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1 **Waste water treatment plants as sources of polyfluorinated compounds, polybrominated**
2 **diphenyl ethers and musk fragrances to ambient air**

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19 **Abstract**

20 To investigate waste water treatment plants (WWTPs) as sources of polyfluorinated
21 compounds (PFCs), polybrominated diphenyl ethers (PBDEs) and musk fragrances to the
22 atmosphere, air samples were simultaneously taken at two WWTPs and two reference sites
23 using high volume samplers. Contaminants were accumulated on glass fiber filters and
24 PUF/XAD-2/PUF cartridges, extracted compound-dependent by MTBE/acetone, methanol, or
25 hexane/acetone and detected by GC-MS or HPLC-MS/MS. Total (gas + particle phase)
26 concentrations ranged from 97 to 1004 pg m⁻³ (neutral PFCs), <MQL to 13 pg m⁻³ (ionic
27 PFCs), 5781 to 482163 pg m⁻³ (musk fragrances) and <1 to 27 pg m⁻³ (PBDEs) and were

28 usually higher at WWTPs than at corresponding reference sites, revealing that WWTPs can be
29 regarded as sources of musk fragrances, PFCs and probably PBDEs to the atmosphere.
30 Different concentrations at the two WWTPs indicated an influence of WWTP size or waste
31 water origin on emitted contaminant amounts.

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33

34 **Capsule**

35 Waste water treatment plants can be regarded as sources of musk fragrances, polyfluorinated
36 compounds (PFCs) and polybrominated diphenyl ethers (PBDEs) to the atmosphere

37

38

39 **Keywords**

40 PBDE, PFC, PFAS, WWTP, air

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42

43 **1 Introduction**

44 Due to their persistence in the environment, their potential to accumulate worldwide in biota
45 and/or their toxic properties, numerous studies investigated the occurrence and distribution of
46 synthetic musk fragrances, polybrominated diphenyl ethers (PBDEs) and poly- and
47 perfluorinated compounds (PFCs) on different spatial and temporal scales in various natural
48 and urban systems (Conder et al., 2008; De Wit, 2002; Dreyer et al., 2009b; Giesy and
49 Kannan, 2001; Heberer, 2002; Kallenborn et al., 1999b; Lau et al., 2007; Schultz et al., 2006;
50 Xie et al., 2007). Many studies brought to question the sources of these compounds to the
51 environment. However, in contrast to the aquatic environment, specific sources to the
52 atmosphere were less studied. The few investigated point sources of synthetic musk
53 fragrances, PBDEs and PFCs to the atmosphere include manufacturing sites, cosmetic plants,

54 waste incineration facilities, electronic waste dismantling sites or landfills (Agrell et al., 2004;
55 Barton et al., 2006; Chen et al., 2009; Chen et al., 2007; St-Amand et al., 2008; Weinberg et
56 al., submitted). Except for these point sources, elevated atmospheric concentrations of
57 PBDEs, PFCs and synthetic musk fragrances usually originate from areas of high industry
58 and/or population density, indicating rather diffuse sources to the atmosphere caused by their
59 widespread everyday use (Agrell et al., 2004; Barber et al., 2007; Dreyer et al., 2009a; Peck
60 and Hornbuckle, 2006; St-Amand et al., 2008). Synthetic musk fragrances, PBDEs and PFCs
61 can be released during application (e.g. musk fragrances, PFCs) (Fiedler et al., 2010; Reiner
62 and Kannan, 2006; Roosens et al., 2007) or by volatilization from products they are
63 incorporated in or attached to (PFCs, PBDEs) (Dinglasan-Panlilio and Mabury, 2006; Fiedler
64 et al., 2010; Kim et al., 2006). Thus, it is not surprising that enhanced concentrations of some
65 of these compounds were detected in indoor air (Fromme et al., 2004; Langer et al., 2009;
66 Shoeib et al., 2004). This also indicates the importance of indoor air as outdoor air
67 contamination sources.

68 Waste water treatment plants (WWTPs) were identified as significant sources of synthetic
69 musk fragrances, PBDEs and PFCs to the aquatic environment (Arnold et al., 2008; Becker et
70 al., 2008; Bester, 2004; Bossi et al., 2008; North, 2004; Schultz et al., 2006; Simonich et al.,
71 2002). Although these compounds were studied throughout the entire waste water treatment
72 process, air measurements at or close to WWTPs are usually lacking. Except for one study
73 suggesting spray irrigation of treated municipal waste water as PBDE source (Goel et al.,
74 2006), the potential of WWTPs to contribute to the atmospheric contamination with musk
75 fragrances, PBDEs and PFCs is still unknown. In WWTPs, chemicals can be released to the
76 atmosphere by two processes: 1st by volatilization from the waste water. This process will
77 most likely apply to the volatile synthetic musk fragrances, volatile lower brominated PBDEs
78 as well as neutral volatile PFCs present in waste water (perfluoroalkyl sulfonamids (FASAs);
79 perfluoroalkylsulfonamido ethanols (FASEs)). 2nd by aerosol formation. In aeration tanks of

80 WWTPs, aerosols are formed during bubble bursting at the air-water interface. Since many
81 chemicals accumulate in the micro layer at the air-water interface (Hardy et al., 1990), they
82 can be released to the atmosphere as aerosols by that pathway. The process of bubble bursting
83 as release mechanism of chemicals to the atmosphere at WWTPs was for example described
84 for polycyclic aromatic hydrocarbons and sterols (Beck and Radke, 2006; Radke and
85 Herrmann, 2003) but also for PFCs in sea spray (Ellis and Webster, 2009; Mader, 2009;
86 McMurdo et al., 2008).

87 The objective of this study was to investigate if synthetic musk fragrances, PBDEs and PFCs
88 are being released from WWTPs to the atmosphere. Therefore, air samples were taken at two
89 WWTPs and analyzed for synthetic musk fragrances, PBDEs and PFCs. Concentrations were
90 then compared to those observed in samples taken simultaneously at reference sites that were
91 not influenced by the WWTPs.

92

93

94 **2 Experimental**

95 *1.1 Chemicals*

96 All chemicals, standard compounds, and gases were of high quality and purity. Details on
97 chemicals and corresponding abbreviations are presented in Table S3.

98

99 *1.2 Sampling*

100 Air sampling was conducted above the aeration tanks of two WWTPs in Northern Germany
101 from 04.08.2009 to 11.08.2009 (WA) and 20.08.2009 to 27.08.2009 (WB). WA is located
102 north of Lüchow (about 9500 inhabitants, Figure S1) and characterized by a population
103 equivalent of 86500. One-third of WA's waste water originates from households and two-
104 thirds from industrial processes. WB is situated in the north of the city of Lüneburg (about
105 72500 inhabitants, Figure S1). The population equivalent of WB is estimated to 210000. Two-

106 thirds of WB's waste water originates from private households and one-third from industrial
107 processes. Both waste water treatment plants were equipped with mechanical sewage
108 treatment, followed by primary sedimentation basins, aeration tanks, secondary sedimentation
109 basins, and digestion towers. Waste water of RB was also treated by a biological phosphorus
110 elimination system. Average waste water volumes at the WWTP effluent were about 2900 m³
111 (RA) and 23000 m³ (RB). However, a higher waste water flow-through has to be considered
112 for the aeration tanks (waste water + returned activated sludge + internal water circulation).
113 The amount of oxygen pumped through the water in the aeration tanks depended on the waste
114 water 'quality'. Simultaneously to the sampling at the WWTPs, air samples were taken at two
115 reference sites (RA, RB, respectively). The reference sites were located in a distance of about
116 5 km south (RA) or west (RB) to the WWTPs and were not supposed to be influenced by the
117 corresponding WWTP under predominant ('normal') meteorological conditions of this region
118 which are characterized by westerly winds. Details on meteorological conditions during
119 sampling campaign are displayed in table S1, S2.

120 At each site, two high volume samplers (HV1, HV2) (Schulze, Asendorf, Germany; Digital,
121 Hegnau, Switzerland) were operated simultaneously directly above the aeration tanks (Figure
122 S2) because maximum emissions were assumed to occur there. HV1 was used to collect
123 PFCs. HV2 collected PBDEs and synthetic musk fragrances. At each site four daily (Monday,
124 Tuesday, Wednesday, Thursday) and one three-day (Friday-Monday) air samples were taken.
125 The average sampling volume was about 350 m³ d⁻¹. Gas-phase target compounds were
126 enriched on PUF/XAD-2/PUF cartridges (Orbo PUF/XAD-2/PUF cartridges 2500, Supelco,
127 Munich, Germany). Particle-associated analytes were accumulated on glass fibre filters (150
128 mm, Macherey&Nagel, Germany). Prior to the sampling, cartridges for PFC analyses were
129 spiked with 50 µL of an internal standard solution containing ¹³C 4:2 FTOH, ¹³C 6:2 FTOH,
130 ¹³C 8:2 FTOH, ¹³C 10:2 FTOH, MeFOSA D₃, EtFOSA D₅, MeFOSE D₇, and MeFOSE D₉
131 (c=200 pg µL⁻¹). PBDE and synthetic musk fragrances' cartridges were spiked with an

132 internal standard solution containing ATHN D₁₃, MX D₁₅, ¹³C BDE28, ¹³C BDE47,
133 ¹³C BDE99, ¹³C BDE153, ¹³C BDE183 and ¹³C BDE209 (c=200 pg μL⁻¹). After sampling,
134 cartridges and GFF were packed separately in alumina-coated polypropylene bags, sealed air
135 tightly, and stored at -20 °C until analysis.

136

137 *1.3 Sample Preparation*

138 Figure 1 depicts an overview about the analytical process. PFCs in gas-phase samples were
139 extracted according to the method of Dreyer et al. (2009b). Briefly, PUF/XAD-2/PUF
140 cartridges were cold extracted three times (1 h, 1 h, 30 min) using methyl-tert butyl ether
141 (MTBE)/acetone 1:1 (v:v). The extract volume was reduced to 150 μL by rotary evaporators
142 and a gentle stream of nitrogen. Prior to the measurement, 50 μL of an injection standard
143 solution containing ¹³C HCB and TCB D₃ (c=400 pg μL⁻¹) were added. Prior to the extraction
144 of particle-phase PFCs, 50 μL of standard solutions containing ¹⁸O₂ PFH_xS, ¹³C PFOS, ¹³C
145 PFBA, ¹³C PFH_xA, ¹³C PFOA, ¹³C PFNA, ¹³C PFDA, ¹³C PFUnDA and ¹³C PFD_oDA
146 (c=200 pg μL⁻¹) were added to the filters. PFCs were extracted by fluidized bed extraction
147 using methanol. The extract volume was reduced to 150 μL. Prior to the measurement, 50 μL
148 of an injection standard (EtFOSAA D₅ (c=400 pg μL⁻¹) were added.

149 Synthetic musk fragrances and PBDEs in the gas phase were extracted three times (1 hr, 1 hr,
150 ½ hr) by cold column extraction using hexane/acetone 1:1 (v:v) (Weinberg et al., submitted.
151 The extract volume was reduced to 150 μL as described above. Prior to the measurement,
152 50 μL of an injection standard solution containing ¹³C HCB and Fluoranthene D₁₅ (c=400
153 pg μL⁻¹) were added. Particle-bound PBDEs and synthetic musk fragrances were extracted
154 with hexane/acetone 1:1 (v:v) using accelerated solvent extraction. Prior to the extraction 50
155 μL of a solution containing mass-labelled synthetic musks and PBDEs (see above) were
156 added. The volume of the extracts was reduced to about 1 mL. Clean-up of the extracts was
157 performed using glass columns filled with 5 g of silica gel (0 % deactivated) and covered by

158 3 g aluminium oxide (15 % deactivated). Evaporated extracts were transferred to the glass
159 columns and eluted with 35 mL hexane and 30 mL hexane/dichloromethane 3:1 (v:v). Prior to
160 the measurements, 50 μL of an injection standard solution containing Fluoranthene D₁₅ and
161 ¹³C HCB (c=400 pg μL^{-1}) were added.

162

163 **Place Figure 1 here**

164

165 *1.4 Instrumental Analysis & Quantification*

166 Separation and detection of neutral and ionic PFC was performed by GC-MS and HPLC-
167 MS/MS, respectively, as described by Dreyer et al. (2009b). Details on the instrumental
168 analysis of synthetic musk fragrances and PBDEs are given by Weinberg et al. (submitted).

169 Quantification was based on peak areas of molecular mass to charge ratios in the respective
170 detection mode. Analyte concentrations were calculated with the internal standards method
171 using a seven point calibration. Internal standards were used to correct for analytes losses.
172 Compounds were classified as not detected (n.d.) with signal to noise ratio (S/N) below 3 and
173 not quantified (n.q.) with S/N below 10. Instrumental detection and quantification limits are
174 presented in Table S6 and S7.

175

176 *1.5 Quality Assurance & Quality Control*

177 All sample preparations and extractions were performed in a clean lab (class 10000). PFC
178 containing laboratory equipment was avoided. Glassware was dish-washed and heated at
179 250 °C for at least 10 h. Prior to the sampling, GFF were baked at 400 °C for at least 12 h.
180 PUF/XAD-2/PUF cartridges were thoroughly cleaned using acetone/MTBE 1:1 for PFC
181 samples and hexane/acetone 1:1 for PBDE and synthetic musk fragrance samples. All
182 standard solutions were only used at room temperature. Seven point calibrations were used to
183 quantify target analytes. Mass-labelled internal standards were used to correct for analyte

184 losses during analysis and measurements. Average recovery rates of spiked mass-labelled
185 compounds ranged from 13 % (^{13}C 4:2 FTOH) to 57 % (EtFOSE D₉) for PFC, 83 % (^{13}C
186 BDE47) to 156 % (^{13}C BDE153) for PBDE as well as 97 % (AHTN D₃) and 79 % (MX D₁₅)
187 for musk fragrances. (Table S8, S9).

188 To determine the level of contamination, field blanks were taken during the sampling
189 campaigns. Additionally, solvent blanks (for gaseous samples) and filter blanks (for particle
190 samples) were analyzed with each set of samples that was extracted. Blank concentrations are
191 reported in the supplemental information (Table S10-13). Field blanks were occasionally
192 contaminated with HHCB and AHTN in the low pg m^{-3} and reached 3 pg m^{-3} for HHCB.
193 Field blanks were not contaminated with PFCs or PBDEs. Two solvent blanks were
194 contaminated with ADBI, HHCB and MX at the low pg m^{-3} range. Some PFC solvent blanks
195 contained small amounts of 8:2 FTOH and 10:2 FTOH ($\leq 1 \text{ pg m}^{-3}$). Ionic PFC concentrations
196 in filter blanks were generally below 1 pg m^{-3} . Filter blanks were slightly contaminated with
197 HHCB (about 1 pg m^{-3}) and MX (4 pg m^{-3}). All PBDE filter blanks were contaminated with
198 BDE183 in the range of 2 pg m^{-3} and highly contaminated with BDE209 ranging from 647 to
199 1202 pg m^{-3} . The source for the BDE209 contamination remained unclear. Therefore,
200 BDE209 was excluded from further discussion. Concentrations of the remaining analytes
201 were blank-corrected.

202 The uncertainty of the entire method (sampling, sample preparation, detection) was calculated
203 according to Eurachem CITAC guidelines. It was between 2.6 % (AHMI) and 49 % (ADBI)
204 for musk fragrances, 45 % for BDE183 (Table S14), and between 13 % (8:2 FTOH) and
205 163 % (PFOSA) for PFCs (Dreyer et al., 2009b).

206

207

208

209 *1.7 Statistical Analysis*

210 Statistical analyses were performed using Winstat (version 2007). Due to the low number of
211 samples, differences between concentrations at WWTPs and reference sites were evaluated
212 using the Mann-Whitney-U-test. Correlation analyses were performed by Pearson correlation.

213

214 *1.8 Air Mass Back Trajectories*

215 To monitor the air mass origin, seven-days air mass back trajectory were calculated using
216 Hysplit 4.8 (Draxler and Rolph, 2003) using NCEP's GDAS data with a resolution of one
217 degree latitude/longitude. Trajectories were calculated for 3 h intervals (one day samples) and
218 6 h intervals (three day samples).

219

220

221 **3 Results**

222 *3.1 PFCs*

223 Volatile and semi-volatile PFCs were detected in all gas-phase samples taken at WWTPs and
224 reference sites (Figure 2, Table S15). Total concentrations of neutral PFCs in gas-phase
225 samples at WA ranged from 97 (WA4) to 228 pg m^{-3} (WA1) and from 74 (RA4) to 193 pg m^{-3}
226 (RA2) at the corresponding reference site. Total PFC concentrations at WB and its
227 corresponding reference site were between 290 (WB2) and 1004 pg m^{-3} (WB5) and between
228 23 (RB5) and 345 pg m^{-3} (RB4), respectively. Compositions of semi-volatile and volatile
229 PFCs in gas-phase samples are given in Figure S4. At WA, the group of FTOHs were
230 observed in highest proportions (75 %), followed by FTAs (10 %), FASAs (9 %) and FASEs
231 (6 %). At the corresponding reference site RA, average contribution decreased in the order of
232 FTOH (74 %), FASA (11 %), FTA (9 %), and FASE (7 %). At WB, average proportions were
233 76 % for FTOHs, 17 % for FASAs, 5 % for FTAs and 2 % for FASEs. At the corresponding

234 reference site RB, average contribution decreased in the order of FTOH (88 %), FTA (5 %),
235 FASA (4 %) and FASE (3 %).

236

237 **Place Figure 2 here**

238

239 Ionic PFCs were detected in all particle-phase samples (Figure S3, Table S16). Total
240 concentrations at WA and RA ranged from 2 to 13 pg m^{-3} and <1 to 25 pg m^{-3} , respectively.
241 At WB, concentrations were between <MQL and 5 pg m^{-3} and at the RB between 2 and 27 pg
242 m^{-3} . Compositions of PFSA and PFCA are given in Figure S5. PFBA, PFOS and PFOA
243 were the most abundant compounds and were detected in more than two-thirds of the
244 samples. With exceptions of WB1, WB5, RA5 and RB1 the proportion of PFBA was
245 observed at >60 %. At WA and WB proportions of PFOSA were 17 % and 26 %, respectively.
246 Contributions of other compounds varied but were usually below 10 %. Ionic
247 PFCs were also analysed in three-day gas-phase samples. PFBS, PFOS, PFBA, PFPA,
248 PFHxA, PFHpA, PFOA, PFNA were detected at very low concentrations (usually below 0.1
249 pg m^{-3}) at WA and/or WB.

250

251

252 *3.2 Synthetic Musk Fragrances*

253 Synthetic musk fragrances were observed in all gas-phase samples and reference sites (Figure
254 3, Table S17). Total musk fragrance concentrations at WA ranged from about 5.52 (WA1) to
255 128 ng m^{-3} (WA4) and from 73 (RA3) to 961 pg m^{-3} (RA4, note the different units) at the
256 corresponding reference site. At WB and RB, total concentrations of synthetic musk
257 fragrances were between 75 (WB1) and 480 ng m^{-3} (WB5) and between 116 (RA1) and

258 826 pg m^{-3} (RA5). HHCB and AHTN were the only analytes that were detected in all air
259 samples. ADBI and AHMI were often detected at both WWTPs with concentrations ranging
260 from 11 to 1741 pg m^{-3} (ADBI) and from 16 to 6551 pg m^{-3} (AHMI). At reference sites,
261 ADBI was detected only occasionally at concentrations of about 9 pg m^{-3} . ATII as well as
262 nitro musks were not detected in any sample. The percental composition of musk fragrances
263 are displayed in Figure S6. At WA/WB, average proportions decreased in the order of HHCB
264 (93 %/82 %), AHTN (5 %/15 %), AHMI (1 %/2 %), and ADBI (1 %/1 %). At reference sites,
265 87 % of the musk fragrances were made of HHCB, the remaining 13 % by AHTN.

266

267 **Place Figure 3 here**

268

269 Particle-bound synthetic musk fragrances were only observed in air samples at WA, WB and
270 RB (Figure S3, Table S18). At RA, particle-phase concentrations were below the limit of
271 detection. Except for ADBI and AHMI in some samples, usually less than 1 % of the total
272 musk fragrance concentration was observed in the particle phase. Total particle-phase
273 concentrations ranged from 49 to 534 pg m^{-3} (WA), 152 to 1615 pg m^{-3} (WB) and 7 to
274 24 pg m^{-3} (RB). HHCB (3-1362 pg m^{-3} ; 33-86 %) and AHTN (4-211 pg m^{-3} ; 10-67 %) were
275 the dominant analytes (Figure S7). Except for WB2, ADBI and AHMI were detected in all air
276 samples of both WWTPs at concentrations ranging from 3 to 22 pg m^{-3} . ATII, MX and MK
277 were not observed in any particle-phase sample.

278

279 3.3 PBDEs

280 Of those PBDEs analysed in this study, only BDE154 and BDE183 were occasionally
281 detected in gas-phase samples (Table S19). BDE154 was observed in samples WA2 and RA5
282 at concentrations around 2 pg m^{-3} . BDE183 was only observed in samples RA3 and RA5

283 (4 pg m^{-3}). BDE28, BDE48, BDE99, BDE100, BDE153, BDE154 were not detected in any
284 particle-phase sample and concentrations of BDE209 were below those detected in the filter
285 blanks. BDE183 was detected in all particle-phase samples of WWTPs and reference sites
286 (Table S20). Concentrations of particle-phase BDE183 were between <1 and 2 pg m^{-3} (WA)
287 and between 2 and 27 pg m^{-3} (WB). BDE183 concentrations at reference sites were usually
288 around 1 pg m^{-3} .

289

290

291 **4 Discussion**

292 *4.1 PFCs*

293 Overall, PFC concentrations determined at WWTPs and reference sites were in the same
294 order of magnitude as those observed in other studies for rural and semi-urban areas of
295 Northern Germany, (Dreyer et al., 2009a; Jahnke et al., 2007) as well as for other semi-urban
296 and urban sites around the world (Barber et al., 2007; Kim and Kannan, 2007; Stock et al.,
297 2004). The gas-phase composition observed in this study was usually in agreement to that of
298 recently published studies on perfluoroalkyl compounds in air (Barber et al., 2007; Dreyer et
299 al., 2009a; Dreyer et al., 2009b; Jahnke et al., 2007); however, the particle phase composition
300 was not. Whereas Dreyer et al. (2009a) observed PFOS in highest abundances and Barber et
301 al. (2007) and Harada et al. (2005) PFOA, results of this study indicate PFBA as most
302 dominant particle-bound PFC. This result was likely not caused by WWTPs as PFBA sources
303 since high PFBA abundances were observed in air of both WWTPs and both reference sites
304 (Figure S3, S5). It could be a result of the recent change from long-chain PFCA to short-chain
305 PFCA such as PFBA (Renner, 2006). Moreover, concentrations of perfluoroalkyl
306 carboxylates and sulfonates at WWTPs were not higher than those of corresponding reference
307 sites. In comparison to their particle-phase concentrations, gas-phase concentrations of

308 selected PFCA and PFSA were about two orders of magnitude lower and thus negligible.
309 Although controversially discussed, it may be that ionic PFC, potentially occurring in the gas
310 phase (Mc Murdo et al. 2008, Mader 2009), were adsorbed to the glass fibre filters and were
311 thus calculated as particle phase PFC (Arp and Goss, 2008; Arp and Goss, 2009; Barton et al.,
312 2009). However, it should be noted that data on ionic PFC in the gas phase is quite uncertain
313 because of concentrations at the detection limit and low recovery rates (about 50 % for PFOS,
314 < 10 % for PFCA). Overall, these results indicate that emission of PFC-loaded aerosols or
315 gaseous PFCA and PFSA is, if at all, of rather minor importance.

316

317 In contrast to ionic PFCs, total concentrations of airborne volatile PFCs were higher at
318 WWTPs than at corresponding reference sites by a factor of 1.5-2 (WA/RA) and 1.5-4
319 (WB/RB). This difference was significant ($p < 0.05$) only at WB. Sum concentration
320 differences were mainly caused increased FTOH concentrations at WWTPs. At WB, this
321 difference was statistically significant ($p < 0.05$). Additionally, concentrations of gas-phase
322 EtFOSA and MeFBSA were significantly higher at WB than at RB. The presence of FASAs
323 and FASEs in waste water or activated sludge was demonstrated in various studies (2009;
324 Becker et al., 2008; Rhoads et al., 2008; Schultz et al., 2006; Sinclair and Kannan, 2006) and
325 FTOH have been reported in WWTP effluents (Mahmoud et al., 2009). Due to their high air-
326 water partition coefficient (Lei et al., 2004), these compounds will likely partition to the
327 atmosphere. In WWTPs, partitioning from waste water will be further enhanced by the
328 aeration process and results in increased air concentrations close to WWTPs. This process
329 may have caused elevated concentrations and proportions of some analytes in WA and
330 particularly in WB samples. The altered PFC profile observed for samples WA4 and WB2
331 (three-days-samples) may indicate different waste water discharge profiles on weekends (e.g.
332 a shift of incoming waste waters from industrial sources to households).

333

334 *4.2 Musk Fragrances*

335 Air concentrations of musk fragrances at both reference sites were in good agreement with
336 those reported by Xie et al. (2007) from coastal and semi-rural areas in Northern Germany, by
337 Kallenborn et al. (1999a) in ambient air samples from Norway, and by Peck and Hornbuckle
338 (2004) from samples over Lake Michigan, USA. Comparison of this study's concentrations
339 detected at WWTPs to those observed at an urban US site (Peck and Hornbuckle, 2006) or
340 close to a Chinese cosmetic plant (Chen et al., 2007) indicate the source potential of WWTPs.
341 Maximum urban values (5300 pg m⁻³) reported by Peck and Hornbuckle (2006) were similar
342 to low concentration samples (WA1, WA3). Concentrations of the remaining WA and WB
343 samples were at least one order of magnitude higher. Concentrations at WB were 3 to 49
344 times higher than those of WA but still lower than those observed in the cosmetic plant (Chen
345 et al., 2007). This study's musk fragrance profiles with HHCB and AHTN as predominant
346 compounds corroborate with production data from Europe (OSPAR, 2004) as well as findings
347 of other authors (Chen et al., 2007; Kallenborn and Gatermann, 2004; Peck and Hornbuckle,
348 2006; Peck and Hornbuckle, 2004) The non-detects of nitro musk fragrances are likely due to
349 the voluntary phase out of these compounds in the 1990s (Käfferlein and Angerer, 2001).

350 Musk fragrances concentrations were significantly higher ($p < 0.05$) at both WWTPs than at
351 corresponding reference sites revealing that musk fragrances volatilize from waste water
352 where they occur in high quantities (Bester, 2004; Chen et al., 2007). In contrast to studies
353 reporting ATII in waste water (Heberer, 2002), it was not observed in air samples at WA and
354 WB. Since only 6 % of the musk fragrances were detected in the particle phase, volatilization
355 from the waste water and not aerosol formation seems to be the main removal mechanism of
356 these compounds from waste water into the atmosphere.

357

358 *4.3 PBDEs*

359 PBDE contamination of this study's WWTP and reference site samples was rather low and, if
360 detected at all, similar to those reported by Jaward et al. (2004), Lee et al. (2004) or Law et al.
361 (2008) for rural or background samples in Europe (usually below 5 pg m^{-3}). Only particle-
362 bound BDE183 was detected constantly in all samples of this sampling campaign. In contrast
363 to WA, BDE183 concentrations at WB were significantly higher ($p < 0.05$) compared to the
364 reference site, indicating that BDE183 might be subject to aerosol-related emission from the
365 aerated waste water. That BDE183 was the only PBDE frequently detected was surprising
366 since other studies reported BDE47 and BDE99 in much higher concentrations than BDE183
367 in waste water or in air (Agrell et al., 2004; Arnold et al., 2008; Chen et al., 2009; North,
368 2004; Shoeib et al., 2004). However, results of our QA/QC procedures or follow-up
369 measurements did not question these observations. As reviewed by De Wit (2002), lower
370 brominated PBDEs may have also been generated by debromination of BDE209 during
371 analyses or by photolysis by UV light and sunlight.

372

373 *4.4 Synopsis of PFC, PBDE and Musk Fragrance Concentrations & Comparison Between the*
374 *two WWTPs*

375 Generally air concentrations increased in the order of PBDEs < PFCs < musk fragrances. Air
376 concentrations of musk fragrances at reference sites usually exceeded those of semi-volatile
377 and volatile PFCs by a factor of 2 to 3 (figures 2, 3). In contrast to reference sites, air
378 concentrations of musk fragrances exceed those of semi-volatile and volatile PFCs by several
379 orders of magnitude at WWTPs. Reported concentrations for musk fragrances in German
380 WWTP influents were between 100 and 1700 ng L^{-1} (AHTN) and between 200 and 3700
381 ng L^{-1} (HHCB) (Bester, 2004; Ternes et al., 2007). For PFC, reported European
382 concentrations ranged from 1.5 to 340 ng L^{-1} (PFOS), 0.2 to 220 ng L^{-3} (PFOA) or 0.2 to 4

383 ng L⁻¹ (PFOSA) (Becker et al., 2008; Bossi et al., 2008; Clara et al., 2008). In Japanese
384 WWTP effluent samples, 17 ng L⁻³ 8:2 FTOH was detected (Mahmoud et al., 2009). Thus,
385 concentrations differences between musk fragrances and PFCs in water are similar to
386 differences observed at WA and WB. Gas-phase concentrations of musk fragrances and PFCs
387 of both WWTPs were not correlated indicating different sources over the sampling period
388 and/or different partitioning or release from the aeration tanks of WWTPs.

389

390 Except for ionic PFCs in the filter samples, gas- and particle phase concentrations of musk
391 fragrances, PFCs and BDE183 were higher at WB than at WA. At WA and RA, FASA and
392 FASE proportions were quite similar, whereas they were increased at WB compared to RB.
393 Enhanced particle-phase PFOSA proportions were observed at both WWTPs compared to the
394 corresponding reference sites, however, this increase was higher at WB than at WA. Increased
395 concentrations and proportions of most target analytes at WB may be caused by different
396 reasons: 1st the size of the WWTPs. The population equivalent was higher at WB (210000)
397 than at WA (86500) which may have resulted in enhanced emissions at WB and thus elevated
398 differences between air concentrations at WB and RB than at WA and RA. 2nd the waste
399 water origin. At WA, waste water mainly originated from industrial sources (2/3) and less
400 from private households (1/3). At WB, about 2/3 of the waste water originated from
401 households which were reported to be the dominant sources of musk fragrances (Kallenborn
402 et al., 1999b; OSPAR, 2004; Reiner and Kannan, 2006) and important sources for PFCs
403 (Becker et al., 2008; Bossi et al., 2008; Clara et al., 2008) in waste water. 3rd differences of
404 WWTP operation parameters. WWTP operation parameters such as detention periods, waste
405 water flow-through or aeration power may influence the volatilization of waste water
406 contaminants. Correlation analysis ($R^2 < 0.16$) indicated that waste water flow-through did
407 not have an obvious influence on the different concentrations of target analytes at the
408 WWTPs. Information on other parameters was not provided by the WWTP operators. 4th the

409 location of reference sites and WWTPs in relation to the air mass origin. During sampling at
410 WA and RA, air masses arrived from mainly northern and eastern directions (Figure S8). RA
411 was located south of WA and the town of Lüchow (figure S1). Thus, air sampled at RA may
412 have had contact to nearby urban areas and thus elevated concentrations. In contrast, air
413 masses were arriving from western and southern regions during sampling at WB and RB
414 (figure S8). Thus, RB was probably not contaminated from close-by urban areas. On the other
415 hand, concentrations observed at WB may contain an urban signal. Furthermore, elevated
416 concentrations observed at RB2 and RB4 indicate an influence of rather distant sources since
417 air masses arrived from areas that were identified as source regions of airborne PFCs and
418 other pollutants (Dreyer et al., 2009a; EEA, 2008).

419

420

421 **5. Conclusions & Outlook**

422 For the first time, it was demonstrated that musk fragrances, neutral PFCs and BDE183 may
423 be released from waste water in aeration tanks of WWTPs to the atmosphere. WWTPs can
424 therefore be regarded as sources of these compounds to the atmosphere. However, since
425 sampling was conducted in summer time and waste water temperatures are roughly 10 °C
426 higher in summer than in winter, partitioning from the waste water to the air might have been
427 elevated. Overall, results of this study suggest that volatilization from waste water is probably
428 the more important release mechanism compared to aerosol formation. WWTPs appeared to
429 be rather minor sources for PFCs and PBDEs if their concentrations are compared to the
430 tremendously elevated ones of musk fragrances. Thus, future studies on mass balance should
431 include this loss mechanism at least for musk fragrances. Further studies should also
432 investigate the influence of WWTP operational conditions on emitted concentrations to

433 comprehensively estimate source strength or emission factors. Therefore longer time series
434 and sampling at more than on reference site are needed.

435

436

437 **Supplemental Information**

438 Supplemental information is available covering details on the target analytes, methodological
439 aspects, compound concentrations and composition, and results of trajectory analysis.

440

441

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449

450

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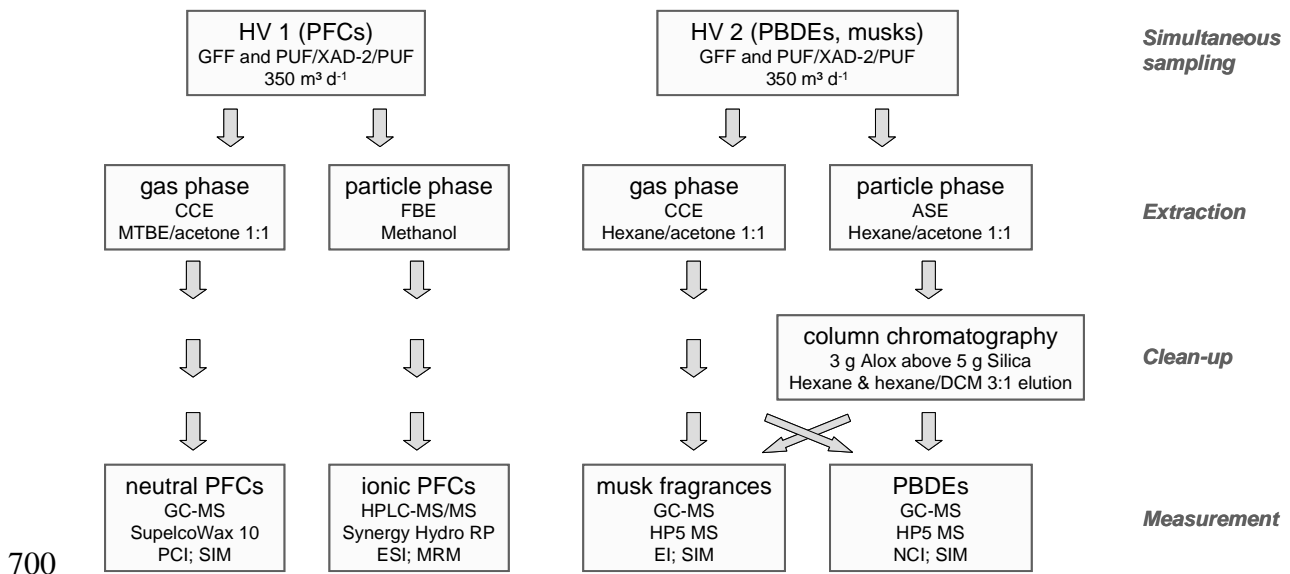
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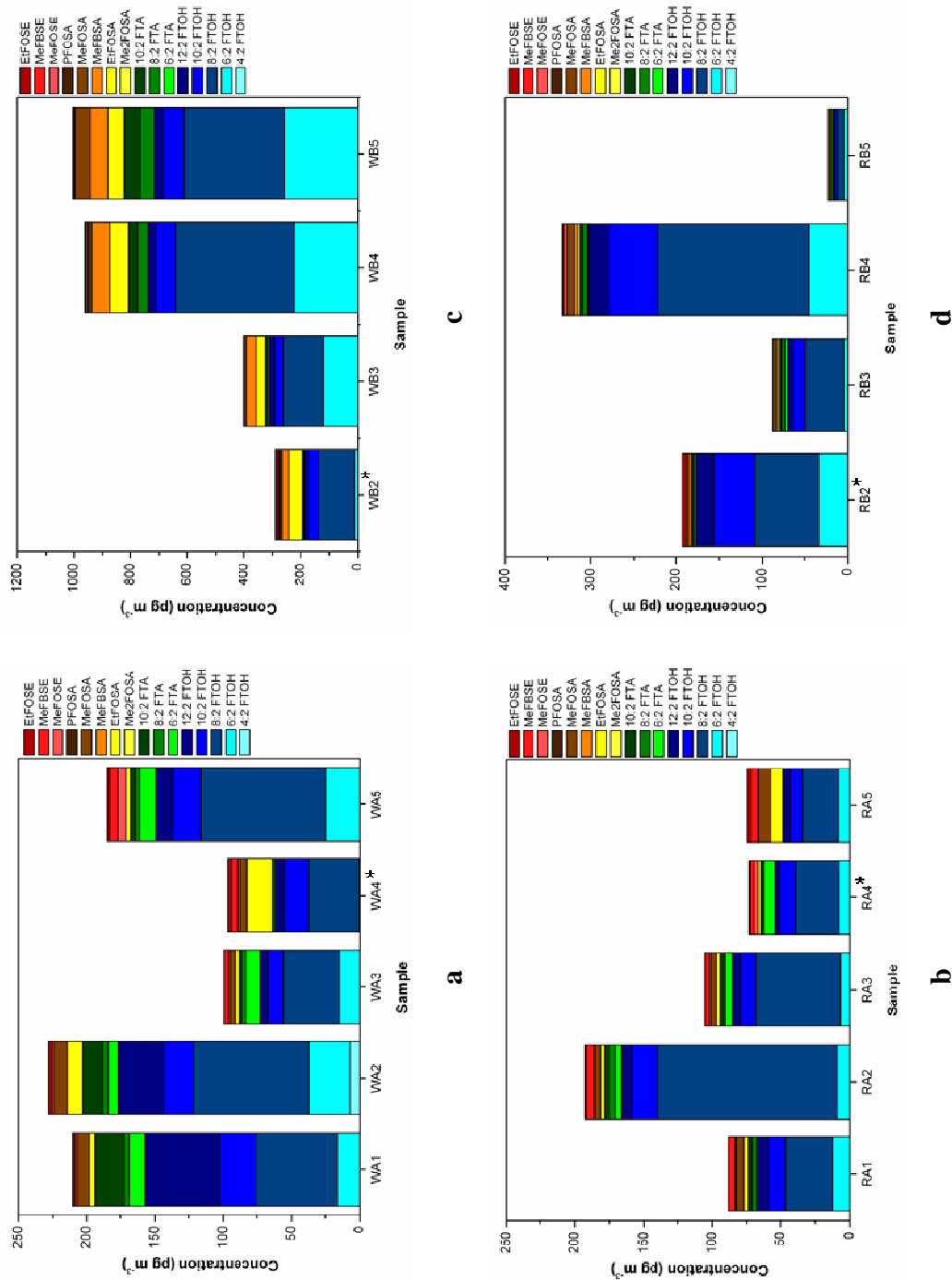
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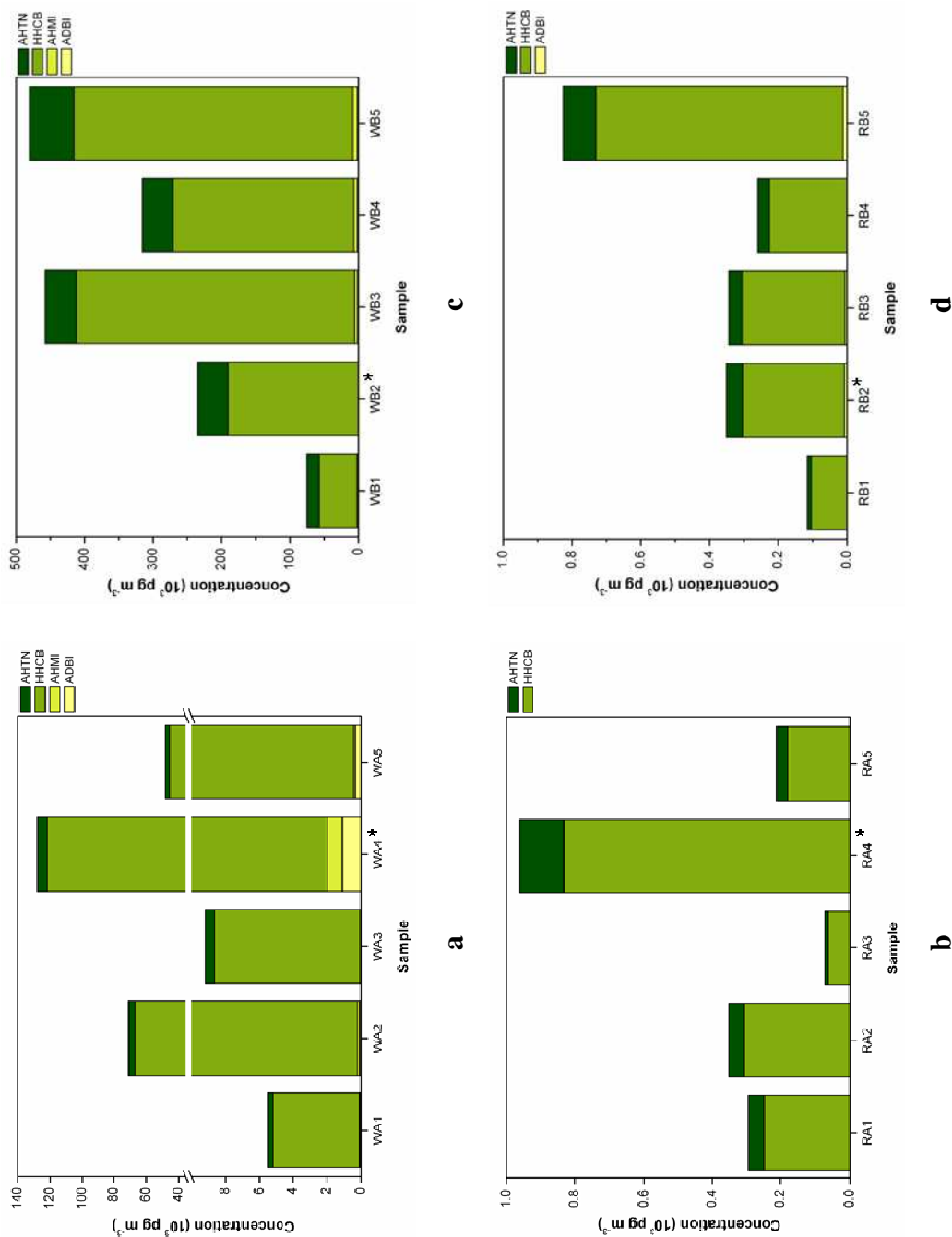
701 Figure 1: Overview about the analytical processes. HV: high volume sampler. GFF: glass
 702 fiber filter. CCE: cold column extraction. FBE: fluidized bed extraction. ASE: accelerated
 703 solvent extraction. EI: electron impact ionization. PCI: positive chemical ionization. NCI:
 704 negative chemical ionization. SIM: selected ion monitoring. ESI: electrospray ionization.
 705 MRM: multi reaction monitoring. DCM: dichloromethane. MTBE: methyl tert-butyl ether.



707 Figure 2: Concentrations (pg m⁻³) of semi-volatile and volatile PFCs in gas-phase samples
 708 taken at two waste water treatment plants (WA (a) and WB (c)) and at the corresponding
 709 reference sites (RA (b) and RB (d)). Sampling periods: 04.08. - 11.08.2009 (WA) and 20.08. -
 710 27.08.2009 (WB). Asterisks mark the 3-day samples. WB1 and RB1 were not measured due
 711 to the high water content of the sample which resulted in serious analytical problems. RB5

712 may not be representative due to technical problems with the high-volume sampler. Note the
 713 different scales.

714



715 Figure 3: Concentrations (10³ pg m⁻³) of musk fragrances in gas-phase samples taken at two
 716 two waste water treatment plants (WA (a) and WB (c)) and at the corresponding reference
 717 sites (RA (b) and RB (d)). Sampling periods: 04.08. - 11.08.2009 (WA) and 20.08. -
 718 27.08.2009 (WB). Asterisks mark the 3-day samples. Note the different scales.