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Atmospheric fate of poly- and perfluorinated alkyl substances (PFASs): I. Day–night patterns of air concentrations in summer in Zurich, Switzerland

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ABSTRACT

Poly- and perfluorinated alkyl substances (PFASs) are anthropogenic pollutants ubiquitously found in the environment. Volatile PFASs are likely transported atmospherically over long ranges, but identification and quantification of emission sources is a challenging task. In this work, special meteorological conditions were utilized to quantify atmospheric emissions of Zurich City, Switzerland with a dual approach of modeling and field measurements. During high pressure systems in summer, a stable nocturnal boundary layer is formed in which pollutants are enriched. For volatile PFASs, a diel pattern of high concentrations in the night and low concentrations during the day was observed in Zurich, which is likely due to the atmospheric boundary layer dynamics. These results enable to model the emission source strength of Zurich City with a multimedia mass balance model in an accompanying paper. Cluster analyses suggested that perfluorocarboxylates (PFCAs) are a result of degradation of volatile precursors and direct emissions.

1. Introduction

Poly- and perfluorinated alkyl substances (PFASs) are a broad group of anthropogenic chemicals that can be divided into various subgroups. A first group consists of neutral volatile PFASs such as fluorotelomer alcohols (FTOHs) and perfluoroalkyl sulfonamides and sulfonamidoethanols (FASAs/FASEs), which herein are called nPFASs. These chemicals are often bound to polymers via acrylate or urethane linkages (so-called fluorinated polymers). The main application areas of nPFASs and their polymers are surface coatings for textiles, paper, or carpets, as well as in impregnation agents. Global annual production of nPFASs is estimated to be in the range of $10–20 \times 10^6$ kg/a. Between 2000 and 2002, $4–5 \times 10^6$ kg/a of FTOHs were produced and production increased to $11–14 \times 10^6$ kg/a in 2004 (Dinglasan-Panlilio and Mabury, 2006). In 2000, more than 3×10^6 kg/a of FASEs and FASAs were produced, but the production has largely decreased since 2002 due to the production stop of the main producer 3 M (Lange et al., 2006). A second group consists of acidic PFASs named perfluoroalkyl acids (PFAAs) consists mainly of perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFSAs). These chemicals are most often used as surfactants, *e.g.* in fire fighting foams (not in use anymore) or as mist suppressants in chromium plating, and are present in many products as residues, *e.g.*, fluorinated polymers. Additionally, it is known that nPFASs partially degrade to PFAAs via biotic and abiotic processes (D'Eon et al., 2006; Ellis et al., 2004; Martin et al., 2006; Rhoads et al., 2008; Schenker et al., 2008; Wang et al., 2009).

Many PFASs are ubiquitously found in all environmental compartments from urban to remote locations (Giesy and Kannan, 2001). Additionally, PFAAs exhibit some critical properties: extreme stability, bioaccumulation (PFAAs with more than seven fluorinated carbons (Kelly et al., 2009; Müller et al., 2011a)), as well as toxic effects, including hepatic and developmental toxicity (Lau et al., 2007). Understanding the sources and pathways of the environmental pollution by PFASs is, therefore, crucial in order to identify and reduce the relevant emissions. Sources of PFAAs to the aquatic environment are rather well studied: industrial production and application, as well as use and disposal of PFAAs containing consumer products have been identified as important emission sources, resulting in PFAA entering the surface waters via wastewater treatment plants (WWTPs) (Huset et al., 2008; Lin et al., 2009). Additional inputs are shown to come from diffuse sources such as rain or street runoff (Müller et al., 2011b; Murakami et al.,

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2009). Atmospheric sources of volatile nPFASs have been less studied and are still not well understood. nPFASs are contained in many products, therefore, populated areas can be expected to act as a diffusive source to the atmosphere. Indoor air samples from residential homes and stores (especially for outdoor equipment) showed elevated nPFAS concentrations (Langer et al., 2010). Additionally, concentration gradients were observed between urban areas and background sites (Barber et al., 2007; Jahnke et al., 2007). Moreover, volatilization from WWTPs and landfills was identified as an additional point source to the atmosphere (Ahrens et al., 2011; Weinberg et al., 2010).

To identify and quantify bulk atmospheric emissions of semivolatile organic compounds from a city, a specific weather phenomenon can be utilized. During stable high pressure systems in summer, the boundary layer, defined as the part of the atmosphere that comes into contact with the surface within an hour, follows a diel (*i.e.* day–night) trend. At night, air near the surface has a lower temperature than the air above, preventing convective mixing. When a city acts as a (constant) source of volatile or semivolatile pollutants, their enrichment can be observed in this small boundary layer. This has been determined for chlorofluorocarbons and hydrochlorofluorocarbons in Dübendorf, Switzerland (Buchmann et al., 2003) and polychlorinated biphenyls (PCBs) in Chicago, USA (MacLeod et al., 2007). During daytime, the surface has a higher temperature than the air above and the atmosphere is mixed up to a height of 1000–2000 m. The atmospheric pollutants are therefore diluted and a diel pattern of high nighttime and low daytime concentrations can be observed.

In this study, this effect was used to characterize and quantify the atmospheric emissions of nPFASs in the city of Zurich, Switzerland, with a combination of field measurements and modeling. Gasic et al. (2009) and Moeckel et al. (2010) have previously shown the applicability of this approach for PCBs and polybrominated diphenyl ethers (PBDEs). For the investigation of PFASs in the present study, high volume air samples were taken during four consecutive days in summer 2010 at two sites, one in the center of Zurich and the other one on the nearby Mount Uetliberg. The samples were analyzed for nPFASs and PFAAs. In the first part of this study, results from high-resolution air measurement are shown including methodology, gas-particle partitioning, and discussion of the atmospheric fate and its significance. An accompanying paper presents the modeling of nPFASs and the emission estimates (Wang et al., 2012).

2. Materials and methods

2.1. Sampling locations

High volume air sampling was performed at two sites, one site representing an urban region and the other one representing a suspected background site without known direct sources. The urban site is located within the city center of Zurich, Switzerland, at 47°22′39″ North and 8°31′50″ East on 410 m above sea level (m.a.s.l.). Zurich is the largest city in Switzerland with around 390'000 inhabitants in the center, about 1.1 million in its urban catchment and a population density of 4000 inhabitants per km^2. The sampler was placed at a station of the Swiss National Air Pollution Monitoring Network (NABEL), which is located in a small park (NABEL, 2010). The NABEL station continuously measures the air quality. High resolution data on ozone (O_3), carbon monoxide (CO), nitrogen oxide (NO_2), sub-10 μm particulate matter (PM10), and volatile organic compounds (VOCs) are available. Additionally, a meteorological station is located on the site and provides data on temperature and wind speed.

The second sampling site was located on top of Mount Uetliberg approximately 5 km south-west of the city site on 850 m.a.s.l. Due to the altitude difference of more than 400 m, the hill-top is expected to be above the nocturnal boundary layer of the city, which has a height of 50–200 m. The sampler was installed on the enclosed site of a telecommunication company, which is situated in a forest. Meteorological and air quality data from the nearby Mount Laegern are used to represent this site. The conditions at Mount Laegern are very similar to the conditions on Mount Uetliberg: the mountain is 870 m.a.s.l. and is also forested. A NABEL station is also located there allowing us to retrieve air quality data typical for a background site.

2.2. Sampling

High volume air sampling was conducted from Friday, August 20, 2010, 8:00 to Monday, August 23, 24:00. Four 4-h samples were taken per day at the urban site (sampling times: 0–4, 8–12, 12–16, 20–24). At the background site, two 4-h samples were taken during day and one 6-h sample during the night, because it was expected that the concentrations would be low during the night (sampling times: 8–12, 12–16, 22–4). The air samplers DA-80 (Digitel, Hagenau, Switzerland) were equipped with 15 cm quartz fiber filters (Whatman International, Maidstone, England) to sample total suspended particulates (TSP) with particle size smaller 70 μm (the major part are however sub 10 μm particles). Polyurethane (PUF, Ziemer Chromatographie, Langerwehe, Germany) polystyrol beads (Amberlite XAD-2, Sigma–Aldrich, Buchs, Switzerland) cartridges were employed after the filter to sample the gas phase. The volume of air passing through the system was controlled by a rotameter and was held at a constant flowrate of 500 L/min.

Weather conditions were very stable during the first three days with a stable high pressure system, high temperatures, light winds (<3 m/s), and clear sky. In the afternoon of the fourth day, the weather started to change with clouds and more wind. Data from the NABEL station in the city showed that during the night, concentrations of NO_2, CO, PM10, and VOC increased (Fig. 1). PM10 and CO are traffic related and additional spikes of high concentrations can be seen in the morning due to rush hour road traffic. Our study was however performed partially on a weekend and these daytime emissions are therefore low. VOCs on the other hand are constantly emitted due to leaking gas pipes (especially methane (Lanz et al., 2008)) and a steady increase of concentrations was observed in the evening. All these observations can be seen as clear indications for the formation of a stable nocturnal boundary layer during the sampling campaign. Ozone concentrations on the other hand had high concentrations during the day due to generation by sunlight. At Mount Laegern, no diel pattern was observed for NO_2 due to the absence of local sources.

Before sampling, filters were pre-extracted with methanol and baked out at 450 °C overnight. Then they were weighed, wrapped in clean aluminum foil, and sealed in plastic bags. After sampling, the filters were again wrapped in the same aluminum foil and sealed again in the same plastic bag. The PUF and XAD-2 were pre-extracted in a Soxhlet with toluene followed by acetone. Two pieces of PUF (10 cm diameter, 6 cm length) were place in an aluminum roll with 30 g of XAD-2 resins in between. The cartridges were sealed in plastic bags until use. After sampling, the cartridges were covered with aluminum foil and sealed in the plastic bag. Both filters and cartridges were stored at −20 °C until analysis.

2.3. Sample preparation

2.3.1. Filters

The filters were weighed, then cut in half with clean scissors, weighed again individually and one half was placed in a pre-cleaned 50-mL polyethylene vial for PFAS analysis. The other half was used for the analysis of PCBs and other organic pollutants, which were not part of this work. A mix of internal standards was added to the vial (see Table S2) and the filter was extracted three times with 25, 15, and 15 mL of methanol in an ultrasonic bath. The extracts were decanted and then gently concentrated to 1 mL with a rotary evaporator (Büchi Labortechnik, Flawil, Switzerland). The concentrated extract was cleaned with a Supelclean ENVI-carb cartridge (Supelco, Bellfonte, USA). The cartridge was pre-cleaned with 5 mL of methanol, the extract was added and eluted with 2 mL of methanol. The 3 mL of extract and eluate were collected and then concentrated again to 0.5 mL under a gentle stream of nitrogen. The final extract was divided into two fractions: the first fraction was used for PFAA and the second for nPFAS analysis.

2.3.2. Cartridges

After addition of a mix of internal standards, the whole cartridge was Soxhlet extracted for 6 h with acetone/MTBE (1:1). The extract was concentrated to around 100 mL with the rotary evaporator and then further to 1 mL with the SyncorVap (Büchi). The solvent was exchanged to ethyl acetate/cyclohexane (1:1) and the extract was divided into two equal fractions. One fraction was used for the analysis of other organic pollutants (not part of this work). The second part of the extract was cleaned with a gel permeation column with S-X3 beads (200–400 mesh, Bio-Rad Laboratories, Hecules, USA). This step was necessary due to residual matrix (from XAD-2) disturbing otherwise the instrumental analysis. The extract was added to the column at 5 mL/min and was eluted with ethyl acetate/cyclohexane (1:1). The fraction of 15–25 min was collected, the rest was discarded. The fraction was then gently concentrated and solvent exchanged to ethyl acetate with a final volume of 0.3 mL. As the final step, 10 μL of D_3-Tonalide solution was added as a recovery standard. This extract was analyzed only for nPFASs.

2.4. Instrumental analysis

In total, 24 PFASs were studied including eight nPFASs, 14 PFAAs, and two degradation products of nPFASs, the fluorotelomer unsaturated acids (FTUCAs). The group of nPFASs contains three FTOHs (6:2, 8:2, and 10:2 FTOH), two FASE (N-methyl- and N-ethyl-perfluorooctanesulfonamidoethanol, Me/EtFOSE), and