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EMISSION OF PER- AND POLYFLUOROALKYL SUBSTANCES FROM A TEXTILE MANUFACTURING PLANT IN CHINA

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Introduction

The manufacturing of high-performance fabrics requires numerous chemical treatment steps that involve, among others, the use of durable water repellent (DWR) finishes. DWRs are based on per- and polyfluoroalkyl substances (PFASs) and impart water, oil, soil, and stain repellency to textiles by lowering the fiber's surface energy.¹ However, PFASs may be emitted to the environment during the manufacturing of textiles via wastewater and air. PFASs are environmentally concerning because of their high persistence, their ability to undergo long-range transport, their potential to bioaccumulate, and their potential to cause toxic effects.²

This study reports on the emission of PFASs via wastewater, air (gas and particle phase), and dust along the textile manufacturing chain in a manufacturing plant in China. The results are compared with concentration levels from other environments, in general, and with concentration levels emitted from the fluorochemical and fluoropolymer industry, in particular.

Materials and methods

The textile manufacturing plant is specialized on the weaving, dyeing, and finishing of polyester textiles and produces functional fabrics, such as sportswear and outdoor clothing, for numerous national and international brands. In total, 34 samples containing water, air (gas and particle phase), and settled dust were collected in two workshops in April 2014, involving the following manufacturing steps (Fig. 1): Scouring, DWR treatment, Drying, Heat Setting, Coating, and Quality Inspection.

One liter of fresh tap water and effluent water was collected in pre-cleaned polyethylene terephthalate bottles and filtrated through glass fiber filters (GFFs, Whatman, Ø 47 mm). Airborne particles were sampled in duplicate using GFFs (Ø 147 mm) deployed on lockers or production machines, at heights of approximately 1.5 to 2 m, for 17 days. Settled dust was wiped off from the same lockers or production machines using GFFs. Air was sampled using polyurethane foam (PUF) disk passive samplers (14 cm x 1.35 cm, Tisch Environmental, Cleves, OH) deployed for 17 days.³

The extraction of the water samples was modified based on a previous study, using 500 mg sorbent (Waters Oasis Wax, 6 cm³, 60 µm particle size) for the solid phase extraction (SPE) and Envi-Carb (Supelclean ENVI-Carb, 250 mg, 3 cm³) for a clean-up.⁴ Particles from the water samples were extracted with methanol using the ultrasonic bath (2 x 60 min). Air and particle samples were halved to extract both neutral and ionic PFASs via Soxhlet extraction using dichloromethane and methanol as solvents, respectively. Dust samples were extracted with methanol for ionic PFASs. All samples were extracted for approximately 20 h. Samples were spiked with appropriate mass-labeled internal standards before extraction. Before instrumental analysis, mass labeled [¹³C₂]-Perfluorooctanoic acid (PFOA) and 9:1 Fluorotelomer alcohol (FTOH) were added as injection standards (10 µL, 100 pg/µL) for HPLC-MS/MS and GC-MS, respectively. The instrumental analyses for ionic and neutral PFASs were described elsewhere.^{4,6}

Mean recovery rates for the mass-labeled internal standards ranged from 33 ± 15% ([¹³C₄]-PFOA) to 195 ± 60% (2-(N-ethyl-d₅-perfluoro-1-octane-sulfonamido)-ethan-d₄-ol) (d₉-EtFOSE). Procedural blank concentrations were taken into consideration when calculating sample concentrations and method detection limits (MDLs). MDLs ranged from 0.01 ng/L (Perfluoroundecanoic acid) (PFUnDA) to 4.37 ng/L (8:2 Fluorotelomer unsaturated carboxylic acid) (8:2 FTUCA) for the SPE of water samples, from

0.02 ng/L (Perfluorotridecanoic acid) (PFTrDA) to 0.55 ng/L (Perfluoroheptanoic acid) (PFHpA) for the ultrasonic extraction, and from 0.002 ng/(sample·d) (PFHpA) to 16.8 ng/(sample·d) (6:2 FTOH) or 0.85 ng/g ((Perfluorododecanoic acid) (PFDoDA) to 493 ng/g (8:2 FTOH) for the Soxhlet extraction.

Results and discussion

PFASs in effluent water. The mean Σ PFASs concentration in the dissolved phase of the effluent was 6690 ng/L, with PFHpA and PFOA contributing 54% to the overall burden. The concentration level was 2 orders of magnitude higher than the mean Σ PFASs concentration of 47.9 ng/L in fresh tap water. Perfluoropentanoic acid (PFPeA), Perfluorodecanoic acid (PFDA), and 8:2 FTUCA contributed with approximately 11% to the Σ PFASs concentration, respectively. FTUCAs were only detected in the effluent water. These compounds are intermediates formed during the biotransformation or aerobic biodegradation of FTOHs to PFCAs.⁷⁻⁹ Hence, findings of perfluoroalkyl carboxylic acids (PFCA) have probably resulted from the use of DWR finishes that are based on FTOHs. About 95% of the Σ PFASs were distributed in the dissolved phase, whereas 5% were found on suspended particulate matter with a mean Σ PFASs concentration of 372 ng/L. With respect to the enhanced adsorption potential to particles with increasing carbon chain length, the main compound was PFDA with a percentage of 38%.

PFASs in air. PUF disks were dominated by 8:2 FTOH and 10:2 FTOH, which accounted for $53 \pm 7\%$ and $32 \pm 11\%$ of the total PFASs concentration, respectively. Σ PFASs concentrations ranged from 193 ng/(sample·d) (outdoors) to 3340 ng/(sample·d) (drying). Concentrations of neutral PFASs were, in general, 2 orders of magnitude higher than that of ionic PFASs. Concentrations referred to 1 m³ air were between 5.1 and 91.3 $\mu\text{g}/\text{m}^3$ and 1.2 and 18.2 $\mu\text{g}/\text{m}^3$ for 8:2 FTOH and 10:2 FTOH, respectively. Previously reported air concentrations typically ranged from a few pg/m^3 to several ng/m^3 for both outdoor and residential indoor air. Elevated indoor air concentrations of up to 458 ng/m^3 were detected in stores selling furniture and outdoor equipment.^{10,11} However, those concentrations were still 2 orders of magnitude lower than the concentrations observed in our study.

PFASs in airborne particles. The Σ PFASs concentrations in airborne particles ranged from 38.5 $\mu\text{g}/\text{g}$ (coating) to 1330 $\mu\text{g}/\text{g}$ (office). Samples were dominated by 10:2 FTOH with a mean proportion of $49 \pm 7\%$, followed by 8:2 FTOH with $28 \pm 5\%$. FTOHs accounted, in general, for approximately 96% of total neutral PFASs. The average concentrations of ionic PFASs totaled approximately 14% of those for neutral PFASs, with PFOA and PFDA accounting for 71% of total ionic PFASs. These results were consistent with the dominating findings of their precursor compounds 8:2 FTOH and 10:2 FTOH. PFAS concentrations were highest in the office, which is located within the DWR workshop, contributing with 66% to the total concentration. Mainly responsible for the elevated concentrations were only a few compounds, namely 8:2 FTOH, 10:2 FTOH, and 12:2 FTOH, N-Methylperfluorobutanesulfonamide (MeFBSA), N-Methylperfluorooctanesulfonamide (MeFOSA), PFOA, and PFDA. These compounds had concentrations 1 order of magnitude higher in the office than during the manufacturing steps. There may be several reasons for the high concentrations in the office: (1) A lower room temperature and lower humidity, resulting in an enhanced adsorption to particles. (2) A lesser air exchange and lesser air circulation, leading to a trapping and accumulation of particles in the office. (3) A smaller particle-size and consequently a higher particle-surface, assuming that coarse particles are rather found in the workshops because of abrasion from the production machines, whereas finer particles predominate in an office environment. (4) The office provides entrance to a laboratory for quality tests, where the final product is tested on, among others, color fastness and elasticity. Therefore, the textile is prepared and cut in the office, possibly resulting in fine textile fibers depositing onto the GFFs. However, amounts of particle-bound PFASs in the office are concerning, especially if fine particles are predominant because of their potential to reach the alveoli after inhalation.

PFASs in settled dust. In contrast to the Σ PFASs concentrations in airborne particles, the Σ PFASs concentrations in settled dust were up to 2 orders of magnitude lower and in a comparable range across the samples. Concentrations ranged from 1390 ng/g (coating) to 6580 ng/g (workshop 1). The main compound was PFOA with a mean percentage of 28%, followed by PFDA and Perfluorononanoic carboxylic acid (PFNA) with mean percentages of 18% and 12%, respectively. In principle, the distribution pattern for settled dust showed a greater variety than that for airborne particles with average percentages of up to 7% for carboxylic acids with more than 11 carbon atoms.

Limited data is available about the emission of PFASs during their production or application. Peer-reviewed studies mainly focused on their emission from the fluorochemical or fluoropolymer industry.¹²⁻¹⁷ Concentrations of ionic PFASs in settled dust and effluent water from fluorochemical or fluoropolymer manufacturing sites were typically up to 3 orders of magnitude higher than those from the textile manufacturing plant of this study. However, PFASs were detected along the textile manufacturing chain, involving high emissions discharging into the atmosphere and into effluent water. The long-chain 8:2 FTOH, 10:2 FTOH, PFOA, and PFDA were the compounds emitted most from the manufacturing plant, although the plant owners stated to use “C6” chemistry instead of “C8” chemistry. Besides, PFASs were found in the workshop of the coating process, although they were not used intentionally as coating ingredients. MeFBSA and EtFOSE were also found in elevated concentrations in airborne particles during the coating compared with the other manufacturing steps and other substance classes, such as PFCAs and FTOHs. These points may indicate that PFASs were not only used as ingredients for DWR finishes but also as surfactants in scouring and coating agents or dyes.

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Weaving ⇒ Scouring ⇒ Dyeing ⇒ DWR treatment ⇒ Drying ⇒ Heat Setting ⇒ Coating ⇒ Quality Inspection

Fig. 1. Manufacturing steps in the textile manufacturing plant.