



# Are perfluoroalkyl acids in waste water treatment plant effluents the result of primary emissions from the technosphere or of environmental recirculation?



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## ABSTRACT

Wastewater treatment plants (WWTP) have been suggested to be one of the major pathways of perfluoroalkyl acids (PFAAs) from the technosphere to the aquatic environment. The origin of PFAAs in WWTP influents is either from current primary emissions or a result of recirculation of PFAAs that have been residing and transported in the environment for several years or decades. Environmental recirculation can then occur when PFAAs from the environment enter the wastewater stream in, e.g., tap water. In this study 13 PFAAs and perfluorooctane sulfonamide were analyzed in tap water as well as WWTP influent, effluent and sludge from three Swedish cities: Bromma (in the metropolitan area of Stockholm), Bollebygd and Umeå. A mass balance of the WWTPs was assembled for each PFAA. Positive mass balances were observed for PFHxA and PFOA in all WWTPs, indicating the presence of precursor compounds in the technosphere. With regard to environmental recirculation, tap water was an important source of PFAAs to the Bromma WWTP influent, contributing >40% for each quantified sulfonic acid and up to 30% for the carboxylic acids. The PFAAs in tap water from Bollebygd and Umeå did not contribute significantly to the PFAA load in the WWTP influents. Our results show that in order to estimate current primary emissions from the technosphere, it may be necessary to correct the PFAA emission rates in WWTP effluents for PFAAs present in tap water, especially in the case of elevated levels in tap water.

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## 1. Introduction

Perfluoroalkyl acids (PFAAs) are man-made organic surfactants that have been produced since the 1950s (Prevedouros et al., 2006; Paul et al., 2009) and used in several industrial and commercial applications such as aqueous film-forming foams, surface treatment and the production of fluoropolymers (Kissa, 2001). Due to their persistence in the environment, PFAAs are today detected worldwide in, e.g., the aquatic environment (Ahrens et al., 2010), wildlife (Houde et al., 2011) and humans (Kannan et al., 2004). The presence of PFAAs in the environment results from emissions during their manufacturing and use as well as from the release and subsequent environmental transformation of precursor compounds (Ellis et al., 2004).

The widespread use of products containing PFAAs and PFAA precursors in households (Herzke et al., 2012) leads to environmental emissions via wastewater treatment plants (WWTPs). Furthermore, PFAAs are only poorly removed by the

purification techniques currently used in WWTPs (Guo et al., 2010). Consequently, WWTPs have been suggested to be one of the most important PFAA pathways to the aquatic environment (Becker et al., 2008; Clara et al., 2008). To assess the magnitude of PFAA emissions from WWTPs, concentrations of PFAAs in effluents are usually used to calculate PFAA emission rates for a certain WWTP (e.g.,  $\mu\text{g PFAA d}^{-1}$ ) or population normalized emission rates (e.g.,  $\mu\text{g PFAA d}^{-1} \text{Pe}^{-1}$ , with Pe being the population equivalent connected to the WWTP) (Filipovic et al., 2013).

Environmental emission rates from WWTPs calculated in this way do not only encompass recent or current primary releases from consumer products and the technosphere, as there are also other pathways of PFAAs to WWTPs. One such pathway is PFAAs in atmospheric deposition and subsequent street runoff (Murakami et al., 2009; Müller et al., 2011). Another pathway is PFAAs ubiquitously present in tap water (Ullah et al., 2011). PFAA levels in tap water reflect the concentrations in the environmental source water (e.g., lake, river or groundwater) used for tap water production (Eschauzier et al., 2012), and thus cumulative historical releases including long-range transported PFAAs or precursors to this water body. Since tap water is in most cases the major water

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source to WWTPs, the PFAAs present in tap water could potentially make a significant contribution to PFAA concentrations in WWTP influents and, consequently, also in effluents. However, this contribution, which reflects an environmental recirculation rather than a recent primary emission of PFAAs, has not been evaluated up to date.

The distinction between primary releases from the technosphere and environmental recirculation is not sharp, as all anthropogenic contaminants ultimately originate from industrial activities or from products. In the present study we distinguish between “recent” emissions from the technosphere (which we consider as new releases, e.g., from products used in households to WWTPs) and “historic” releases (such as industrial emissions of PFOS prior to its phase-out in 2002 or the use of PFAA containing fire-fighting foams, if it happened many years ago). Historic releases thus means that the PFAAs have been present and transported in the environment for many years, often decades. If these contaminants reach a WWTP then we consider this to be an environmental recirculation (since they are discharged to the environment “again”), as opposed to a recent or new release.

Due to industry commitment in industrialized countries to reduce PFAA emissions and PFAA residuals in products it becomes more and more unlikely that there are considerable direct and current emissions from products to groundwater or surface water bodies used for tap water production. Thus we can assume that the majority of PFAAs present in tap water nowadays are environmentally recirculated.

The objective of this study was to verify if the levels of PFAAs present in tap water can make a significant contribution to PFAAs measured in WWTPs, and thus to distinguish between PFAAs originating from environmental recirculation of historical releases and recent direct emissions from the technosphere. To this end, tap water from the drainage areas of three different WWTPs in Sweden as well as influents, effluents and sludge from the three WWTPs were collected and analyzed. In addition, a mass balance of PFAAs in the WWTPs was assembled to investigate the potential contribution of precursor degradation within the WWTPs to the PFAA concentrations measured in the effluents (Schultz et al., 2006).

## 2. Materials and methods

### 2.1. Sample collection

Influent water, effluent water and sewage sludge samples were collected from three WWTPs in three different Swedish cities: Bromma (in the metropolitan area of Stockholm), Bollebygd and Umeå. The WWTPs were chosen to represent different geographical locations within Sweden, different degrees of urbanization and different population equivalents connected. Detailed information on the location and characteristics of the different WWTPs is given below and in the Electronic Supplementary Material (ESM, Table S1 and Fig. S1). Tap water samples from all different water suppliers present in the drainage areas of the three WWTPs were collected directly from the outlets of the water purification facilities. In order to minimize the contribution of additional water sources to the WWTP influents such as atmospheric deposition/urban runoff, the WWTP samples were collected during a week with cold (below freezing) or dry weather conditions (no or low precipitation). All water samples were collected and stored in high-density polyethylene bottles. Sludge samples were stored in polyethylene bottles. All samples were kept at 4 °C until extraction.

#### 2.1.1. Bromma WWTP

Twenty-four-hour composite influent and effluent water samples were collected continuously between May 1–5, 2013,

using a Bühler 1027 sampler (Hach-Lange, Sköndal, Sweden). Dewatered sludge samples were collected on May 2, 6 and 7, 2013. Bromma WWTP receives water originating from two tap water suppliers, Stockholm Vatten (20%) and Norrvatten (80%), both of which use water from Lake Mälaren as their water source. Grab samples of tap water were collected at Lovö (Stockholm Vatten) and Norrvatten between May 7–25, 2013.

#### 2.1.2. Bollebygd WWTP

Twenty-four-hour composite influent and effluent water samples were collected continuously between March 5–8, 2013. Primary sludge samples were collected daily from the primary clarifier during the same period. Bollebygd WWTP receives tap water from one supplier which uses a ground water source. Grab samples of tap water were collected during the same period of time as the WWTP samples.

#### 2.1.3. Umeå WWTP

Twenty-four-hour composite influent and effluent water samples were collected continuously between February 25–28, 2013, using a Bühler 1027 sampler (Hach-Lange). Dewatered sludge samples were collected during the same period. Umeå WWTP receives tap water from one supplier. The source water is taken from the river Umeälven after bank filtration. Grab samples of tap water were collected during the same period of time as the WWTP samples.

## 2.2. Chemicals and reagents

All native and isotope-labeled standard compounds were purchased from Wellington Laboratories (Guelph, ON, Canada) in 2 µg mL<sup>-1</sup> solution mixtures. The 14 target analytes were perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), perfluorododecanoic acid (PFDoDA), perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), perfluorooctane sulfonic acid (PFOS), perfluorodecane sulfonic acid (PFDS) and perfluorooctane sulfonamide (FOSA). For simplicity, we included FOSA in the generic term PFAAs in this study.

<sup>13</sup>C<sub>4</sub>-PFBA, <sup>13</sup>C<sub>3</sub>-PFPeA, <sup>13</sup>C<sub>2</sub>-PFHxA, <sup>13</sup>C<sub>4</sub>-PFHpA, <sup>13</sup>C<sub>4</sub>-PFOA, <sup>13</sup>C<sub>5</sub>-PFNA, <sup>13</sup>C<sub>2</sub>-PFDA, <sup>13</sup>C<sub>2</sub>-PFUnDA, <sup>13</sup>C<sub>2</sub>-PFDoDA, <sup>18</sup>O<sub>2</sub>-PFHxS, <sup>13</sup>C<sub>4</sub>-PFOS and <sup>13</sup>C<sub>8</sub>-FOSA were used as isotope-labeled surrogate internal standards (IS). <sup>13</sup>C<sub>8</sub>-PFOA and <sup>13</sup>C<sub>8</sub>-PFOS were used as volumetric standards in the calculation of total method recovery of the internal standards. All isotope-labeled standards were certified to contain <0.5% of their native analogues. Solvents and reagents used in this work were of HPLC grade or highest commercial purity. Methanol and 1-methyl piperidine were purchased from Merck (Hohenbrunn, Germany) and acetonitrile was purchased from Sigma Aldrich (Steinheim, Germany). All laboratory materials were rinsed with methanol and tested for background contamination before using. No significant contamination with any of the target PFAAs was observed.

## 2.3. Chemical analysis and quality control

### 2.3.1. Water extraction

Tap water, influent and effluent water samples were extracted and cleaned up using a modification of a method originally described for tap water analysis (Ullah et al., 2011). Briefly, aliquots of 50 mL (all influents) or 200 mL (all other samples) were spiked with 20 µL (tap water from Umeå and Bollebygd) or 60 µL (all other samples) of IS solution (10 pg µL<sup>-1</sup> of each IS in methanol) and extracted on pre-washed (16 mL of 2 vol% 1-methyl

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