.97
TDMPP	-5.53, -9.17, -2.60						-5.35
TEHP	-2.41, -4.37, -0.94	-2.41		-5.21	-5.49		-3.39
TEP	-4.26, -5.99, 0.18	-4.62			-5.11, -5.83		-4.87
TIBP*		-3.88	-2.79				-3.34
TiPP	-4.25, -5.81, 1.24	-4.25			-4.56		-4.25
TmCP	-5.66, -9.92, -2.89						-5.66
TMP	-4.99, -6.27, 0.50	-4.99			-6.53, -4.89		-4.99
TnBP	-3.88, -5.40, -0.41	-3.88			-4.24		-3.88
ToCP	-5.66, -9.92, -2.72						-5.66
TpCP	-5.66, -9.92, -2.89						-5.66
TPhP	-5.79, -10.69, -2.90	-5.79		-4.73	-3.87, -4.24		-4.73
TPPP	-4.92, -9.47, -2.72						-4.92
TTBNPP	-11.96, -10.12, -8.76	-11.96	-11.1				-11.10
TTBPP	-4.55, -8.65, -2.35						-4.55

*less than 3 data points available

Table S3: Data sets for log K_{OW} values; references are presented in[].

Acronym	[26, 50] (EPISuite, SPARC, Absolv)	[36]	[8]	[39]	[30]	[23]	[9]	[10-13, 15-18]	[3]	[35]	[47]	[32]	[14]	[31]	[1]	[46]	[41-45]	[48]
BCMP-BCEP	3.31, 4.25							2.83 [10]					2.83			1.9		
BDCPP	2.18, 1.93																	
BEHP	6.07, 5.75												2.67					
BPA-BDPP	15.68, 8.29, 10.02												6	4.5		4.5		
DCP	7.84, 4.56, 5.25									4.51						4.51		
DOPO	3.49, 1.87																	
EHDPP	6.3, 5.57									5.73		6.64	5.87			5.73	5.73 [41]	
IDDPP	7.28, 6.63									5.44			6.11			5.44	5.44 [42]	
MC 984	5.03, 6.29																	
PBDMPP	16, 10.28, 11.79												6.2					
PBDPP	12.6, 7.08, 7.41												4.93	4.4		7.41	5.5 [44]	
TBEP	3, 5.38		3.75	3.0	3.65				4.02			3.75	4.56			3.65		4.78
TCEP	1.63, 2.01, 1.44		1.44	, 1.63	1.48	1.7		1.78 [13,17,18]	0.47			1.44	1.7			1.44		
TCIPP	2.89, 3.25, 2.59		2.59	2.89		2.59	2.68	3.33 [11,16,34]	1.4			2.59	2.68			2.59		
TCP	6.34, 5.14, 5.48			6.34					5.95	5.11	3.42		5.93			5.11	5.11 [43]	
TDBPP	4.19, 5.37, 4.29														4.98			
TDCIPP	3.65, 4.39	3.76	3.65		3.74	3.8	3.69	3.69 [15]	1.59			3.65	3.69			3.8		
TDCPP	3.65, 3.89,6.24																	
TDMPP	7.98, 7.01																	
TEHP	9.49, 10.15		5.04	9.49	4.23				9.42	4.23		9.49	4.2			4.22		4.22

Table S3 continued: Data sets for log K_{OW} values; references are presented in[].

Acronym	[26, 50] (EPISuite, SPARC, Absolv)	[36]	[39]	[30]	[23]	[3]	[35]	[47]	[32]	[14]	[31]	[1]	[46]	[41-45]	[48]
TEP	4.21, 0.8, 1.08, 0.87									1.11			0.8		
TIBP	6.7, 3.71, 3.6									3.7			3.6		
TiPP	2.12, 2.35, 1.87, 2.67												2.12	6.1 [45]	
TmCP	6.34, 5.14		6.34			5.95							5.48		
TMP	-0.6, -0.71, -0.65, -0.52								-0.65				-0.65		
TnBP	3.82, 4.10, 4.26	3.99	3.82	4.0		3.46	4		4	4.0			4		
ToCP	6.34, 5.14		6.34			5.95							5.48		
TpCP	6.34, 5.14		6.34			5.95							5.48		
TPhP	4.7, 3.26, 4.59, 4.1, 4.7	4.76	4.7	4.61	4.61	4.46	4.63		4.59	4.63			4.59		
TPPP	9.07, 7.99														
TTBNPP	8.05, 10.84									4.87					
TTBPP	10.43, 9.46														

Table S4: Median log K_{OW} and log K_{AW} used in the input datasets “Input all”, “Modelled input data” and “Outlier removed”

		Input all		Modelled input data		Outlier removed	
Acronym	MW (g/mol)	log K_{AW}	log K_{OW}	log K_{AW}	log K_{OW}	log K_{AW}	log K_{OW}
BCMP-BCEP	583	-12.20	3.07	-12.20	3.31	-12.20	3.07
BDCPP	320	-8.82	2.05*	-8.82	1.93*	-8.82	2.05*
BEHP	322	-5.77	5.75	-5.77	5.75	-5.77	5.91
BPA-BDPP	693	-5.41	7.15	-11.72	9.16	-5.41	7.15
DCP	340	-5.75	4.56	-5.75	4.91	-5.75	4.54
DOPO	216	-5.65*	2.68	-5.65*	1.87	-5.65*	2.68
EHDPP	362	-4.99	5.73	-4.99	5.57	-4.99	5.73
IDDPP	390	-4.75	6.11	-4.75	6.63	-4.75	6.11
MC 984	582	-8.10	5.66*	-8.10	5.03*	-8.10	5.66*
PBDMPP	687	-10.58*	11.04	-10.58*	11.04	-10.58*	11.04
PBDPP	574	-8.23*	7.08	-10.92*	7.25	-8.23*	6.29
TBEP	398	-8.68	3.75	-9.12	3.00	-8.93	3.75
TCEP	285	-6.04	1.63	-5.98	1.63	-6.04	1.63
TCIPP	328	-5.61	2.68	-5.61	2.89	-6.16	2.68
TCP	368	-5.66	5.71	-5.66	5.48	-5.66	5.93
TDBPP	698	-9.78	4.29	-9.83	4.19	-9.78	4.29
TDCIPP	431	-6.97	3.69	-6.97	3.65	-6.97	3.69
TDCPP	431	-6.97	3.89	-6.97	3.77	-6.97	3.89
TDMPP	410	-5.35	7.49*	-5.53	7.01*	-5.53	7.49*
TEHP	435	-3.39	9.42	-2.41	9.49	-3.39	9.42
TEP	182	-4.87	0.88	-4.62	0.88	-4.87	0.88
TIBP	266	-3.34*	3.70	-3.44*	3.66	-3.34*	3.65
TiPP	224	-4.25	2.13	-4.25	2.13	-4.25	2.12
TmCP	368	-5.66	5.95	-5.66	5.14	-5.66	5.95
TMP	140	-4.99	-0.65	-4.99	-0.60	-4.99	-0.65
TnBP	266	-3.88	4.00	-3.88	3.82	-3.88	4.00
ToCP	368	-5.66	5.95	-5.66	5.14	-5.66	5.95
TpCP	368	-5.66	5.95	-5.66	5.14	-5.66	5.95
TPhP	326	-4.73	4.61	-5.79	4.10	-4.49	4.62
TPPP	453	-4.92	8.53*	-8.76	7.99*	-4.92	8.53*
TTBNPP	1018	-11.10	8.05	-11.04	8.05	-11.10	8.05
TTBPP	495	-4.55	9.94*	-4.55	9.46*	-4.55	9.94*

*less than 3 data points available

Table S5: log K_{OA} of the input datasets “Input all”, “Modelled input data” and “Outlier removed”

Acronym	MW (g/mol)	Input all log K_{OA}	Modelled input data log K_{OA}	Outlier removed log K_{OA}
BCMP-BCEP	583	15	16	15
BDCPP*	320	11	11	11
BEHP	322	12	12	12
BPA-BDPP	693	13	21	13
DCP	340	10	11	10
DOPO*	216	8.3	7.5	8.3
EHDPP	362	13	11	13
IDDPP	390	13	11	13
MC 984*	582	14	13	14
PBDMPP*	687	22	22	22
PBDPP*	574	15	18	15
TBEP	398	13	12	13
TCEP	285	7.7	7.6	7.7
TCIPP	328	8.8	8.5	8.3
TCP	368	12	11	11
TDBPP	698	14	14	14
TDCIPP	431	11	11	11
TDCPP	431	11	11	11
TDMPP*	410	15	13	15
TEHP	435	14	12	14
TEP	182	6.1	5.6	6.0
TIBP*	266	7.0	7.5	7.0
TiPP	224	6.5	6.4	6.4
TmCP	368	14	11	14
TMP	140	4.3	4.4	4.3
TnBP	266	8.1	7.7	7.9
ToCP	368	14	11	14
TpCP	368	14	11	14
TPhP	326	10	10	9.3
TPPP*	453	16	13	16
TTBNPP	1018	20	19	20
TTBPP*	495	17	14	17

*less than 3 data points available for either log K_{OW} or log K_{AW}

Table S6: Data and sources of vapour pressure at 25^{o}C unless otherwise indicated; references are presented in[].

Acronym	[2]	[30]	[39]	[5,24]	[4,21]	[32]	[14]	[10,11,13,25]	[46]	[27]	[20]	[19]
BCMP-BCEP							2.3E-3	2.8E-06[10]	1.6E-12	1.2E-5		2.7E-6
BDCPP										1.4E-5		3.4E-6
BEHP										2.4E-5		2.4E-5
BPA-BDPP									1.2E-03	2.7E-6		1.2E-3
DCP									6.3E-4			1.2E-4
DOPO												
EHDPP						8.9E-5			8.7E-5	4.5E-3	6.2E-4[41]	4.5E-3
IDDPP									1.1E-5	2.6E-5		6.3E-6
MC 984										1.2E-5		2.7E-6
PBDMPP												4.0E-4
PBDPP									2.8E-6			
TBEP		4 (150ºC); 1.33 (20ºC)	1.6E-4	3.7E-5	2.8E-5	3.3E-6			2.8E-5	1.7E-4		1.6E-4
TCEP	2.7 (90ºC); 0.25 (70ºC); 0.082(60ºC);0.017 (46ºC), 3.7 E-04 (20ºC)	67 (145°C)	5.2E-2	6.7[5]	43 (137°C)[4]	8.2		1.1E-3[13]	1.5E-2	5.2E-2	0.22	5.2E-2
TCIPP			7.5E-3			2.7E-3		1.4[11]	100	7.5E-3	4.7E-2	7.5E-3
TCP		<2.7 (150ºC); 39 (200ºC)							2.4E-5	1.6		1.6
TDBPP										1.2E-5	2.1E-8	1.2E-5

Table S6 continued: data and sources of vapour pressure at 25^{o}C unless otherwise indicated; references are presented in[].

Acronym	[2]	[23,30]	[39]	[38,40]	[33]	[21]	[28]	[32]	[25]	[46]	[27]	[20]	[19]
TDCIPP		1.3 (30ºC) [23]	4.0E-5	5.6E-6[38]				9.8E-6	5.6E-6	9.9E-6	4.0E-5	1.8E-5	3.8E-5
TDCPP											3.E-5		3.0E-5
TDMPP											1.2E-5		2.75E-6
TEHP	53 (160ºC); 133 (180ºC); 330 (200ºC)	31 (150 ºC)	8.1E-5	1.10E-5		1.1E-5		1.1E-5		2.7E-4	8.1E-5	1.1E-5	8.09E-5
TEP										39			22
TIBP										1.7			2.0E-2
TiPP										20	18		18
TmCP				9.9E-5 (20ºC)						2.4E-5	1.5E-5		4.7E-6
TMP								113		0.75	55	113	55
TnBP	100 (97ºC); 1000 (144ºC), 0.8 (20ºC)		0.47	0.15	100 (114ºC); 2000 (162ºC)	16900 (177ºC)	7.1E-2	0.15		0.15	0.47		0.47
ToCP				5.5E-5 (20ºC)						2.4E-5	1.5E-5		1.5E-5
TpCP				4.4E-5 (20ºC)						2.4E-5	1.5E-5		4.7E-6
TPhP		20 (150ºC); 253 (200ºC) [23]	6.3E-5	4.1E-3				8.4E-4		1.6E-4	6.3E-5	8.4E-4	6.3E-5
TPPP											1.2E-5		2.7E-6
TTBNPP													2.7E-6
TTBPP											1.2E-5		2.7E-6

Table S7: Mesured, EPISuite, SPARC subcooled vapour pressure (P_L, Pa), median P_L and log of median P_L input data for the f_{part} calculations with the Junge-Pankow (J-P) model

Acronym	Median P_L	Median log P_L	Measured P_L	P_L EPISuite	P_L SPARC
BCMP-BCEP	2.8E-06	-5.6	1.2E-03	1.2E-05	1.7E-09
BDCPP	8.6E-06	-5.1		1.4E-05	2.2E-03
BEHP	2.4E-05	-4.6		2.4E-05	3.0E-04
BPA-BDPP	1.2E-03	-2.9	1.2E-03	7.5E-02	0.21
DCP	3.7E-04	-3.4	6.3E-04	1.5E-05	2.4E-06
DOPO				1.5E-05	1.6E-06
EHDPP	4.5E-03	-2.4	8.8E-05	2.3E-03	6.7E-03
IDDPP	1.1E-05	-5.0	1.1E-05	2.6E-05	
MC 984	7.2E-06	-5.1		1.2E-05	
PBDMPP	4.0E-04	-3.4		1.5E-03	6.9E-05
PBDPP	2.8E-06	-5.6	2.8E-06	1.2E-05	2.0E-08
TBEP	9.6E-05	-4.0	2.8E-05	1.6E-04	2.8E-05
TCEP	1.4E-01	-0.87	3.1E-02	5.2E-02	0.11
TCIPP	7.5E-03	-2.1	3.5E-02	2.7E-03	2.4E-02
TCP	8.0E-05	-4.1	4.5E-05		8.0E-05
TDBPP	1.2E-05	-4.9		1.2E-05	1.3E-02
TDCIPP	1.4E-05	-4.9	7.7E-06	4.0E-05	1.7E-05
TDCPP	3.0E-05	-4.5		4.1	0.22
TDMPP	7.2E-06	-5.1		3.8E-03	4.7E-02
TEHP	4.6E-05	-4.3	1.6E-05	8.0E-05	6.2E-06
TEP	3.0E+01	1.5		1.2E-05	1.9E-14
TIBP	8.8E-01	-0.057		1.2E-05	1.0E-09
TiPP	1.8E+01	1.3		2.5E-02	2.1E-08
TmCP	1.5E-05	-4.8	2.4E-05	2.7E-05	3.6E-05
TMP	5.5E+01	1.7	7.5E-01	57	1.3E-05
TnBP	1.5E-01	-0.82	1.5E-01	0.15	8.8E-08
ToCP	1.5E-05	-4.8	2.4E-05	1.3E-05	7.3E-07
TpCP	1.5E-05	-4.8	2.4E-05	1.5E-05	
TPhP	1.6E-04	-3.8	2.7E-04	6.3E-05	8.4E-04
TPPP	7.2E-06	-5.1		1.2E-05	
TTBNPP	2.7E-06	-5.6		1.5E-05	1.6E-06
TTBPP	7.2E-06	-5.1	1.2E-03	1.2E-05	

Table S8: Initial $f_{\text{part,T}}$ (left), sensitivity of $f_{\text{part,T}}$ to individually changed log K_{OW} and log K_{AW} (middle) and resulting maximum and minimum $f_{\text{part,T}}$ values (right) for all OPEs from the Outlier Removed data set. Values highlighted in orange are resulting $f_{\text{part,T}}$ values that differ by more than 10% from the initial $f_{\text{part,T}}$ of the compound.

		Sensitivity, S to individual input parameters				Resulting $f_{\text{part,T}}$ extreme values	
Acronym	Initial $f_{\text{part,T}}$	high log K_{AW}	low log K_{AW}	high log K_{OW}	low log K_{OW}	max $f_{\text{part,T}}$	min $f_{\text{part,T}}$
BCMP-BCEP	1.00	0.18	0.013	-1.5 x 10^{-3}	-2.8 x 10^{-3}	1.00	1.00
BDCPP	0.48	152	154	-10	-10	0.88	0.12
BEHP	0.94	10	3.0	-2.7	-8.2	0.99	0.82
BPA-BDPP	0.97	3.9	1.3	-2.0	-8.1	0.99	0.87
DCP	0.14	303	708	-410	-206	0.38	0.046
DOPO	1.8 x 10^{-3}	2.4 x10^{4}	8.4 x10^{4}	-1.3 x10^{4}	-7053	6.6 x 10^{-3}	5.5 x 10^{-4}
EHDPP	0.97	-0.46	-0.12	-3.2	-10	0.99	0.89
IDDPP	0.98	5.0	1.3	-1.2	-4.1	0.99	0.91
MC 984	1.00	0.77	0.13	-0.08	-0.27	1.00	0.99
PBDMPP	1.00	2.7 x10^{-8}	2.8 x10^{-9}	-2.9 x10^{-9}	-3.2 x10^{-8}	1.00	1.00
PBDPP	1.00	0.15	0.025	-0.018	-0.069	1.00	1.00
TBEP	0.98	12	2.0	-0.54	-1.2	1.00	0.86
TCEP	4.5 x 10^{-4}	1.1 x10^{5}	4.2 x10^{5}	-1.6 x10^{4}	-1.1 x10^{4}	1.8 x10^{-3}	1.3 x10^{-4}
TCIPP	1.6 x 10^{-3}	2.6E x10^{4}	9.0 x10^{4}	-1.4 x10^{4}	-7.7 x10^{3}	6.0 x10^{-3}	5.1 x10^{-4}
TCP	0.66	41	28	-29	-42	0.88	0.37
TDBPP	1.00	1.8	0.21	-0.065	-0.17	1.00	0.99
TDCIPP	0.28	194	342	-93	-67	0.66	0.08
TDCPP	0.38	135	180	-59	-49	0.75	0.12
TDMPP	1.00	0.050	0.010	-0.010	-0.053	1.00	1.00
TEHP	1.00	0.14	0.053	-0.16	-1.2	1.00	0.99
TEP	8.0 x 10^{-6}	4.6 x10^{6}	1.4 x10^{7}	-2.4 x10^{5}	-2.0 x10^{5}	2.6 x10^{-5}	2.8 x10^{-6}
TIBP	8.1 x 10^{-5}	2.3 x10^{5}	4.7 x10^{5}	-5.9 x10^{5}	-2.6 x10^{5}	1.9 x10^{-4}	3.8 x10^{-5}
TiPP	2.0 x 10^{-5}	1.4 x10^{6}	3.5 x10^{6}	-6.6 x10^{5}	-4.2 x10^{5}	5.4 x10^{-5}	8.3 x10^{-6}
TmCP	1.00	0.75	0.14	-0.096	-0.35	1.00	0.99
TMP	1.8 x 10^{-7}	1.9 x10^{8}	5.8 x10^{8}	-4.9 x10^{6}	-5.6 x10^{6}	5.8 x10^{-7}	6.5 x10^{-8}
TnBP	6.4 x 10^{-4}	3.7 x10^{4}	8.7 x10^{4}	-9.4 x10^{4}	-3.9 x10^{4}	1.6 x10^{-3}	2.8 x10^{-4}
ToCP	1.00	0.75	0.14	-0.10	-0.35	1.00	0.99
TpCP	1.00	0.75	0.14	-0.10	-0.35	1.00	0.99
TPhP	0.018	1800	4900	-4586	-1727	0.052	6.8 x 10^{-3}
TPPP	1.00	6.2 x10^{-3}	1.3 x10^{-3}	-0.0016	-0.010	1.00	1.00
TTBNPP	1.00	4.0 x10^{-6}	3.4 x10^{-7}	-2.1 x10^{-7}	-1.2 x10^{-6}	1.00	1.00
TTBPP	1.00	7.4 x10^{-4}	1.8 x10^{-4}	-3.1 x10^{-4}	0.0	1.00	1.00

Table S9: Median log K_{AW} and log K_{OW} values with the respective 25 and 75 percentile, the interquartile range (IQR) and the upper and lower data fence used to determine outliers. For data sets with less than three data points as input data the individual data points are presented in () with the used median value marked with *.

		Median,Percentiles and fences of log K_{AW}						Median,Percentiles and fences of log K_{OW}					
Acronym	MW (g/mol)	Median log K_{AW}	25‰	75‰	IQR	Upper fence	Lower fence	Median log K_{OW}	25‰	75‰	IQR	Upper fence	Lower fence
BCMP-BCEP	583	-12.2	-12.2	-8.6	3.6	-3.2	-17.6	3.07	2.8	3.3	0.48	4.0	2.1
BDCPP	320	-8.82	-9.08	-7.40	1.6	-5.0	-11.4	2.05* (1.99, 2.12)	n.a.	n.a.	n.a.	n.a.	n.a.
BEHP	322	-5.77	-6.40	-4.74	1.7	-2.2	-8.9	5.75	4.2	5.9	1.7	8.5	1.7
BPA-BDPP	693	-5.41	-8.57	-5.09	3.48	0.14	-13.79	7.15	4.9	9.6	4.7	16.7	-2.2
DCP	340	-5.75	-5.76	-5.62	0.14	-5.42	-5.96	4.56	4.5	5.3	0.7	6.4	3.4
DOPO	216	-5.65*	n.a.	n.a.	n.a.	n.a.	n.a.	2.68	2.3	3.1	0.8	4.3	1.1
EHDPP	362	-4.99	-6.78	-3.39	3.4	1.7	-11.9	5.73	5.7	6.1	0.6	6.6	1.88
IDDPP	390	-4.75	-6.57	-3.28	3.3	1.6	-11.5	6.11	5.4	6.6	1.2	8.4	3.7
MC 984	582	-8.10	-8.14	-6.79	1.3	-4.8	-10.1	2.74* (2.59, 2.89)	n.a.	n.a.	n.a.	n.a.	n.a.
PBDMPP	687	-10.58*	n.a.	n.a.	n.a.	n.a.	n.a.	11.04	9.3	12.8	3.6	18.2	3.9
PBDPP	574	-8.23	-9.57	-6.88	2.70	-2.84	-13.62	7.08	5.2	7.4	2.2	10.7	1.9
TBEP	398	-8.68	-9.22	-8.05	1.2	-6.3	-11.0	3.75	3.3	4.3	1.0	5.7	1.9
TCEP	285	-6.04	-6.67	-5.98	0.7	-4.9	-7.7	1.63	1.4	1.7	0.3	2.1	1.1
TCIPP	328	-5.61	-6.74	-5.49	1.2	-3.6	-8.6	2.68	2.6	2.9	0.3	3.3	2.1
TCP	368	-5.66	-5.99	-5.66	0.3	-5.2	-6.5	5.71	5.1	6.2	1.1	7.9	3.4
TDBPP	698	-9.78	-9.88	-5.78	4.1	0.40	-16.0	4.29	4.2	5.0	0.8	6.2	3.0
TDCIPP	431	-6.97	-7.22	-5.79	1.4	-3.7	-79.4	3.69	3.7	3.8	0.1	3.9	3.5
TDCPP	431	-6.97	-7.51	-6.35	1.2	-4.6	-9.2	3.89	3.8	5.1	1.3	7.0	1.8
TDMPP	410	-5.35	-7.35	-4.07	3.3	1.0	-13.1	3.91* (3.82, 4.00)	n.a.	n.a.	n.a.	n.a.	n.a.
TEHP	435	-3.39	-5.00	-2.41	2.6	1.5	-8.9	9.42	4.23	9.49	5.3	17.4	-3.7

*less than 3 data points available

Table S9 continued: Median log K_{AW} and log K_{OW} values with and without removed outliers as well as the respective 25 and 75 percentile, the interquartile range (IQR) and the upper and lower data fence used to determine outliers. For data sets with less than three data points as input data the individual data points are presented in () with the used median value marked with *.

		Median,Percentiles and fences of log K_{AW}						Median,Percentiles and fences of log K_{OW}					
Acronym	MW (g/mol)	Median log K_{AW}	25‰	75‰	IQR	Upper fence	Lower fence	Median log K_{OW}	25‰	75‰	IQR	Upper fence	Lower fence
TEP	182	-4.87	-5.65	-4.62	1.0	-3.1	-7.2	0.88	0.9	1.1	0.2	1.5	0.5
TIBP	266	-3.34	-3.61	-3.06	0.55	-2.25	-4.43	3.70	3.6	3.7	0.1	3.9	3.4
TiPP	224	-4.25	-4.56	-4.25	0.3	-3.8	-5.0	2.13	2.1	2.3	0.2	2.6	1.9
TmCP	368	-5.66	-7.79	-4.28	3.5	1.0	-13.1	5.95	5.5	6.3	0.9	7.6	4.2
TMP	140	-4.99	-5.59	-4.92	1.0	-3.4	-7.5	-0.65	-0.7	-0.6	0.1	-0.5	-0.7
TnBP	266	-3.88	-4.24	-3.88	0.4	-3.3	-4.8	4.00	3.8	4.0	0.2	4.3	3.5
ToCP	368	-5.66	-7.79	-4.19	3.6	1.3	-13.2	5.95	5.5	6.3	0.9	7.2	4.2
TpCP	368	-5.66	-7.79	-4.28	3.5	1.0	-13.1	5.95	5.5	6.3	0.9	7.2	4.2
TPhP	326	-4.73	-5.79	-4.06	1.7	-1.5	-8.4	4.61	4.6	4.7	0.1	4.8	4.5
TPPP	453	-4.92	-7.20	-3.82	3.4	1.2	-12.3	8.53* (7.99, 9.07)	8.3	8.8	0.5	9.6	7.4
TTBNPP	1018	-11.10	-11.96	-10.85	1.11	-9.20	-13.62	8.05	7.26	8.75	1.5	11.0	5.0
TTBPP	495	-4.55	-6.60	-3.45	3.1	1.3	-11.3	9.94	9.7	10.2	0.5	10.9	9.0

*less than 3 data points available

Table S10: Initial $f_{part,T}$ from the “input all” dataset and median $f_{part,T}$ as well as 1. and 3. quartile of the Monte Carlo uncertainty analysis with calculated and default dispersion factors

Acronym	log K_{AW}	log K_{OW}	Initial $f_{part,T}$	Median $f_{part,T}$	Median $f_{part,T}$ default dispersion factor
BDCPP median	-8.8	2.1	0.48	0.45	0.50
BDCPP Quartile 1	-9.0	2.0		0.40	0.30
BDCPP Quartile 3	-8.6	2.1		0.52	0.65
DCP median	-5.8	4.6	0.15	0.14	0.16
DCP Quartile 1	-5.8	4.5		0.04	0.07
DCP Quartile 3	-5.6	5.3		0.29	0.26
DOPO median	-5.7	2.7	1.8E-03	1.7E-03	1.8E-03
DOPO Quartile 1	-5.7	2.3		1.3E-03	9.9E-04
DOPO Quartile 3	-5.7	3.1		2.3E-03	4.3E-03
TCEP median	-6.0	1.6	4.5E-04	4.5E-04	4.5E-04
TCEP Quartile 1	-6.7	1.4		4.0E-04	2.0E-04
TCEP Quartile 3	-6.0	1.7		5.2E-04	1.1E-03
TCIPP median	-6.6	2.7	5.8E-03	5.8E-03	6.2E-03
TCIPP Quartile 1	-6.7	2.6		5.0E-03	2.7E-03
TCIPP Quartile 3	-6.5	2.9		6.6E-03	1.2E-02
TDCIPP median	-7.0	3.7	0.28	0.28	0.28
TDCIPP Quartile 1	-7.2	3.7		0.27	0.17
TDCIPP Quartile 3	-5.8	3.8		0.29	0.45
TDCPP median	-7.0	3.9	0.38	0.38	0.36
TDCPP Quartile 1	-7.5	3.8		0.33	0.17
TDCPP Quartile 3	-6.4	5.1		0.43	0.55
TEP median	-4.9	0.9	1.0E-05	1.0E-05	9.5E-06
TEP Quartile 1	-5.7	0.9		8.6E-06	4.8E-06
TEP Quartile 3	-4.6	1.1		1.2E-05	2.3E-05
TiBP median	-3.3	3.7	9.1E-05	8.8E-05	8.2E-05
TiBP Quartile 1	-3.6	3.6		3.5E-05	4.3E-05
TiBP Quartile 3	-3.1	3.7		2.7E-04	2.1E-04
TiPP median	-4.3	2.1	2.9E-05	2.1E-05	2.8E-05
TiPP Quartile 1	-4.6	2.1		1.8E-05	1.3E-05
TiPP Quartile 3	-4.3	2.3		2.3E-05	6.1E-05
TMP median	-5.0	-0.7	1.8E-07	1.8E-07	1.8E-07
TMP Quartile 1	-6.0	-0.7		8.0E-08	1.6E-07
TMP Quartile 3	-4.9	-0.6		4.3E-07	2.1E-07
TnBP median	-3.9	4.0	9.7E-04	1.5E-03	1.0E-03
TnBP Quartile 1	-4.2	3.8		1.4E-03	4.5E-04
TnBP Quartile 3	-3.9	4.0		1.6E-03	2.1E-03
TPhP median	-4.7	4.6	0.059	0.058	0.054
TPhP Quartile 1	-5.8	4.6		0.051	0.026
TPhP Quartile 3	-4.1	4.7		0.066	0.11

We compared f_{part} obtained from model predictions with results reported by Wolschke et al. (2016) [49] who measured weekly OPE air concentrations over one year at the sea-side town of Büsum in northern Germany.

58 air samples (each sample about 2800 m^3 over a 7-day period) were collected using a high-volume air sampler. A glass fibre filter (GFF, pore size: 0.7 μm) and a self-packed polyurethane foam (PUF)/XAD-2 cartridge (PUF: Ø5.0 cm × 2.5 cm; 35 g XAD-2, particle size: 0.3-1.0 mm) were employed simultaneously to collect particle and gas phase separately. PUF/XAD-2 was extracted with a modified Soxhlet extractor for 16 h using dichloromethane (DCM). Particle samples (GFF) were extracted using a standard Soxhlet extractor using DCM for 16 h.

Instrumental analysis was performed on an Agilent 7010 gas chromatograph - tandem mass spectrometer (GC-MS/MS), fitted with an HP-5MS column (30m 0.25mm i.d. 0.25 mm film thickness, J&W Scientific).

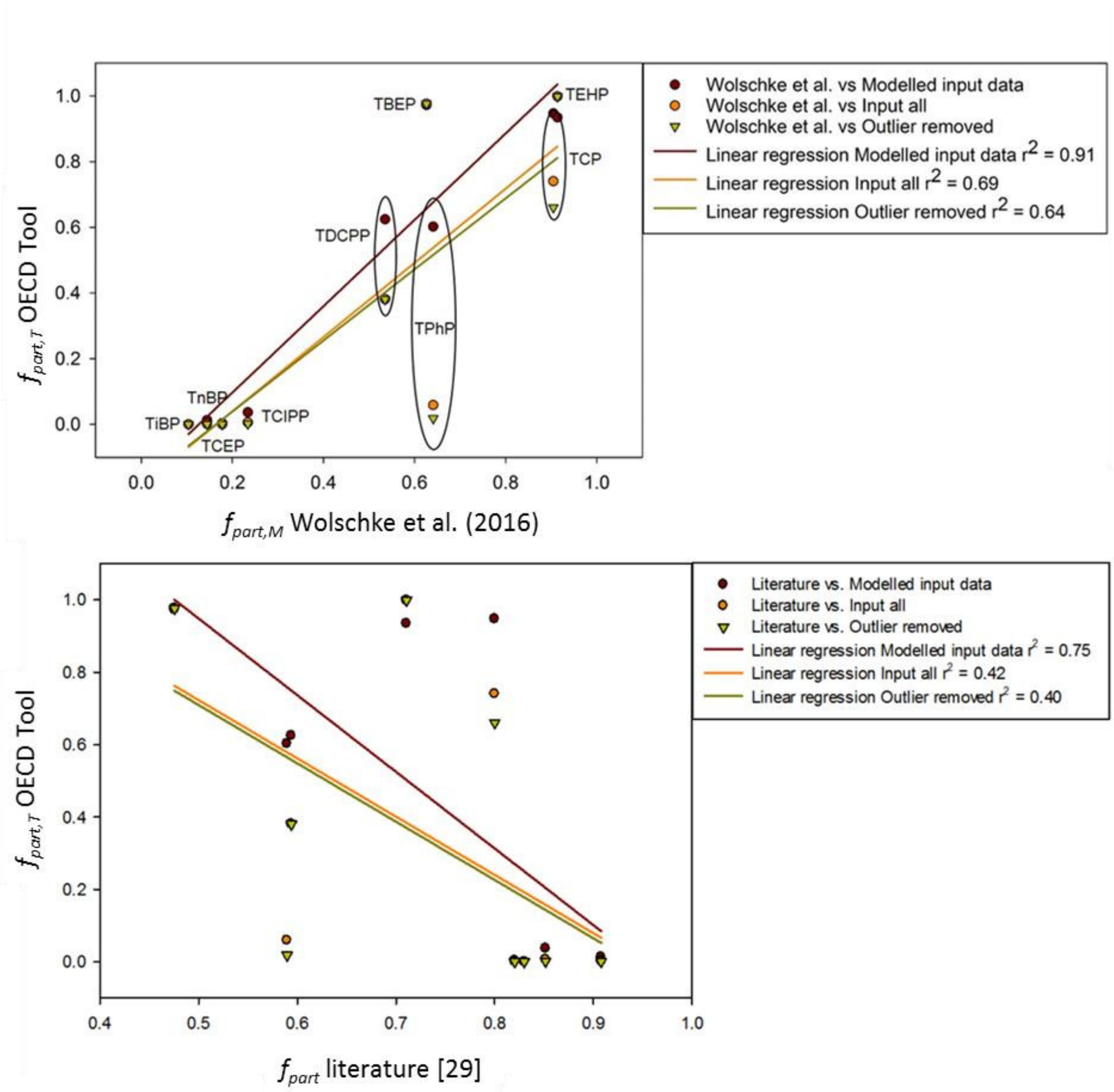

Figure S1: Correlation of f_{part} predicted by the Tool for the different input datasets vs. f_{part} reported by Wolschke et al. (2016) [49] (top) and in the literature [29] (bottom)

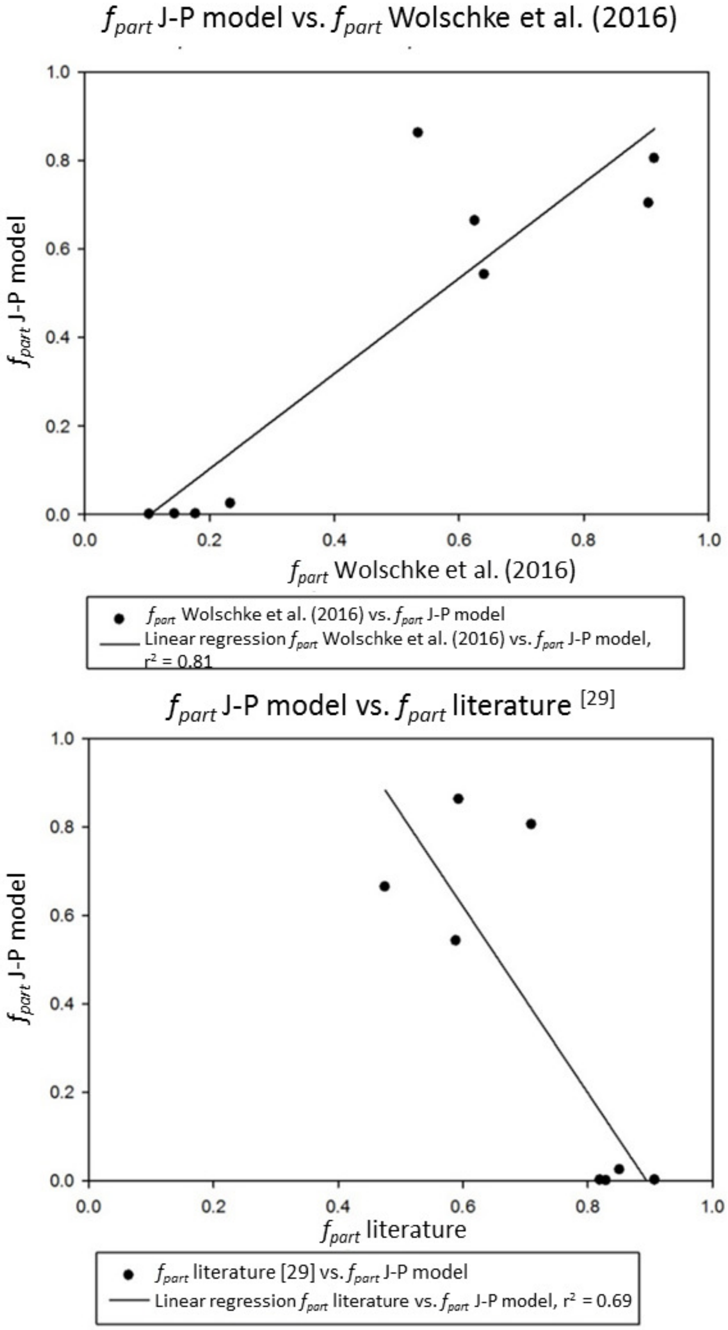

Figure S2: Correlation of f_{part} predicted by the J-P model vs. f_{part} reported by Wolschke et al. (2016) [49] (top) and in the literature [29] (bottom)

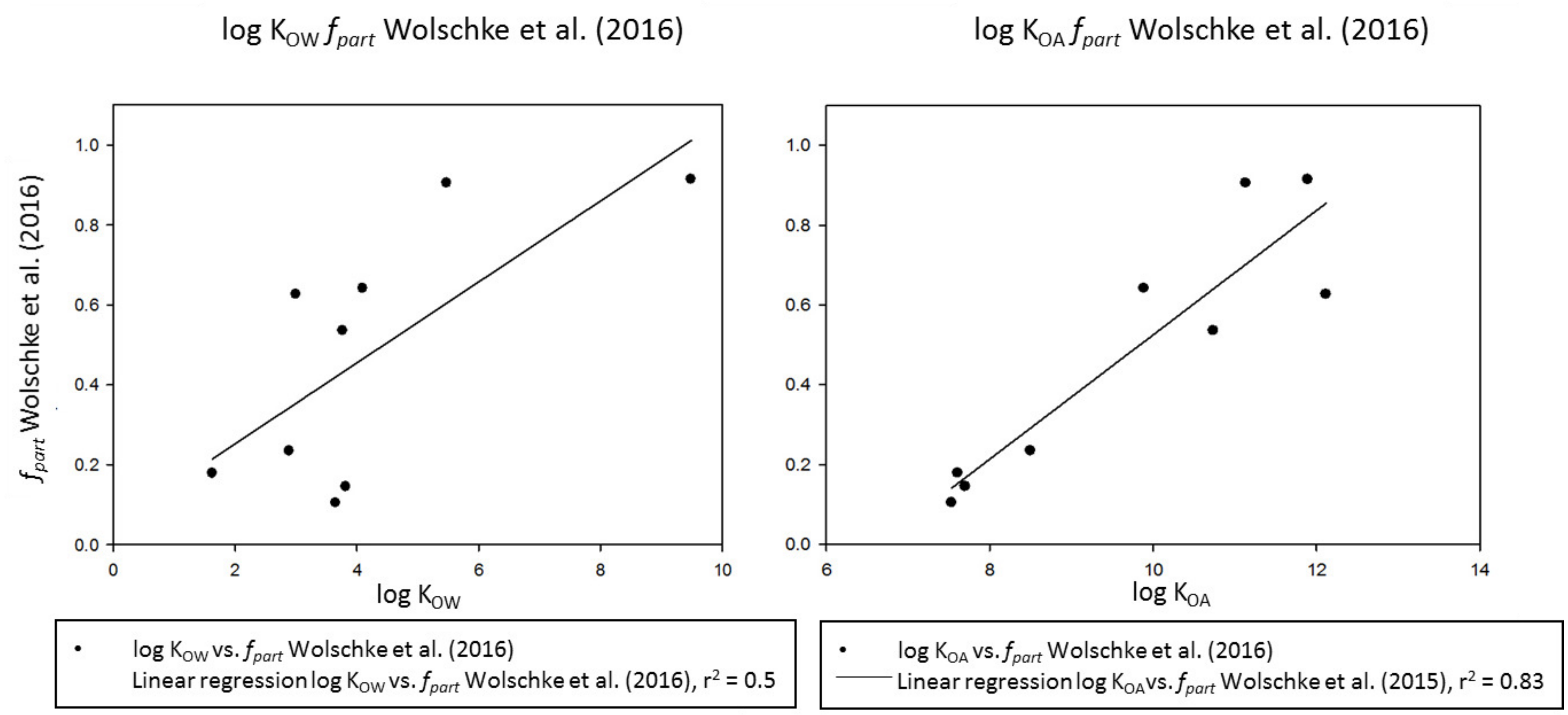

Figure S3: Correlation of f_{part} reported by Wolschke et al. (2016) [49] vs. log K_{OW} and log K_{OA}

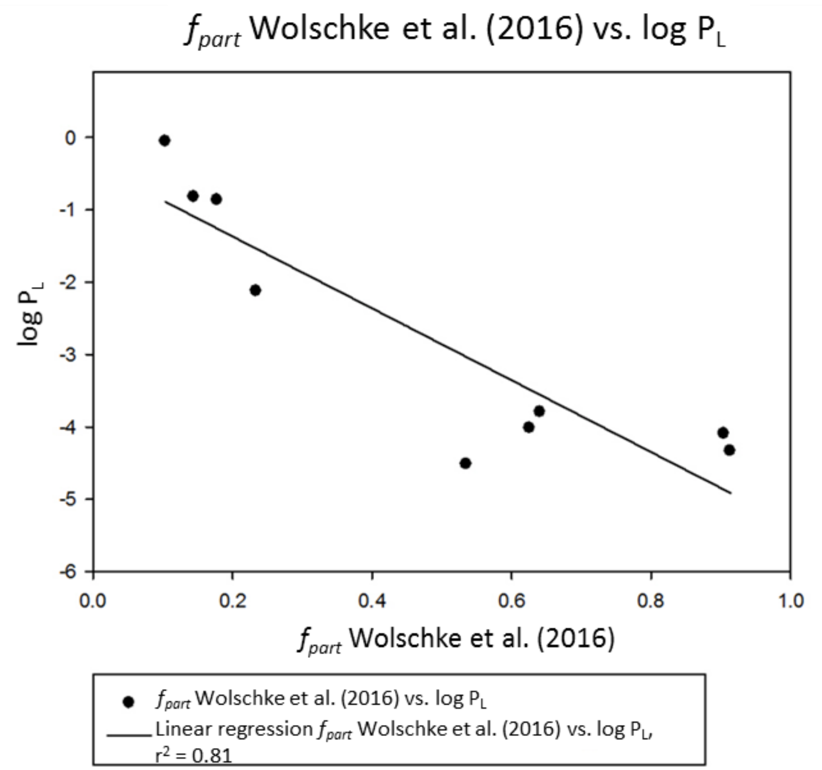

Figure S4: Correlation of f_{part} reported by Wolschke et al. (2016) [49] vs. log P_L

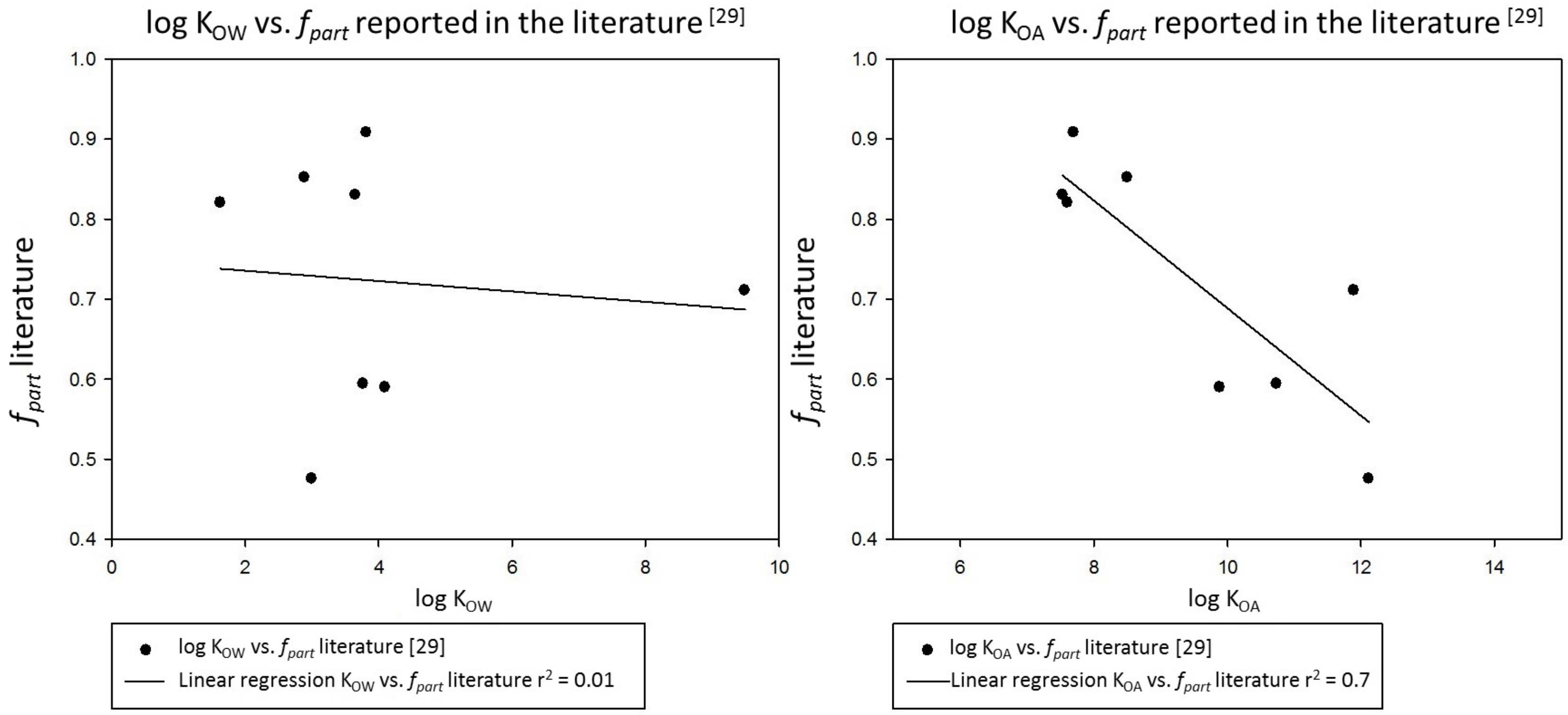

Figure S5: Correlation of f_{part} reported in the literature [29] vs. log K_{OW} and log K_{OA}

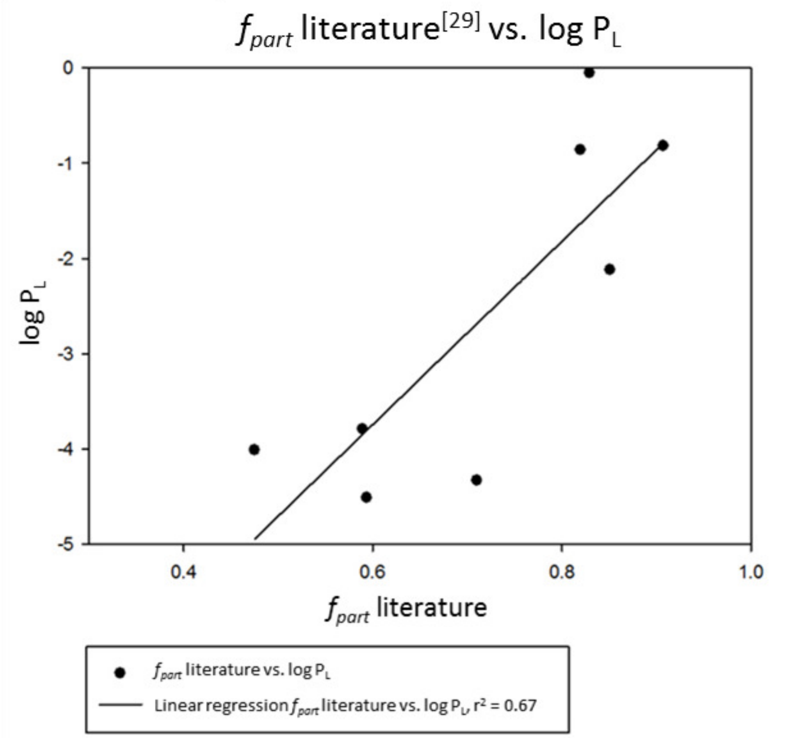

Figure S6: Correlation of f_{part} reported in the literature [29] vs. P_L

Table S11: f_{part} estimated by the Junge-Pankow model ($f_{part,J\text{-}P}$), the Harner-Bidleman model ($f_{part,H\text{-}B}$) and the Tool ($f_{part,T}$) using measured P_L (left), log P_L and log K_{OA} estimated by EPISuite (middle) and log P_L and log K_{OA} estimated by SPARC (right) in relation to log P_L and log K_{OA}.

	measured P_L		EPISuite					SPARC				
Acronym	$f_{part,J\text{-}P}$	logP_L	$f_{part,J\text{-}P}$	$f_{part,H\text{-}B}$	$f_{part,T}$	log P_L	log K_{OA}	$f_{part,J\text{-}P}$	$f_{part,H\text{-}B}$	$f_{part,T}$	log P_L	log K_{OA}
BCMP-BCEP	0.015	-2.9	0.6	1.0	1.0	-4.9	16	1.0	1.0	1.0	-8.8	14
BDCPP			0.6	0.3	0.3	-4.9	11	0.0	9.5×10^{-3}	0.012	-2.7	9.4
BEHP			0.4	0.7	0.8	-4.6	12	0.1	0.1	0.1	-3.5	11
BPA-BDPP	0.014	-2.9	2.3×10^{-4}	1.0	1.0	-1.1	22	0.0	1.0	1.0	-0.7	20
DCP	0.03	-3.2	0.5	0.3	0.2	-4.8	11	0.9	0.1	0.1	-5.6	10
DOPO			0.5	1.2×10^{-4}	1.5×10^{-4}	-4.8	7.5	0.9			-5.8	
EHDPP	0.16	-4.1	7.5×10^{-3}	0.4	0.5	-2.6	11	0.0	0.1	0.2	-2.2	11
IDDPP	0.61	-5.0	0.4	0.8	0.8	-4.6	12		0.6	0.7		12
MC 984			0.6	1.0	1.0	-4.9	13		0.9	0.9		13
PBDMPP			0.011	1.0	1.0	-2.8	22	0.2	1.0	1.0	-4.2	21
PBDPP	0.86	-5.6	0.6	1.0	1.0	-4.9	18	1.0	1.0	1.0	-7.7	18
TBEP	0.38	-4.6	0.1	0.9	0.9	-3.8	12	0.4	0.6	0.7	-4.6	12
TCEP	5.5×10^{-4}	-1.5	3.3×10^{-4}	1.5×10^{-4}	1.9×10^{-4}	-1.3	7.6	1.6×10^{-4}	3.7×10^{-5}	4.6×10^{-5}	-1.0	7.0
TCIPP	4.9×10^{-4}	-1.5	6.4×10^{-3}	1.2×10^{-3}	1.5×10^{-3}	-2.6	8.5	7.3×10^{-4}	1.4×10^{-4}	1.8×10^{-4}	-1.6	7.6
TCP	0.28	-4.3		0.8	0.8		12	0.2	0.7	0.7	-4.1	12
TDBPP			0.6	1.0	1.0	-4.9	14	1.4×10^{-3}	1.0	1.0	-1.9	13
TDCIPP	0.69	-5.1	0.3	0.1	0.2	-4.4	11	0.5	0.1	0.1	-4.8	10
TDCPP			4.2×10^{-6}	0.1	0.2	0.6	11	7.7×10^{-5}	0.2	0.2	-0.7	11
TDMPP			4.6×10^{-3}	1.0	0.9	-2.4	14	3.6×10^{-4}	1.0	1.0	-1.3	13
TEHP	0.52	-4.8	0.2	0.7	0.8	-4.1	12	0.7	0.8	0.8	-5.2	12
TEP			0.6	1.2×10^{-6}	1.4×10^{-6}	-4.9	5.5	1.0	4.0×10^{-8}	4.9×10^{-8}	-14	4.0
TIBP			0.6	1.1×10^{-4}	5.7×10^{-5}	-4.9	7.5	1.0	1.5×10^{-4}	1.5×10^{-4}	-9.0	7.6
TiPP			6.8×10^{-4}	8.8×10^{-6}	1.1×10^{-5}	-1.6	6.4	1.0	1.7×10^{-6}	1.7×10^{-7}	-7.7	4.6
TmCP	0.42	-4.6	0.4	0.8	0.8	-4.6	12	0.3	0.7	0.7	-4.4	12
TMP	2.3×10^{-5}	-0.1	3.0×10^{-7}	9.2×10^{-8}	1.1×10^{-7}	1.8	4.4	0.6	1.9×10^{-9}	1.7×10^{-9}	-4.9	2.6
TnBP	1.2×10^{-4}	-0.8	1.1×10^{-4}	1.9×10^{-4}	2.3×10^{-4}	-0.8	7.7	1.0	3.5×10^{-5}	4.3×10^{-5}	-7.1	7.0
ToCP	0.42	-4.6	0.6	0.8	0.8	-4.9	12	1.0	0.6	0.7	-6.1	12
TpCP	0.42	-4.6	0.5	0.8	0.8	-4.8	12		0.7	0.7		12
TPhP	0.06	-3.6	0.2	0.1	0.1	-4.2	11	0.02	0.1	0.1	-3.1	10
TPPP			0.6	1.0	1.0	-4.9	14		1.0	1.0		14
TTBNPP			0.5	1.0	1.0	-4.8	20	0.9	1.0	1.0	-5.8	18
TTBPP			0.6	1.0	1.0	-4.9	15		1.0	1.0		15

Table S12: f_{part} predicted by the Tool for the "Outlier removed" dataset at the default temperature (left), 253.15 K (middle) and 308.15 K (right)

Acronym	Initial f_{part}	f_{part} at 253.15 K	f_{part} at 308.15 K
BCMP-BCEP	1.00	1.00	1.00
BDCPP	0.48	0.48	0.48
BEHP	0.94	0.94	0.94
BPA-BDPP (BADP)	0.97	0.97	0.97
DCP	0.14	0.14	0.14
DOPO	1.8E-03	1.8E-03	1.8E-03
EHDPP	0.97	0.97	0.97
IDDPP	0.98	0.98	0.98
MC 984	1.00	1.00	1.00
PBDMPP	1.00	1.00	1.00
PBDPP (RDP)	1.00	1.00	1.00
TBEP	0.98	0.98	0.98
TCEP	4.5E-04	4.5E-04	4.5E-04
TCIPP	1.6E-03	1.6E-03	1.6E-03
TCP	0.66	0.66	0.66
TDBPP	1.00	1.00	1.00
TDCIPP	0.28	0.28	0.28
TDCPP	0.38	0.38	0.38
TDMPP	1.00	1.00	1.00
TEHP	1.00	1.00	1.00
TEP	8.0E-06	8.0E-06	8.0E-06
TIBP	8.1E-05	8.1E-05	8.1E-05
TiPP	2.0E-05	2.0E-05	2.0E-05
TmCP	1.00	1.00	1.00
TMP	1.8E-07	1.8E-07	1.8E-07
TnBP	6.4E-04	6.4E-04	6.4E-04
ToCP	1.00	1.00	1.00
TpCP	1.00	1.00	1.00
TPhP	0.018	0.018	0.018
TPPP	1.00	1.00	1.00
TTBNPP	1.00	1.00	1.00
TTBPP	1.00	1.00	1.00

Table S13: fpart, temperature (Temp) [°C] and TSP_{coarse} [µg m^{-3}] per analyte and sample reported in Wolschke et al. (2016) [49], including the Pearson correlation coefficient for the correlation of temperature and $f_{part,M}$ (correl temp) and the correlation of TSP_{coarse} and $f_{part,M}$ (correl TSP).

Sample	TiBP	TnBP	TCEP	TCIPP	TDCPP	TPhP	TBEP	TEHP	TCP	Temp	TSP_{coarse}
BUE-07	0.00	0.00	0.00	0.00	0.00	0.00	n.a.	0.45	0.00	13.9	10
BUE-08	0.37	0.56	0.00	0.51	0.82	0.77	n.a.	0.97	1.00	14.4	42
BUE-09	0.00	0.05	0.00	0.10	0.80	0.46	1.00	0.90	0.92	16.2	34
BUE-10	0.00	0.02	0.00	0.06	0.55	0.31	1.00	0.96	0.93	12.1	22
BUE-11	0.23	0.26	0.62	0.42	0.41	0.29	n.a.	0.89	n.a.	9.0	50
BUE-12	0.00	0.00	0.00	0.00	0.36	0.38	n.a.	0.91	0.73	7.9	14
BUE-13	0.11	0.21	0.00	0.41	0.89	0.88	1.00	0.89	0.95	10.2	65
BUE-14	0.02	0.05	0.41	0.11	0.83	0.67	1.00	0.98	1.00	9.6	54
BUE-15	0.08	0.03	0.00	0.10	0.79	0.73	1.00	0.96	0.96	3.3	n.a.
BUE-16	0.08	0.17	0.75	0.38	0.77	0.91	1.00	1.00	1.00	3.4	19
BUE-17	0.07	0.05	0.00	0.16	0.67	0.73	1.00	0.98	1.00	6.4	30
BUE-18	0.17	0.09	0.00	0.11	0.13	0.29	0.00	0.79	0.55	6.2	n.a.
BUE-19	0.00	0.06	0.00	0.18	0.00	0.00	0.00	0.56	0.00	4.3	4
BUE-20	0.00	0.16	0.00	0.00	0.00	0.69	n.a.	0.83	1.00	4.3	3
BUE-21	0.09	0.00	0.53	0.25	0.00	0.29	0.00	0.33	0.20	5.7	4
BUE-22	0.19	0.10	0.00	0.13	0.00	0.48	n.a.	0.73	0.53	5.7	15
BUE-23	0.00	0.00	0.00	0.00	0.00	0.00	n.a.	0.00	n.a.	4.7	38
BUE-24	0.00	0.00	0.00	0.00	0.00	0.00	n.a.	n.a.	n.a.	3.8	2
BUE-25	0.00	0.00	0.00	0.00	0.00	0.00	n.a.	0.00	n.a.	-1.1	47
BUE-26	0.19	0.28	0.73	0.70	1.00	0.96	1.00	0.99	1.00	-7.5	21
BUE-27	0.48	0.92	1.00	0.96	1.00	0.98	1.00	1.00	1.00	-3.4	39
BUE-28	0.14	0.00	0.00	0.00	0.37	0.63	n.a.	0.81	0.79	2.4	5
BUE-29	0.13	0.00	0.00	0.04	0.00	0.15	0.00	0.00	0.00	4.6	3
BUE-30	0.00	0.00	0.00	0.15	0.00	0.10	0.00	0.75	0.13	5	23
BUE-31	0.33	0.51	0.00	0.31	0.69	0.86	1.00	0.91	0.93	5.6	20
BUE-32	0.00	0.00	0.00	0.00	0.00	0.00	n.a.	n.a.	0.00	6.7	23
BUE-33	0.00	0.10	0.35	0.38	0.76	0.73	1.00	0.85	0.85	6.6	17
BUE-34	0.21	0.29	0.31	0.46	1.00	0.75	n.a.	1.00	1.00	6.5	17
BUE-35	0.00	0.00	0.00	0.00	0.00	0.00	n.a.	n.a.	n.a.	4.7	11
BUE-36	0.32	0.19	0.00	0.12	0.47	0.61	n.a.	1.00	1.00	6.7	16
BUE-37	0.46	0.80	0.78	0.86	1.00	0.95	n.a.	1.00	1.00	8.8	13
BUE-38	0.22	0.52	0.39	0.39	0.51	0.71	0.66	0.92	1.00	11.9	13
BUE-39	0.00	0.00	0.19	0.31	0.62	0.63	0.51	0.94	1.00	9.8	7
BUE-40	0.00	0.11	0.00	0.32	0.27	0.47	0.46	0.93	1.00	11	12
BUE-41	0.23	0.33	0.00	0.35	0.00	0.48	0.00	0.81	1.00	14.7	25
BUE-42	0.00	0.00	0.00	0.01	0.74	0.33	1.00	0.95	1.00	17.1	18
BUE-43	0.00	0.00	0.00	0.11	0.81	0.45	1.00	0.99	1.00	n.a.	15

Table S13 continued:

Sample	TiBP	TnBP	TCEP	TCIPP	TDCPP	TPhP	TBEP	TEHP	TCP	Temp	TSP_{coarse}
BUE-44	1.00	1.00	1.00	1.00	1.00	1.00	n.a.	1.00	1.00	13.8	6
BUE-45	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.79	0.57	14.1	7
BUE-46	0.21	0.32	0.00	0.48	0.37	0.43	0.51	0.90	1.00	15	34
BUE-47	0.25	0.18	0.47	0.34	0.64	0.73	n.a.	0.94	1.00	17.4	18
BUE-48	0.00	0.00	0.00	0.14	0.31	0.46	0.44	0.71	1.00	18	7
BUE-49	0.09	0.10	0.00	0.17	0.00	0.00	0.00	0.64	n.a.	15.6	5
BUE-50	0.12	0.19	0.19	0.26	0.43	0.45	n.a.	0.87	1.00	16.6	14
BUE-51	0.00	0.13	0.00	0.25	0.71	0.59	1.00	0.91	1.00	17.7	12
BUE-52	0.22	0.31	0.00	0.13	0.57	0.83	1.00	0.92	1.00	17.3	9
BUE-53	0.00	0.00	0.00	0.00	0.38	0.24	1.00	0.86	1.00	20.3	19
BUE-54	0.00	0.09	0.00	0.07	0.59	0.21	1.00	0.88	1.00	17.2	16
BUE-55	0.03	0.15	0.21	0.17	0.72	0.56	1.00	0.94	1.00	16.6	13
BUE-56	0.08	0.18	0.17	0.40	0.66	0.54	n.a.	0.86	1.00	16.8	7
BUE-57	0.06	0.12	0.00	0.13	0.58	0.46	n.a.	0.89	1.00	14.6	17
BUE-58	0.08	0.27	0.28	0.39	0.61	0.61	n.a.	0.76	1.00	11.8	2
BUE-59	0.12	0.34	0.00	0.27	0.27	0.59	n.a.	0.82	1.00	12.5	34
BUE-60	0.00	0.12	0.00	0.15	0.39	0.54	0.00	0.84	1.00	11.4	15
median	0.07	0.10	0.00	0.16	0.49	0.48	1.00	0.89	1.00		
correl temp	-0.056	-0.026	-0.26	-0.11	0.084	-0.068	0.029	0.23	0.28		
correl TSP	0.057	0.14	0.068	0.15	0.26	0.15	0.45	0.040	0.24		

Table S14: Impact of TSP$_{coarse}$ on the partitioning behaviour of OPEs predicted by the Tool for the "Outlier removed" dataset as well as the fraction of OPEs partitioning into the gas phase (%). Compounds with f_{part} < 0.5 are marked light blue.

Acronym	f_{part} at TSP$_{coarse}$ = 10^{-9}	f_{part} at TSP$_{coarse}$ = 10^{-10}	f_{part} at TSP$_{coarse}$ = 10^{-11}	f_{part} at TSP$_{coarse}$ = 10^{-12}
BCMP-BCEP	1.0	1.0	1.0	1.0
BDCPP	1.0	0.9	0.5	0.1
BEHP	1.0	1.0	0.9	0.6
BPA-BDPP (BADP)	1.0	1.0	1.0	0.8
DCP	0.9	0.6	0.1	1.6E-02
DOPO	0.2	0.02	1.8E-03	1.8E-04
EHDPP	1.0	1.0	1.0	0.8
IDDPP	1.0	1.0	1.0	0.8
MC 984	1.0	1.0	1.0	1.0
PBDMPP	1.0	1.0	1.0	1.0
PBDPP (RDP)	1.0	1.0	1.0	1.0
TBEP	1.0	1.0	1.0	0.8
TCEP	0.04	4.5E-03	4.5E-04	4.5E-05
TCIPP	0.1	0.02	1.6E-03	1.6E-04
TCP	1.0	1.0	0.7	0.2
TDBPP	1.0	1.0	1.0	1.0
TDCIPP	1.0	0.8	0.3	0.04
TDCPP	1.0	0.9	0.4	0.1
TDMPP	1.0	1.0	1.0	1.0
TEHP	1.0	1.0	1.0	1.0
TEP	8.0E-04	8.0E-05	8.0E-06	8.0E-07
TIBP	8.0E-03	8.1E-04	8.1E-05	8.1E-06
TiPP	2.0E-03	2.0E-04	2.0E-05	2.0E-06
TmCP	1.0	1.0	1.0	1.0
TMP	1.8E-05	1.8E-06	1.8E-07	1.8E-08
TnBP	0.1	6.4E-03	6.4E-04	6.4E-05
ToCP	1.0	1.0	1.0	1.0
TpCP	1.0	1.0	1.0	1.0
TPhP	0.6	0.2	0.02	1.8E-03
TPPP	1.0	1.0	1.0	1.0
TTBNPP	1.0	1.0	1.0	1.0
TTBPP	1.0	1.0	1.0	1.0
% in gas phase	25	28	41	44

Table S15: Impact of TSP$_{coarse}$ on the partitioning behaviour of OPEs predicted by the Tool for the "Modelled input" dataset as well as the fraction of OPEs partitioning into the gas phase (%). Compounds with f_{part} < 0.5 are marked light blue.

Acronym	f_{part} at TSP$_{coarse}$ = 10^{-9}	f_{part} at TSP$_{coarse}$ = 10^{-10}	f_{part} at TSP$_{coarse}$ = 10^{-11}	f_{part} at TSP$_{coarse}$ = 10^{-12}
BCMP-BCEP	1.0	1.0	1.0	1.0
BDCPP	1.0	0.8	0.3	0.04
BEHP	1.0	1.0	0.7	0.2
BPA-BDPP (BADP)	1.0	1.0	1.0	1.0
DCP	1.0	0.8	0.3	3.7E-02
DOPO	0.03	2.8E-03	2.8E-04	2.8E-05
EHDPP	1.0	0.8	0.2	0.03
IDDPP	1.0	1.0	0.7	0.2
MC 984	1.0	1.0	1.0	0.9
PBDMPP	1.0	1.0	1.0	1.0
PBDPP (RDP)	1.0	1.0	1.0	1.0
TBEP	1.0	1.0	0.9	0.5
TCEP	0.03	3.4E-03	3.4E-04	3.4E-05
TCIPP	0.2	0.03	2.7E-03	2.7E-04
TCP	1.0	0.9	0.5	0.1
TDBPP	1.0	1.0	1.0	1.0
TDCIPP	1.0	0.8	0.3	0.03
TDCPP	1.0	0.8	0.3	0.04
TDMPP	1.0	1.0	1.0	0.7
TEHP	1.0	1.0	0.9	0.4
TEP	3.3E-04	3.3E-05	3.3E-06	3.3E-07
TIBP	2.8E-02	2.9E-03	2.9E-04	2.9E-05
TiPP	2.0E-03	2.0E-04	2.0E-05	2.0E-06
TmCP	1.0	0.8	0.3	0.1
TMP	2.1E-05	2.1E-06	2.1E-07	2.1E-08
TnBP	0.04	4.2E-03	4.2E-04	4.2E-05
ToCP	1.0	0.8	0.3	0.1
TpCP	1.0	0.8	0.3	0.1
TPhP	0.9	0.4	0.06	6.5E-03
TPPP	1.0	1.0	1.0	0.9
TTBNPP	1.0	1.0	1.0	1.0
TTBPP	1.0	1.0	1.0	1.0
% in gas phase	25	28	53	66

Literature

[1] OECD. eChemPortal at http://www.echemportal.org/echemportal/, 2014. [accessed]

[2] Bayer. 1980. Technical data sheet, Disflamoll® TCA. Leverkusen, Germany: Bayer AG.

[3] BioByte. 2004. BioLoom [computer program]. version 1.0. (ClogP 4.0). Claremont, CA: BioByte Corporation.

[4] Boerdijk GB. 2000. Polymer Chemicals, Safety-Detail Report, Determination of the vapour pressure of Fyrol CEF, measured with vacuum DSC. Arnhem, the Netherlands: Akzo Nobel. Unpublished work.

[5] Brodsky J, Brodesser J, Bauer C, Römbke J. 1997. The environmental fate of six existing chemicals in laboratory tests. Chemosphere 34: 515-538.

[6] Brooke D N, Crookes M J, Quarterman P, J B. Environmental risk evaluation report: Cresyl diphenyl phosphate, 2009a

[7] Brooke D N, Crookes M J, Quarterman P, J B. Environmental risk evaluation report: Tetraphenyl resorcinol diphosphate, 2009b

[8] CITI (Chemicals Inspection and Testing Institute) - MITI (Ministry of International Trade and Industry). 1992. Biodegradation and Bioaccumulation Data of Existing Chemicals Based on the CSCL Japan: Japan Chemical Industry Ecology-Toxicology and Information Center.

[9] Cuthbert JE, Mullee DM. 2002a. TCPP: Determination of general physicochemical properties. Derby, UK: SafePharm Laboratories. Report 1613/002.

[10] European Communities (EC). European Union Risk Assessment Report, 2,2-BIS(CHLOROMETHYL) TRIMETHYLENE BIS[BIS(2-CHLOROETHYL) PHOSPHATE] (V6); 2008a

[11] European Communities (EC). European Union Risk Assessment Report, TRIS(2-CHLORO-1-METHYLETHYL) PHOSPHATE (TCPP); 2008b

[12] European Communities (EC). European Union Risk Assessment Report, TRIS[2-CHLORO-1-(CHLOROMETHYL)ETHYL] PHOSPHATE (TDCP); 2008c

[13] European Communities (EC). European Union Risk Assessment Report, TRIS (2-CHLOROETHYL) PHOSPHATE, TCEP; 2009

[14] http://echa.europa.eu/information-on-chemicals/registered-substances?p_auth=HjYvbyn5&p_p_id=registeredsubstances_WAR_regsubsportlet&p_p_lifecycle=1&p_p_state=normal&p_p_mode=view&p_p_col_id=column-1&p_p_col_pos=1&p_p_col_count=2&_registeredsubstances_WAR_regsubsportlet_javax.portlet.action=registeredSubstancesAction; accessed 04.08.2014

[15] European Commission (Joint Research Centre). 2004a. Tris[2-chloro-1-(chloromethyl)ethyl]phosphate (TDCP). European Risk Assessment Report, Vol. 426 draft of environmental part. Ispra, Italy: European Chemicals Bureau, Institute for Health and Consumer Protection.

[16] European Commission (Joint Research Centre). 2004b. Tris(2-chloro-1-methylethyl) phosphate (TCPP). European Risk Assessment Report, Vol. 425 draft of environmental part. Ispra, Italy: European Chemicals
Bureau, Institute for Health and Consumer Protection.

[17] European Commission (Joint Research Centre). 2004c. Tris (2-chlorethyl) phosphate, TCEP. European Risk Assessment Report, Vol. 68 draft. Ispra, Italy: European Chemicals Bureau, Institute for Health and Consumer
Protection.

[18] Hazelton Europe. 1994b, 20 April. Physical chemistry section, Test: Partition coefficient.

[19] S.H. Hilal, L.A. Carreira and S.W. Karickhoff,: "Prediction of the Vapor Pressure, Boiling Point, Heat of Vaporization and Diffusion Coefficient of Organic Compounds" QSAR & Combinatorial Science, 565 22 (2003).

[20] S. H Hilal, L.A. Carreira and S.W. Karickhoff, "Prediction of the Solubility, Activity Coefficient, Gas/Liquid and Liquid/Liquid Distribution Coefficients of Organic Compounds", QSAR & Combinatorial Science, 23,709(2004).

[21] Hinckley DA, Bidleman TF, Foreman WT, Tuschall JR. 1990. Determination of vapor pressures for nonpolar and semipolar organic compounds from gas chromatograhic retention data. J. Chem. Eng. Data 35: 232-237.

[22] Huckins JN, Fairchild JF, Boyle TP. 1991. Role of exposuremode in the bioavalability of triphenyl phosphate to aquatic organisms. Bull Environ Contam Toxicol 21: 481-485

[23] IPCS (International Programme on Chemical Safety). 1998. Flame Retardants: Tris(Chloropropyl) Phosphate and Tris(2-Chloroethyl) Phosphate. Environmental Health Criteria, Vol. 209. Geneva, Switzerland: World Health Organization.

[24] IPCS (International Programme on Chemical Safety). 2000. Flame Retardants: Tris(2-Butoxyethyl) Phosphate,
Tris (2-Ethylhexyl) Phosphate and Tetrakis(Hydroxymethyl) Phosphonium Salts. Environmental Health Criteria, Vol. 218. Geneva, Switzerland: World Health Organization.

[25] Krawetz A. 2000.Phoenix Chemical Laboratory. Report 00 5 22 2-10.

[26] Liagkouridis, I., Cousins, A., Cousins, I. 2015. Physical–chemical properties and evaluative fate modelling of'emerging' and'novel' brominated and organophosphorusflame retardants in the indoor and outdoor environment. Science of the Total Environment 524–525 (2015) 416–42, http://dx.doi.org/10.1016/j.scitotenv.2015.02.106

[27] Lyman, W.J. 1985. In: Environmental Exposure From Chemicals. Volume I., Neely,W.B. and Blau,G.E. (eds), Boca Raton, FL: CRC Press, Inc., Chapter 2.

[28] Midwest Research Institute. 1991. Assessment of the need for limitation on triaryl and trialkyl/aryl phosphates.
Washington, DC: U.S. Environmental Protection Agency. EPA Contract No. 68-01-4313.

[29] Möller, A., Xie, Z., Caba, A., Sturm, R., Ebinghaus, R., (2011). Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea. Environmental Pollution, 159, 3660–3665.

[30] Muir DCG. 1984. Phosphate esters. In: Hutzinger O, ed. Anthropogenic compounds. The handbook of environmental chemistry 3C. Germany, Berlin: Springer-Verlag. pp. 41-66.

[31] Pakalin S, Cole T, Steinkellner J, Nicolas R, Tissier C, Munn S, et al. Review on Production Processes of Decabromodiphenyl Ether (decaBDE) Used in Polymeric Applications in Electrical and Electronic Equipment, and Assessment of the Availability of Potential Alternatives to decaBDE. European Chemicals Bureau, 2007

[32] Reemtsma, T., Quintana, J., Rodil, R., Garcia-Lopez, M., Rodriguez, I. 2008. Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. Trends in Analytical Chemistry, Vol. 27, No. 9, 2008, doi:10.1016/j.trac.2008.07.002

[33] Riddick JA, Bunger WB, Sakano TK eds. 1985. Organic Solvents: Physical Properties and Methods of Purification. 4th edition. Techniques of Chemistry, Vol. II. New York, NY: John Wiley and Sons.

[34] Robson M. 1994. Test result certificate, Hazelton to Courtaulds Chemicals. Courtaulds Study, SGS Redwood Limited. In European Commission (2004b)

[35] Saeger VW, Hicks O, Kaley RG, Michael PR, Mieure JP, Tucker ES. 1979. Environmental fate of selected phosphate esters. Environ Sci Technol 13: 840-844.

[36] Sasaki K, Takeda M, Uchiyama M. 1981. Toxicity, absorption and elimination of phosphoric acid triesters by killifish and goldfish. Bull Environ Contam Toxicol 27: 775-782.

[37] Tremain SP. 2002a. TCPP determination of vapour pressure. SPL project number 1613/001. in European Commission (2004b)

[38] Tremain SP. 2002b. TDCP: determination of vapour pressure. Derby, UK.: SafePharm Laboratories. Report 1613/003.

[39] U.S. EPA. 2003. EPI Suite. [computer program]. version 3.11. Washington, DC: U.S. Environmental Protection Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC). Modelled data

[40] U.S. EPA. 2003. EPI Suite. [computer program]. version 3.11. Washington, DC: U.S. Environmental Protection Agency (EPA) Office of Pollution Prevention Toxics and Syracuse Research Company (SRC). Measured data

[41] Environment Agency (UK EA, 2009a). Environmental risk evaluation report: 2-Ethylhexyl diphenyl phosphate (CAS No. 1241-94-7). Environment Agency. United Kingdom. Available at: http://publications.environmentagency.gov.uk/PDF/SCHO0809BQTY-E-E.pdf

[42] Environment Agency (UK EA 2009b). Environmental risk evaluation report: Isodecyl diphenyl phosphate (CAS no. 29761-21-5). Environment Agency. United Kingdom. Available at: http://publications.environmentagency.gov.uk/PDF/SCHO0809BQUF-EE.pdf

[43] Environment Agency (UK EA 2009c). Environmental risk evaluation report: Tricresyl phosphate (CAS no. 1330-78-5). Environment Agency. United Kingdom. Available at: http://publications.environment-agency.gov.uk/PDF/SCHO0809BQUJ-E-E.pdf

[44] Environment Agency (UK EA, 2009d). Environmental risk evaluation report: Tetraphenyl resorcinol diphosphate (CAS nos. 57583-54-7). Environment Agency. United Kingdom. Available at: http://publications.environmentagency.gov.uk/PDF/SCHO0809BQUL-E-E.pdf

[45] Environmental risk evaluation report: Isopropylated triphenyl phosphate (CAS nos. 28108-99-8, 26967-76-0 & 68937-41-7). Environment Agency. United Kingdom. Available at: http://publications.environment-agency.gov.uk/PDF/SCHO0809BQUG-E-E.pdf

[46] van der Veen, I., de Boer, J., 2012.Phosphorusflame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere 88, 1119–1153.

[47] Veith GD, Defoe DL, Bergstedt BV. 1979. Measuring and estimating the bioconcentration factor of chemicals in fish. J Fish Res Board Can 36: 1040-1048.

[48] World Health Organization Geneva, 2000. Flame retardants: tris(2-butoxyethyl) phosphate, tris(2-ethylhexyl) phosphate and tetrakis(hydroxymethyl) phosphonium salts. Environmental Health Criteria 218, http://apps.who.int/iris/bitstream/10665/42248/1/WHO_EHC_218.pdf

[49] Wolschke H, Sühring R, Mi W, Möller A, Xie Z, Ebinghaus R. Atmospheric occurrence and fate of organophosphorus flame retardants and plasticizer at the German coast. Atmospheric Environment 2016, 137, 1-5
DOI: 10.1016/j.atmosenv.2016.04.028

[50] Zhang, X.; Sühring, R.; Serodio, D.; Bonnell, M.; Sundin, N.; Diamond, M. L. Novel flame retardants: Estimating the physical-chemical properties and environmental fate of 94 halogenated and organophosphate PBDE replacements. Chemosphere 2016, 144, 2401–2407; DOI 10.1016/j.chemosphere.2015.11.017

Paper V

Regional variations of organophosphorus flame retardants - Fingerprint of large river basin estuaries/deltas in Europe compared with China

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Regional variations of organophosphorus flame retardants - Fingerprint of large river basin estuaries/deltas in Europe compared with 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^{-1} 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.

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 absorb 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 diphenyethers (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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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; Sühring 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; Sühring 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 °C prior to analysis. Sampling sites are shown in Fig. 1. From the Xiaoquing 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 presented by Sühring et al. (2016a). Larger pieces (>2 mm) were removed by hand from the sediment samples. The samples were homogenized with anhydrous sodium sulfate (Na_2SO_4) using an agate mortar. The samples were extracted using accelerated solvent extraction (Thermo Fisher ASE-350) with an in-cell clean-up (Sühring 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.

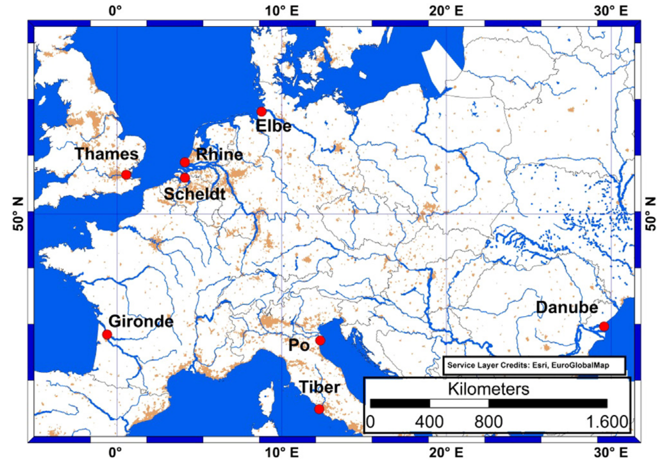

Fig. 1. European sampling sites.

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 °C, pressure: 120 bar, heat: 5 min, static (2x): 8 min, flush: 100%, purge: 60 s. The second faction 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 μL under a gentle stream of heated nitrogen (40 °C). Finally, 500 pg (absolute) ^{13}C-PCB-141 and ^{13}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 °C) for the gravimetrical 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 °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 m × 0.25 mm i.d. × 0.25 μm 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 °C for 0.1 min and 300 °C min^{-1} until 300 °C and held for a final 20 min. The GC oven program was as follows: initial 60 °C for 4 min, 25 °C min^{-1} until 100 °C, 7 °C min^{-1} until 310 °C and held for 1 min. The backflush was performed at 310 min with a flow of 1.5 mL min^{-1} at the first column for 5 min. The temperature of the MS transfer line was held at 280 °C. The ion source and quadrupole temperatures were 150 °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 °C and rinsed with acetone. Na_2SO_4 was cleaned by Soxhlet extraction with DCM for 12 h and baked at 450 °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 ± 0.02 ng for TiBP to 0.5 ± 0.15 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 value. Based on a sample amount of 10 g, MDLs ranged from 37 pg g^{-1} for TiBP to 250 pg g^{-1} for TCPP. The average recoveries of the surrogates were 76 ± 18% for TCEP-d12, 56 ± 18% for TnBP-d27, and 74 ± 16% for TPhP-d15. All reported concentrations were corrected for blanks and recoveries.

3. Results and discussion

3.1. Analytical method

The use of a GC-MS/MS system with a (mid-column) backflush system compared to classic GC-MS systems provided a strong increase of condition stability, while reducing matrix effects. After each run the first half part of the column was flushed backwards with high temperature carrier gas to eliminate matrix debris on the column. These advantages compared with the GC-MS/MS-System lead to a more robust analysis with increased sensitivity and selectivity for the analyses of OPEs in environmental samples (Wolschke et al., 2016). Due to the wide range of physical-chemical properties, instability of compounds and blank contamination, using classic GC-MS, it has been challenging to develop an extraction and cleanup method for complex sediment matrices that reduces the matrix effects enough while not impairing the analytes. With the describe advantage of the GC-MSMS method with mid-column backflush the clean-up process can be simplified.

3.2. Environmental occurrence and fate

OPEs were detected in all analyzed sediment samples. The sum concentrations for the European river sediments ranged from 2.5 ng g^{-1} dry weight (dw) at an up-stream position in the river Gironde to 181 ng g^{-1} dw in the Belgian river Scheldt. In general, the absolute concentrations were highly variable between the individual rivers. Individual concentrations are provided in Table S3. The concentrations are comparable to other studies from Europe. In Greece sediment concentrations in the Evrotas river between 10.5 and 248 ng g^{-1} dw were reported (Giulivo et al., 2017). In the Adige river, Italy OPE concentrations in sediments ranged from 11.5 to 549 ng g^{-1} dw and in Slovenia in the Sava river basin from 0.31 to 310 ng g^{-1} dw (Giulivo et al., 2017). Interestingly, Brandsma et al. (2015) reported lower OPE concentrations in the river Scheldt river (<0.1–19.6 ng g^{-1} dw) compared to this study. A possible explanation could be that the OPE concentrations have increased over the years, as the samples from Brandsma et al. (2015) were collected in 2008, compared to 2014 for this study. But local differences in accumulation capacities and discharge patterns could also be a reason for the differences in detected concentrations. To ensure comparability between the sampling sites, the contamination levels and patterns in this study are therefore being discussed normalized for TOC (Fig. 2). The results indicated that the river Scheldt with OPEs concentration up to 18 μg g^{-1} TOC is the most contaminated river for OPEs in Europe (Fig. 2), followed by the Rhine, Thames and Po. The rivers Elbe, Danube, Tiber and Gironde displayed overall lower OPEs contaminations (Fig. 2). These differences in concentrations was expected, the catchment area of the rivers Scheldt (Antwerp), Rhine (Rotterdam, Ruhr area) and Thames (London) are highly populated and strongly influenced by industry. An interesting exemption to this observation were the high OPEs concentrations (17 μg g^{-1} TOC) at a sampling station in the river Gironde near the city of Blaye (Gironde 2 in Fig. 2), suggesting that there might be local sources for OPEs in that area.

In all samples, the chlorinated tris(2-chloroethyl) phosphate (TCPP) was the dominating (highest concentrated and detection frequency) compound with a contribution to the sum of OPEs up to 70% (average 63%). The high contributions of TCPP were congruent with findings reported in other matrices from Europe (Malarvannan et al., 2015; Möller et al., 2011; Regnery and Püttmann, 2009; Wolschke et al., 2015, 2016). The second highest concentrated and prevalent compound was Tris(2-butoxyethyl) phosphate (TBEP) with an average contribution of 18%. However, compared to TCPP, TBEP showed a higher variability of contributions to sum OPEs in different rivers. In Elbe and Gironde TBEP had the highest contributions to the OPEs contamination pattern with up to 30%, whereas its contributions in the river Scheldt were lower (0–15%). The reason is not clear, and it can indicate a higher input of TBEP in this river catchments but a specific usage or production is not known in this area. Another OPE with river specific contamination pattern was Tri-cresly-phosphate (TCP) - in the rivers Elbe and Thames its contribution was comparably high with around 10% of total compared to the average contribution in other rivers of only 3%. These findings indicated that for many OPEs, the contamination patterns are location specific, forming an individual fingerprint.

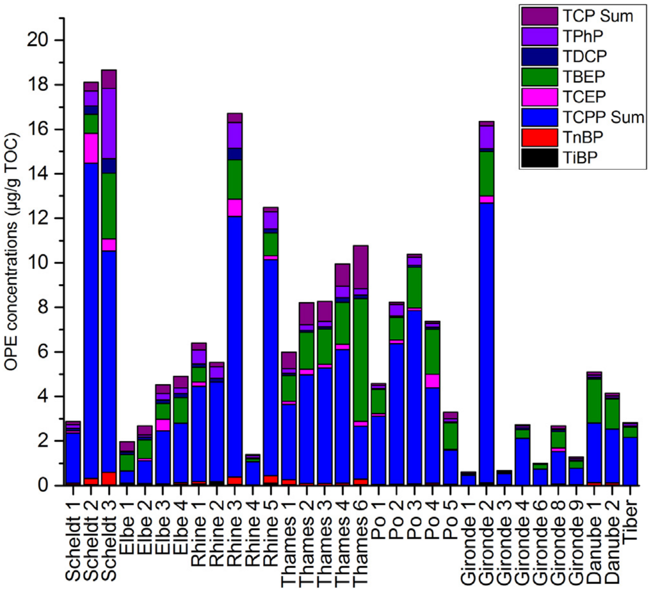

Fig. 2. Individual sediment concentrations along the estuaries in ng g^{-1} TOC dry weight.

To compare the contamination patterns from a use area (Europe) and a production area (China), five samples from the Xiaoquing River, Shandong, China were analyzed. The catchment area of the river encompasses industrial areas around the cities Weifang, Zibo and Jinan. The results of the estuare from Xiaoquing River are match able with investigations of the connected Bohai Sea published by Zhong et al., 2018, which implicate a representative set for the region.

The OPE patterns in the Xiaoquing were noticeably different compared to the patterns found in European rivers (Fig. 3). The major component was TCEP (46%), a component that is restricted in Europe (European Commission, 2014). Consequently, the contributions of TCEP in Europe are significantly lower ($p < 0.01$). At the same time, the major component in Europe, TCPP, only contributed around 20% to the OPE pattern in China (Fig. 3). TCPP is the main replacement for TCEP (World Health Organization, 1998). The differences in patterns between Europe and China highlight the effectiveness of restrictions of TCEP, but also the problem of “regrettable substitution”, since the overall use of OPEs has not declined but the pattern has merely shifted to other OPE components. An interesting similarity between the OPE patterns in China and Europe were the high contribution of TCP which were also

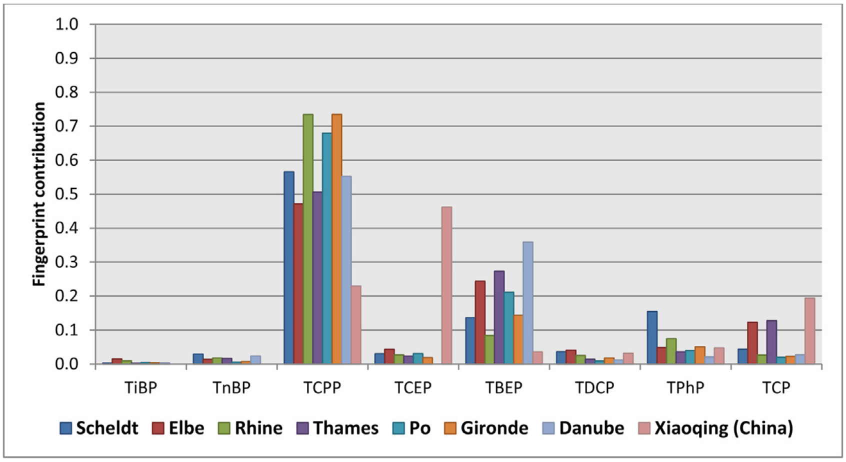

Fig. 3. Fingerprint of different estuaries/deltas.

Table 1
Pearson correlations of fingerprint analyses.

		Elbe	Rhine	Thames	Po	Gironde	Danube	Xiaoqing (China)
Scheldt	Pearson corr	**0.910**	**0.998**	**0.894**	**0.976**	**0.993**	**0.861**	**0.265**
	Sig.	1.67E-03	1.09E-08	2.71E-03	3.28E-05	6.38E-07	0.00596	0.524
Elbe	Pearson corr	**1**	**0.908**	**0.997**	**0.966**	**0.941**	**0.969**	**0.218**
	Sig.		1.78E-03	2.44E-08	8.77E-05	4.78E-04	6.74E-05	0.603
Rhine	Pearson corr		**1**	**0.892**	**0.976**	**0.995**	**0.859**	**0.244**
	Sig.			2.84E-03	3.39E-05	2.97E-07	0.00621	0.559
Thames	Pearson corr			**1**	**0.958**	**0.928**	**0.974**	**0.191**
	Sig.				1.74E-04	8.51E-04	3.98E-05	0.650
Po	Pearson corr				**1**	**0.992**	**0.948**	**0.221**
	Sig.					1.03E-06	3.33E-04	0.598
Gironde	Pearson corr					**1**	**0.905**	**0.229**
	Sig.						0.00198	0.585
Danube	Pearson corr						**1**	**0.089**
	Sig.							0.832

present in Elbe and Thames.

3.3. *Fingerprint analyses*

To analyze individual contamination “fingerprints” of the different estuaries, a method for the “Fingerprint Analysis of Contaminant Data” (Russell, 2004) by the United States Environmental Protection Agency (EPA) was used. The average concentrations [pg g^{-1} dw] of each river were used to determining the contribution to the sum contamination in the investigation area (i.e. specific estuary):

$$con_{xi}[\%] = \frac{c_{xi}\left[pg\, g^{-1}\, dw\right]}{\sum_{i=1}^{n} c_{xi}\left[pg\, g^{-1}\, dw\right]}$$

With

$con_x[\%]$: Contribution in % of compound $X_{i=1-n}$ to the sum concentration in the investigation area.

$c_{xi}[pg\, g^{-1}\, dw]$: Concentration of compound $X_{i=1-n}$ in pg g^{-1} dw.

$d\sum_{x=1}^{n} c_x[pg\, g^{-1}\, dw]$: Sum concentration of all compounds X in the investigation area in pg g^{-1} dw.

The resulting contribution of individual substances to the contamination pattern in an investigated area was then used to create a “fingerprint” of the contamination patterns in that area (Fig. 3). For comparison of the different investigation areas, the determined patterns were correlated with each other, using a Pearson correlation analyses (Table 1). As expected, the OPE patterns in European rivers were very similar with Pearson correlation coefficients between 0.86 and 0.99 (Table 1, Fig. 3). Particularly, the Scheldt and Rhine with a similar catchment and in parts water mixing were highly correlated ($r > 0.99$); but high correlations were also found for the Gironde in France and the Po in Italy ($r > 0.99$). The correlation of Po and Gironde are interesting, because of the different catchment areas the Po with highly industrialised areas and the large cities Turin and Milan in contrast to the rural area around Bordeaux. The other “group” was the Elbe estuary in Germany, the Thames in England and the Danube Rumania. These had highly intercorrelated patterns ($r > 0.99$), but were slightly less correlated with the Scheldt, Rhine, Gironde and Po patterns ($r < 0.97$) (Table 1).

The pattern in the Xiaoquing River as an example for China was significantly different from all analyzed European estuaries ($p < 0.01$) with correlation coefficients between 0.08 (Danube) and 0.27 (Scheldt) (Table 1). The different profile highlighted the differences between production and usage areas, as well as the differences in legislations. The presented study showed that a common market and harmonised regulations generates a comparable fingerprint of contamination and can effectively reduce contamination from specific hazardous compounds such as the chlorinated TCEP in a large area.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.01.061.

References

Bollmann, U.E., Möller, A., Xie, Z., Ebinghaus, R., Einax, J.W., 2012. Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. Water Res. 46 (2), 531–538.

Brandsma, S.H., Leonards, P.E.G., Leslie, H.A., de Boer, J., 2015. Tracing organophosphorus and brominated flame retardants and plasticizers in an estuarine food web. Sci. Total Environ. 505, 22–31.

Ernst, W., Boon, J., Weber, K., 1988. Occurrence and fate of organic micropollutants in the north sea. In: Salomons, W. (Ed.), Pollution of the North Sea. An Assessment. Springer-Verlag, Berlin, New York, pp. 285–299.

European Commission, 2014. Commission Directive 2014/79/EU.

Giulivo, M., Capri, E., Kalogianni, E., Milacic, R., Majone, B., Ferrari, F., Eljarrat, E., Barceló, D., 2017. Occurrence of halogenated and organophosphate flame retardants in sediment and fish samples from three European river basins. Sci. Total Environ. 586, 782–791.

Hartmann, P.C., Bürgi, D., Giger, W., 2004. Organophosphate flame retardants and plasticizers in indoor air. Chemosphere 57 (8), 781–787.

Kennish, M.J., 1992. Ecology of Estuaries: Anthropogenic Effects. CRC Press, Boca Raton, Ann Arbor, London, p. 494.

Laane, R., Vethaak, A., Gandrass, J., Vorkamp, K., Köhler, A., Larsen, M., Strand, J., 2013. Chemical contaminants in the Wadden Sea: sources, transport, fate and effects. J. Sea Res. 82, 10–53.

Malarvannan, G., Belpaire, C., Geeraerts, C., Eulaers, I., Neels, H., Covaci, A., 2015. Organophosphorus Flame Retardants in the European Eel in Flanders, Belgium: Occurrence, Fate and Human Health Risk. . (Accessed 29 February 2016).

Martin, J., Brun-Cottan, J., 1988. Estuaries. In: Salomons, W. (Ed.), Pollution of the North Sea. An Assessment. Springer-Verlag, Berlin, New York, pp. 88–99.

Möller, A., Xie, Z., Caba, A., Sturm, R., Ebinghaus, R., 2011. Organophosphorus flame retardants and plasticizers in the atmosphere of the North Sea. Environ. Pollut. 159 (12), 3660–3665.

Muir, D.C.G., 1984. Phosphate esters. In: Atlas, E., Fishbein, L., Giam, C.S., Leonard, J.E., Muir, D.C.G., Powers, M.A., Schoer, J. (Eds.), Anthropogenic Compounds. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 41–66.

Reemtsma, T., Quintana, J.B., Rodil, R., García-López, M., Rodríguez, I., 2008. Organophosphorus flame retardants and plasticizers in water and air I. Occurrence and fate. Trac. Trends Anal. Chem. 27 (9), 727–737.

Regnery, J., Püttmann, W., 2009. Organophosphorus flame retardants and plasticizers in rain and snow from Middle Germany. Clean. - Soil, Air, Water 37 (4–5), 334–342.

Russell, H. Plumb, 2004. Fingerprint Analysis of Contaminant Data: a Forensic Tool for Evaluating Environmental Contamination (Bibliogov).

Staaf, T., Östman, C., 2005. Organophosphate triesters in indoor environments. J. Environ. Monit. 7 (9), 883–887.

Sühring, R., Busch, F., Fricke, N., Kötke, D., Wolschke, H., Ebinghaus, R., 2016a. Distribution of brominated flame retardants and dechloranes between sediments and benthic fish — a comparison of a freshwater and marine habitat. Sci. Total Environ. 542, 578–585.

Sühring, R., Wolschke, H., Diamond, M.L., Jantunen, L., Scheringer, M., 2016b. Distribution of organophosphate ester flame retardants between gas- and particle phase – model predictions vs. measured data. Environ. Sci. Technol. 50 (13), 6644–6651.

van der Veen, I., Boer, J. de, 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere 88 (10), 1119–1153.

Waaijers, S.L., Parsons, J.R., 2016. Biodegradation of brominated and organophosphorus flame retardants. Curr. Opin. Biotechnol. 38, 14–23.

Wang, R., Tang, J., Xie, Z., Mi, W., Chen, Y., Wolschke, H., Tian, C., Pan, X., Luo, Y., Ebinghaus, R., 2015. Occurrence and spatial distribution of organophosphate ester flame retardants and plasticizers in 40 rivers draining into the Bohai Sea, north China. Environ. Pollut. 198, 172–178.

Wang, X., Liu, J., Yin, Y., 2010. The pollution status and research progress on organophosphate ester flame retardants. Prog. Chem. 22 (10), 1983–1992.

Wolschke, H., Sühring, R., Mi, W., Möller, A., Xie, Z., Ebinghaus, R., 2016. Atmospheric occurrence and fate of organophosphorus flame retardants and plasticizer at the German coast. Atmos. Environ. 137, 1–5.

Wolschke, H., Sühring, R., Xie, Z., Ebinghaus, R., 2015. Organophosphorus flame retardants and plasticizers in the aquatic environment: a case study of the Elbe River, Germany. Environ. Pollut. 206, 488–493.

World Health Organization, 1998. Flame Retardants: Tris(chloropropyl) Phosphate and Tris(2-chloroethyl) Phosphate. Environmental Health Criteria 209. World Health Organization, Geneva, p. 106 xix.

Zhang, X., Sühring, R., Serodio, D., Bonnell, M., Sundin, N., Diamond, M.L., 2016. Novel flame retardants: estimating the physical-chemical properties and environmental fate of 94 halogenated and organophosphate PBDE replacements. Chemosphere 144, 2401–2407.

Zhong, M., Wu, H., Mi, W., Li, F., Ji, C., Ebinghaus, R., Tang, J., Xie, Z., 2018. Occurrences and distribution characteristics of organophosphate ester flame retardants and plasticizers in the sediments of the Bohai and Yellow Seas, China. Sci. Total Environ. 615, 1305–1311. https://doi.org/10.1016/j.scitotenv.2017.09.272.

Supplementary Information

Regional variations of organophosphorus flame retardants - Fingerprint of large river basin estuaries/deltas in Europe compared with China

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S1: Sampling sites

Sample	Sampling Date	Latitude	Longitude	Location	TOC [%]
Elbe 1	17.09.2014	53°50.359	008°46.336	Mud Flat Cuxhaven	0,35
Elbe 2	17.09.2014	53°49.897	008°51.677	Near Otterndorf	0,30
Elbe 3	17.09.2014	53°50.150	009°18.740	Near Freiburg (Elbe)	0,87
Elbe 4	17.09.2014	53°35.440	009°34.891	Near Hollern - Twielenfleth	0,64
Danube 1	01.08.2013	45°27.471	28°15.707	DS Rheni	0,24
Danube 2	01.08.2013	45°11.67	28°57.56	Danube's river mouth	0,36
Gironde 1	03.09.2015	45°02,701	0°36.698		0,42
Gironde 2	03.09.2015	45°07,650’	0°42.172’		0,45
Gironde 3	03.09.2015	45°12.116	0°43.714		0,34
Gironde 4	07.09.2015	45°17.189	0°44.054		0,44
Gironde 6	04.09.2015	45°28.341’	0°53.052’		0,69
Gironde 8	05.09.2015	45°43.637	1°37.066		0,15
Gironde 9	04.09.2015	45°31.562	1°0.179		1,05
Po1	03.09.2013	44°98.460	11°97.490	Villanova Marchesana (RO)	0,90
Po2	02.09.2013	44°88.753	11°60.554	Pontelagoscuro	0,89
Po3	04.09.2013	44°92.925	12°13.865	Mesola(FE)	0,80
Po4	05.09.2013	44°85.499	12°30.402	Goro (FE)	0,30
Po5	06.09.2013	44°79.390	12°33.617	Bagnasciuga Zona Est	0,45
Rhine 1	24.02.2015	51°58.847	4°06.710	Hook van Holland Atlantic Wall Museum	0,22
Rhine 2	24.02.2015	51°54.75	4°15.41	Maasluis	0,06
Rhine 3	24.02.2015	51°53.521	4°35.64	Beverwaard, small branch	0,65
Rhine 4	24.02.2015	51°43.093	4°41.635	Lage Zwaluwe, Pontoon	2,59
Rhine 5	24.02.2015	51°46.383	4°11.49	New Zeeland Harbour, Pontoon	1,24
Scheldt 1	25.02.2015	51°23,848	3°52.071	Scheldt river mouth	1,30
Scheldt 2	25.02.2015	51°18.269	4°17.314	After Anvers	1,00
Scheldt 3	25.02.2015	51°11.731	4°20.527	Before Anvers	0,21
Tiber	17.10.2013	42°05'13.06''	12°36'07.05''	Ponte Grillo	0,78
Thames 1	22.11.2013	51,461	0,4391	East Tisbury	0,41
Thames 2	22.11.2013	51,4974	0,45579	Standfort le Hope	0,68
Thames 3	22.11.2013	51,46662	0,5566	Decoy Fleet	0,34
Thames 4	22.11.2013	51,4864	0,6405	Allhallows	0,43
Thames 5	22.11.2013	51,517	0,7503	Southend On the Sea	0,33
Thames 6	22.11.2013	51,51	0,54999	Southend On the Sea	0,08
Xiaoqing 1	20.04.2014	37,07085	117,9169		0,44
Xiaoqing 2	22.04.2014	37,24972	118,7191		0,10
Xiaoqing 3	23.04.2014	37,2785	118,8924		0,75
Xiaoqing 4	23.04.2014	37,29627	119,0558		0,69
Xiaoqing 5	23.04.2014	37,27602	118,9335		0,07

S2 Mass transitions GC-MSMS

	Quantifier			**Qualifier**		
Compound	Precurser Ion	Product Ion	CE (V)	Precurser Ion	Product Ion	CE (V)
dTnBP	*103*	*83*	*15*	*167*	*103*	*15*
dTCEP	*261*	*196*	*5*	*261*	*103*	*25*
dTPhP	*341*	*223*	*35*	*341*	*178*	*35*
INJ-PCB141	*372*	*302*	*40*			
INJ-PCB208	*476*	*406*	*40*			
TiBP	99	81	25	155	99	5
TnBP	99	81	35	155	99	5
TCEP	249	187	5	249	99	35
TCPP	277	125	5	157	117	5
TDCPP	381	159	15	191	75	5
TPhP	326	215	25	326	170	25
TBEP	299	199	5	227	101	5
TCP	368	198	30	368	165	30

S3: Individual concentration in pg/g dw

	TiBP	TnBP	TCPP *	TCEP	TBEP	TDCP	TPhP	TCP *
Scheldt 1	478	855	29230	1305	0	1605	2073	1706
Scheldt 2	291	2848	141549	13417	8576	3826	6597	3916
Scheldt 3	50	1197	20890	1168	6188	1383	6648	1709
Elbe 1	208	169	1962	0	2520	420	183	1438
Elbe 2	167	123	3072	259	2545	369	277	1274
Elbe 3	354	348	20757	4593	6217	1399	2444	3412
Elbe 4	384	418	17253	0	7439	1125	1668	3276
Rhine 1	174	213	9610	422	1482	335	1421	663
Rhine 2	102	0	2681	0	0	97	315	110
Rhine 3	260	2143	75555	5051	11449	3420	7393	2635
Rhine 4	181	215	27181	0	3606	926	3017	893
Rhine 5	1298	4149	120031	2261	12640	2361	9353	2585
Thames 1	110	938	13912	545	4732	377	947	2985
Thames 2	71	552	33195	1814	11230	548	1763	6648
Thames 3	38	280	17631	568	5421	306	819	3043
Thames 4	75	357	25870	1022	8064	840	2271	4309
Thames 6	25	197	1914	168	4415	124	234	1542
Po 1	180	177	27606	1058	9844	348	1296	715
Po 2	229	275	56283	1434	8944	550	4673	805
Po 3	290	357	62196	951	14687	689	2847	1055
Po 4	95	212	12882	1817	6084	240	538	254
Po 5	139	116	6938	168	5325	186	648	1287
Gironde 1	0	60	1895	0	0	283	82	262
Gironde 2	229	275	56283	1434	8944	550	4673	805
Gironde 3	34	63	1720	0	0	191	63	224
Gironde 4	0	0	9317	0	1719	335	360	248
Gironde 6	0	93	5096	0	1352	136	70	154
Gironde 8	32	71	2170	241	1078	115	73	196
Gironde 9	95	261	7865	0	3383	383	721	679
Danube 2	34	283	6442	0	4731	159	252	319
Danube 1	58	375	8711	0	4838	162	331	440
Tiber	0	0	16868	0	3654	427	816	278
Xiaoqing 1	0	0	3757	39664	1799	2148	2236	3542
Xiaoqing 2	0	0	311	2274	732	487	463	2031
Xiaoqing 3	0	0	15836	15621	2003	1308	2392	17715
Xiaoqing 4	0	0	16873	13890	888	1038	2339	7150
Xiaoqing 5	0	0	40	2662	338	145	168	627

*Sum of Isomeres

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Sprachkenntnisse:

Deutsch	Muttersprache
Englisch	Fließend in Wort und Schrift (C1)

List of publications

Included in this thesis

Wolschke, H., Sühring, R., Massei, R., Tang, J., Ebinghaus, R. Regional variations of organophosphorus flame retardants - Fingerprint of large river basin estuaries/deltas in Europe compared with China. Environmental Pollution (*under review*).

Wolschke, H., Sühring, R., Mi, W., Möller, A., Xie, Z., Ebinghaus, R., 2016. Atmospheric occurrence and fate of organophosphorus flame retardants and plasticizer at the German coast. Atmospheric Environment 137, 1–5.

Sühring, R., **Wolschke, H**., Diamond, M.L., Jantunen, L.M., Scheringer, M., 2016. Distribution of Organophosphate Esters between the Gas and Particle Phase–Model Predictions vs Measured Data. Environ. Sci. Technol. 50 (13), 6644–6651.

Wolschke, H., Sühring, R., Xie, Z., Ebinghaus, R., 2015. Organophosphorus flame retardants and plasticizers in the aquatic environment: A case study of the Elbe River, Germany. Environmental Pollution 206, 488–493.

Wang, R., Tang, J., Xie, Z., Mi, W., Chen, Y., **Wolschke, H**., Tian, C., Pan, X., Luo, Y., Ebinghaus, R., 2015. Occurrence and spatial distribution of organophosphate ester flame retardants and plasticizers in 40 rivers draining into the Bohai Sea, north China. Environmental Pollution 198, 172–178.

Further publications

Massei, R., Busch, W., **Wolschke, H**., Schinkel, L., Bitsch, M., Schulze, T., Krauss, M., Brack, W. CHARACTERIZATION OF PESTICIDE PATTERNS AND RISK DRIVERS IN SEDIMENTS OF EUROPEAN RIVER BASINS: EUROPEAN WIDE OR RIVER BASIN SPECIFIC CONTAMINATION?". Environ. Sci. Technol. (*under review*).

Freese, M., Sühring, R., Marohn, L., Pohlmann, J.-D**., Wolschke, H.**, Byer, J.D., Alaee, M., Ebinghaus, R., Hanel, R., 2017. Maternal transfer of dioxin-like compounds in artificially matured European eels. Environmental Pollution 227, 348–356.

Chen, W.-L., Xie, Z., **Wolschke, H**., Gandrass, J., Kötke, D., Winkelmann, M., Ebinghaus, R., 2016. Quantitative determination of ultra-trace carbazoles in sediments in the coastal environment. Chemosphere 150, 586–595.

Freese, M., Sühring, R., Pohlmann, J.-D., **Wolschke, H**., Magath, V., Ebinghaus, R., Hanel, R., 2016. A question of origin: dioxin-like PCBs and their relevance in stock management of European eels. Ecotoxicology 25 (1), 41–55.

Sühring, R., Busch, F., Fricke, N., Kötke, D., **Wolschke, H**., Ebinghaus, R., 2016. Distribution of brominated flame retardants and dechloranes between sediments and benthic fish — A comparison of a freshwater and marine habitat. Science of the Total Environment 542, 578–585.

Wolschke, H., Meng, X.-Z., Xie, Z., Ebinghaus, R., Cai, M., 2015. Novel flame retardants (N-FRs), polybrominated diphenyl ethers (PBDEs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in fish, penguin, and skua from King George Island, Antarctica. Marine Pollution Bulletin 96 (1-2), 513–518.

Sühring, R., Barber, J.L., **Wolschke, H**., Kötke, D., Ebinghaus, R., 2015. Fingerprint analysis of brominated flame retardants and Dechloranes in North Sea sediments. Environmental Research 140, 569–578.

Sühring, R., Freese, M., Schneider, M., Schubert, S., Pohlmann, J.-D., Alaee, M., **Wolschke, H**., Hanel, R., Ebinghaus, R., Marohn, L., 2015. Maternal transfer of emerging brominated and chlorinated flame retardants in European eels. Science of the Total Environment 530-531, 209–218.

Wang, Z., Xie, Z., Mi, W., Möller, A., **Wolschke, H**., Ebinghaus, R., 2015. Neutral Poly/Per-Fluoroalkyl Substances in Air from the Atlantic to the Southern Ocean and in Antarctic Snow. Environ. Sci. Technol. 49 (13), 7770–7775.

Wang, Z., Xie, Z., Möller, A., Mi, W., **Wolschke, H**., Ebinghaus, R., 2015. Estimating dry deposition and gas/particle partition coefficients of neutral poly-/perfluoroalkyl substances in northern German coast. Environmental Pollution 202, 120–125.

Xie, Z., Wang, Z., Mi, W., Möller, A**., Wolschke, H**., Ebinghaus, R., 2015. Neutral Poly-/perfluoroalkyl Substances in Air and Snow from the Arctic. Sci. Rep. 5, 8912.

Sühring, R., Byer, J., Freese, M., Pohlmann, J.-D., **Wolschke, H**., Möller, A., Hodson, P.V., Alaee, M., Hanel, R., Ebinghaus, R., 2014. Brominated flame retardants and Dechloranes in European and American eels from glass to silver life stages. Chemosphere 116, 104–111.

Trautwein, C., Berset, J.-D., **Wolschke, H**., Kümmerer, K., 2014. Occurrence of the antidiabetic drug Metformin and its ultimate transformation product Guanylurea in several compartments of the aquatic cycle. Environment International 70, 203–212.

Wang, Z., Xie, Z., Möller, A., Mi, W., **Wolschke, H**., Ebinghaus, R., 2014. Atmospheric concentrations and gas/particle partitioning of neutral poly- and perfluoroalkyl substances in northern German coast. Atmospheric Environment 95, 207–213.

Sühring, R., Möller, A., Freese, M., Pohlmann, J.-D., **Wolschke, H**., Sturm, R., Xie, Z., Hanel, R., Ebinghaus, R., 2013. Brominated flame retardants and dechloranes in eels from German Rivers. Chemosphere 90 (1), 118–124.

Xie, Z., Zhao, Z., Möller, A., **Wolschke, H.**, Ahrens, L., Sturm, R., Ebinghaus, R., 2013. Neutral poly- and perfluoroalkyl substances in air and seawater of the North Sea. Environ Sci Pollut Res 20 (11), 7988–8000.

Sheppard, C.R.C., Ateweberhan, M., Bowen, B.W., Carr, P., Chen, C.A., Clubbe, C., Craig, M.T., Ebinghaus, R., Eble, J., Fitzsimmons, N., Gaither, M.R., Gan, C.-H., Gollock, M., Guzman, N., Graham, N.A.J., Harris, A., Jones, R., Keshavmurthy, S., Koldewey, H., Lundin, C.G., Mortimer, J.A., Obura, D., Pfeiffer, M., Price, A.R.G., Purkis, S., Raines, P., Readman, J.W., Riegl, B., Rogers, A., Schleyer, M., Seaward, M.R.D., Sheppard, A.L.S., Tamelander, J., Turner, J.R., Visram, S., Vogler, C., Vogt, S., **Wolschke, H**., Yang, J.M.-C., Yang, S.-Y., Yesson, C., 2012. Reefs and islands of the Chagos Archipelago, Indian Ocean: why it is the world's largest no-take marine protected area. Aquatic Conserv: Mar. Freshw. Ecosyst. 22 (2), 232–261.

Wolschke, H., Xie, Z., Möller, A., Sturm, R., Ebinghaus, R., 2011. Occurrence, distribution and fluxes of benzotriazoles along the German large river basins into the North Sea. Water Research 45 (18), 6259–6266.

Book chapters

Readman, J.W., DeLuna, F., Ebinghaus, R., Guzman, A., Price, A.R.G., Readman, E.E., Sheppard, A.L.S., Sleight, V.A., Sturm, R., Thompson, R.C., Tonkin, A., **Wolschke, H**., Wright, R.J., Sheppard, C.R.C., 2013. Contaminants, Pollution and Potential Anthropogenic Impacts in Chagos/BIOT, in: Sheppard, C. (Ed.), Coral reefs of the United Kingdom Overseas Territories, vol. 4. Coral reefs of the world 4. Springer, Dordrecht, New York, pp. 283–298.

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https://scholar.google.de/citations?user=fBTpB0QAAAAJ&hl=de