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Concentrations and patterns of perfluoroalkyl and polyfluoroalkyl substances in a river and three drinking water treatment plants near and far from a major production source

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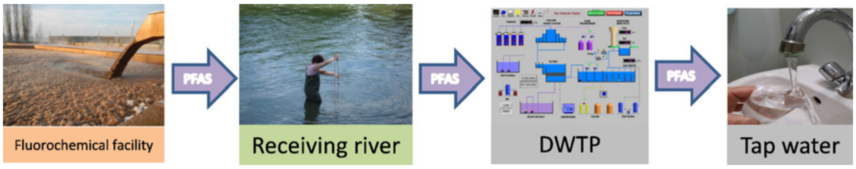
HIGHLIGHTS

- River and well fields were contaminated by the release of PFASs from a facility.
- A poorly studied PFAS (6:2 FTAB) was the predominant PFAS found in the river.
- The oxidative conversion method showed evidence for the presence of PFCA precursors.
- Conventional water treatments were unable to remove PFASs efficiently.
- Ozonation and activated carbon filtration may lead to the breakdown of certain FTs.

GRAPHICAL ABSTRACT



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ABSTRACT

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are emerging contaminants that have been detected in the environment, biota and humans. Drinking water is a route of exposure for populations using water contaminated by PFAS discharges. This research entailed measuring concentrations, mass flows and investigating the fate of dozens PFASs in a river receiving effluents from a fluorochemical manufacturing facility. To measure the total concentration of perfluoroalkyl carboxylic acid (PFCA) precursors, an oxidative conversion method was used. Several dozen samples were collected in the river (water and sediment), in drinking water resources and at different treatment steps on four sampling dates. One PFCA and three fluorotelomers (FTs) were detected up to 62 km downstream from the manufacturing facility. 6:2 Fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) was the predominant PFAS with a mass flow of 3830 g/day 5.2 km downstream from the facility. At all sampling points, PFAS concentrations in sediment were quite low (<6 ng/g dw). Five of the 11 investigated wells showed detectable concentrations of PFASs. Interestingly, their profile patterns were different from those observed in the river, suggesting a transformation of PFCA precursors in the sediments of alluvial groundwater. Conventional drinking water treatments (aeration, sand or granular activated carbon filtration, ozonation or chlorination) did not efficiently remove PFASs. Furthermore, an increase in

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Abbreviations: DWTP, drinking water treatment plant; FT, fluorotelomer; FTSA, fluorotelomer sulfonic acid; FTOH, fluorotelomer alcohol; GC–MS, gas chromatography/mass spectrometry; LC-MS/MS, liquid chromatography/tandem mass spectrometry; PFAA, perfluoroalkyl acid; PFAS, perfluoroalkyl and polyfluoroalkyl substances; PFCA, perfluoroalkyl carboxylic acid; PFSA, perfluoroalkane sulfonic acid.

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concentration of certain PFASs was observed after ozonation, suggesting that some FTs such as 6:2 FTAB can break down.

Only nanofiltration was able to remove all the analyzed PFASs. In the treated water, total PFAS concentrations never exceeded 60 ng/L. The oxidative conversion method revealed the presence of unidentified PFCA precursors in the river. Therefore, 18 to 77% of the total PFCA content after oxidation consisted of unidentified chemical species. In the treated water, these percentages ranged from 0 to 29%, relatively and reassuringly low values.

1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are a group of aliphatic chemicals in which all of the carbon atoms, except that of the terminal functional group, are fully fluorinated (prefix: per) or in which hydrogen atoms are still attached to one or more carbon atoms (prefix: poly) (Buck et al., 2011). A perfluoroalkyl chain with 7 or more perfluorinated carbons is referred to as "long-chain" (Buck et al., 2011). PFASs have been produced extensively since the second half of the 20th century and are components of many industrial, commercial and consumer products (Kissa, 2001; Prevedouros et al., 2006). For instance, they are used as surfactants in aqueous film-forming foams (AFFF), mist suppressants for metal-plating baths and semiconductors, processing aids in the manufacture of fluoropolymers, and surface protectors in carpets, leather, textiles, paper, packaging, building and construction materials (Buck et al., 2011; Kissa, 2001).

The chemical structure of perfluoroalkyl substances, such as perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs), makes them extremely resistant to the degradation processes that occur in the environment (e.g. hydrolysis, photolysis and biodegradation). Thus, they are stable in both water and soil, and are present in the environment due to direct emissions or as end-stage metabolites of polyfluoroalkyl substance breakdown processes that take place in the environment (Buck et al., 2011; Prevedouros et al., 2006). Polyfluoroalkyl substances can potentially be transformed into intermediate transformation products and perfluoroalkyl substances due to their $-CH_2$ moiety which is more prone to oxidation (Buck et al., 2011; Frömel and Knepper, 2010; Liu and Mejia Avendaño, 2013). Given their resilience and the volatility of certain PFASs such as fluorotelomer alcohols (FTOHs), PFASs have become ubiquitous in the environment (Ahrens, 2011; Houde et al., 2011; Valsecchi et al., 2013).

There is a growing concern about the potential environmental and toxicological impact of PFASs due to their persistence and bioaccumulative properties. Routes of exposure in the general population remain unclear, although some research suggests that food intake is the major contemporary pathway (Vestergren and Cousins, 2009). Drinking water exposure also appears to dominate in populations that use heavily contaminated resources (Hoffman et al., 2011; Vestergren and Cousins, 2009; Wilhelm et al., 2008), because conventional drinking water treatments do not remove PFASs (Appleman et al., 2014; Quiñones and Snyder, 2009; Rahman et al., 2014). Moreover, an increase in PFCA concentrations in treated water has been observed in a few cases (Boiteux et al., 2012; Dauchy et al., 2012; Takagi et al., 2008).

The objectives of this study were to determine the behavior and fate of several PFASs, including perfluoroalkyl acids (PFAAs) and fluorotelomers (FTs), in a river receiving wastewater from a large facility that manufactures fluorotelomer-based products and side-chain fluorinated polymers and to assess the impact on drinking water resources. Furthermore, we also assessed the ability of three drinking water plants (DWTPs) to remove PFASs, including conventional processes and advanced technologies such as nanofiltration. In addition to the specific analytical methods used to identify and quantify PFASs, we also employed an oxidative conversion of PFAAs precursors (Houtz and Sedlak, 2012). The aim was to infer the proportion of PFASs that cannot be identified using individual PFAS analysis and reveal the presence of unidentified PFASs.

2. Materials and methods

2.1. Standards and reagents

The suite of 48 native target PFASs and 19 mass-labeled PFASs used in the present study (Table S1-1) were from Wellington Laboratories (Guelph, ON, Canada) and purchased from BCP Instruments (Oullins, France) with the following exceptions. 6:2 FTAB, and M4 were a gift from the fluorotelomer manufacturer and assumed to be 100% pure. These two PFAS were discovered during the study, and therefore were not monitored in every sample, but primarily in the water samples of the last sampling campaign. The structure and acronyms of all the monitored PFASs are given in Table S1-1. All solvents and reagents were at the highest purity available.

2.2. Sites description and sample collection

The river selected for this study is located in northern France and receives wastewater from an industrial wastewater treatment plant (WWTP) (Dauchy et al., 2017). This WWTP treats raw sewage coming from a facility that manufactures fluorotelomer-based products and side-chain-fluorinated polymers used in fire-fighting foams and stain repellents. In 2013, the average daily flow of the WWTP effluent was about 900 m^3/d.

Four sampling campaigns were carried out for sample collection. In May, July, October and December 2013, grab samples of water and sediment were collected on the same day from seven locations along the river, from the riverbank (Fig. S1), starting nearly 1.2 km upstream of the WWTP discharge. The field study encompassed approximately 65 km of the river. In addition to the four sampling campaigns, river flow was recorded at sampling point #4 (Table S3-1). The average historical flow rate from 1960 to present is 108 m^3/s.

Three DWTPs located downstream of the WWTP discharge were investigated (Fig. S1). The first DWTP (sampling point #6) is located 15 km downstream from the WWTP. Raw water of this DWTP (named DWTP A) is supplied by five alluvial wells (hereafter referred as F1b, F2b, F4, F6 and F11). The plant uses sand filtration and chlorine dioxide to treat water. The drinking water produced by this plant (1200 m^3/h) is consumed by 80,000 people. The second DWTP (sampling point #8) is located 20 km downstream of the WWTP. Raw water of this DWTP (named DWTP B) is supplied by four alluvial wells (hereafter referred as F1, F2, F3, and F4). The water treatment process includes, in succession, sand filtration, activated carbon filtration and chlorination (chlorine dioxide). The drinking water produced by this plant (1200 m^3/h) is consumed by 40,000 people. The third DWTP (sampling point #10) is located 39 km downstream of the WWTP. Raw water of this DWTP (named DWTP C) is directly pumped from the river. Two treatment processes are used in parallel: a membrane filtration process and a biological treatment. Membrane filtration (nanofiltration) contributes to 80% of the drinking water flow. The biological treatment technique includes settling, sand filtration, ozonation, activated carbon filtration and