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1   Organophosphorus flame retardants and plasticizers in the atmosphere of

2   the North Sea

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4   Axel Möller[1*], Zhiyong Xie[1], Armando Caba[1], Renate Sturm[1], Ralf Ebinghaus[1]

5   [1]Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Institute of

6   Coastal Research, Department for Environmental Chemistry, Max-Planck-Strasse 1,

7   21502 Geesthacht, Germany

8   * corresponding author phone: +49 4152 87 2353 fax: +49 4152 87 2332

9   email: axel.moeller@hzg.de

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20 **Abstract**

21   Air samples collected in the German part of the North Sea from March to July 2010

22 were investigated for organophosphorus compounds (OPs) being applied as flame

23 retardants and plasticizers. The $\sum_8$OPs concentration ranged from 110 to 1400 pg m^{-3}

24 while tris(2-chloroisopropyl) phosphate (TCPP) dominated all samples with individual

25 concentrations up to 1200 pg m^{-3}. The highest concentrations were observed in

26 continental air masses showing the high influence of industrialized regions including

27 production sites on atmospheric emissions and concentrations. The occurrence of OPs

28 even in oceanic/Arctic air masses shows that OPs can undergo long-range atmospheric

29 transport. Dry particle-bound deposition fluxes from 9 to 240 ng m^{-2}d^{-1} for $\sum_8$OPs were

30 estimated leading to a minimum annual flux of 710 ± 580 kg y^{-1} OPs into the German

31 North Sea. This study presents the first occurrence of OPs in the marine atmosphere

32 together with important information on their long-range transport potential.

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34   *Capsule:* Organophosphorus flame retardants, in particular tris(2-chloroisopropyl)

35 phosphate, are emitted into the North Sea atmosphere by Western European countries.

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1. Introduction

Organic flame retardants (FRs) have been applied for several decades to reduce the inflammability of various industrial and commercial products. Besides halogenated, mainly brominated organic FRs (BFRs) such as polybrominated diphenyl ethers (PBDEs), halogenated and non-halogenated organophosphorus compounds (OPs) have been commonly used. While chlorinated OPs (e.g., tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP) and tris(1,3-dichloro-2-isopropyl) phosphate (TDCP)) are mainly used as FRs, non-chlorinated OPs (e.g., triphenyl phosphate (TPhP), tri-n-butyl phosphate (TnBP) and tris(2-butoxyethyl) phosphate (TBEP)) are additionally widely applied as plasticizers, antifoaming agents and additives in hydraulic fluids (Marklund et al., 2003). Caused by the ongoing worldwide phase-out and restrictions of PBDEs since the early 2000s and the recent banishment of PBDEs by the Stockholm Convention on persistent organic pollutants (POPs) in 2009 (UNEP, 2009), the production and usage and, therefore, emissions into the environment of OPs are expected to increase (Reemtsma et al., 2008). Even though they were firstly reported in environment in the 1970s (Meijers and van der Leer, 1976; Sheldon and Hites, 1978), they can therefore be considered as "re-emerging" pollutants (Reemtsma et al., 2008).

Similar to PBDEs, OPs are not chemically bound in the fire-proofed material and can easily leach into the environment via volatilization, abrasion and dissolution. As a result, OPs have been frequently detected in the environment, mainly in the water compartment (e.g., rivers (Fries and Püttmann, 2003; Bacaloni et al., 2007; Rodil et al., 2009), groundwater (Fries and Püttmann, 2003), seawater (Weigel et al., 2005; Andresen et al., 2007)), and, since the report of OPs in indoor air up to 250 ng m^{-3} by

65 Carlsson et al. (1997), in increasing numbers in indoor environments (Tollback et al.;

66 Marklund et al., 2003; Marklund et al., 2005a; Saito et al., 2007; Stapleton et al., 2009).

67 Several OPs have known or suspected adverse health effects including skin irritation,

68 carcinogenicity, dermatitis and neurotoxicity (WHO, 1991a, b ; Camarasa and

69 Serrabaldrich, 1992; Matthews et al., 1993; Sato et al., 1997; WHO, 1998; 2000). As

70 one result, TCEP was replaced by TCPP in Europe, but its production is still not

71 prohibited (Quednow and Püttmann, 2009). Halogenated OPs have been shown to be

72 fairly persistent towards biodegradation (Kawagoshi et al., 2002; Meyer and Bester,

73 2004) while the persistence of the non-halogenated OPs increases with increasing alkyl

74 chain length (Saeger et al., 1979).

75   Although OPs are discussed to undergo long-range atmospheric transport (LRAT)

76 and can be classified as semi-volatile compounds (Wensing et al., 2005), data on OPs in

77 the outdoor atmospheric environment are still very limited. In the 1990s, they have been

78 detected in aerosols from Antarctica (Ciccioli et al., 1994) and in pine needles from the

79 Sierra Nevada, U.S. (Aston et al., 1996) as a result of atmospheric transport. Further

80 reports in snow and precipitation (Laniewski et al., 1998; Marklund et al., 2005b;

81 Regnery and Püttmann, 2009; Regnery and Püttmann, 2010) showed potential wash-out

82 mechanisms from the atmosphere and, more important, potential transport pathways of

83 OPs into the marine environment in addition to riverine discharges. Bacaloni et al.

84 (2008) reported OPs in volcanic lakes in Italy as a result of atmospheric deposition.

85   In this study, we present the occurrence of chlorinated and non-chlorinated OPs in

86 the marine atmosphere for the first time. Thereby, we focused on those used as flame

87 retardants – TCEP, TCPP, TDCP, TBEP, TPhP, tris(2-ethylhexyl) phosphate (TEHP) –

88 and on TnBP and tri-iso-butyl phosphate (TiBP) which have been shown to be major

89   OPs in air, snow and remote lakes in recent studies (Marklund et al., 2005; Bacaloni et

90   al., 2008; Regnery and Püttmann, 2009; 2010;). OP concentrations were studied in the

91   atmosphere of the North Sea with respect to the spatial distribution and source regions,

92   seasonal fluctuations and dry deposition fluxes into the North Sea as important input

93   pathway into the marine environment.

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95   **2.   Material and Methods**

96   *2.1. Chemicals*

97   TnBP, TEHP, TBEP, TCEP, TCPP (mixture of isomers), TDCP, TPhP, and [D$_{27}$]-

98   TnBP were purchased from Sigma Aldrich; TiBP from Merck; [D$_{15}$]-TPhP from Dr.

99   Ehrenstorfer and [^{13}C]-Hexachlorobenzene (HCB) from Cambridge Isotope

100   Laboratories. Acetone, hexane and dichloromethane (DCM) were pico grade

101   (PromoChem) and silica gel (0.063-0.200 mm) was purchased from Merck.

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103   *2.2. Sampling*

104   In total, 20 air samples from the German part of the North Sea were collected during

105   the cruises no. H319 (6 samples), H325 (7 samples) and H331 (7 samples) of the

106   German research vessel *Heincke* in March, May and July 2010. Integrated high-volume

107   air samples were taken at the ship's upper deck using a high-volume pump operated for

108   one day to obtain a volume of ~300 m^3. A glass fiber filter ([GFF], pore size: 0.7 µm)

109   was used to trap the airborne particles and the gaseous OPs were collected on a glass

110   column packed with PUF/Amberlite® XAD-2 resin. Samples were stored at -20 °C until

111   extraction. Detailed sampling information are included in Table S1 of the Supporting

112   Information (SI).

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2.3. Extraction, cleanup and analysis

The PUF/XAD-2 columns and the GFFs were extracted separately. They were spiked with 20 ng [D_{27}]-TnBP and [D_{15}]-TPhP as internal standards prior to extraction. Both air columns and GFFs were Soxhlet extracted for 16 h using DCM. The extracts were roti-evaporated to 2 mL and purified on a 2.5 g 10% water deactivated silica gel column topped on 3 g of anhydrous granulated sodium sulfate. Firstly, non-polar compounds were removed using 20 mL hexane (no OPs were detected in this fraction) and the target analytes were eluted in the second fraction using 30 mL DCM/Acetone (1:1 v/v), then roti-evaporated to 2 mL following a further nitrogen evaporation step to the final volume of 200 µL while the solvent was exchanged to hexane. Ten ng of ^{13}C-HCB was added as injection standard.

Analysis was done by an Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass spectrometer (GC-MS) equipped with a programmed temperature vaporizer (PTV) injector. The GC was fitted with a HP-5MS column (30 m×0.25 mm i.d.×0.25 μm film thickness, J&W Scientific) and the GC was operated in electron impact mode. The initial oven temperature was 40 °C for 4 min, 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 to 300 °C. The injection volume was 1 μL and the helium carrier gas flow was 1.3 mL min^{-1}. The PTV inlet was operated in pulsed splitless mode with an initial temperature of 60 °C for 0.1 min, and then increased at 500 °C min^{-1} to 300 °C. The temperatures of the MS transfer line and the ion source were held at 280 °C and 230 °C, respectively. The masses for the detection of OPs and IS in selective ion monitoring mode are included in Table S2.

136   The content of total organic carbon (TOC) in the air filter samples was analyzed

137   using a multiphase carbon, hydrogen, moisture detector (RC-612, LECO Corporation).

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139   *2.4. Air mass back trajectories*

140   Air mass origins were calculated for the air samples using NOAA's HYSPLIT

141   model (Draxler and Hess, 1997). Back trajectories (BTs) were calculated for each

142   sample in 4 h steps along the sampling cruises. BTs were traced back for 120 h with the

143   sampling height as arrival height (see Figure S1 for individual BTs).

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145   *2.5. QA/QC*

146   Samples were taken during 'good' weather conditions only, i.e., stopped during ship

147   stations and back winds. Air columns and filters were installed directly on the ship's

148   upper deck and not exposed to the ships lab air. The air columns were protected against

149   UV-sunlight during sampling using aluminum foil in order to avoid degradation of the

150   target compounds on the column. All air columns were precleaned with solvents of

151   different polarity. GFFs were baked at 450 °C for 12 h prior to usage. All used glass

152   ware was baked at 250 °C for 10 h and rinsed with acetone and silica gel was cleaned

153   with acetone for 12 h and baked at 450 °C for 12 h prior to usage. Breakthrough of the

154   target compounds was checked using tandem columns during the present cruises. No

155   target compounds were observed above the method detection limits (MDLs) in the

156   lower column. Three field blanks were taken for each cruise by exposing the column

157   and filter to the routine sampling and extraction method. In general, air column blanks

158   were in the absolute one-digit ng range or even below while air filters showed even

159   lower blank values (see Table S3 for individual blanks). MDLs were derived from mean

160   blank values plus three times the standard deviation or, for those compounds showing

161   no blanks, from the instrumental detection limits at signal-to-noise (S/N) ratios of three.

162   MDLs ranged from 1 pg m^{-3} to 94 pg m^{-3} (see Table S4 for individual MDLs). The

163   recoveries of the IS were 131 ± 46% and 176 ± 40% for the filter and 241 ± 130% and

164   224 ± 15% in air columns for [D$_{27}$]-TnBP and [D$_{15}$]-TPhP, respectively. All

165   concentrations were recovery corrected. Relative recoveries of the analytes corrected by

166   the surrogate ranged from 77 ± 5% for TCEP to 111 ± 4% for TEHP (mean all OPs 91 ±

167   13%).

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169   **3.   Results and discussion**

170   *3.1. Atmospheric concentrations*

171   All investigated OP flame retardants and plasticizers were detected in the North Sea

172   atmosphere with TCPP (calculated as sum of isomers) being the predominating OP

173   which was detected in all samples contributing 60 ± 16% of the sum of eight

174   investigated OPs (defined as $\sum_8$OPs hereafter). Thereby, the concentrations of TCPP

175   were 2 to 23 fold higher than for TCEP as a result of the industrial replacement of

176   TCEP by TCPP. TCEP and TPhP were detected in all samples too, while TiBP, TnBP

177   and TCEP were detected in approximately 90% of the samples, TEHP in 65%, TBEP in

178   50% and TDCP in 20 % of the samples, respectively. The $\sum_8$OPs concentration

179   (particulate + gaseous) ranged from 110 to 1400 pg m^{-3} (median 369 ± 362 pg m^{-3}) with

180   individual concentrations for TCPP, TCEP, TPhP, TiBP, and TnBP ranging from 38 to

181   1200 pg m^{-3}, 6 to 160 pg m^{-3}, 4 to 290 pg m^{-3}, not detected (n.d.) to 150 pg m^{-3} and n.d.

182   to 150 pg m^{-3}, respectively. TBEP and TEHP ranged from n.d. to 80 pg m^{-3} and from

183   n.d. to 31 pg m^{-3}, respectively. Individual concentrations are given in Table S5. OPs in

184   the North Sea atmosphere were mainly distributed in the particulate phase with a mean

185   particulate associated fraction of 86 ± 25% for $\sum_8$OPs and individual percentages of

186   ranging from 61 ± 46% for TBEP to 100% for TDCP. This is in good agreement with

187   the previous results reported by Carlsson et al. (1997) of >99% for the particulate

188   fraction, while the lower particle-associated percentage in this study might partly be

189   caused by fine aerosol particles in the offshore sampling area passing the filter and

190   being trapped on the column.

191   There is only very little peer-reviewed data for comparison of OPs in outdoor air,

192   especially in non-urbanized or even remote areas. Carlsson et al. (1997) reported

193   outdoor concentrations of T*n*BP, T*i*BP, TCEP, TCPP, TPhP, TBEP and TEHP below

194   1 ng m^{-3} close to buildings and Takimoto et al. (1999) reported tricresyl phosphate

195   (TCP), another arylated OP, up to 200 pg m^{-3} in the atmosphere of a Japanese non-urban

196   area. Saito et al. (2007) detected T*n*BP, TCPP and TBEP up to 1.7 ng m^{-3}, 3.1 ng m^{-3}

197   and 1.1 ng m^{-3}, respectively, outside of Japanese houses and office buildings. Marklund

198   et al. (2005) reported concentrations in remote air from Northern Finland of 12000 pg

199   m^{-3}, 810 pg m^{-3}, 210 pg m^{-3}, 20 pg m^{-3} and 1.6 pg m^{-3} for TPhP, TCPP, T*n*BP, TDCP

200   and TCEP, respectively, while they stated traffic (i.e., hydraulic fluids, oils, emissions

201   from car interiors) to be a major source of OPs in the atmosphere. Their observed TPhP

202   concentration was 1000 times higher than in the present study while the remaining OPs

203   are in relatively good comparison what might be a result of air masses which passed

204   urbanized or industrialized areas (Marklund et al. ,2005). Interestingly, TCEP observed

205   in the North Sea atmosphere was ~25 times higher than in Northern Finland and the OP

206   profile was generally dominated by the halogenated OP and not by non-halogenated

207   OPs as observed by Marklund et al. (2005b) what might be a result of different sources

208   influencing the airborne concentrations. In a screening of new pollutants in the

209   Norwegian Arctic, TiBP (32-230 pg m^{-3}), TCEP (270 pg m^{-3}), TCPP (330 pg m^{-3}),

210   TDCP (87-250 pg m^{-3}) and TBEP (150 pg m^{-3}) were detected in remote air from New

211   Ålesund, Svalbard (Green et al., 2008) which are in good comparison to the

212   concentrations observed in this study. Indoor concentrations of OPs are typically several

213   orders of magnitude higher, e.g., up to 950 ng m^{-3} (Marklund et al., 2005a) as a result of

214   emissions from building materials, furniture and consumer products in private and

215   office housings.

216   In terms of the industrial shift from PBDEs to alternative non-PBDE FRs, likely

217   including OP flame retardants, it is important to note that the observed OP

218   concentrations, especially TCPP, in the North Sea atmosphere are several times higher

219   than typical PBDE concentrations in the European outdoor environment which are

220   usually in the one to two digit pg m^{-3} range (Hites, 2004; Jaward et al., 2004; Pozo et

221   al., 2008). More demonstratively, Stapleton et al. (2009) detected OPs, namely TPhP,

222   TCPP and TDCP, in house dust in concentrations similar or even higher than PBDEs.

223   Since there are no data on OP flame retardants in the outdoor environment from the

224   early 2000s where PBDEs were still allowed to be used, it is not possible to compare

225   temporal trends of OPs and PBDEs in the atmospheric environment. Nevertheless, it is

226   likely that atmospheric OP concentrations have increased in recent years and might

227   further increase in response to a possible industrial shift towards OP flame retardants.

228

229   *3.2.   Spatial variations, seasonal trends and possible sources*

230   The spatial distribution of OPs in the atmosphere of the North Sea is shown in

231   Figure 1. The spatial variations in the sampling area of the cruises are more a result of

232   varying air masses rather than spatial differences of the sampling stations. Samples of

233   H319 were mainly dominated by air masses passing the Scandinavian countries and by

234   oceanic air from north-northwest. As a result, the observed concentrations, especially

235   for the dominating OP, TCPP, were relatively homogenous during the cruise H319. In

236   cruise H325, the highest concentrations of TnBP, TiBP, TCEP and TCPP were observed

237   at station H325 A1 which was taken partly in the estuary of the river Weser and

238   influenced by continental air masses passing industrialized areas of Germany, the

239   Netherlands, the English Channel and the United Kingdom (U.K.). This resulted in ~5

240   times higher concentrations compared to stations H325 A2-A7 which were dominated

241   by oceanic and Scandinavian air masses showing industrialized regions of Western

242   Europe being source regions of OPs in the marine atmospheric environment. The

243   production of TCPP in the EU in 2000 (36000 tonnes) was stated to take place at three

244   sites in Germany and one site in the U.K. (EC, 2007) showing, together with the results

245   of this study, the importance of these countries as sources of TCPP in the North Sea

246   environment. The lowest concentrations observed at stations H325 A4 and A5 are a

247   result of mainly oceanic air masses traveling southwards from the European Arctic to

248   the North Sea (see Figure 2 for representative BTs). During the cruise H331, the

249   sampled air masses were mainly continental based passing Germany, the Netherlands,

250   Belgium, France (H331 A1-4, A7) and the U.K. (H331 A5-A6) (see Figure 2 and S1).

251   The highest TCPP was again observed at the first station of the cruise in the river Weser

252   estuary while the concentrations during H331 are generally higher compared to cruises

253   H319 and H325 showing again the influence of continental air masses. Interestingly,

254   TPhP as well as TiBP, TnBP and TCEP were found in comparably high concentrations

255   at H331 A7 up to 280 pg m^3 (TPhP) while the observed TCPP concentration was lower

256   than at other stations during H331. This might be a result of a specific, possibly

257   industrial, source leading to a different OP mixture in the atmosphere. It should be

258   noted that sample H331 A7 consisted only of a volume of 41 m^3 sampled within 3 hours

259   what might lead to a higher uncertainty. Within the three cruises, significant correlations

260   were observed for TCPP and TCEP, TnBP, TPhP and further significant correlations

261   were found for the investigated OPs (see Table S6, excluding H331 A7) indicating that

262   the investigated OPs have generally similar source regions (Western Europe) and

263   sources (i.e., emissions from industrial and commercial products, emissions from

264   households, traffic).

265   Comparing the three cruises in March, May and July, the highest concentrations of

266   the dominating OP, TCPP, were observed in July when the ambient air temperature was

267   the highest. This might either be caused by a temperature dependence of atmospheric

268   OP emissions and transport behaviour or a result of the continental air mass origin

269   during H331 passing urbanized or industrialized areas of Western Europe in contrast to

270   Scandinavian or oceanic air masses during H319 and H325. During all three cruises,

271   the TCPP concentration, as well as the TPhP concentration was significantly ($p < 0.01$

272   and $p < 0.05$, respectively) correlated with the ambient air temperature, while no

273   correlation with the air temperature was observed for other OPs. This might be a result

274   of the increasing volatilization of TCPP as well as other FRs from flame-proofed

275   products and houses to the outdoor environment with increasing temperature (1.2 ± 0.8

276   °C during H319, 7.2 ± 0.7 during H325 and 18.1 ± 1.6 °C during H331). On the other

277   hand, increasing temperature and increasing solar irradiation might lead to faster

278   atmospheric degradation. Calculated atmospheric half-lives of investigated OPs for the

279   reaction with OH-radicals range between <1 h for TnBP to 21.3 h for TDCP while

280   halogenated OPs are generally more persistent than non-halogenated (Regnery and

281   Püttmann, 2009). Therefore, emissions of other, non-halogenated OPs might be higher

282   in summer, too, while they are more readily counterbalanced by higher degradation

283   rates with increasing air temperature and solar irradiance during atmospheric transport

284   leading to any correlations with the ambient air temperature. Anyway, since cruise

285   H325 showed air mass origin driven concentration variations and Regnery and

286   Püttmann (2010) reported any seasonal trends in precipitation, too, it is likely that the

287   high concentrations during H331 can be mainly traced back to the air mass origins. In

288   addition, a significant correlation was observed for the TOC and several OPs (i.e.,

289   TiBP, TnBP, TCEP, TCPP and TEHP) which strengthen the conclusions of (1)

290   continental sources and (2) air mass origin dominated variations rather than temporal

291   and seasonal variations of OPs in the North Sea atmosphere.

292   Since OPs in the atmosphere are predominantly adsorbed to airborne particles and

293   half-lives of particle-bound OPs towards photodegradation are neither known nor

294   predicted (Regnery and Püttmann, 2009), they might have different, likely longer

295   atmospheric half-lives. The occurrence of OPs in the present study in samples even

296   originating from oceanic and partly Arctic air masses, together with earlier findings of

297   OPs in snow, precipitation and remote areas, shows that OPs can undergo long-range

298   atmospheric transport despite their relatively short estimated atmospheric half-lives

299   compared to legend POPs.

300

301   *3.3.   Dry deposition flux into the North Sea*

302   Since OPs are known to be widely emitted, distributed and transported in the surface

303   waters (Fries and Püttmann, 2001; Andresen et al., 2004; Martinez-Carballo et al., 2007;

304   Quednow and Püttmann, 2008), riverine inputs are major sources of OPs in the marine

305   aqueous environment. But, OPs have been detected in remote volcanic lakes (Bacaloni

306   et al., 2008) showing atmospheric transport and deposition processes to be important

307   sources of OPs in remote aqueous environments, too, including the marine offshore

308   environment. Therefore, we estimated the particulate dry deposition flux (F_d, ng m^{-2}d^{-1}),

309   which is an important deposition process for particle-associated pollutants using

310   equation (1):

311
$$F_d = V_d C_p \tag{1}$$

312   where V_d is the dry deposition velocity (m d^{-1}) and C_p is the OP concentration in the

313   particulate phase (ng m^{-3}). The dry deposition velocity is highly influenced by

314   physicochemical properties of the pollutant and the airborne particle as well as

315   meteorological parameters such as wind speed (Franz et al., 1998). Since neither

316   measured velocities for OPs, nor for other pollutants in the North Sea atmosphere are

317   available, we used a value of 0.2 cm s^{-1} (172.8 m d^{-1}) which was proposed by Castro-

318   Jiménez et al. (2010) for the deposition of polychlorinated dibenzo-p-dioxins and

319   dibenzofurans (PCDD/Fs) into the Open Mediterranean Sea representing offshore

320   marine aerosols influenced by continental sources. Since the North Sea is influenced by

321   continental sources (i.e., Western Europe), too, we adopted this value for the North Sea

322   which is also in good comparison with the modeled velocities for Northern Atlantic

323   given by Jurado et al. (2004). Since the wind speeds during the three cruises are

324   relatively comparable (5.8 ± 3.1 m s^{-1}, 8.4 ± 3.0 m s^{-1} and 7.6 ± 2.4 m s^{-1} for H319,

325   H325 and H331, respectively), we used the same deposition velocity for all three

326   cruises. Nevertheless, an uncertainty of a factor of three has to be assumed caused by

327   the unknown deposition velocities in the North Sea, the difference between continental

328 and oceanic air masses caused by different particle size distribution and possible

329 variations between the different OPs.

330   The dry deposition fluxes for the three cruises are shown in Figure 3. According to

331 the particle associated concentrations, the highest fluxes occurred during H331 in July

332 with a sum flux for $\sum$(TiBP, TnBP, TCEP, TCPP, TPhP, TBEP) from 46 to 240 ng m^{-2}

333 d^{-1} and individual fluxes from 3 ± 3 ng m^{-2} d^{-1} for TBEP up to 91 ± 51 ng m^{-2} d^{-1} for

334 TCPP caused by continentally, and likely industrially influenced air masses delivering

335 OPs to the North Sea. Lower fluxes were calculated for H319 and H325 which were in

336 the same range with sum fluxes from 24 to 97 ng m^{-2} d^{-1} and from 9 to 150 ng m^{-2} d^{-1},

337 respectively.

338   With an estimated area for the German North Sea (including the estuaries of the

339 rivers Elbe, Weser and Ems) of 42000 km² (Bundesamt für Seeschifffahrt und

340 Hydrographie [BSH], personal communication), and based on the mean values of H319

341 and H325 an annual flux of at least 710 ± 580 kg y^{-1} for $\sum$(TiBP, TnBP, TCEP, TCPP,

342 TPhP, TBEP) can be estimated, while continental air masses from Western Europe can

343 temporary lead to significantly higher input fluxes (e.g., 1900 ± 870 kg y^{-1} for $\sum$(TiBP,

344 TnBP, TCEP, TCPP, TPhP, TBEP) based on H331). Even though these deposition

345 fluxes into the North Sea might be comparably low to riverine discharges (e.g., rivers

346 Elbe, Weser, Rhine, Ems), which will be in two digit tonnes/year range based on

347 riverine concentrations of several hundreds ng/L (Fries and Püttmann, 2001; Andresen

348 et al., 2007;), atmospheric transport leads to a fast distribution from source regions

349 towards the open ocean contributing significantly to the transport of OPs and their

350 deposition into open oceans. Furthermore, the occurrence of OPs in oceanic or even

351 Arctic air masses shows that they are transported, and therefore also deposited, into

352 remote areas such as the Arctic, and their occurrence and deposition need to be studied

353 in future research. Once deposited into remote oceans by atmospheric deposition, they

354 can be further transported in the ocean and, possibly, accumulated by marine organisms

355 as shown by Marklund Sundkvist et al. (2010). In addition to that, the possible

356 degradation products of the different OPs need to be studied, together with their

357 occurrence, persistence and transport in the atmospheric and aquatic environment.

358

359 **4.   Conclusions**

360   Taken together, the results of this study show that several OPs applied both as FRs

361 and plasticizers are widely distributed in the marine atmospheric environment

362 originating from continental source regions such as Germany and the U.K.. Thereby,

363 TCPP was found to be the predominating compound with concentrations up to 1 ng m^{-3}.

364 This study proves that OPs can undergo mainly particle-bound long-range atmospheric

365 transported and (can) be deposited into the marine environment. In future research these

366 findings should be affirmed by investigating remote areas such as the Arctic and

367 Antarctica to evaluate the transport and deposition of OPs from source regions to highly

368 sensitive environments and their risk assessment as emerging pollutants.

369   The observed OP concentrations are several magnitudes higher compared to typical

370 PBDE concentrations in European off-source regions showing the importance of OP in

371 the field of environmental analysis of organic flame retardants. In addition, the usage

372 and emissions of OPs used as FRs might further increase worldwide due to the ongoing

373 banishment of PBDEs and need of replacement compounds. Therefore, the occurrence

374 of OPs, especially in off-source regions, should be studied in other highly-industrialized

375 countries such as the U.S. and China. Even though estimated atmospheric half-lives of

376 OPs seem to be comparably low and possibly too low for LRAT, this study, together

377 with recent investigations, clearly indicates that their environmental transport behaviour

378 allows longer half-lives and traveling distances.

379

385

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558   **Fig. 1**. Spatial distribution of OPs in the atmosphere of the North Sea during (a) H319,

559   (March), (b) H325 (May) and (c) H331 (July).

560   **Fig. 2.** Air mass back trajectories and height of H325 A4 (a) and H331 A2 (b)

561   representing oceanic/Arctic and continental air masses, respectively.

562   **Fig. 3.** Dry deposition flux of OPs into the North Sea.