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# Parameters affecting the formation of perfluoroalkyl acids during wastewater treatment

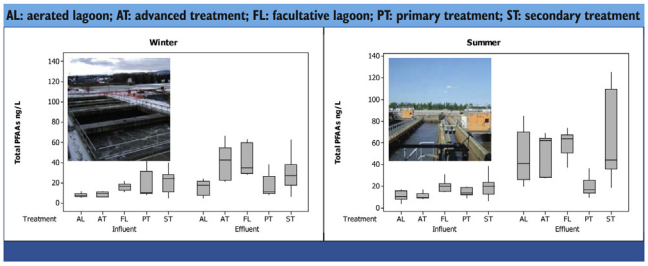
P. Guerra, M. Kim, L. Kinsman, T. Ng, M. Alaee, S.A. Smyth*

*Science and Technology Branch, Environment Canada, 867 Lakeshore Road, Burlington, Ontario L7R 4A6, Canada*

## 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.


## 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

* Corresponding author at: 867 Lakeshore Road, P.O. Box 5050, Burlington, Ontario L7R 4A6, Canada. Tel.: +1 905 336 4509; fax: +1 905 336 6420.
*E-mail addresses:* Shirleyanne.Smyth@ec.gc.ca, guerra.paulac@gmail.com (S.A. Smyth).

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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 μm Nylon filter; therefore, the concentrations of PFAAs reported in this study only considered the dissolved phase. The surrogate standard solution containing $^{13}C_4$-PFBA, $^{13}C_2$-PFHxA, $^{13}C_2$-PFOA, $^{13}C_5$-PFNA, $^{13}C_2$-PFDA, $^{13}C_2$-PFDoA and $^{13}C_4$-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 μm 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 μL polypropylene micro-vial and $^{13}C_2$-2H-perfluoro-2-decenoic acid (FOUEA) and $^{13}C_4$-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

ranged from 1.0 to 220 ng/L (median 3.9 ng/L, $n = 72$) in RI and 1.4 to 290 ng/L (median 8.7 ng/L, $n = 75$) in FE.

Compared to previous studies, current PFOA levels were higher than reported in 10 Danish WWTPs (RI: <0.2–23.5 ng/L, FE: <0.2–24.4 ng/L) [5]; and similar to values reported in 18 Korean WWTPs employing mostly secondary aerobic biological treatment and nutrient removal treatment [6]. PFOS and PFHxA concentrations were similar to the levels from studies in Greece [12] and Hong Kong [13]. However, these studies focused on a total of four secondary aerobic biological treatment WWTPs, providing limited information on environmental and treatment factors that may affect occurrence of PFAAs.

Using the extensive dataset available in this study, the influences of two important factors on PFAAs occurrence were examined: industrial input and season. For industrial input, plant T served a small population (3000 inhabitants) and received approximately 80% industrial (aviation) wastewater. The industry can still use certain PFAAs such as PFOS in hydraulic fluid that has been exempted from the ban [14]. As a result, plant T contained the highest concentrations of all studied PFAAs and WWTPs. In previous investigations, some industrial wastewater discharged high concentrations of PFAAs as well; for example, one study reported up to 8400 ng/L that was 30-fold higher than the levels in municipal wastewater [15]. Therefore, it was corroborated that wastewater inputs from industry using PFAA can influence PFAA levels in the wastewater system.

The effect of seasonal water temperature on PFAA concentrations during wastewater treatment was evident for most compounds (Fig. S1). In this study, winter and summer process temperatures ranged from −3 °C to 24 °C, respectively. Overall for RI, higher concentrations were observed during summer ($p < 0.05$) for PFHxA, PFHpA, PFNA, PFDA and PFHxS. A similar pattern was observed in FE where PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, and PFDA were statistically higher ($p < 0.05$) in summer as well. Among these compounds, PFHxA, PFHpA, PFNA, PFDA showed seasonal differences in both RI and FE whereas the seasonal influence to PFBA, PFPeA, and PFOA appeared only in FE. The latter case may imply that these compounds were influenced by seasonal operation of WWTPs, which will be discussed below.

### 3.2. Formation

In order to evaluate the performance of different WWTPs and seasonal differences, PFAA formation percentage was calculated using the follow equation:

$$\%\,\text{formation} = \frac{C_{FE} - C_{RI}}{C_{RI}} \times 100 \quad (1)$$

where $C_{RI}$ and $C_{FE}$ are the concentrations of different PFAAs measured in RI and FE, respectively to be used to show the net change of PFAA concentrations during treatment without reflecting partitioning of the compounds into sludge. The median PFAA formation ranged from −60 to 740% (Table S3), indicating that in some cases measured PFAAs were formed during wastewater treatment. This trend of PFAAs formation during wastewater treatment was also reported in previous studies of ST/AT [10,16], but our study also included AL, FL, and PT. The formation of PFAAs is likely due to the breakdown of PFAA precursors during wastewater treatment [10]. Previous investigations showed that fluorotelomer alcohols (FTOHs), industrial intermediates used in the synthesis of fluorotelomer intermediates, surfactants, and polymeric materials, were transformed to PFOA, PFNA, and PFHxA [17] while N-ethyl perfluorooctane sulfonamidoethanol (N-etFOSE) was transformed to PFOS [18]. Precursors were also detected in the atmosphere above the primary clarifier of a Canadian WWTP and their levels decreased at the aeration tank (∼50%), probably due to their conversion to PFAAs [19]. Therefore, based on our observations of PFAAs formation, it can be assumed that precursors were present in the studied RIs.

### 3.3. Effects of wastewater treatment

To further investigate the parameters affecting PFAAs formation, treatment types, hydraulic retention times (HRTs), temperatures, and other factors affecting PFAAs generation during wastewater treatment were evaluated. These parameters were primary factors that also affect WWTP operation.

#### 3.3.1. Treatment type

A wide variability in the formation of PFAAs was observed, indicating that process types may influence PFAAs formation. The Kruskal–Wallis test confirmed that calculated formations of PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, PFOS, and PFHxS were statistically different between various treatment types. Their rank order from high to low formation was: AT (median: 160%) > AL/FL (150%) > ST (55%) > PT (-1%). Hence, formation of PFAAs varied based on treatment type.

#### 3.3.2. Seasonal effect

In this study, samples were collected in winter (8.7 ± 4.2 °C) and summer (17.5 ± 4.4 °C), with statistically different ($p < 0.05$) temperatures. The Mann–Whitney test indicated that higher formation was observed during summer for PFBA, PFHpA, and PFNA in AL ($p < 0.05$), PFHpA and PFOS in PT ($p < 0.05$), and PFHxA in FL ($p < 0.05$). These results are summarized in Fig. 1 where seasonal formations, differentiated by wastewater process type are presented for (a) PFOA, (b) PFOS, and (c) PFHxA. Formations of the rest of PFAAs are shown in Fig. S2. Only PT showed lower formation in summer for PFOA (−18 to 40%), PFOS (−59 to 160%), and PFHxA (−40 to 31%), and in winter when formations ranged from −38 to 25%, −73 to 47%, and −14 to 92% for PFOA, PFOS, and PFHxA, respectively. In contrast, greater conversion of precursors into PFAAs was observed in AL, FL, ST, and AT plants, and was higher during summer. This could be related to the higher temperatures that may increase microbial activity, favouring the transformation of precursors [20]. Previously, Loganathan et al. [10] examined concentrations of PFAAs in wastewater during different seasons, reporting no seasonal variations. However, the study used grab samples collected from two WWTPs. In comparison, the present study, which used composite samples, showed seasonal differences in PFAAs formation during different wastewater treatments.

#### 3.3.3. HRT

HRT indicates the average length of time that a soluble compound remains in a reactor. In order to examine the relationship between HRT and PFAA formation, correlations of PFHxA, PFOA, PFNA, and PFOS were performed for plants using ST and AT processes. Lagoons and PT were not included because of their relatively long (20 days and 6 months) and short (0.3–2.8 h) HRTs, respectively, which unduly influenced the correlation. Spearman correlation coefficients were between −0.7 to 0.5 with the strongest correlations obtained for PFOA and PFHxA. Overall formations ranged from −34% to 1200% (median: 64%) and from −30% to 4000% (median: 60%) for PFOA and PFHxA, respectively. When HRT was higher than 15 h, formations increased to between −16% and 1200% (median: 140%), and from −11% to 4000% (median: 130%), for PFOA and PFHxA, respectively. In both cases, linear correlations were observed at HRTs longer than 15 h (Fig. 2) that were affected by the temperature, in agreement with the discussion above. The correlations obtained were better in summer, with $R^2 = 0.71$ for PFHxA and $R^2 = 0.88$ for PFOA while in winter they were $R^2 = 0.26$ for PFHxA

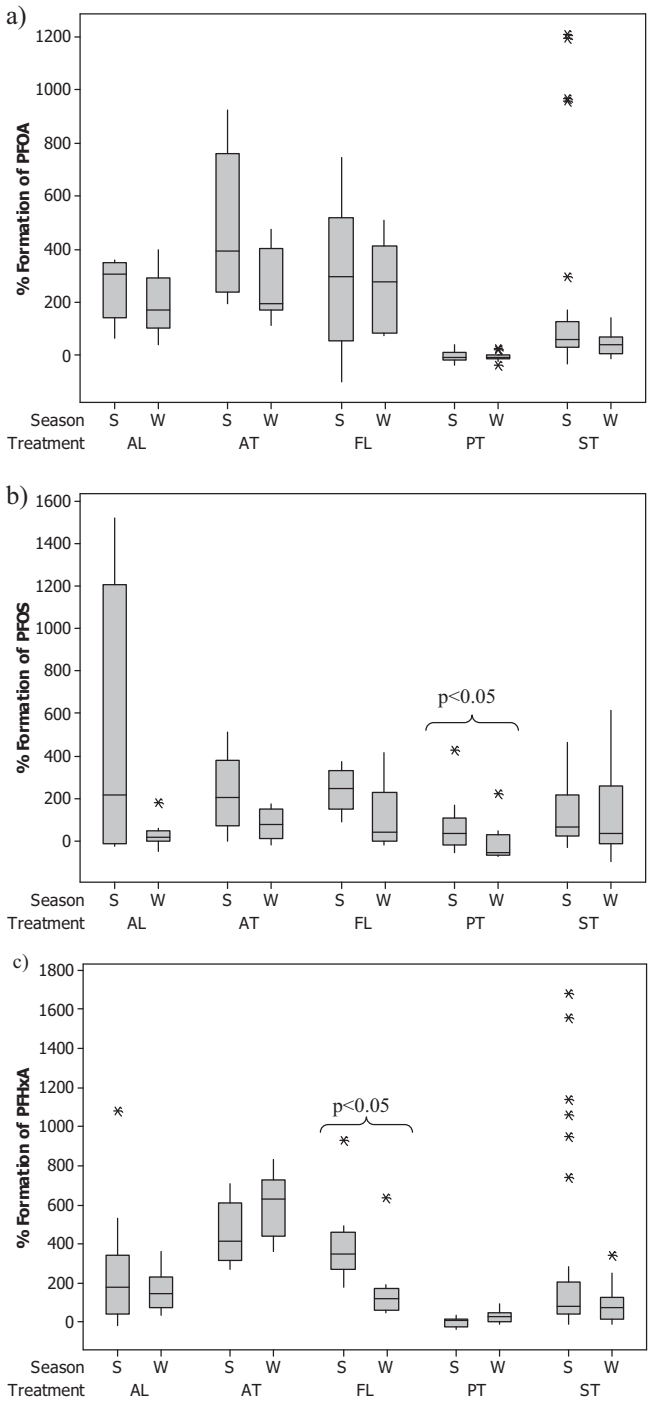


**Fig. 1.** Formation percentages (%) of (a) PFOA, (b) PFOS and (c) PFHxA grouped by treatment type (AL: aerated lagoon, AT: advanced biological nutrient removal treatment, FL: facultative lagoon, PT: chemically assisted primary treatment, ST: secondary biological treatment) and season (S: summer, W: winter). The graph indicates sample minimum, lower quartile, median, upper quartile, sample maximum, and outliers.

and $R^2 = 0.70$ for PFOA. This pattern can be attributed to degradation of precursors such as 8:2 FTOHs that may biodegrade to PFOA and PFHxA [17], and also to the effect of the seasonal temperatures.

In the case of lagoons, formation was also observed for PFHxA (median: 190%), PFOA (280%), and PFOS (25%); however, somewhat higher formation was observed in FL (PFHxA median: 230%), PFOA (330%), and PFOS (120%)). This could be related to the longer HRT in FL than AL, and was confirmed by the lower formation in PT that had even lower HRTs (PFHxA median: −7.0%), PFOA (−7.8%), and PFOS (−5.9%). Overall, the observed trend during wastewater treatment indicated that longer HRT provides more opportunity for PFAAs to be formed from their precursors.

### 3.3.4. Other factors

Other parameters such as mixed liquor volatile suspended solids, solid retention times (SRTs), chemical oxygen demand, and total suspended solids were also analyzed and compared to PFAA data; however, there was no clear evidence of correlations.

## 3.4. PFAAs in solids and effect factors

Although PFAAs were formed in the liquid stream, they could be partially removed through partitioning to sludge due to their physico-chemical properties. To investigate the removal of PFAAs via sorption, their levels were evaluated in 110 PS, 76 WBS, and 108 treated biosolid samples. In the scientific literature only one investigation evaluated the levels of PFOS and PFOA in PS and WBS [7]. To the best of our knowledge, this is the most comprehensive dataset available in the literature for these analyses. Examination of the variability in concentrations of PFAAs over three days resulted in median RSDs of 29%, 26% and 20%, for PS, WBS and biosolids, respectively. PFAA levels were least variable in biosolids. The treatment processes may reduce the matrix effect of interfering compounds and also equalize and homogenize the material, which would explain the lower PFAAs variability in biosolids.

PFDA, PFDoA, and PFOS were detected in 55% (2.9–22 ng/g, median 7.3 ng/g), 8.3% (8.2–13 ng/g, median 5.1 ng/g), and 25% (6.4–2900 ng/g, median 13 ng/g) of PS samples, respectively; the other PFAAs were not detected. Since removals in the primary clarifier were negligible probably due to the low HRT (up to 4.6 h), levels in PS were also low, as Yu et al. [7] observed as well. On the other hand, PFAA levels increased in WBS (PFHxA, PFOA, PFNA, PFUnA, PFDA, PFDoA, and PFHxS) with concentrations from 15 to 120 ng/g. PFOS concentrations ranged from 9.7 to 8200 ng/g (median: 35 ng/g) in 87% of samples. The higher concentrations of PFAAs in WBS over PS could be due to the longer contact time and recirculation of WBS in the aeration tank and secondary clarifier, which gave more opportunity for PFAAs sorption onto sludge. This observation may be a result of increased PFAAs formation from its precursors. PS and WBS may also have different sorption tendencies as Arvaniti et al. [12] recently reported in one WWTP; this affected the PFAA levels found in both matrices.

Removal of PFAAs via sorption can be influenced by their partitioning affinity. To examine this, the solid–liquid distribution coefficient ($K_d$) were estimated for the most frequently detected compounds (PFHxA, PFOA, PFNA, PFDA and PFOS). It was calculated by dividing PFAAs concentration in WBS (ng/kg) by their concentration in FE (ng/L); obtained $K_d$ values were summarized in Fig. S3. Median calculated $\log K_d$ followed the order PFOS (3.73) > PFDA (3.68) > PFNA (3.25) > PFOA (2.49) > PFHxA (1.93), confirming the values presented by previous studies [7,12]. Thus, the higher sorption tendency of PFOS compared to PFOA explain the relatively lower concentration of PFOS in the FE (median: 4.7 ng/L) and higher in WBS (35 ng/g).

Biosolids were obtained from the blending and the solids treatment of PS and WBS. PFAAs were detected in all samples (Table S4). PFOS was the most prevalent compound, with the highest concentrations found in plant T (median: 6200 ng/g). Median levels of PFOS (13 ng/g) were similar to previous studies [7,21]. The next highest concentrated compounds were PFOA > PFDA > PFNA, and even-chain length perfluorinated carboxylic acids (PFCAs) like PFOA, PFDA, and PFDoA accounted for 79 ± 12% of total PFAAs. This predominance of PFCAs was also reported in digested sludge from 20 WWTPs in Switzerland [22]; and is consistent with FTOHs'

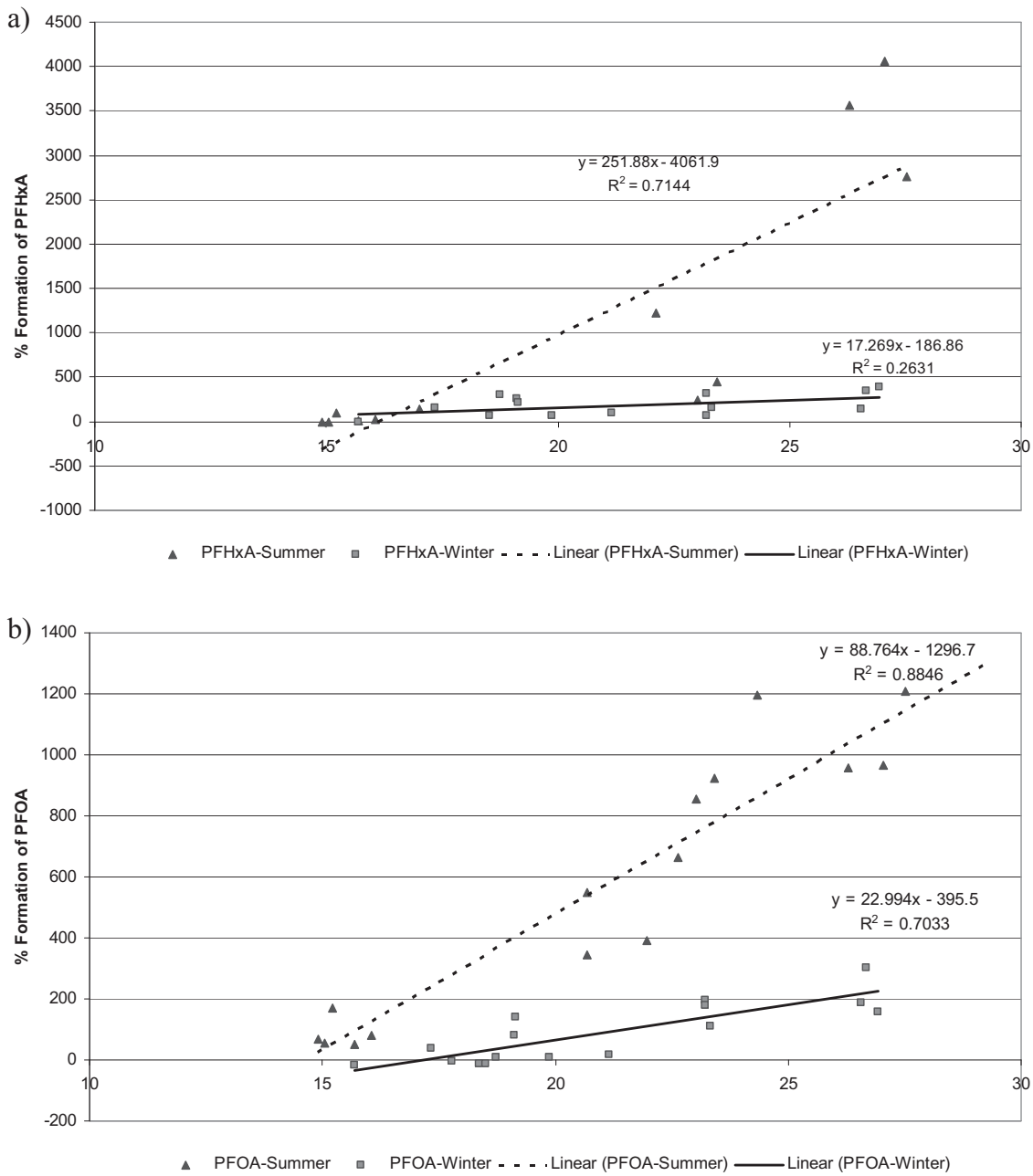


**Fig. 2.** Correlation between HRT (h) and removal efficiencies of (a) PFHxA and (b) PFOA.

aerobic biodegradation, which yield predominantly even-chain length PFCAs [23].

In this study, ten of fifteen plants employed digestion, of these nine were anaerobic and one aerobic. When comparing digested and non-digested biosolids, higher concentrations of PFAAs were observed in digested samples (Fig. S4). These values were statistically significant in the case of PFOS, PFNA, PFDA, and PFUnA ($p < 0.05$). Sludge digestion has an important role in the stabilization of solids, volume reduction, and production of digester gas [24]. The high concentration of PFAAs in digested biosolids may be due to the breakdown of precursors in the digester, increasing PFAA levels. Another possible reason for PFAAs' increase in digested biosolids is the reduction of volatile solids in the digester, resulting in the accumulation of recalcitrant PFAAs in digested biosolids. Digestion treatment can also enhance sorption propensity of hydrophobic compounds [25]. Thus, higher PFAA levels in digested biosolids may be attributed to precursor's breakdown, decrease of volatile solids, and improved sorption tendency during digestion.

### 3.5. Mass balance

Finally, using the analysis of PFAAs in RI, FE, and biosolids, mass balances were conducted to evaluate the formation of PFAAs and the mass loadings in FE and biosolids. Mass loadings were calculated by multiplying substance concentrations by volumetric flow rates for the liquid stream and by production rate for biosolids. The results for winter and summer mass balances are presented in Table 1. PS and WBS were not included because their flow information was not available.

Total PFAAs mass loadings in FE were significantly higher (median 5400 mg/d) compared to biosolids (median 160 mg/d). Estimation of the FE:biosolids ratio in mass loadings ranged from

**Table 1**
Median mass loadings (mg/day) of different PFAAs.

| | Raw influent | | | | | | | Final effluent | | | | | | | Biosolids | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | PFHxA | PFHpA | PFOA | PFNA | PFDA | PFHxS | PFOS | PFHxA | PFHpA | PFOA | PFNA | PFDA | PFHxS | PFOS | PFOA | PFNA | PFDA | PFHxS | PFOS |
| *Winter* | | | | | | | | | | | | | | | | | | | |
| H | 90 | 110 | 190 | 95 | – | – | 110 | 110 | 87 | 170 | 84 | 21 | 42 | 42 | – | – | – | – | 30 |
| M | 480 | 400 | 1600 | 570 | – | – | 1200 | 660 | 320 | 1400 | 520 | 350 | 280 | 1800 | – | – | – | – | – |
| N | 580 | 230 | 610 | 77 | – | 210 | 410 | 550 | 230 | 540 | 84 | 20 | 200 | 140 | – | 2.2 | – | – | 12 |
| A | 4500 | 2800 | 5200 | – | 1300 | 2000 | 7400 | 7200 | 3100 | 8300 | – | 1300 | 3200 | 7700 | 86 | – | 410 | 32 | 400 |
| C | 74 | 43 | 93 | – | – | – | – | 190 | 70 | 180 | – | 51 | 100 | 130 | 3.7 | 4.5 | – | 2.3 | 30 |
| F | 190 | 120 | 210 | 100 | – | 86 | 140 | 210 | 130 | 240 | 78 | 36 | 120 | 120 | – | – | – | 4.4 | 25 |
| L | 120 | 76 | 200 | 140 | – | 54 | 140 | 270 | 120 | 330 | 210 | 79 | 190 | 160 | 9.0 | 28 | – | 8.4 | 86 |
| P | 2800 | 1400 | 4200 | 1300 | – | 2100 | 12,000 | 5100 | 1600 | 4000 | 1600 | 1100 | 1100 | 27,000 | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] |
| Q | 5400 | 2700 | 4400 | – | 230 | 1700 | 1800 | 6400 | 3100 | 6400 | | 1100 | 2700 | 11,000 | – | 37 | 500 | 33 | 730 |
| T | 360 | 120 | 190 | 25 | 2.0 | 790 | 1700 | 350 | 100 | 200 | 23 | 2.3 | 580 | 1500 | 100 | 27 | 12 | 120 | 1800 |
| W | 530 | 79 | 1100 | 330 | – | 150 | 1500 | 810 | 330 | 1100 | 280 | 250 | | 2800 | – | 200 | – | 86 | 780 |
| B | 710 | 790 | 1300 | 1200 | 290 | – | – | 5000 | 1300 | 8800 | 1500 | 1700 | 1900 | 840 | 210 | 320 | 1900 | 140 | 710 |
| E | 36 | 51 | 80 | – | – | – | – | 140 | 75 | 410 | – | 130 | 37 | 87 | 30 | 18 | – | 11 | 50 |
| *Summer* | | | | | | | | | | | | | | | | | | | |
| H | 250 | 170 | 330 | 120 | – | – | 300 | 230 | 190 | 310 | 150 | 33 | 230 | 140 | – | – | 28 | – | 70 |
| M | 940 | 430 | 2000 | 410 | – | – | 390 | 700 | 590 | 2400 | 410 | 450 | 320 | 660 | – | – | 160 | – | – |
| N | 160 | 51 | 190 | 100 | – | 62 | 84 | 200 | 81 | 180 | 120 | 42 | 65 | 170 | – | 6.9 | 52 | – | 5.7 |
| B | 1300 | 1100 | 1700 | 1600 | 660 | – | – | 9300 | 2000 | 11,000 | 2100 | 2500 | 670 | 1200 | 430 | 350 | 2400 | 310 | 1500 |
| E | 71 | 100 | 130 | – | – | – | – | 290 | 100 | 380 | 180 | 230 | 88 | 170 | 30 | 31 | 120 | 12 | 110 |
| A | 1700 | 2200 | 4000 | 1800 | 840 | 1800 | 1400 | 4800 | 2000 | 5500 | 2100 | 1400 | 5200 | 2600 | 88 | 180 | 240 | 30 | 210 |
| C | 76 | 49 | 77 | – | – | – | – | 1000 | 91 | 690 | 110 | 220 | 33 | 60 | 6.1 | 9.3 | 75 | 4.8 | 16 |
| F | 270 | 150 | 190 | – | 30 | 39 | 63 | 510 | 140 | 370 | 130 | 36 | 76 | 80 | 6.0 | | 20 | 4.8 | 34 |
| L | 260 | 150 | 290 | 210 | – | 350 | 400 | 480 | 230 | 510 | 320 | 180 | 480 | 480 | 7.6 | 38 | 66 | 7.6 | 190 |
| P | 2900 | 1100 | 2200 | 1000 | – | 1300 | 93,000 | 6000 | 2600 | 5600 | 1300 | 2000 | 3500 | 12,000 | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] |
| Q | 1700 | 1000 | 2100 | 640 | – | 1400 | 1300 | 2800 | 1100 | 3400 | 900 | 1600 | 940 | 2300 | – | – | 480 | 31 | 460 |
| T | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] | n/a[a] |
| W | 1700 | 710 | 1600 | 780 | – | 240 | 1100 | 1900 | 800 | 2200 | 680 | 520 | – | 3600 | – | 160 | 220 | 26 | 620 |
| B | 1300 | 1100 | 1700 | 1600 | 660 | – | – | 9300 | 2000 | 11,000 | 2100 | 2500 | 670 | 1200 | 430 | 350 | 2400 | 310 | 1500 |
| E | 71 | 100 | 130 | – | – | – | – | 290 | 100 | 380 | 180 | 230 | 88 | 170 | 30 | 31 | 120 | 12 | 110 |

[a] Not available, not possible to calculate mass loading.

0.8 to 38 (median: 11) and from 0.2 to 170 (median: 5.8) in plants with PT and ST/AT, respectively, indicating a higher burden of PFAAs to the environment through effluent. No seasonal differences were observed for FE:biosolids ($p > 0.05$). In general, PFAAs median removals via sorption were 8% for PT and 15% for ST/AT, indicating that PFAAs removal through sorption was low. However, different trends were observed by compounds. PFOA, PFNA, PFDA, and PFOS were mainly released to the environment through FE at 98%, 89%, 69%, and 79%, respectively. This trend is directly related to their previously calculated $K_d$, where PFOS is more highly sorbed to WBS than PFOA.

Estimated mass loadings showed that the sum of FE and biosolids loading exceeded the influent loadings, substantiating the formation of PFAAs in some WWTPs. Formation percentage was estimated in plants with ST/AT by: % formation = (((mg/day in FE + mg/day in Biosolids) − mg/day in RI)/mg/day RI) × 100. The compounds most highly formed were PFOS (median: 92%), PFHxA (70%), PFOA (56%), PFNA (47%), and PFHpA (32%). PFCAs and perfluorinated sulfonic acids (PFSAs) are converted from FTOHs and N-etFOSE, respectively. Assuming that only these two precursors were present in the influents, it was estimated that FTOHs were in the RI of 90% of the studied ST/AT plants while N-etFOSE was in the 70%. In addition, using the formation of PFOS and PFOA, it was calculated that the levels of PFOS and PFOA precursors present in the influent ranged from 3 to 620%, and from 5 to 81% of the respective PFAAs entering to the WWTPs. This wide variation was related to season, HRT, and solids treatment in addition to the amount of precursors.

## 4. Conclusions

This study investigated the occurrence, fate, and behaviour of PFAAs in 20 Canadian WWTPs to better understand their formation in different wastewater treatment processes. PFAAs were detected in all RI (7.5–2100 ng/L) with PFOA, PFOS, and PFHxA at the highest concentrations. In FE, PFAAs were found at higher levels with values ranging from 15 to 2500 ng/L, indicating PFAAs formation during wastewater treatment, which may be due to degradation of precursors. The low concentrations of PFAAs in PS and the high concentrations of PFAAs in WBS confirmed that there is a potential to generate PFAAs during the aerobic biological step.

Investigation of parameters affecting PFAAs formation showed that PT processes formed the least PFAAs compared to biological treatment processes, possibly due to minimum biological activity and short HRT. Higher temperature and longer HRT increased the formation of PFAAs. The removal of PFAAs by sorption to sludge was influenced by their different sorption tendencies: PFOS (3.73) > PFDA (3.68) > PFNA (3.25) > PFOA (2.49) > PFHxA (1.93). Mass balances confirmed the formation of PFAAs, the low sorption of PFAAs onto biosolids and their consequent release to the aquatic environment at mass loadings up to 140 g/day. Additional studies on levels of PFAA precursors and their transformation patterns would be beneficial to better understand how PFAA are formed in WWTPs.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2014.03.016.

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