

Final Draft
of the original manuscript:

Bollmann, U.E.; Moeller, A.; Xie, Z.; Ebinghaus, R.; Einax, J.W.:
**Occurrence and Fate of Organophosphorus Flame Retardants
and Plasticizers in Coastal and Marine Surface Waters**
In: Water Research (2011) Elsevier

DOI: 10.1016/j.watres.2011.11.028

1 **Occurrence and Fate of Organophosphorus Flame**
2 **Retardants and Plasticizers in Coastal and Marine**
3 **Surface Waters**

4
5 Ulla E. Bollmann^{a,b,1}, Axel Möller^{a,*}, Zhiyong Xie^a, Ralf Ebinghaus^a, and Jürgen W. Einax^b

6 ^a Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, Department for Environmental
7 Chemistry, Max-Planck-Straße 1, 21502 Geesthacht, Germany

8 ^b Friedrich-Schiller-University of Jena, Institute for Inorganic and Analytical Chemistry, Lessingstraße 8,
9 07743 Jena, Germany

10 * Corresponding author: telephone: +49 4152 872353, e-mail: axel.moeller@hzg.de

11 ¹ Present address: Aarhus University, Department for Environmental Science, Frederiksborgvej 399,
12 4000 Roskilde, Denmark; telephone: +45 871 58462, e-mail: ueb@dmu.dk

Abstract

This comprehensive study focused on the spatial and seasonal variation of organophosphorus flame retardants and plasticizers (OPs) in surface water from the estuary of the River Elbe and the German Bight (North Sea). 100 surface water samples were extracted by solid phase extraction (SPE) and analyzed by gas chromatography-mass spectrometry (GC-MS) with regard to 16 different OPs. The dominating substance was found to be tris(1-chloro-2-propyl) phosphate (TCPP) (Elbe: 40 – 250 ng L⁻¹, German Bight: 3 – 28 ng L⁻¹). Furthermore, triethyl phosphate (TEP), tri-*iso*-butyl phosphate (TiBP), tris(2-butoxyethyl) phosphate (TBEP), and triphenylphosphine oxide (TPPO) were detected in concentrations up to 180 ng L⁻¹. Seasonal trends were detected for the longitudinal profile of the Elbe estuary. Besides the dilution of river water with North Sea water towards the mouth, leading to decreasing concentrations at the four sampling cruises (March, May, August, and October, 2010), an additional depletion of non-halogenated OPs was observed in summer which is supposed to be due to biodegradation or photodegradation.

In addition, a comparison of all important tributaries of the German Bight (Elbe, Ems, and Weser) as well as the indirect tributaries Meuse, Rhine, and Scheldt was done by multivariate statistical methods. It could be shown that the contribution of non-halogenated alkylated OPs in the Rhine was higher than in all other tributaries. The riverine input of OPs into the North Sea via the investigated tributaries was estimated to be about 50 t yr⁻¹.

Keywords: TCPP; TCEP; River; Estuary; North Sea; Seasonal variations

33 **1 Introduction**

34 Flame retardants and plasticizers based on organophosphorus acid esters (OPs) are a widely-used
35 substance group. Varying alkyl- and aryl-ester groups, some of them halogenated, lead to a large variation
36 of their physico-chemical properties – ranging from very polar and volatile (e.g. trimethyl phosphate) to
37 non-polar and non-volatile (e.g. tri(ethylhexyl) phosphate) (Reemtsma et al., 2008; SRC PhysProp
38 Database, 2010). This makes them useful for various different applications from flame retardants in
39 polyurethane foam (especially the halogenated OPs) and plasticizers in flexible PVC (primarily non-
40 halogenated OPs) to some minor applications as additives in computer housings or hydraulic fluids. A
41 good overview of the usage of different OPs is given by Marklund et al. (2003).

42 The worldwide usage of OPs was 207,200 t in 2004 (EFRA, 2010) and especially due to the replacement
43 of the banned polybrominated diphenylethers (PBDEs) by OPs an increasing trend can be noticed
44 (Stapleton et al., 2009). Already in the late 1970s first studies on the occurrence and fate of OPs in the
45 aquatic environment were published (Sheldon and Hites, 1978; Saeger et al., 1979). Due to the fact that
46 the emissions into the environment are still increasing, the OPs can be classified as “re-emerging
47 pollutants” (Reemtsma et al., 2008).

48 Since OPs are not chemically bonded to the polymeric materials, they can undergo diffusion processes
49 and be emitted into the environment. By the reason of the large variation in physical-chemical properties,
50 OPs can be transported in different environmental media and have been detected in various environmental
51 compartments. High concentrations up to a few $\mu\text{g m}^{-3}$ were detected in indoor environments (Tollbäck et
52 al., 2010) whereas in outdoor air concentrations of a few ng m^{-3} were measured (Saito et al., 2007; Möller
53 et al., 2011). Surface water concentrations ranged between a few ng L^{-1} up to a few hundred ng L^{-1}
54 (Andresen et al., 2004; Regnery and Püttmann, 2010). Especially the halogenated OPs are supposed to be
55 highly persistent in the environment and only slightly biodegradable. Due to this they are insufficient
56 degraded in sewage treatment plants and enter the aquatic environment (Andresen et al., 2004; Marklund
57 et al., 2005). Several OPs are known to be toxic (e.g. neurotoxic or carcinogen) and additionally, the
58 lipophilic OPs have the potential to bioaccumulate (Reemtsma et al., 2008).

59 This is the first comprehensive study of organophosphorus acid triesters (OPs) in the estuaries of all
60 important tributaries of the German Bight (North Sea), i.e. the rivers Elbe, Weser, and Ems, as well as the
61 indirect tributaries Meuse, Rhine and Scheldt, and the German Bight (North Sea) itself. Within this
62 sampling region, OPs were analyzed in order to determine possible seasonal trends, and to compare the
63 substance patterns of the different tributaries using multivariate statistical methods. Finally, the riverine
64 input of OPs into the German Bight (North Sea) was estimated. This study covered 16 different OPs;
65 thereunder three chlorinated alkyl phosphates (tris(2-chloroethyl) phosphate, TCEP; tris(1-chloro-2-
66 propyl) phosphate, TCPP; tris(dichloroisopropyl) phosphate, TDCPP), ten non-halogenated alkyl
67 phosphates (trimethyl phosphate, TMP; triethyl phosphate, TEP; tri-*n*-propyl phosphate, TPrP; tri-*iso*-
68 propyl phosphate, TiPrP; tri-*n*-butyl phosphate, TBP; tri-*iso*-butyl phosphate, TiBP; tripentyl phosphate,
69 TPeP; trihexyl phosphate, THP, tris(2-ethylhexyl) phosphate, TEHP; tris(2-butoxyethyl) phosphate,
70 TBEP), two aryl phosphates (triphenyl phosphate, TPhP; tricresyl phosphate, TCP), and also the synthetic
71 intermediate triphenyl phosphine oxide (TPPO). A list of the OPs analyzed in this study with their
72 chemical structures, applications, and physico-chemical properties is given in Table S1 of the
73 supplementary material.

74 **2 Material and Methods**

75 **2.1 Chemicals**

76 Information on CAS-No., producers, and purities of the used OP standards are listed in Table S3 in the
77 supplementary material. SERDOLITH[®] PAD 2 and 3 (analytical grade) were purchased by Serva (Germany)
78 and mineral water was from Bismarck-spring (Germany). All solvents were of highest purity (picograde)
79 and obtained from Promochem (Germany). Sodium sulphate (granular, anhydrous for organic trace
80 analysis) and hydrochloric acid (suprapur[®], 30 %) were purchased from Merck (Germany).

81 **2.2 Sampling area and sampling**



82
83 Figure 1

84 Sampling area and sampling stations.

85

86 The sampling area (Figure 1) is located in the south eastern part of the North Sea, called the German
87 Bight, with the estuaries of its tributaries. On the one hand the North Sea has the largest intertidal
88 mudflats in the world and on the other hand it is highly anthropogenic influenced by fishery, shipping and
89 recreational activities. The German Bight is heavily influenced by the Elbe plume and in lower quantities
90 by the Weser and Ems. In addition the diluted plume of the Rhine-Meuse-Scheldt-Delta enters the
91 German Bight due to an easterly coastline flow.

92 1 L surface water samples were taken from the shores of the rivers Elbe, Weser, Ems, Rhine, Meuse, and
93 Scheldt in August 2010. In addition samples from the estuary of the Elbe were taken during four
94 expeditions with the German research vessel R/V LUDWIG PRANDTL. They were performed in March,
95 May, August, and October 2010. The samples from the German Bight were taken during three
96 expeditions with the German research vessel R/V HEINCKE in March, July, and September 2010. River
97 water samples were immediately filtered (glass fiber filter, Whatman GF/C) and acidified with
98 concentrated HCl for conservation. All samples were stored at 4 °C until further analytical procedure
99 (storage time max. five months).

2.3 Analytical Procedure

The analytical process was performed in a Varipro[®] cleanroom (class 10000, Daldrop + Dr. Ing. Huber, Neckartaltingen, Germany). Throughout the whole analytical procedure no plastic lab ware was used in order to reduce blanks.

500 mL (estuary) and 1000 mL (North Sea) surface water were spiked with 30 ng surrogates (TMP-d9, TEP-d15, TPrP-d21, TBP-d27, TPhP-d15), respectively, and extracted by solid phase extraction (SPE) with 3 g SERDOLITH[®] PAD 3 (cleaned with acetone, Soxhlet, 4 h) as adsorption material. The SPE-material was conditioned by 5 mL acetone and 10 mL pre-cleaned mineral water (cleaned by rinsing over 25 g SERDOLITH[®] PAD 2) and washed with 5 mL pre-cleaned mineral water after sample loading. Before elution with 50 mL dichloromethane the cartridges were dried by centrifugation (3000 rpm, 5 min). The extracts were reduced by rotary evaporation to 5 – 10 mL. Afterwards, the water was frozen out over night at -18 °C and residual water was removed by rinsing over Na₂SO₄. During further reduction in a constant nitrogen flow to 150 µL the solvent was changed to *n*-hexane. Finally, 200 pg ¹³C-hexachlorobenzene was added as injection standard.

Analysis was done by an Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC-MS). The injection was done by a PTV injector in 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⁻¹ to 300 °C. The injection volume was 1 µL and the helium carrier gas flow was 1.3 mL min⁻¹. The GC was equipped with an HP-5MS column (30 m × 0.25 mm i.d. × 0.25 µm film thickness, J&W Scientific) and the oven temperature was 40 °C for 4 min, afterwards increased by 5 °C min⁻¹ to 170 °C (5 min), 10 °C min⁻¹ to 230 °C (5 min), 5 °C min⁻¹ to 250 °C, then 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 operated in selected ion monitoring (SIM) mode. Masses for the detection of OPs and IS are included in Table S1 and S2 in the supplementary material, respectively.

2.4 Quality assurance

Recovery tests (500 mL pre-cleaned mineral water spiked to 60 ng L⁻¹ of each OP) showed absolute recoveries between 30 (TMP) and 105 % (TPhP). Surrogates were used to compensate losses during the

127 extraction process, hence, all concentrations were corrected by the recovery of the corresponding
128 surrogate (see Table S4 in suppl. mat.). Relative recoveries ranged between 82 (TPPO) and 118 %
129 (TiBP). In some tests sodium chloride (to adjust a salinity of 30 PSU) and hydrochloride acid (to adjust
130 pH 1) were added to confirm the robustness of the method within the present sample conditions.

131 The limits of detection (LODs), calculated at a signal-to-noise (S/N) ratio of 3, ranged between 0.1 and
132 3.9 ng L⁻¹ and limits of quantification (LOQs), calculated at a S/N ratio of 9, ranged between 0.2 and
133 11.7 ng L⁻¹. Method blanks were detected for TiBP, TPhP, TEHP, and TPPO ranging from 0.2 to
134 1.8 ng L⁻¹. Based on this the LODs and LOQs are calculated for these four substances using blank
135 standard deviation method. Recoveries (Table S4), LODs and LOQs (Table S5) for all analytes are given
136 in the supplementary material.

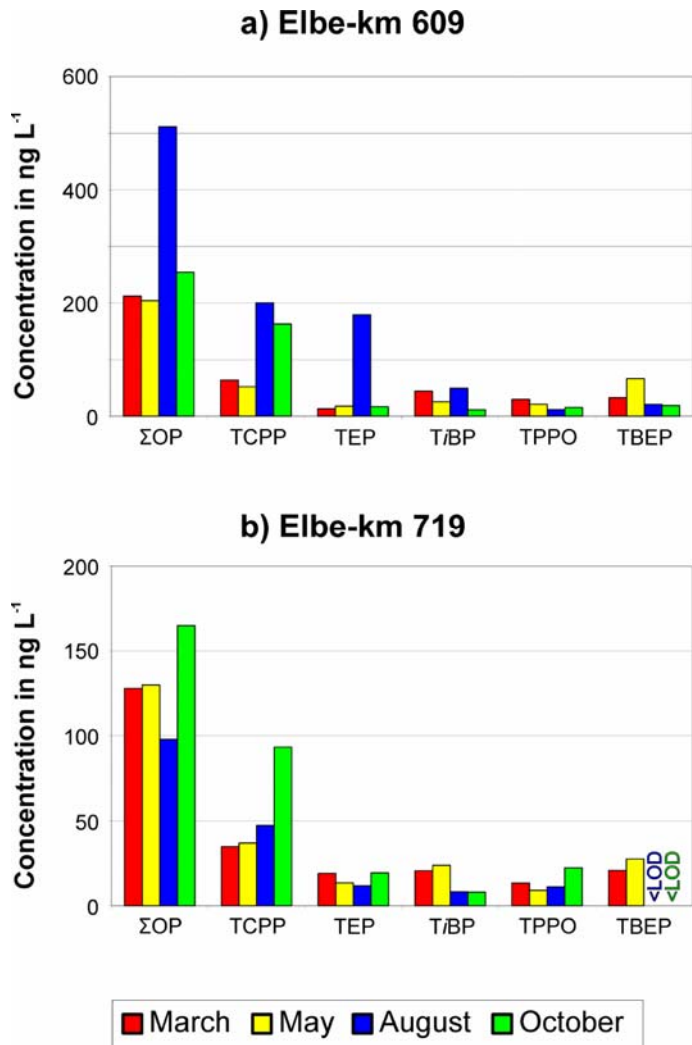
137 2.5 Data treatment

138 The chromatographic evaluation was done by use of *Agilent MSD ChemStation*. Further data treatment
139 was performed with *Microsoft® Office Excel 2003* and *Statistica 6*.

140 3 Results and Discussion

141 3.1 Riverine and marine concentrations

142 In the estuary of the River Elbe up to 11 out of 16 analyzed OPs were detected in the dissolved phase.
143 Most abundant OP in all samples was TCPP with individual concentrations from 40 to 250 ng L⁻¹.
144 Furthermore, TEP (10 – 180 ng L⁻¹), TiBP (10 – 50 ng L⁻¹), TPPO (10 – 40 ng L⁻¹), and TBEP (<LOD –
145 80 ng L⁻¹) were identified as major OPs. Upstream of the city of Hamburg a total OP concentration of
146 about 500 ng L⁻¹ was observed in August; in March, May, and October it was 200 – 250 ng L⁻¹. At the
147 mouth (Elbe-km 724) the total OP concentration ranged between 80 and 150 ng L⁻¹ (Figure 2 and
148 Table S6 in suppl. material).



149

150 Figure 2

151 Total measured OP concentration (Σ OP) and concentrations of selected OPs at the beginning of the
 152 estuary (a, Elbe-km 609) and the mouth of the river Elbe (b, Elbe-km 719) in 2010 in ng L^{-1} .

153

154 The concentrations in the different tributaries are equivalent to those in the estuary of the Elbe. In the
 155 non-tidal influenced part of the river the total OP concentration ranged between 400 and 550 ng L^{-1} . Only
 156 in the River Scheldt total OP concentrations up to 1092 ng L^{-1} were detected. Individual concentrations
 157 ranged from a few ng L^{-1} up to 570 ng L^{-1} (Table 1). The dominating OP in all tributaries was TCPP (44 –
 158 570 ng L^{-1}). Otherwise some differences in substance patterns were noticeable and, therefore, analyzed
 159 with multivariate statistical methods (see paragraph 3.3).

160

161

162

163 **Table 1:** Total (Σ OP) and individual concentrations in ng L^{-1} and total loadings (Σ OP-load) in t yr^{-1} in the
 164 analyzed tributaries of the North Sea in August, 2010.

River	Station	Σ OP	TCPP	TCEP	TDCPP	TEP	TiBP	TBEP	alk OP ¹	TPhP	TPPO	Σ OP-load ²
		in ng L^{-1}	in ng L^{-1}	in ng L^{-1}	in ng L^{-1}	in ng L^{-1}	in ng L^{-1}	in ng L^{-1}	in ng L^{-1}	in ng L^{-1}	in ng L^{-1}	in t yr^{-1}
Elbe	E1	435	134	35.5	30.8	22.3	19.2	94.3	7.4	10.3	80.7	8.1
	E2	249	84.3	9.25	10.9	33.9	15.4	24.2	3.5	<LOQ	65.2	5.0
	E3	96.9	44.0	4.93	6.4	6.99	4.31	<LOD	1.4	3.8	25.2	2.1
Weser	W1	386	167	34.0	26.6	13.2	13.2	48.4	5.5	<LOQ	77.2	1.6
	W2	58.3	24.3	3.29	5.3	5.16	<LOQ	<LOD	1.7	<LOD	15.1	0.3
Ems	Em1	397	175	34.2	35.3	49.2	11.1	42.7	7.7	<LOD	42.1	0.4
	Em2	222	89.8	11.5	8.0	27.9	4.81	38.9	2.8	<LOD	38.0	n.a.
Rhine	R1	360	79.2	12.6	14.3	55.1	84.0	30.3	9.5	<LOQ	73.7	23
	R2	326	74.8	12.4	13.2	37.2	78.6	32.6	9.4	<LOQ	65.6	n.a.
	R3	466	139	22.0	30.6	52.2	80.6	53.9	20.4	<LOQ	64.8	4.9
	R4	375	159	25.8	20.5	29.7	16.8	38.7	38.7	<LOQ	43.6	1.0
	R5	586	115	18.4	18.6	82.7	78.2	51.7	37.8	<LOQ	183	23
	R6	485	122	14.9	15.7	55.0	68.7	28.5	44.8	<LOQ	133	10
Meuse	M1	542	196	38.4	37.3	48.6	20.7	103	15.3	3.6	79.6	n.a.
Scheldt	S1	1092	570	69.9	67.0	84.5	5.27	72.0	36.6	<LOQ	185	n.a.
	S2	355	164	19.0	19.2	67.7	5.04	<LOD	7.3	<LOD	71.5	n.a.

¹TMP, TiPrP, TBP, TEHP ²calculated by daily mean water discharge of specific sampling day

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

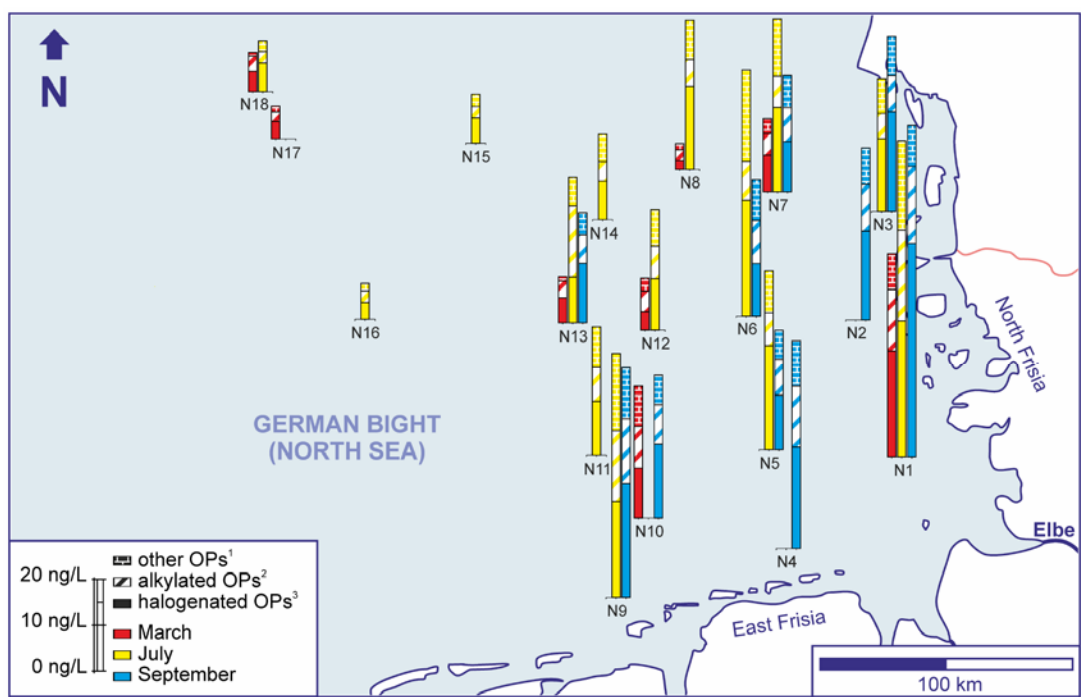
165

166 The concentrations in all investigated rivers in this study are comparable to those in former studies
 167 (Table 2). Comparing the results for the Elbe to the concentrations measured by Andresen et al. (2007)
 168 and by the ARGE Elbe (2000) the levels for all substances are nearly similar. Indeed, the concentration of
 169 TCEP was slightly higher in the 1990's (ARGE Elbe, 2000). This is assumedly due to the consumption
 170 decrease of TCEP since 1989 (WHO, 1998). Fries and Püttmann (2001) observed TCEP in a
 171 concentration in the Upper Rhine similar to the Delta concentration in the present study. In contrast, the
 172 concentrations of the non-halogenated OPs TBP and TBEP are ten times higher in the Upper Rhine which
 173 is probably caused by production sites located at the Rhine and can be a reason for the different substance
 174 pattern, which will be discussed later (paragraph 3.3). The high consumption decrease in TCEP since
 175 1989 is also noticeable in the Rhine: Knepper et al. (1999) detected up to 500 ng L^{-1} in 1994, whereas in
 176 the later studies it decreased to less than 25 ng L^{-1} .

River	Location (Country)	TCP	TEP	TiBP	TBP	TBEP	TPhP	Ref.
Elbe	Hamburg – Cuxhaven (D)	40 – 250	5 – 20	10 – 50	2 – 7.5	<LOD – 80	0.3 – 4	This study
	Magdeburg – Hamburg (D)	200	60					ARGE Elbe, 2000
	Dresden / Hamburg		<LOD / 17		789 / 399	494 / 103		Fries and Püttmann, 2001
	Stade (D)	90	22		19	23	3.1	Andresen et al., 2007
Rhine	Delta (NL)	75 – 160	12 – 25	17 – 84	6 – 28	28 – 54	1 – 2	This study
	Rüsselsheim (D)		24		218	321		Fries and Püttmann, 2001
	Colone (D)	30 – 150	50 – 500					Knepper et al., 1999
Ruhr	Spring – Mouth (D)	20 – 200	13 – 130			< 40	10 – 200	Andresen et al., 2004
Streams	Hesse (D)	502	118		276	183		Quednow and Püttmann, 2008
Danube	Vienna (A)	33 – 43	13 – 23		20 – 110	24 – 52	<LOQ – 6	Martinez-Carballo et al., 2007
Tiber	Rome (I)	54 – 117	<LOD – 7	98 – 137	82 – 114	87 – 323	11 – 165	Bacaloni et al., 2007
Streams	Arkansas (USA)		48 - 700		31 - 560			Haggard et al., 2006

178

179 The total OP concentration in the German Bight (North Sea) ranged from 5 to 50 ng L⁻¹. Similar to the
 180 estuary of the River Elbe, the major OPs were TCP (3 – 28 ng L⁻¹), TEP (0.7 – 7 ng L⁻¹), TiBP (0.5 –
 181 5 ng L⁻¹), TBEP (<LOD – 6 ng L⁻¹) and TPPO (<LOD – 12 ng L⁻¹). The highest concentrations were
 182 detected in the Elbe plume (sample point N1). A high negative correlation (r = -0.94, July) between
 183 salinity and total OP concentration was noticed which led to decreasing concentrations towards the open
 184 sea (Figure 3).



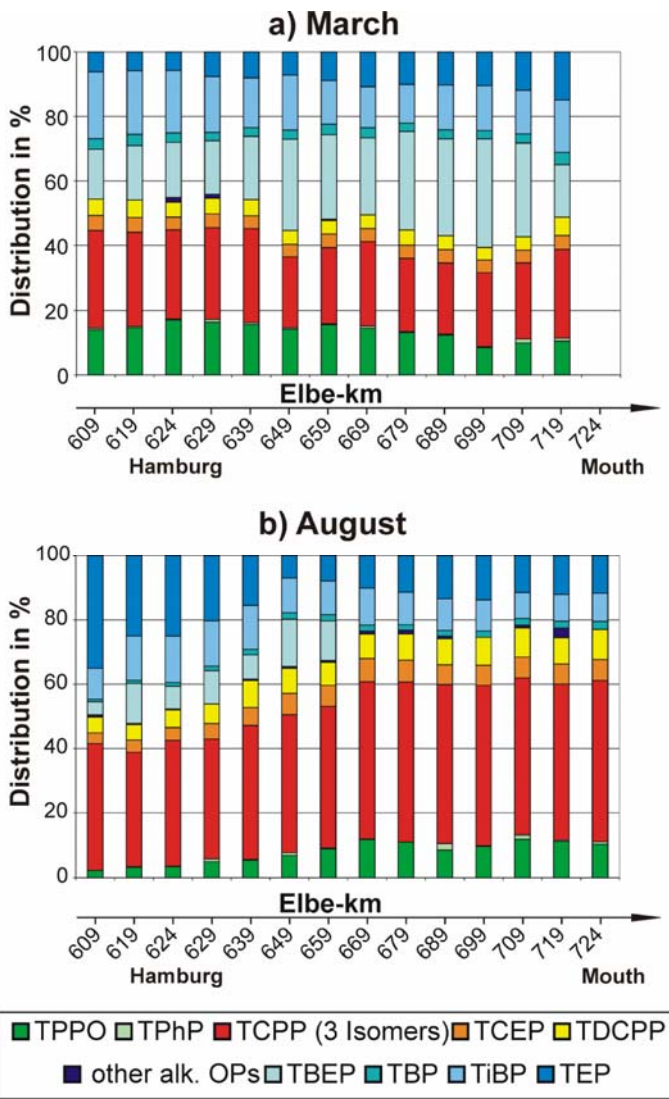
185 ¹ TPhP, TPPO ² TEP, TiBP, TBP, TBEP, TEHP ³ TCP, TCEP, TDCPP

186 Figure 3

187 OP concentrations in the German Bight (North Sea) in ng L^{-1} in March, July, and September, 2010 (no
188 column = not analyzed).

189 3.2 Spatial and seasonal variations

190 To obtain a better comparison of the OP-concentrations along the River Elbe regarding the four different
191 sampling months, the OP-load was calculated as the product of the OP-concentration and the water
192 discharge, estimated for the sampling stations from the daily mean discharge data at the water gauge
193 measuring station in Neu-Darchau. Upstream of Hamburg the total OP loading ranged between 0.1 and
194 0.5 g s^{-1} . Besides two slightly higher loadings at Elbe-km 639 and 649 in October the loading is nearly
195 constant until Elbe-km 689 (near Brunsbüttel) in March, May and October. With increasing salinity
196 towards the mouth a decreasing trend in the OP loading was observed downstream from Elbe-km 689. In
197 contrast, in August the total OP concentration decreased over the entire estuary.



198

199 Figure 4

200 Distribution of the OP-concentrations in the Elbe-estuary in March (a) and August (b) 2010 (blue: non-
201 halogenated alkylated OPs, yellow-red: halogenated OPs).

202 As shown in Figure 4, also the substance pattern changed in August along the entire Elbe estuary while it
203 was similar for the three other campaigns. Especially the contribution of non-halogenated alkylated OPs
204 decreased towards the mouth in August. In March and May the non-halogenated OPs predominated
205 (50 %) whereas in August and October the contribution of halogenated was higher (70 %).

206 Similar to the river Elbe, changes in the percentages of halogenated and non-halogenated OPs were also
207 observed for the German Bight (North Sea). In March and September the ratio of halogenated to non-
208 halogenated OPs was 1.4 ± 0.4 and 1.9 ± 0.5 , respectively, whereas in July the amount of halogenated
209 OPs was slightly higher by a medium factor of 2.2 ± 0.8 (see Figure 3 and Figure S1 in suppl. material).

210 The decreasing concentrations in the Elbe estuary towards the open sea in March, May, and October were
211 caused by mixing processes with sea water which is confirmed by high negative correlation with salinity.

212 In August an additional depletion occurred affecting the non-halogenated OPs. In the literature different
213 degradation pathways for OPs can be found: biodegradation (Saeger et al., 1979) predominantly under
214 aerobic conditions (Fries and Püttmann, 2003), alkaline hydrolysis (Mabey and Mill, 1978), as well as
215 photodegradation (Muir et al., 1989; Regnery and Püttmann, 2009). Especially the short chain alkylated
216 OPs are highly volatile and evaporation might occur with increasing temperature. In addition sorption
217 processes (WHO, 2000; WHO, 1990) can be expected as reasons for decreasing concentrations in the
218 dissolved phase. Due to the fact that sorption processes would occur for those OPs with high *n*-octanol-
219 water partition coefficients and not only for non-halogenated OPs these processes can be excluded as a
220 reason for the decreasing concentrations in August. Concluded from the comparison to secondary
221 parameters such as pH-value and temperature, alkaline hydrolysis can also be excluded. This means that
222 biodegradation as well as photodegradation and evaporation are likely the mechanisms leading to
223 decreasing concentrations in August and affecting mostly the non-halogenated OPs. Consequently in
224 summer halogenated OPs predominate, whereas in winter time it is nearly equalized with non-

225 halogenated OPs. To conclude which one of the processes might be the leading process causing the
226 decreases in OP concentrations in the water phase further research is necessary.

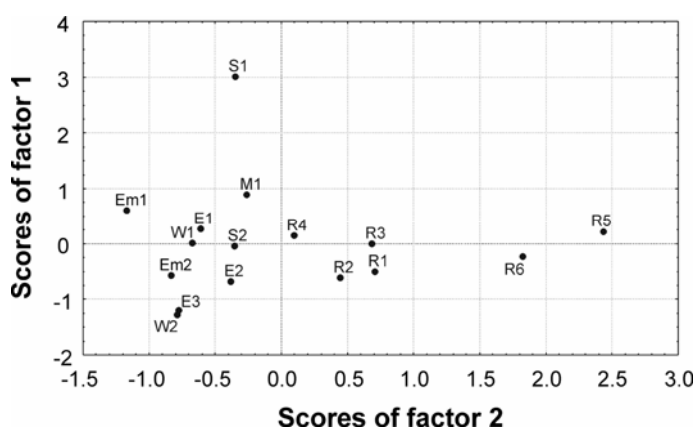
227 Former studies for seasonal variations of OP concentrations in urban and rural lake water and in
228 precipitation by Regnery and Püttmann (2009) showed no seasonal dependence. This can be confirmed
229 with the results of this study by comparing single substance concentrations of the four different sampling
230 months at the same sampling point of the Elbe estuary, e.g. TCPP or TiBP at Elbe-km 609. The variations
231 of the single substance concentrations follow no seasonal trends. However, as mentioned above the
232 longitudinal profile of the Elbe estuary shows obvious seasonal dependent variations, which are caused by
233 the different rates of degradation of the different substances.

234 **3.3 Substance pattern**

235 As mentioned in paragraph 3.1 the substance pattern in the different tributaries seemed to be different.
236 For this reason two multivariate statistical methods (cluster analysis and factor analysis) were conducted
237 to find structures in the set of data and to make them visible. To neglect the seasonal variations in the
238 substance pattern (see paragraph 3.2) the following analysis was only based on the sampling in August,
239 2010, in all tributaries. In addition the values were standardized (from each value the average was
240 subtracted and divided by the standard deviation) to allow comparisons of many variables with different
241 dimensions (Einax et al., 1997).

242 By means of a cluster analysis groups, i.e. clusters, are formed on the basis of multivariate distances to
243 visualize similarities in a high-dimensional set of data (for further information see Einax et al., 1997). The
244 final output of a cluster analysis, in this case conducted as hierarchical agglomerative clustering according
245 to WARD, is a dendrogram (Figure S2 in suppl. material). This shows that one sample of the Scheldt (S1)
246 and the samples from the two largest effluents of the Rhine (Nieuwe Waterweg, R5, and Hollandsch
247 Diep, R6) differed a lot from all the other samples and formed separate clusters. In a smaller impact also a
248 separation between the other samples of the Rhine and the remaining samples of the other rivers could be
249 seen. For the interpretation of the hidden relationships a factor analysis was conducted converting
250 correlated variables to so-called factors (for further information see Einax et al., 1997). In this case three
251 factors with eigenvalues above 1 were extracted, which explain together about 80 % of the total variance.

252 A scatterplot of factor 1 and 2 (Figure 5) shows a separation of the Scheldt sample S1 from the other
 253 samples due to factor 1 and of the Rhine samples caused by factor 2. This reveals that the Rhine differed a
 254 lot from the other rivers due to a higher fraction of non-halogenated OPs as TMP, TiBP, and TiPrP,
 255 which have highest loadings in factor 2. The separation of the Scheldt sample S1 in the cluster analysis is
 256 caused by the very high OP concentrations at this sampling site (see Table 1). This is assumed because
 257 TCP, TDCP, TCEP, and TBP, substances which are common for all investigated rivers have high
 258 loadings in factor 1 (Table S7 in suppl. material).



259 Figure 5

260 Scatterplot of the scores of factor 1 and 2 (E: Elbe, Em: Ems, M: Meuse, R: Rhine, S: Scheldt, W:
 261 Weser); Loadings factor 1: TCP (0.958), TDCP (0.966), TCEP (0.963), TBP (0.795); Loadings factor
 262 2: TMP (0.816), TiPrP (0.872), TiBP (0.832).

263
 264
 265 The reasons for these differences in the substance patterns of the different rivers can only be assumed. As
 266 indicated in paragraph 3.1 there are some production sites of OPs located along the river Rhine which can
 267 cause these differences. The patterns of all the other river is might be due to normal usage of OP-
 268 containing products and other diffuse sources. Indeed, this needs to be confirmed by further research.

269 Concluded from the comparison of the substance patterns in the different tributaries the slightly higher
 270 amount of non-halogenated OPs in samples from the East Friesian coast (N4, N9) compared to those from
 271 the North Friesian coast (N2, N3) (see Figure 3) are ascribed to a coastline inflow of the Rhine into the
 272 German Bight. In former studies this coastline flow was also recognized for other organic pollutants
 273 (Möller et al., 2010).

3.4 Riverine input into the North Sea

Based on the sampling campaign in August, 2010, and daily mean water discharge values, the total riverine input of OPs was estimated to be 50 t yr⁻¹. The highest amount was discharged by the Rhine-Meuse delta (82 %). Smaller amounts entered the North Sea via the rivers Elbe (11 %), Scheldt (5 %), Weser, and Ems (1 % each). Annually, about 13 t TCPP, 6.1 t TEP, 5.8 t TiBP, and 3.5 t TBEP were discharged into the North Sea via the investigated tributaries.

In contrast, Möller et al. (2011) estimated the atmospheric input of OPs into the German Bight to be about 50 – 70 times lower than the riverine input. This means, that the main OP fraction in the marine environment enters the sea via the rivers.

A comparison to other organic pollutants shows the relevance for analyzing OPs in the marine environment. For example the input of poly- and perfluorinated compounds (PCFs), another important group of persistent organic pollutants, was estimated to be about 800 kg yr⁻¹ via the Elbe and 6 – 20 t yr⁻¹ via the Rhine (Möller et al., 2010), whereas it was 5.5 and 42.5 t yr⁻¹ of OPs, respectively.

4 Conclusions

This study shows a seasonal dependency of the OP substance pattern. In summer non-halogenated OPs are affected by degradation processes, assumed to be biodegradation and photodegradation. This leads to a predomination of halogenated OPs in summer whereas in winter it is nearly equalized with non-halogenated OPs.

Moreover, it could be pointed out that the substance pattern of the River Rhine differs from that of all other tributaries of the German Bight (North Sea), that were investigated in this study. It could be seen that the contribution of non-halogenated OPs is much higher in this river, which is probably due to OP production sites along the Rhine.

The riverine input of OPs into the German Bight (North Sea) could be estimated to be 50 t yr⁻¹. This very high input reveals that further research in fate and transportation behavior of OPs in the marine environment is necessary.

5 Acknowledgment

The authors would like to thank Thorben Ammann (University of Hamburg, Germany), FGG Elbe, FGG Weser, WSA Meppen, and Helpdesk Water of Rijkswaterstraat Waterdienst (Netherlands) for providing secondary parameters of the rivers. In addition, the captains and crews of R/V HEINCKE and R/V LUDWIG PRANDTL should be thanked as well as the Alfred-Wegener-Institut (Bremerhaven, Germany) for the possibility of taking part in the cruises of R/V HEINCKE. Moreover the authors would like to thank Armando Caba (Helmholtz-Zentrum Geesthacht) for taking the North Sea samples.

6 References

- Andresen, J. A., Grundmann, A., and Bester, K. (2004) Organophosphorus flame retardants and plasticisers in surface waters. *Science of the Total Environment* 332(1-3), 155-166.
- Andresen, J.A., Muir, D., Ueno, D., Darling, C., Theobald, N., and Bester, K. (2007) Emerging pollutants in the North Sea in comparison to Lake Ontario, Canada, data. *Environmental Toxicology and Chemistry / SETAC* 26, 1081-1089.
- Arbeitsgemeinschaft zur Reinhaltung der Elbe (ARGE Elbe) (2000) Selected organic trace pollutants in the river Elbe and its tributaries in 1994 – 1999. http://www.arge-elbe.de/tl_fgg_neu/veroeffentlichungen.html (in German).
- Bacaloni, A., Cavaliere, C., Foglia, P., Nazzari, M, Samperi, R., and 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, 1123-1130.
- Einax, J.W., Zwanziger, H.W., and Geiss, S. (1997) *Chemometrics in environmental analysis*. WILEY-VCH, Weinheim.
- European Flame Retardants Association (2010) Market statistics, www.cefic-efra.com (Accessed May 25, 2010).

- 322 Fries, E. and Püttmann, W. (2001) Occurrence of organophosphate esters in surface water and ground
323 water in Germany. *Journal of Environmental Monitoring* 3, 621-626.
- 324 Fries, E. and Püttmann, W. (2003) Monitoring of the three organophosphate esters TBP, TCEP and TBEP
325 in river water and ground water (Oder, Germany). *Journal of Environmental Monitoring* 5, 346-352.
- 326 Haggard, B. E., Galloway, J. M., Green, W. R., and Meyer, M. T. (2006) Pharmaceuticals and other
327 organic chemicals in selected north-central and northwestern Arkansas streams. *Journal of*
328 *Environmental Quality* 35(4), 1078-1087.
- 329 Knepper, T.P., Sacher, F., Lange, F.T., Brauch, H.J., Karrenbrock, F., Roerden, O., and Lindner, K.
330 (1999) Detection of polar organic substances relevant for drinking water. *Waste Management* 19, 77-
331 99.
- 332 Mabey, W. and Mill, T. (1978) Critical Review of Hydrolysis of Organic Compounds in Water Under
333 Environmental Conditions. *J. Phys. Chem. Ref. Data* 7, 383-415.
- 334 Marklund, A., Andersson, B., and Haglund, P. (2003) Screening of organophosphorus compounds and
335 their distribution in various indoor environments. *Chemosphere* 53(9), 1137-1146.
- 336 Marklund, A., Andersson, B., and Haglund, P. (2005) Organophosphorus flame retardants and plasticizers
337 in Swedish sewage treatment plants. *Environmental Science & Technology* 39(19), 7423-7429.
- 338 Martínez-Carballo, E., González-Barreiro, C., Sitka, A., Scharf, S., and Gans, O. (2007) Determination of
339 selected organophosphate esters in the aquatic environment of Austria. *Science of the Total*
340 *Environment* 388, 290-299.
- 341 Muir, D. C. G., Yarechewskiab, A. L., and Grift, N. P. (1989) Biodegradation of four triaryl/alkyl
342 phosphate esters in sediment under various temperature and redox conditions. *Toxicological &*
343 *Environmental Chemistry* 18, 269-286.

344 Möller, A., Ahrens, L., Sturm, R., Westerveld, J., van der Wielen, F., Ebinghaus, R., and de Voogt, P.
345 (2010) Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed.
346 *Environmental Pollution* 158(10), 3243-3250.

347 Möller, A., Xie, Z., Caba, A., Sturm, R., and Ebinghaus, R. (2011) Organophosphorus flame retardants
348 and plasticizers in the atmosphere of the North Sea. *Environmental Pollution* 159, 3660-3665.

349 OECD (2010) Screening Information Data Set (SIDs) for High Production Volume Chemicals: Triethyl
350 phosphate, <http://www.inchem.org/documents/sids/sids/78400.pdf> (Accessed May12, 2011).

351 Quednow, K. and Püttmann, W. (2008) Organophosphates and Synthetic Musk Fragrances in Freshwater
352 Streams in Hesse/Germany. *CLEAN - Soil, Air, Water* 36(1), 70-77.

353 Reemtsma, T., Quintana, J. B., Rodil, R., Garía-Lopéz, M., and Rodríguez, I. (2008) Organophosphorus
354 flame retardants and plasticizers in water and air I. Occurrence and fate. *Trends in Analytical*
355 *Chemistry* 27(9), 727-737.

356 Regnery, J. and Püttmann, W. (2009) Organophosphorus Flame Retardants and Plasticizers in Rain and
357 Snow from Middle Germany. *CLEAN - Soil, Air, Water* 37(4-5), 334–342.

358 Regnery, J. and Püttmann, W. (2010) Occurrence and fate of organophosphorus flame retardants and
359 plasticizers in urban and remote surface waters in Germany. *Water Research* 44, 4097-4104.

360 Saeger, V., Hicks, O., Kaley, R., Michael, P.R., Mieure, J.P., and Tucker, E.S. (1979) Environmental fate
361 of selected phosphate esters. *Environmental Science & Technology* 13(7), 840-844.

362 Saito, I., Onuki, A., and Seto, H. (2007) Indoor organophosphate and polybrominated flame retardants in
363 Tokyo. *Indoor Air* 17, 28-36.

364 Sheldon, L. S. and Hites, R. A. (1978) Organic compounds in the Delaware River. *Environmental Science*
365 *& Technology* 12(10), 1188-1194.

366 SRC PhysProp Database Demo (2010) <http://www.syrres.com/what-we-do/databaseforms.aspx?id=386>
367 (Accessed December 28, 2010).

368 Stapleton, H. M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J. D., Blum, A., and Webster, T.F. (2009)
369 Detection of organophosphate flame retardants in furniture foam and U.S. house dust. *Environmental*
370 *Science & Technology* 43(19), 7490-7495.

371 Tollbäck, J., Isetun, S., Colmsjö, A., and Nilsson, U. (2010) Dynamic non-equilibrium SPME combined
372 with GC , PICI , and ion trap MS for determination of organophosphate esters in air. *Analytical and*
373 *Bioanalytical Chemistry* 396, 839-844.

374 World Health Organization (WHO) (1990) *Environmental Health Criteria 110: Tricresyl phosphate.*
375 Geneva.

376 World Health Organization (WHO) (1998) *Environmental Health Criteria 209: Tris(chloropropyl)*
377 *phosphate, Tris(2-chloroethyl)phosphate.* Geneva.

378 World Health Organisation (WHO) (2000) *Environmental Health Criteria 218: Tris(2-butoxyethyl)*
379 *phosphate, Tris(2-ethylhexyl) phosphate, and tetrakis(hydroxymethyl) phosphonium salts.* Geneva.
380