PER- AND POLYFLUOROALKYL SUBSTANCES IN DRINKING WATER: OCCURRENCE, REMOVAL, AND HUMAN HEALTH RISKS

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Introduction

Per- and polyfluoroalkyl substances (PFASs) are of rising concern due to their persistence in the environment and their potential for bioaccumulation in organisms.[1] PFASs are used in food packaging, textile, personal care products and aqueous film forming foams (AFFFs) or in industrial processes like as surfactants and emulsifiers. PFASs can be released into the aquatic environment through point sources such as landfills, sewage treatment plants (STPs) or firefighting exercises with PFAS-containing AFFFs or nonpoint sources such as surface runoff.[2, 3] PFASs can potentially contaminate drinking water source areas such as groundwater and surface water, and be an exposure route for human.[4] PFASs have half-lives of several years in the human body and high exposure to PFASs is possibly connected to adverse health effects such as the risk of high cholesterol and blood lipid levels, delayed puberty, decreased fertility, increased Body Mass Index (BMI), bladder cancer, kidney cancer, prostate cancer, testicular cancer.[5, 6] Some countries have established guideline values for PFASs in drinking water; for example, the National Food Agency in Sweden recommends that the concentration of the sum of 11 different PFASs (i.e. C_4-C_{10} perfluorocarboxylates (PFCAs), C_4, C_6, C_8 perfluorosulfonates (PFSAs) and 6:2 fluorotelomer sulfonates (6:2 FTSA)) should not exceed 90 ng L^{-1} in drinking water.

Conventional drinking water treatment plants (DWTPs) are not designed to remove organic micropollutants such as PFASs, and previous studies have reported that treatment processes such as sand-filtration, coagulation, flocculation, sedimentation, disinfection are ineffective in the removal of PFASs.[7] On the other hand, treatment methods like granular activated carbon (GAC) and anion exchange (AIX) can effectively remove PFASs from water.[8] However, these treatment techniques have shown low removal efficiency for shorter chained PFASs and decreasing removal efficiency over time due to saturation of the filter material such as GAC and AIX.[8] Little is known about PFAS concentrations in drinking water source areas and finished drinking water on national scale and associated risks for human health.

The aim of this study was to assess the occurrence, treatment efficiency and human health risks for PFASs in drinking water in Sweden. Specific objectives include i) investigation of the PFAS concentrations in drinking water source areas and finished drinking water on national scale in Sweden, ii) evaluation of the removal efficiency of PFASs in the full-scale DWTPs, and iii) assessment of the potential human health risks for PFASs in drinking water.

Materials and methods

The target analytes included C_3–C_{13}, C_{15}, C_{17} perfluorocarboxylates (PFCAs, $C_nF_{2n+1}COO^-$) (i.e. PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA), C_4, C_6, C_8, C_{10} perfluorosulfonates (PFSAs, $C_nF_{2n+1}SO_3^-$) (i.e. PFBS, PFHxS, PFOS, PFDS), 6:2, 8:2 and 10:2 fluorotelomer sulfonates (FTSAs, $C_6F_{13}CH_2CH_2SO_3^-$), perfluorooctanesulfonamide (FOSA, $C_8F_{17}SO_2NH_2$), and perfluorooctanesulfonamidoacetic acid (FOSAA, $C_8F_{17}SO_2N(H)CH_2CO_2H$), methyl and ethyl FOSAAs ($C_8F_{17}SO_2N(C_nH_{2n+1})CH_2CO_2H$). In addition, 12 mass-labelled internal standards (ISs) were used for quantification.

Drinking raw water and finished drinking water samples were collected from almost 50 DWTPs in Sweden in June and October 2018. The samples were collected in 1 L polypropylene (PP) bottles and stored cold (6 °C) until extraction. The samples (500 mL) were extracted using an established method based on solid phase extraction (SPE) as described elsewhere.[3]

Results and discussion:

The mean ∑PFAS concentrations in the incoming raw water for the full-scale DWTPs ($n = 47$) was 9.4 ng L^{-1} (median: 1.3 ng L^{-1}), with a maximum ∑PFAS concentration of 150 ng L^{-1} (Figure 1). In total, 11 out of 24 PFASs were detected in drinking raw water with PFOA, PFHxS, and PFNA showing the highest detection frequency (72%, 55% and 45%, respectively). Dominant PFASs in drinking raw water were PFOA (33% of the ∑PFASs), PFHxS (17%), and FOSA (12%), while the highest concentrations were measured for PFHxS (73 ng

L^{-1}), PFBA (66 ng L^{-1}), and PFOS (46 ng L^{-1}). The median $\sum$PFAS concentrations in drinking raw water in this study (1.3 ng L^{-1}) was in the same range or lower as those reported previously in surface and groundwater in Sweden (median = 3.9 ng L^{-1}, *n* = 289, and 0.04 ng L^{-1}, *n* = 161, respectively).[3] Similar to this study, dominant PFASs in surface and groundwater were generally shorter chain PFCAs and PFSAs in Sweden,[3] tropical French overseas territories,[9] Germany,[10] USA,[11] and Brazil, Frank and Spain.[12]

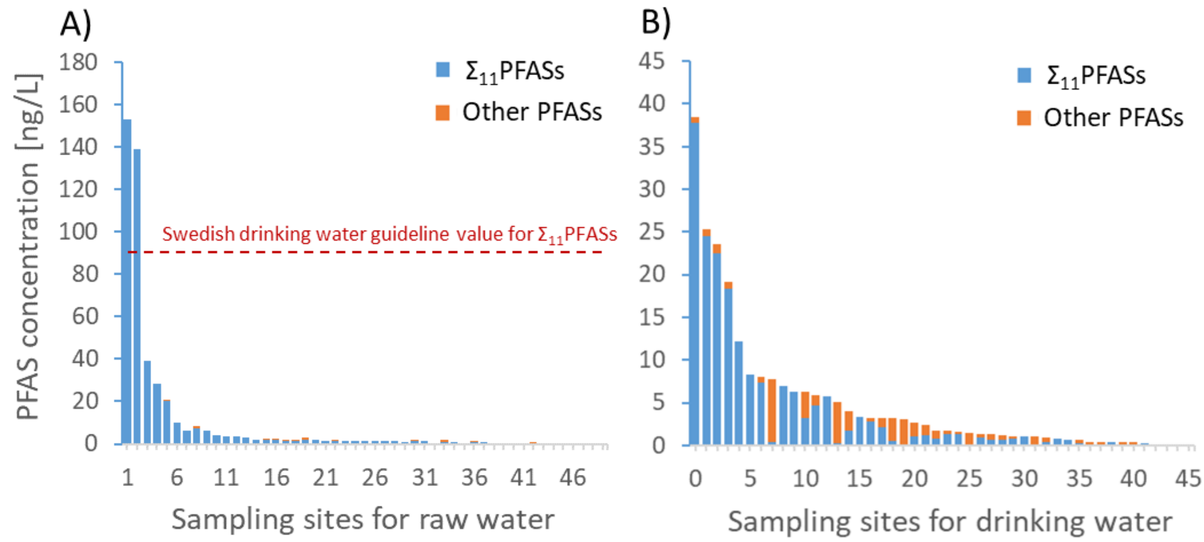

Figure 1: Concentrations of Σ_{11}PFASs and other PFASs in A) drinking water source areas (*n* = 47) and B) finished drinking water (*n* = 46) from June 2018 and comparison with the Swedish drinking water guideline value of 90 ng L^{-1} for the sum of 11 PFASs. The Σ_{11}PFASs include PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFHxS, PFOS, 6:2 FTSA. The other PFASs include PFUnDA, PFDoDA, PFTriDA, PFTeDA, PFHxDA, PFOcDA, PFDS, 8:2 FTSA, 10:2 FTSAs, FOSA, FOSAA, MeFOSAA and EtFOSAA.

The mean $\sum$PFAS concentrations in the drinking water for the full-scale DWTPs (*n* = 46) was by a factor of approximately two lower (4.8 ng L^{-1}) in comparison to the raw water (9.4 ng L^{-1}); however, the median concentration was comparable (1.7 ng L^{-1} and 1.3 ng L^{-1}, respectively). The difference between the mean and median can be explained by the fact that the measured concentrations were positively skewed, i.e. many samples with low concentrations and few with higher concentrations. In total, 10 out of 24 PFASs were detected in drinking water with PFOA, FOSA, PFHxS, and PFNA with the highest detection frequency (66%, 66%, 43 and 43%, respectively). Similar to the drinking raw water, dominant PFASs in drinking water were FOSA (39% of the $\sum$PFASs), PFOA (21%), and PFHxS (10%), while highest concentrations were measured for PFBA (22 ng L^{-1}), 6:2 FTSA (17 ng L^{-1}), PFHxS (7.9 ng L^{-1}) and FOSA (7.4 ng L^{-1}). The drinking water concentration in Sweden were comparable to those reported previously.[13] However, drinking water concentrations of PFASs were 1-2 orders of magnitude higher at sites linked to PFAS contamination by industry, fire training facilities, landfills and wastewater treatment plants.[14, 15]

The measured PFAS concentrations in this study were below the drinking water guideline/health advisory value issued by Sweden (90 ng L^{-1} for $\sum_{11}$PFASs, see Figure 1), Denmark (100 ng L^{-1} for $\sum_{12}$PFASs), United Kingdom (300 ng L^{-1} for PFOS and PFOA, respectively), and USA (70 ng L^{-1} for $\sum$PFOS/PFOA).[3] The number would not increase if $\sum_{24}$PFAS (instead of $\sum_{11}$PFASs) concentrations were considered in the drinking water threshold of the Swedish drinking water guideline. However, in the future it should be considered to include also FOSA in the Swedish drinking water guideline, since it had a detection frequency of 66% and a maximum concentration of 7.4 ng L^{-1} in drinking water. The PFAS concentrations in the incoming raw water exceeded the Swedish guideline in 2 out of the 48 drinking water samples from source areas. However, the removal efficiency of PFASs was high at both of these DWTPs (78% and 95%, respectively) due to the installation of GAC filters.

The median removal efficiency of PFASs in the investigated DWTPs was 10% with a high variation depending on the individual DWTP. This is in agreement with previous studies showing that conventional DWTPs are not designed to remove PFASs in drinking water.[7] For individual PFASs, the median removal efficiency increased with perfluorocarbon chain length for PFSAs in this study, with the lowest median removal efficiency for the short chain PFBS (<0%), followed by PFHxS (13%) and PFOS (32%). This trend can be explained by the high mobility (e.g. high water solubility) of the shorter chain PFASs, and thus their low sorption potential to conventional treatment filter materials (e.g. sand-filtration) as well as advanced treatment filter materials (e.g. GAC and AIX).[8, 16]

Overall, the PFAS concentrations in the finish drinking water were below international drinking water guideline values. However, conventional treatment techniques were ineffective in removing PFASs and thus there is a risk for human exposure of PFASs via drinking water. Furthermore, it is possible that new drinking water guidelines are becoming stricter (i.e. lower PFAS threshold values and inclusion of more PFASs). Due to the occurrence of PFASs both in drinking water source areas and finished drinking water, there is an urgent need for advanced treatment methods for the removal of PFASs in drinking water.

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