



# Parameters affecting the formation of perfluoroalkyl acids during wastewater treatment



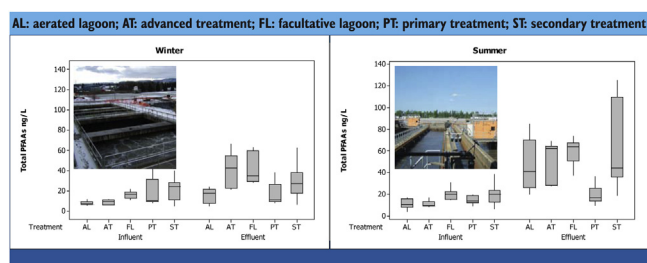
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## HIGHLIGHTS

- Largest PFAA dataset in liquid and solid samples from 5 wastewater treatment types.
- PFAAs generated from precursors breaking down during wastewater treatment.
- Temperature, HRT, and sludge digestion influenced the formation of PFAAs.
- Median log  $K_d$  were PFOS (3.73), PFDA (3.68), PFNA (3.25), PFOA (2.49), and PFHxA (1.93).
- Mass balance showed low PFAAs removal by sorption and high PFAAs loading in effluents.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This study examined the fate and behaviour of perfluoroalkyl acids (PFAAs) in liquid and solid samples from five different wastewater treatment types: facultative and aerated lagoons, chemically assisted primary treatment, secondary aerobic biological treatment, and advanced biological nutrient removal treatment. To the best of our knowledge, this is the largest data set from a single study available in the literature to date for PFAAs monitoring study in wastewater treatment. Perfluorooctanoic acid (PFOA) was the predominant PFAA in wastewater with levels from 2.2 to 150 ng/L (influent) and 1.9 to 140 ng/L (effluent). Perfluorooctanesulfonic acid (PFOS) was the predominant compound in primary sludge, waste biological sludge, and treated biosolids with concentrations from 6.4 to 2900 ng/g dry weight (dw), 9.7 to 8200 ng/g dw, and 2.1 to 17,000 ng/g dw, respectively. PFAAs were formed during wastewater treatment and it was dependant on both process temperature and treatment type; with higher rates of formation in biological wastewater treatment plants (WWTPs) operating at longer hydraulic retention times and higher temperatures. PFAA removal by sorption was influenced by different sorption tendencies; median log values of the solid–liquid distribution coefficient estimated from wastewater biological sludge and final effluent were: PFOS (3.73) > PFDA (3.68) > PFNA (3.25) > PFOA (2.49) > PFHxA (1.93). Mass balances confirmed the formation of PFAAs, low PFAA removal by sorption, and high PFAA levels in effluents.

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## 1. Introduction

Perfluoroalkyl acids (PFAAs) are synthetic chemicals with a variety of applications. They contain dual hydrophobic and hydrophilic moieties that make materials both oil and water resistant [1]. This makes them useful in the production of apparel, carpets, and

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packaging products, as processing additives during fluoropolymer production, and as surfactants in consumer applications. However, they can pose a risk to the environment, having the potential to persist in the environment, to bioaccumulate, and to be toxic [2]. Many PFAAs have been detected in the environment; of these the most studied are perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). Due to the possible negative effects of PFOS on the environment and on human health, it was added to the Stockholm Convention on Persistent Organic Pollutants (POPs) in 2009, resulting in global restrictions of its production and use. PFOA is more water soluble than PFOS (3400 mg/L vs. 67 mg/L), being more likely present at higher concentrations in the aquatic environment [3]. Due to the potential impact of PFOA in the environment, the United States Environmental Protection Agency (USEPA) and 8 leading global companies have agreed to eliminate its use by 2015 [4]. Similarly, the USEPA banned the use of PFOS in 2009.

Since PFAAs can be released from consumer products over their lifespan, they can be discharged into municipal wastewater and thereby enter wastewater treatment plants (WWTPs). Previous studies have reported that wastewater treatment does not effectively remove PFAAs, presenting levels between 7.0 and 1120 ng/L in WWTP effluents from different countries [2,5,6]. Determination of PFAAs in biosolids is more difficult due to matrix complexity. Consequently, there is limited information on PFAA levels in biosolids; to date the highest reported level in biosolids was 700 ng/g dry weight (dw) [7]. PFAA determination in influents, effluents, and biosolids allows the calculation of their removal during wastewater treatment that is primarily accomplished by sorption to sludge, especially for long-chain PFAAs [8]. Removal of these non-degradable compounds through biodegradation could be minimal [9]. In contrast, some studies have reported the formation of PFAAs during wastewater treatment from precursors also present in the influent [10].

Although it has been shown that PFAA levels increase in treated effluents [7], the factors governing PFAA formation during wastewater treatment have not previously been investigated. This study expands the scope of WWTP types beyond previous investigations, which focussed on mass balances from secondary WWTPs. This knowledge is essential to evaluate current regulatory instruments and/or treatment processes in reducing PFAAs discharged to the environment. In this study, the occurrence and behaviour of 13 PFAAs, including PFOA, PFOS, and the perfluorinated analogues: perfluorobutane sulfonic acid (PFBS), perfluorohexane sulfonic acid (PFHxS), perfluorooctane sulfonamide (PFOSA), perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), and perfluorododecanoic acid (PFDoA) were evaluated in 680 liquid and solid samples from 20 Canadian WWTPs. The aims of this investigation were to (1) determine PFAA concentrations in the liquid and solid streams of 5 different wastewater treatment types (facultative (FL) and aerated lagoons (AL), chemically assisted primary treatment (PT), secondary aerobic biological treatment (ST), and advanced biological nutrient removal treatment (AT)); (2) study parameters affecting PFAA removal and fate, and (3) conduct mass balances to delineate the fate of PFAAs. This study contains the largest data set currently available in the scientific literature for PFAA analysis in different compartments of wastewater treatment.

## 2. Materials and methods

In order to maximize data quality for this study, samples were collected based on the approach presented by Ort et al. [11]. Raw influent (RI), primary effluent (PE), and final effluent (FE) samples

were collected using Hach Sigma 900 refrigerated autosamplers (Hach Company, Loveland CO, USA). To obtain 24-h equal volume composite samples 400 mL was collected every 30 min. Primary sludge (PS) was sampled from the underflow of the primary clarification tank and waste biological sludge (WBS) was collected from the underflow of the secondary clarification tank. Treated biosolid was sampled after the final treatment step. PS, WBS and biosolids were collected as grab samples. Wastewater and biosolids samples were sub-sampled into 1000 ml wide-mouth high-density polyethylene bottles and shipped to the laboratory on ice by overnight courier.

Each WWTP was sampled for 3 consecutive days during the summer (June to September) and winter (January to April) seasons, in 2009 or 2010. The main characteristics of the studied WWTPs in this investigation are summarized in Table S1. To prepare liquid samples, 500 ml of wastewater was filtered through a 0.45  $\mu\text{m}$  Nylon filter; therefore, the concentrations of PFAAs reported in this study only considered the dissolved phase. The surrogate standard solution containing  $^{13}\text{C}_4$ -PFBA,  $^{13}\text{C}_2$ -PFHxA,  $^{13}\text{C}_2$ -PFOA,  $^{13}\text{C}_5$ -PFNA,  $^{13}\text{C}_2$ -PFDA,  $^{13}\text{C}_2$ -PFDoA and  $^{13}\text{C}_4$ -PFOS was added to the filtered wastewater. 5 g dw of solid samples containing an aliquot of surrogate standard mixture were extracted by suspending in 10 ml of 3% acetic acid, 15 ml of methanolic ammonium hydroxide (0.3%) and 100 mg of Ultra Carbon. The solution was mixed by shaking and vortexing, and was then centrifuged and filtered using a 0.45  $\mu\text{m}$  Nylon filter. Solid phase extraction (SPE) was used for extraction of liquid samples and clean-up of solid samples. Waters Oasis WAX SPE cartridges (150 mg) were previously conditioned with 5 ml of methanolic ammonium hydroxide (0.3%) and 5 ml of 0.1% of formic acid. The samples were loaded onto the cartridge and washed using 5 ml of reagent water followed by 5 ml of a solution containing 50% methanol and 50% 0.1 M formic acid in water. The cartridges were eluted with 4 ml of methanolic ammonium hydroxide (0.3%). After vortexing, aliquots of the eluate were transferred into a 300  $\mu\text{L}$  polypropylene micro-vial and  $^{13}\text{C}_2$ -2H-perfluoro-2-decanoic acid (FOUEA) and  $^{13}\text{C}_4$ -PFOA were added as recovery standards. Extracts were analyzed by liquid chromatography mass spectrometry (LC/MS/MS). More details on analytical methodology and statistical analysis are described in supplementary data.

## 3. Results and discussion

### 3.1. PFAAs in wastewater

PFAAs were analyzed in 386 liquid samples: RI ( $n=149$ ), PE ( $n=90$ ), and FE ( $n=147$ ). Overall variability in the sampling and analytical system was calculated using the relative standard deviation (RSD) of the three samples that were collected at each sampling point in each season. The median RSDs for RI, PE, and FE were 21%, 20%, and 18%, respectively, which is a reasonably low variation in PFAA concentrations.

Detailed levels of individual PFAAs in RI and FE are presented in Table S2. These results exceed the data set reported by Ratola et al. in a mini review [9]. Concentrations of PFAAs in PE were not included in the table and will not be discussed further because no statistical differences ( $p>0.05$ ) were observed between their levels in RI and PE. This indicates that physical settling of solids in wastewater treatment does not provide any removal as has been previously reported [1]. The predominant PFAA in both RI and FE was PFOA, at concentrations ranging from 2.2 to 150 ng/L (median 5.3 ng/L,  $n=72$ ) and 1.9 to 40 ng/L (median 12 ng/L,  $n=75$ ), respectively. PFOS was the second most abundant compound at levels from 2.0 to 1100 ng/L (median 4.7 ng/L,  $n=60$ ) in RI and 1.0 to 1300 ng/L (median 5.0 ng/L,  $n=69$ ) in FE. Following PFOS, PFHxA

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