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Landfills as sources of polyfluorinated compounds, polybrominated diphenyl ethers and musk fragrances to ambient air

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Abstract

In order to investigate landfills as sources of polyfluorinated compounds (PFCs), polybrominated diphenyl ethers (PBDEs) and synthetic musk fragrances to the atmosphere, air samples were simultaneously taken at two landfills (one active and one closed) and two reference sites using high volume air samplers. Contaminants were accumulated on glass fiber filters (particle phase) and PUF/XAD-2/PUF cartridges (gas phase), extracted by methyl-tert butyl ether/acetone (neutral PFCs), methanol (ionic PFCs) or hexane/acetone (PBDEs, musk

fragrances), and detected by GC-MS (neutral PFCs, PBDEs, musk fragrances) or HPLC-MS/MS (ionic PFCs). Total concentrations ranged from 84 to 706 pg m^{-3} (volatile PFCs, gas phase), from <MQL to 42 pg m^{-3} (ionic PFCs, particle phase), from 204 to 1963 pg m^{-3} (synthetic musk fragrances, gas+ particle phase) and from 1 to 11 pg m^{-3} (PBDEs, gas+ particle phase). Observed sum concentrations of PFCs and synthetic musk fragrances and partly PBDE concentrations were elevated at landfill sites compared to corresponding reference sites. Concentrations determined at the active landfill were higher than those of the inactive landfill. Overall, landfills can be regarded as a source of synthetic musk fragrances, several PFCs and potentially of PBDEs to ambient air.

1. Introduction

Due to their persistence, bioaccumulation and/or toxicity polyfluorinated compounds (PFCs), polybrominated diphenyl ethers (PBDEs) and synthetic musk fragrances have been reported to be chemicals of emerging environmental concern (De Wit, 2002; Peck, 2006; Prevedouros et al., 2006). Although analysed for about a decade, their environmental fate is not fully understood yet. There are still knowledge gaps concerning their sources to the atmosphere. The few investigated direct sources of atmospheric PFCs, PBDEs and synthetic musk fragrances comprise manufacturing sites, cosmetic plants, waste-related facilities or waste water treatment plants (Agrell et al., 2004; Barton et al., 2006; Chen et al., 2009; Chen et al., 2007; St-Amand et al., 2008; Ter Schure et al., 2004; Weinberg et al., in press). Beside these point sources, areas of high industrial impact and population density have also been regarded as sources to the atmosphere (Barber et al., 2007; Dreyer et al., 2009c; Peck and Hornbuckle, 2006; St-Amand, 2008) which is likely due to their widespread distribution in everyday-used products from which they can be released by volatilization or during product application

(Dinglasan-Panlilio and Mabury, 2006; Fiedler et al., in press; Kim et al., 2006; Reiner and Kannan, 2006; Roosens et al., 2007).

After usage, such products or treated items are discarded, pre-treated and finally disposed at landfills as final sink (Eggen et al. 2010, Slack et al 2004) (Figure S1). It is well known that waste treatment, such as recycling and incineration result in atmospheric emissions of PBDEs (Agrell et al., 2004; Chen et al., 2009; Petreas and Oros, 2009; Zhao et al., 2009). Similarly, Ellis et al. (2001) suggested thermolysis of fluoropolymers as source of polyfluorinated acids. Being stored at landfills PFCs, PBDEs and synthetic musk fragrances have the potential of being released into the environment (Prevedouros, 2006; Prevedouros et al., 2004; Slack et al., 2007). In the past years, several efforts have been performed to investigate these compounds in landfill leachates and their contribution to the contamination of the aquatic environment (Bossi et al., 2008; Busch et al., 2010; Eggen et al 2010; Kallenborn et al., 2004; Odusanya et al., 2009; Osako et al., 2004). The atmospheric contamination pathway due to volatilisation from the disposed products was less investigated. To the best of our knowledge, there is only one study dealing with atmospheric emissions of PBDEs from a landfill in Ottawa, Canada (St-Amand, 2008). For PFCs and musk fragrances data is currently not available.

The objective of the present study was to investigate the occurrence and distribution pattern of airborne PFCs, PBDEs and synthetic musk fragrances at landfills and to elaborate if landfills can be regarded as sources of PFCs, PBDEs and musk fragrances to the atmosphere. Therefore, air samples were taken simultaneously at landfills and reference sites which were supposed to be not contaminated by the presumed source and analysed for the compounds of interest.

2. Experimental

2.1 Chemicals

All solvents, native and mass-labelled analytical standards and gases were of high purity. Details on all compounds, their acronyms, suppliers and qualities are listed in table S1.

2.2 Sampling

Air sampling was conducted at two landfills in Northern Germany from 11.08.-18.08.2009 (landfill LC, closed site) and 27.08.-02.09.2009 (landfill LA, active site). LC is a sanitary landfill located in a rural area and was closed in 2003. The former waste dumping site is covered by synthetic sealing lanes, soil and plant covering in order to generally prevent atmospheric emissions and to avoid uncontrolled leakage. However, a small part of LC is still in operation for regional plastic diminishments for pre-treatment and further transport, compost and electronic waste of about 50000 inhabitants. Landfill LA is situated close to a city of about 70000 inhabitants and serves about 170000 people. After pre-treatment, waste is deposited to the active section of this landfill. LA deposits waste from almost all categories, such as sanitary waste, compost, plastics and electronic devices. Two reference sites located at a distance of about 5 km west of the landfills were sampled simultaneously to LC and LA. The reference sites were assumed not to be contaminated by landfills themselves since this part of northern Germany receives winds primarily from west- and south-western directions. At each landfill and each reference site two high volume samplers (HV1, HV2) were deployed and operated for one week. HV1 was used to collect PFCs. Airborne PBDEs and synthetic musk fragrances were sampled with HV2. Four daily air samples (Monday, Tuesday, Wednesday, Thursday) and one three-day sample (Friday-Monday) were taken with each HV at all sites. The average sampling rate was about $350 \text{ m}^3 \text{ d}^{-1}$.

Gas-phase compounds were enriched on PUF/XAD-2/PUF cartridges (ORBO™ PUF/XAD-2/PUF cartridges 2500, Supelco, Munich, Germany). Particle-associated analytes were accumulated on glass fibre filters (GFF; diameter 150 mm, Macherey&Nagel, Düren, Germany). Prior to the sampling, cartridges for PFCs were spiked on the upper PUF slice with 50 µL of a standard solution containing ¹³C 4:2 FTOH, ¹³C 6:2 FTOH, ¹³C 8:2 FTOH, ¹³C 10:2 FTOH, MeFOSA D₃, EtFOSA D₅, MeFOSE D₇, and MeFOSE D₉ (c=200 pg µL⁻¹). PBDE and musk fragrances' cartridges were spiked with 50 µL of an internal standard solution containing ATHN D₁₃, MX D₁₅, ¹³C BDE28, ¹³C BDE47, ¹³C BDE99, ¹³C BDE153, ¹³C BDE183 and ¹³C BDE209 (c=200 pg µL⁻¹). After sampling, cartridges and GFF were separately packed in aluminium-coated polypropylene bags, sealed air tightly and stored at -20 °C until analysis.

2.3 Sample Preparation

2.3.1 PFCs

Sample preparation and analyses of neutral and ionic PFC are summarized in table 1 and are described in detail elsewhere (Dreyer et al., 2008; Dreyer et al., 2009c). Briefly, volatile PFCs accumulated in PUF/XAD-2/PUF cartridges were cold column extracted three times using MTBE/acetone 1:1 (v:v). The volume of the extracts was reduced to 150 µL by rotary evaporation and nitrogen and extracts were transferred to measurement vials. Prior to the measurement, 50 µL of an injection standard solution containing ¹³C HCB and TCB D₃ (c=400 pg µL⁻¹) were added.

Ionic PFCs were methanol-extracted using fluidized bed extraction. Prior to the extraction, 50 µL of standard solutions containing ¹⁸O₂ PFH_xS, ¹³C PFOS, ¹³C PFBA, ¹³C PFH_xA, ¹³C PFOA, ¹³C PFNA, ¹³C PFDA, ¹³C PFUnDA and ¹³C PFDoDA (c=200 pg µL⁻¹) were added. The volume of the extracts was reduced to 150 µL by rotary evaporation and nitrogen and extracts were transferred to measurement vials. Samples were spiked with 50 µL of an

injection standard solution containing EtFOSAA D₅ (400 pg μL⁻¹). After spiking PFC extracts with the injection standard, white solids formed. Therefore, sample vials were centrifuged and remaining liquid fraction was measured.

2.3.2 PBDEs and Musk Fragrances

Table 1 provides an overview about the analysis of PBDEs and musk fragrances. Gas-phase PBDEs and musk fragrances accumulated in PUF/XAD-2/PUF cartridges were cold-column extracted three times (1 h, 1 h, 30 min) using hexane/acetone 1:1 (v:v). After each cycle, remaining solvent in the cartridge was blown out with nitrogen. The extract volume (approximately 450 mL) was reduced to 1 mL using Synchore polyvap (Büchi, Essen, Germany) at 45 °C and 415 to 380 mbar. Samples were further evaporated to 150 μL by a gentle stream of nitrogen (Barkey optocontrol, Leopoldshöhe, Germany). Finally, extracts were transferred to measurement vials. Prior to the measurement, 50 μL of an injection standard solution (¹³C HCB and Fluoranthene D₁₀, c=400 pg μL⁻¹) were added to the samples. Particle-phase PBDEs and musk fragrances at GFFs were filled into stainless steel extraction cells (volume= 22 mL) of an accelerated solvent extractor (ASE 200, Dionex, Idstein, Germany). 50 μL of a standard solution containing mass-labelled ¹³C BDE27, ¹³C BDE47, ¹³C BDE99, ¹³C BDE153, ¹³C BDE183, AHTN D₃ and MX D₁₅ (c=200 pg μL⁻¹) were added. Remaining space within the cells was filled up with pre-cleaned diatomite (Sigma-Aldrich, Munich, Germany). Accelerated solvent extraction was performed with hexane/acetone 1:1 (v:v) at a pressure of 140 bar and a temperature of 100 °C in two static cycles (5 min, hold time 5 min). After the first extraction cycle, the cell volume was rinsed, purged with nitrogen for 60 s and refilled with solvent. The entire extract volume (about 35 mL) was reduced to 1 mL using Synchore polyvap. Clean-up of the particle phase extracts was performed by column chromatography (inner diameter = 1 cm) using 5 g of silica gel (0 % deactivated) covered by 3 g aluminium oxide (15 % deactivated). Columns were conditioned with hexane.

Evaporated extracts were transferred to the glass columns and eluted with 35 mL hexane and 30 mL hexane/dichloromethane 3:1 (v:v). Finally, eluates were rotary evaporated at 30 °C and 240 mbar to about 1 mL, further reduced to 150 μL using nitrogen and transferred to measurement vials. Prior to the measurement, 50 μL of an injection standard solution containing ^{13}C HCB and fluoranthene D_{10} ($c=400 \text{ pg } \mu\text{L}^{-1}$) were added to the samples.

2.4 Detection and Quantification

Instrumental details on the determination of PFCs were published by Dreyer et al. (2008). PBDEs and musk fragrances in gas- and particle-phase samples were measured using gas chromatography (GC; 6890, Agilent Technologies, Waldbronn, Germany) – mass spectrometry (MS; 5975 inert MS, Agilent Technologies, Waldbronn, Germany). PBDEs were detected using negative chemical ionization (NCI) and the selected ion monitoring (SIM) mode. Synthetic musk fragrances were detected by electron impact ionisation (EI) in the SIM mode. A list of mass to charge ratios (m/z) of all analytes is given in table S4. The GC (Agilent) was equipped with a programmed temperature vaporizer (PTV) inlet. The analytes were separated on a HP-5 MS capillary column, (Agilent, 30 m x 0.25 mm) coated with 5 % phenyl-dimethylpolysiloxane stationary phase (0.25 μm film thickness). The following instrumental settings were used: injection volume 2 μL ; injection mode pulsed splitless; pulse pressure 40 psi; initial inlet temperature 70 °C; inlet heating rate 400 °C min^{-1} ; final inlet temperature 300 °C; oven temperature program: initial oven temperature 60 °C, 5 °C min^{-1} to 170 °C hold for 3 min, 5 °C min^{-1} to 200 °C, 15 °C min^{-1} to 300 °C hold for 20 min (PBDEs) or 5 min (musk fragrances); transfer line temperature 250 °C; column flow 1.4 ml min^{-1} carrier gas: helium; reactant gas: methane. Musk fragrances' and PBDE chromatograms are presented in Figures S2, S3.

Quantification was based on peak areas. Analyte concentrations were calculated with the internal standards method using a seven point calibration. Compounds were classified as not

detected (n.d.) with signal to noise ratio (S/N) below 3 and not quantified (n.q.) with S/N below 10. Instrumental detection and quantification limits of all substance classes are presented in Table S5, S6.

2.5 Quality Assurance and Quality Control

All experiments were conducted in a clean lab (class 10000). For PFC analysis, PFC-containing materials were avoided during sampling and sample preparation. Prior to the sampling PUF/XAD-2/PUF cartridges were soxhlet-cleaned for 24 h using acetone (PFCs) and hexane/acetone 1:1 (PBDEs and synthetic musk fragrances). GFF were heated at 400 °C for at least 12 h. Glassware was dish-washed and heated at 250 °C for 10 h. All standard solutions were only used at room temperature. Mass-labelled standards were used to correct for analyte losses during analysis and measurements. Average absolute recovery rates of mass-labelled compounds ranged from 10 ± 7 % (^{13}C FTOH) to 58 ± 13 % (EtFOSE D₉) for PFCs, 92 ± 14 % (AHTN D₃) and 100 ± 40 % (MX D₁₅) for synthetic musk fragrances, and 78 ± 23 % (^{13}C BDE28) to 137 ± 23 % (^{13}C BDE153) for PBDEs (Table S11).

To determine potential contamination during sampling, field blanks were taken. Additionally, solvent blanks (gas phase) and filter blanks (particle phase) were analyzed with each set of samples extracted. Concentrations in blank samples are reported in the supplemental information (Table S13-16). Field blanks were occasionally contaminated with HHCB and AHTN in the low pg m^{-3} and ranged up to 4.7 pg m^{-3} for HHCB. Field blanks were not contaminated with PFCs or PBDEs. Only some neutral PFCs (8:2 FTOH, 10:2 FTOH and 12:2 FTOH) were occasionally detected in solvent blanks ranging from 0.9 to 2.6 pg m^{-3} . Ionic PFC concentrations in filter blanks were generally below 1 pg m^{-3} . Filter blanks revealed a slight contamination with HHCB (about 1 pg m^{-3}) and MX (4 pg m^{-3}). All PBDE filter blanks were contaminated with BDE183 in the range of 2 to 3 pg m^{-3} . Concentrations of BDE183 at samples LC3, LC4, RC1 and RC4 were lower than filter blanks and were thus not

further discussed. All filter blanks were highly contaminated with BDE209 (608 to 1943 pg m^{-3}). Therefore, BDE209 was excluded from further consideration. The reason of this severe BDE209 contamination remained unclear. Concentrations for the remaining analytes were blank-corrected.

The uncertainty of the entire method (sampling, sample preparation, detection) was determined according to Eurachem guidelines (EURACHEM / CITAC guide CG 04, 2000). It was between 16 % (AHTN) and 28 % (HHCB) for musk fragrances, 21 % for BDE183 (table S17), and between 13 % (8:2 FTOH) and 163 % (PFOSA) for PFCs (Dreyer et al., 2009c).

2.6 Trajectory Analysis

Air mass back trajectories were calculated to check if reference sites were not contaminated by potential landfill emissions. To investigate air mass origin during air sampling, back trajectories were calculated by Hysplit 4.8 (Draxler and Rolph, 2003) for an arriving height of 2 m using NCEP's Global Data Assimilation System (GDAS) data with a resolution of one degree latitude/longitude. Seven-days back trajectories were calculated for 3 h intervals (one day samples) and 6 h intervals (three day samples).

2.7 Statistical Analysis

Statistical analysis was performed using Winstat (version 2007.1). The significance ($p < 0.05$) of concentration differences between landfill samples and their corresponding reference sites was evaluated using the Mann-Whitney-U-test. Correlation analyses were performed by Pearson correlation.

3. Results and Discussion

3.1 PFCs

Volatile and semi-volatile PFCs were detected in all gas-phase samples from landfills and reference sites (Figure 1, Table S18). Total neutral PFC concentrations ranged from 84 (LC5) to 126 pg m^{-3} (LC2) at LC and from 42 (RC3) to 80 pg m^{-3} (RC4) at the corresponding reference site. PFC concentrations at LA and its corresponding reference site were between 134 (LA2) and 706 pg m^{-3} (LA1) and between 54 (RA2) to 284 pg m^{-3} (RA1). At LC and RC, FTOHs were detected in highest proportions (>75 %), followed by FASE/FTA (about 6 % each) and FASA (5 %) (Figure S8). Average proportions at LA and corresponding RA decreased in the order FTOHs (>92 %) > FASA (5 %) > FASE/FTA (1 %) each (Figure S8).

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Ionic PFCs were detected in all particle-phase samples (Figure S5, Table S19). Sum concentrations at LC and RC ranged from 6 (LC4) to 15 pg m^{-3} (LC2) and from <1 (RC4) to 15 pg m^{-3} (RC1). At LA, concentrations were between <MQL (LA2) and 42 pg m^{-3} (LA4) and between 11 (RA5) and 16 pg m^{-3} (RA4). Compositions of PFSA and PFCA are given in Figure S9. PFOS, PFBA, PFHxA, and PFOA were detected in all samples. Remaining ionic PFCs were only occasionally detected at low concentrations (<1 pg m^{-3}). Except for samples LA4, LC3 and LC4, PFBA was the predominant ionic PFC with average proportions of 59 %, followed by PFHxA (16 %), PFOS (11 %) and PFOA (9 %).

Concentrations of PFCs determined in the present study, were in the same range as those of other studies from rural and semi-rural areas in Europe (Barber, 2007; Dreyer et al., 2009b;

Jahnke et al., 2007). Gas phase compositions were usually in agreement to those reported for PFCs in air (Barber, 2007; Dreyer and Ebinghaus, 2009; Jahnke, 2007); however, particle-phase compositions were not. Whereas Dreyer et al. (2009b) observed PFOS in highest abundances and Barber et al. (2007) and Harada et al. (2005) PFOA, results of this study indicate PFBA as most dominant particle-bound PFC. This corroborates the study of Weinberg et al. (in press) who detected PFBA in air samples from waste water treatment plants in highest proportions. Our results are probably rather due to a general production shift from C8 to C4-based fluorochemicals than to landfill emissions of PFBA since high abundances were observed in air samples of both landfills and reference sites. Additionally, highly variable particle-phase PFC concentrations and proportions may indicate an elevated uncertainty of particle-phase data (particularly at these low concentrations) and potential adsorption effects of gas-phase PFCA on GFF (Arp and Goss, 2008; Arp and Goss, 2009; Barton, 2006).

In contrast to particle-bound PFC where there was not difference between landfill and reference sites, air concentrations of volatile and semi-volatile PFCs were 1.5-2.5 (LC) and 1.5-3 (LA) times higher than at corresponding reference sites. Total concentration differences were mainly caused by elevated FTOH concentrations which were significantly higher at LC than at RC. At LA, only the concentration average of 8:2 FTOH was significantly different to that of RA ($p < 0.05$). Also, concentrations of FTAs, FASAs and FASEs were higher at landfills compared to the corresponding reference sites. However, this difference was not significant. Previous studies investigating airborne PFCs in northern Germany observed elevated concentrations in stationary and slow air masses arriving at low altitudes from diffuse sources in urban and industrialized areas (Dreyer and Ebinghaus, 2009; Dreyer et al., 2009b). In the present study, trajectory analysis revealed that, except for LA2 and RA2, sampled air masses were originated in similar areas west of the sampling sites indicating a rather urban sample character. This was also reflected by a constant PFC profile in analyzed

samples. Furthermore, trajectory analysis indicated that reference sites were not contaminated by air arriving from the direction of the landfills. That concentrations of some neutral PFCs, mainly FTOHs and to a lesser extent FASAs, FASEs and FTAs, were nevertheless higher at landfills than at corresponding reference sites strongly suggests that these compounds are subject to volatilisation from products disposed at landfills. Particularly FTOHs are incorporated in polymers in a wide array of products such as plastics, paper packaging and surfactants (Jensen et al., 2008; Kissa, 2001) and a laboratory study revealed the release of PFCs from those products (Dinglasan-Panlilio and Mabury, 2006). The difference in deviation significances (landfill vs. reference site) between the different groups of airborne PFCs may also be attributed to the lower volatility of FASEs and FASAs (Dreyer et al., 2009a; Lei et al., 2004).

3.2 Synthetic Musk Fragrances

Synthetic musk fragrances were observed in all gas-phase samples at landfills and reference sites (Figure 2, Table S20). Total synthetic musk fragrance concentrations at LC and RC ranged from 146 (LC3) to 990 pg m^{-3} (LC1) and from 47 (RC4) to 84 pg m^{-3} (RC3). At LA and RA, total concentrations of musk fragrances were between 579 (LA5) and 1947 pg m^{-3} (LA2) and between 50 (RA4) and 1016 pg m^{-3} (RA2). Whereas HHCB (85 % on average) and AHTN (14 % on average) were detected in all air samples, ADBI and AHMI were only occasionally observed. ATII as well as nitro musks were not detected in any air sample (Figure S10).

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With two exceptions (samples RC4, RC5) particle-bound synthetic musk fragrances were only detected in air samples of LA and RA (Figure S7, Table S19). Total particle-phase concentrations ranged from 8 (LA1) to 57 pg m^{-3} (LA3) and 6 (RA1) to 103 pg m^{-3} (RA2). Total concentrations at RC4 and RC5 were 20 and 30 pg m^{-3} , respectively. HHCB and AHTN were the only substances observed in the particle phase. The proportions were mostly dominated by AHTN (60 % on average) (Figure S11).

Total concentrations of gas-phase musk fragrances were in about the same range as those reported in other studies from comparable rural to suburban locations in Northern Germany (Xie et al., 2007), Norway (Kallenborn et al., 1999) and North America (Peck and Hornbuckle, 2006; Peck and Hornbuckle, 2004). However, elevated concentrations of samples LC1, LA5 and RA2 were similar to concentrations reported for urban sites in North America (Peck and Hornbuckle, 2006). As observed previously (Peck and Hornbuckle, 2006; Peck and Hornbuckle, 2004; Xie, 2007), synthetic musk fragrances investigated in the present study were predominantly detected in the gas-phase. Similar to other studies (Chen et al., 2007; Kallenborn, 1999; Peck and Hornbuckle, 2006; Peck and Hornbuckle, 2004), HHCB and AHTN were the predominant substances in all samples. Xie et al. (2007) reported a mean ratio of HHCB/AHTN of 3.5 which was comparable to that of European market volumes in 2000 (ratio 3.9) (OSPAR, 2004). However, the mean ratio of HHCB/AHTN observed in this study was 6.5. This may be due to the enormous variability of HHCB and AHTN content in personal care products, as demonstrated by Roosens et al. (2007) and Reiner and Kannan (Reiner and Kannan, 2006). ADBI and AHMI were only occasionally detected, probably as result of distinctly lower production volumes of these compounds (OSPAR, 2004). That nitro musks were not detected is likely due to their phase out in the 1990s (Käfferlein and Angerer, 2001).

Concentrations of synthetic musk fragrance in the gas phase were significantly higher ($p < 0.05$) at landfills than at corresponding reference sites (factors of 4-12 (LC) and 2-15

(LA)). Because of their relatively short atmospheric residence times (e.g. HHCB 5.3 h, (Aschmann et al., 2001)) synthetic musk fragrances probably result from rather local and regional than distant sources. Overall, this strongly indicates their volatilisation from waste deposited at landfills.

3.3 PBDEs

None of the PBDE congeners was detected in gas-phase samples. These findings are in contrast to those of St-Amand et al. (2008) who detected air concentrations of PBDEs up to 7 pg m^{-3} close to a sanitary landfill in Ottawa, Canada as well as in other studies from Europe (Gioia et al. 2006, Lee et al. 2004) and North America (Strandberg et al. 2001, Gouin et al. 2006) and Canada.

BDE183 was detected in all particle-phase samples (Table S20). BDE183 concentrations were between 1 and 3 pg m^{-3} at LC and between 1 and 11 pg m^{-3} at LA. BDE183 concentrations at reference sites were usually around $<1\text{-}3 \text{ pg m}^{-3}$. In sample RA1, BDE47 (20 pg m^{-3}), BDE99 (15 pg m^{-3}), BDE100 (6 pg m^{-3}) and BDE154 (2 pg m^{-3}) were also detected.

Overall, PBDE contamination of this study's landfill and reference site samples was rather low and, if detected at all, similar to those reported by Jaward et al. (2004a; 2004b) and Law et al. (2008) for European samples ($<2 \text{ pg m}^{-3}$). This may be due to an effect on the recent ban of penta- and octaBDE formulations in the European Union (Directive 2003/11/EC). Surprisingly, the only PBDE congener that was constantly detected was BDE183. This rather unusual PBDE profile may be explained by the degradation of BDE209 to lower brominated BDEs (De Wit, 2002). Only at LA, BDE183 concentrations were significantly higher ($p<0.05$) compared to the reference site (Figure S7), indicating that BDE183 might be subject to emission from diminishments disposed at the active landfill.

4. Summary & Conclusions

For the first time, synthetic musk fragrances, PFCs and PBDEs were analysed at landfills to investigate the source potential of these sites. Particularly air concentrations of synthetic musk fragrances and several PFCs were elevated at landfills compared to corresponding reference sites. Landfills can therefore be regarded as sources of these compounds to the atmosphere. In general, concentrations decreased in the order of musk fragrances > PFCs > PBDEs which was similar to observations at waste water treatment plants (Weinberg et al. in press). Except for 2 samples (LC3, LA1), air concentrations of musk fragrances usually exceed those of PFCs by factors of 3 to 14. Thus, landfills seem to be rather minor sources for PFCs and PBDEs if their concentrations are compared to the elevated ones of musk fragrances. However, since sampling was conducted in summer, observed concentrations might be comparably high and not representative for a yearly average.

Air concentrations of several PFCs, particulate BDE183, and musk fragrances were significantly higher in samples taken at LA than at LC, indicating elevated contamination at the active landfill (LA) compared to the closed landfill (LC). Different types of waste, varying contaminant contents of products disposed at the landfill sites or different contaminant release mechanisms may have also influenced emissions from these sites and resulted in different proportions of individual target analytes. Air concentrations of PFCs and synthetic musk fragrances at reference sites were quite uniform and may thus display background concentrations.

Overall, future studies are needed to further investigate the release potential of landfills for PFCs, PBDEs and synthetic musk fragrances. Studies should also include more than one reference site in order to determine emission factors of high quality. Longer time series are

needed for the observation of seasonal variations and evaluation of the source strength of landfills.

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Supporting information

Supporting information covers chemicals, meteorological conditions during sampling, methodological details, PFCs, PBDEs and musk fragrances concentrations of the gas- and particle phase as well as details of results' analyses.

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Tables

Table 1: Overview of this study's analytical methods for the determination of airborne PFCs, PBDEs and synthetic musk fragrances. GFF: glass fiber filters. CCE: Cold column extraction. FBE: Fluidized bed extraction. ASE: Accelerated solvent extraction. MTBE: Methyl-tert-butyl ether.

	PFCs	PBDEs	Musk fragrances
Sampling	Air sampling at landfills (LC, LA) and reference sites (RC, RA) (350 m ³ d ⁻¹)		
Enrichment	PUF/XAD-2/PUF, GFF	PUF/XAD-2/PUF, GFF	
Extraction (gas phase)	CCE (MTBE/acetone 1:1)	CCE (hexane/acetone 1:1)	
Extraction (particle phase)	FBE (MeOH)	ASE (hexane/acetone 1:1)	
Clean-Up	---	Column chromatography (3g Alox above 5 g Silica) Particle -phase samples only	---
Target analytes	Neutral PFCs: 5 FTOHs, 3 FTAs, 5 FASAs, 3 FASEs Ionic PFCs: 5 PFSA, 9 PFCAs	BDE28, BDE47, BDE99, BDE100, BDE153, BDE154, BDE183, BDE209	HHCB, AHTN, ADBI, AHMI, ATII, MX, MK
Detection	Neutral PFCs: GC-MS (PCI) Ionic PFC: HPLC-MS/MS	GC-MS (NCI)	GC-MS (EI)

Figures

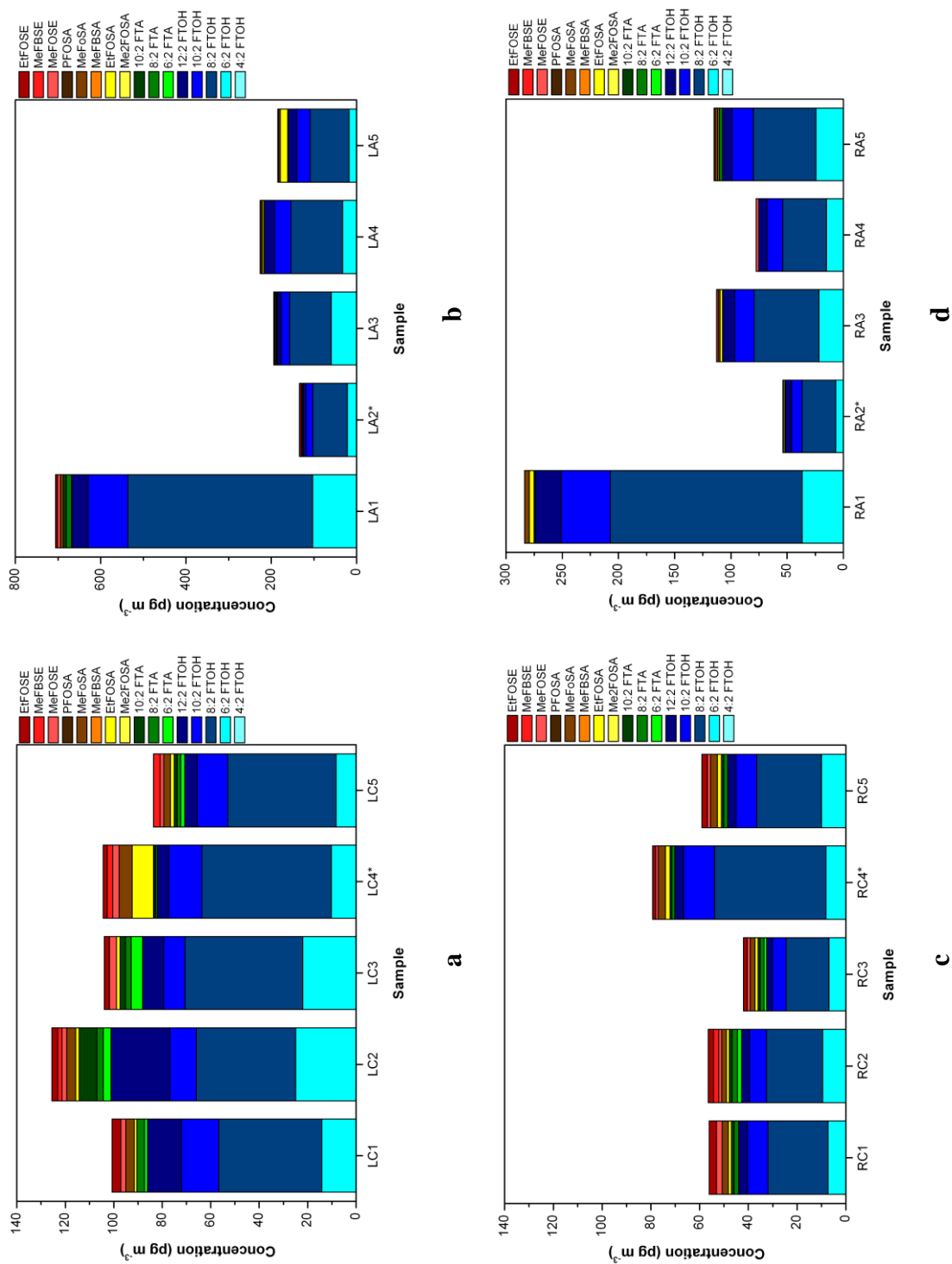


Figure 1: Concentrations (pg m^{-3}) of semi-volatile and volatile PFCs in gas-phase samples taken at landfills LC (a) and LA (b) and at the corresponding reference sites RC(c) and RA (d). Sampling periods: 11.08.-18.08.2009 (LC) and 27.08.-02.09.2009 (LA). Note the different scales. Asterisks mark the 3-day samples.

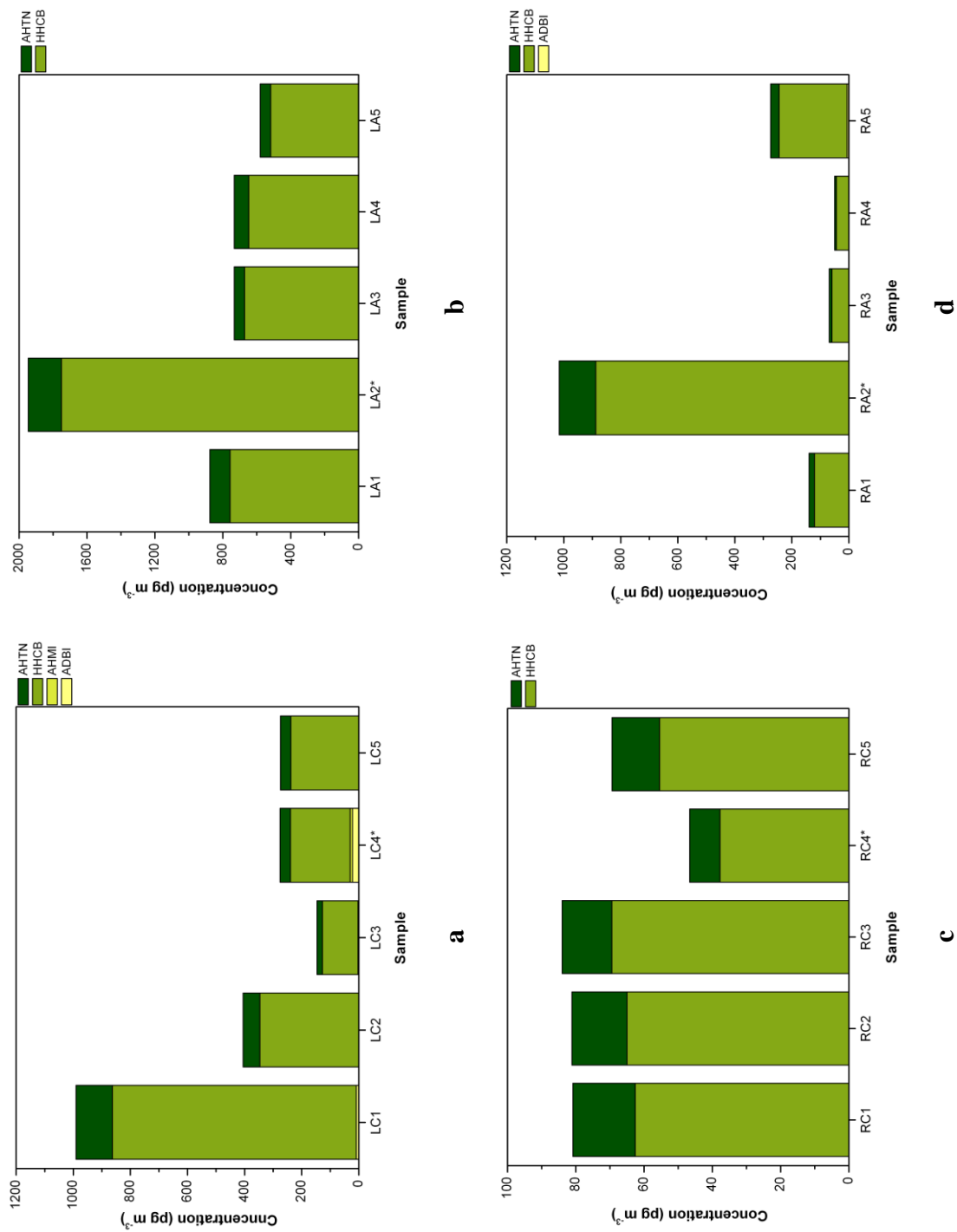


Figure 2: Concentrations (pg m⁻³) of musk fragrances in gas-phase samples taken at two landfills (LC (a) and LA (b)) and at the corresponding reference sites (RC(c) and RA (d)). Sampling periods: 11.08.-18.08.2009 (LC) and 27.08.-02.09.2009 (LA). Note the different scales. Asterisks mark the 3-day samples.

Figures

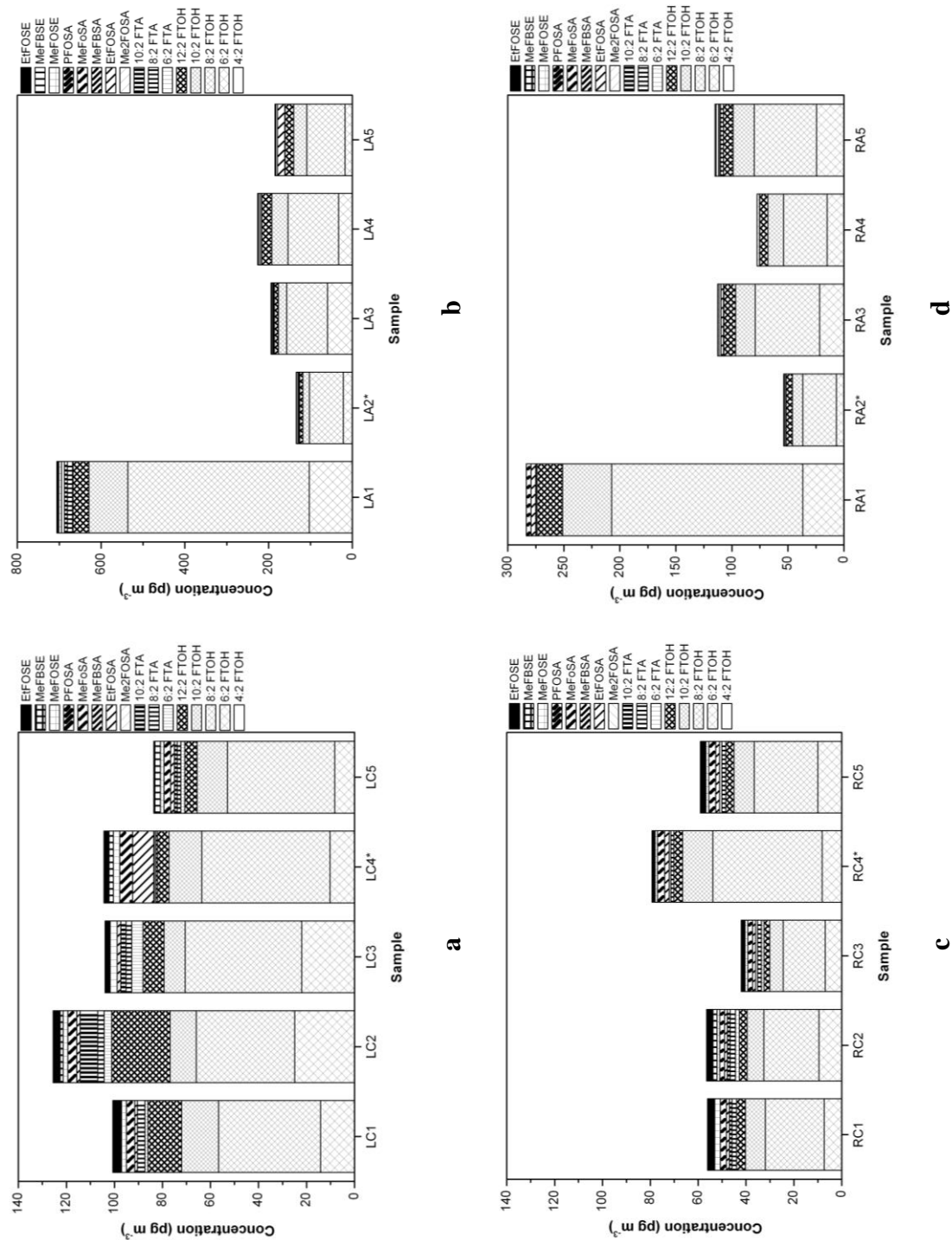


Figure 1: Concentrations (pg m⁻³) of semi-volatile and volatile PFCs in gas-phase samples taken at landfills (LC (a) and LA (b)) and at the corresponding reference sites (RC(c) and RA (d)). Sampling periods: 11.08.-18.08.2009 (LC) and 27.08.-02.09.2009 (LA). Note the different scales. Asterisks mark the 3-day samples.

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