Mass Flow and Fate of Per- and Polyfluoroalkyl Substances in a Landfill

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Introduction

Per- and polyfluoroalkyl substances (PFASs) are man-made chemicals and have received a considerable amount of attention due to their ubiquitous detection in the environment, wildlife and humans all over the world[1, 2]. PFASs have unique physicochemical property of water and oil repellency, which make them usable in various industrial applications and commercial products such as surfactants in textiles, leather, cookware and paper. During production, usage and disposal, PFASs can be released into the environment. This can be problematic since PFASs are extremely high persistent, and potentially bioaccumulative and toxic[3]. Important point sources for PFASs in the aqueous environment are sewage treatment plants (STPs) and landfills[4, 5]. However, little is known about the impact of landfills on the aquatic environment.

The aim of this study is to assess the occurrence and distribution profiles of PFASs at a landfill in Sweden and the impact on the nearby aquatic environment. The specific objectives were to *i)* investigate the distribution of PFASs in leachate, groundwater and sludge and the mass flux of PFASs within the landfill, *ii)* evaluate the treatment efficiency of the on-site sewage treatment system for the removal of PFASs, and *iii)* assess the mass flux of PFASs in the receiving river water.

Materials and methods

In total, 28 PFASs were analyzed including C_4, C_6, C_8, C_{10} perfluoroalkane sulfonates (PFSAs) (PFBS, PFHxS, PFOS, PFDS), $C_{3-13,15,17}$ perfluoroalkyl carboxylates (PFCAs) (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA), three perfluorooctane sulfonamides (FOSAs) (FOSA, MeFOSA EtFOSA), two perfluorooctane sulfonamidoethanols (FOSEs) (MeFOSE, EtFOSE), three perfluorooctane sulfonamidoacetic acids (FOSAAs) (FOSAA, MeFOSAA, EtFOSAA) and three fluorotelomer carboxylate (6:2 FTSA, 8:2 FTSA, 10:2 FTSA). Linear (L) and branched (B) isomers were analysed for PFHxS, PFOS and FOSA. In addition, 16 internal standards were included.

The landfill is located near Uppsala, Sweden, and has mainly deposed ashes from a nearby incineration plant and special waste since 1971. The landfill can be divided into following areas: Old landfill, where mainly ashes were disposed (area A), active landfill area with compost storage, soil and dried sewage sludge storage (from a nearby STP), and deposition of ashes, insulation material and plaster (area B). In addition, the landfill has an on-site STP, which has separated treatment steps including aeration, moving bed biofilm reactor (MBBR), sedimentation, polishing and oxidation ponds.

The samples were collected in 1 L PP bottles in February and March 2017 at the following locations: Landfill leachate and drainage system (*n* = 12), on-site STP (*n* = 9), stored sludge material (*n* = 9), groundwater (*n* = 11), and receiving water (*n* = 11).

The aqueous samples were extracted using solid phase extraction (SPE) using Oasis WAX cartridges (6 cc, 500 mg 60 µm, Waters) as described elsewhere.[6] The solid samples were extracted using solid-liquid extraction and ENVI-Carb cleaned-up as described elsewhere.[7] The instrumental analysis was performed using ultra performance liquid chromatography (UPLC) coupled with a tandem mass spectrometer (MS/MS). As part of the quality control, duplicate measurements and blank control samples were evaluated.

Results and discussion

Distribution of PFASs in landfill leachate and groundwater. In total, 20 out of 28 PFASs were detected in untreated landfill leachate and drainage system with general higher ΣPFAS concentrations at area A (on average, 980 ng L^{-1}) compared to area B (490 ng L^{-1}). The highest ΣPFAS concentration was 1800 ng L^{-1}, which was lower compared to landfill leachate from Norway (up to 6120 ng L^{-1} for Σ_{28}PFASs)[8], Germany (up to 12800 ng L^{-1} for Σ_{43}PFASs)[5], Canada (up to 21300 ng L^{-1} for Σ_{13}PFASs)[9], and China (up to 292000 ng L^{-1} for

Σ_{14}PFASs)[10]. The large variations of PFAS concentrations at different landfill sites can be explained by the type and amount of waste, age of the landfill and treatment process of leachate. In this study, the most abundant PFAS classes were PFCAs (61% of ΣPFASs), followed by PFSAs (31%) and PFAS precursors (7.6%) in area A, whereas in area B, PFAS precursors were dominated (40%), followed by PFCAs (38%) and PFSAs (22%). The dominance of PFAS precursors at the active landfill area (area B) indicates that the content of PFAS precursors in more recent products has increased. Elevated PFAS concentrations were detected in the stored sludge samples (the sludge represent a time period from April 2016 to February 2017 sampled at the nearby STP) with ΣPFAS concentrations ranging from 33 to 440 ng g^{-1} dry weight (dw). Dominating PFAS classes in the sludge samples were FTSAs (37% of the ΣPFASs), followed by PFSAs (33%), FOSAs (15%) and PFCAs (7.6%). In the groundwater samples, 16 out of 28 analysed PFASs were present with a large concentration variation for ΣPFASs ranging from 8.5 to 1800 ng L^{-1} depending on the groundwater depth and location (**Figure 1**). The most abundant classes of PFASs were ΣPFCAs with an average concentration of 230 ng L^{-1} (61% of ΣPFASs), followed by ΣPFSAs (140 ng L^{-1}; 37% ΣPFASs) and ΣPFAS precursors (7.5 ng L^{-1}; 2.0% ΣPFASs).
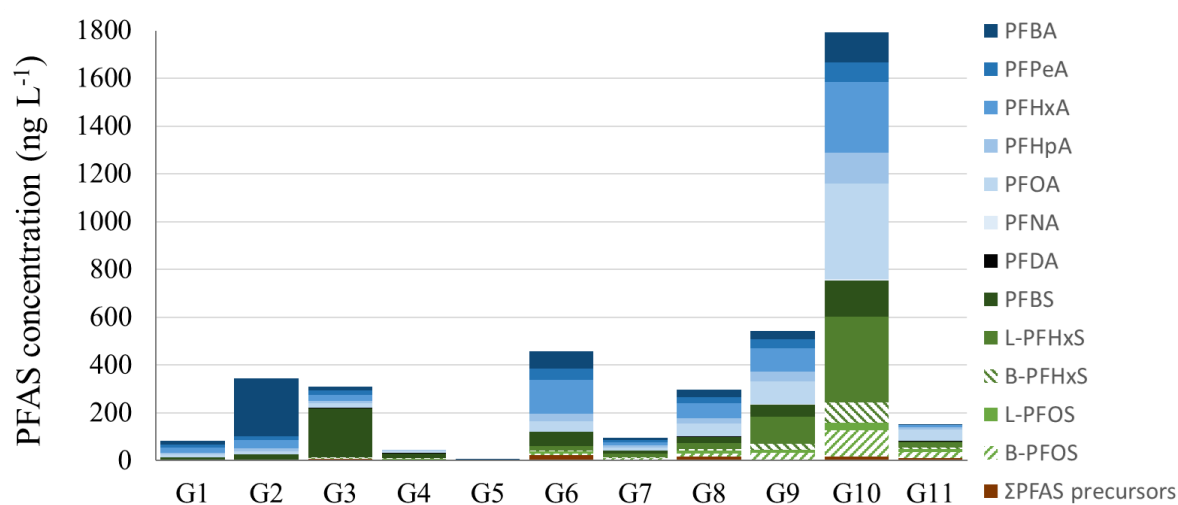
Figure 1: Detected individual PFASs and ΣPFAS precursors in groundwater.

Removal of PFASs at the on-site treatment plant. The average removal efficiency of PFASs at the on-site treatment plant was 40%, 55% and 84% for PFCAs, PFSAs and PFAS precursors, respectively (**Figure 2**). For PFCAs, the removal efficiency of the short chain PFBA (perfluorocarbon chain length C_3) was negative with -10%, while the removal efficiency constantly increased with increasing perfluorocarbon chained for PFCAs to up to 100% for PFDA (C_9 PFCA). For PFSAs, the removal efficiency of PFBS (C_4) was 9.6% and increased to 90% for the linear isomer of PFOS (C_8). For PFAS precursors, the removal efficiency was generally high ranging from 53% for the linear isomer of FOSA to 66% for the branched isomer of FOSA and 77% for 6:2 FTSA and up to 100% for 8:2 FTSA, MeFOSAA and EtFOSAA. The highest removal efficiency was observed after the first aeration step (on average, 36% for ΣPFASs) and after the MBBR treatment (425). Overall, the removal of PFASs in the on-site treatment system might be related to sorption of PFASs to particles and subsequent sedimentation, however, an impact of the PFAS concentrations in the ponds by in-leaking water cannot be ruled out.

PFAS flux estimations and transport in the receiving river water. The highest leaching of ΣPFASs originated from area A (540 mg d^{-1}) which is possibly due to the large area size and amount of deposited waste. In contrast, area B had a smaller flux for ΣPFASs with 41 mg d^{-1}, most likely due to the small amount of waste and temporary storage of both soil and sludge compared to area A. During the treatment process at the on-site treatment plant the flux of ΣPFASs decreased from 412 mg d^{-1} to 220 mg d^{-1}. It is likely that at least parts of the PFAS fluxes has entered the groundwater, which can explain the high PFAS concentrations in some groundwater samples. In the receiving river water samples, 10 out of 28 analysed PFASs were identified and the ΣPFAS concentrations were up to 41 ng L^{-1} close to the landfill site. However, the ΣPFAS concentrations decreased to <5 ng L^{-1} further downstream with a flux of 1400-2000 mg d^{-1} of ΣPFASs.
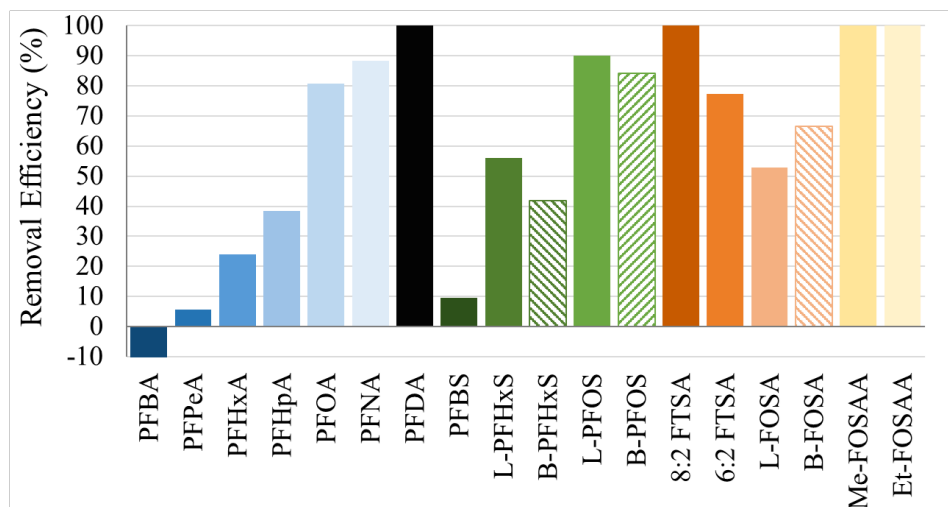
Figure 2: Total removal efficiencies of individual PFASs within the on-site STP after aeration, moving bed biofilm reactor (MBBR), sedimentation, polishing and oxidation ponds.

Overall, PFASs were ubiquitously present in leachate, drainage, sludge, groundwater and receiving water samples at the landfill. In the aqueous phase, the shorter chain PFAS dominating over the longer chain PFASs. It is recommended to implement advanced treatment techniques at the landill in the future[11]. Flux estimations have shown that there is no large impact on the receiving river water, however, future measures are needed to assess the risks for the groundwater and nearby environment.

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