Science of the Total Environment 754 (2021) 142431

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Removal and formation of perfluoroalkyl substances in Canadian sludge treatment systems – A mass balance approach

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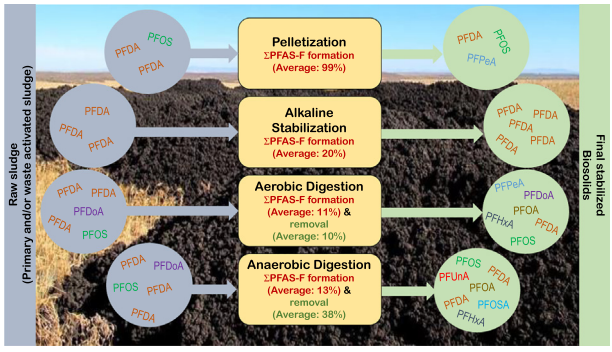
HIGHLIGHTS

- Evaluated the formation and removal of thirteen PFAS in nine different sludge treatment systems
- Increase in ΣPFAS-F mass flow seen during pelletization and alkaline stabilization processes
- Modest removals of ΣPFAS-F were seen in some aerobic and anaerobic digestion processes.
- Behavior of individual PFAS (PFOA, PFDA, and PFOS) varied within and between treatment process types.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 July 2020
Received in revised form 14 September 2020
Accepted 14 September 2020
Available online 21 September 2020

Editor: Dimitra A Lambropoulou

Keywords:
PFAS
Sludge
Biosolids
Pelletization
Alkaline stabilization
Aerobic digestion
Anaerobic digestion

ABSTRACT

Poly- and per-fluoroalkyl substances (PFAS) are an emerging class of anthropogenic contaminants whose occurrence has raised concerns with the beneficial reuse of biosolids from wastewater treatment. This study evaluated the behavior of thirteen PFAS in nine Canadian sludge treatment systems including pelletization, alkaline stabilization, aerobic and anaerobic digestion processes. The composition of the overall PFAS-fluorine (ΣPFAS-F) loading in a system fed with only primary sludge was dominated by perfluorodecanoate (PFDA), whereas systems with blended primary and waste activated sludge feeds had a mix of short and long chain PFAS in raw sludges and treated biosolids. An increase in average ΣPFAS-F mass flow was observed through pelletization (19% formation) and alkaline stabilization (99% formation) processes indicating negative removal or contaminant formation. One of the two aerobic digestion systems and three of the five anaerobic digestion systems showed modest reductions (< 40% removal) in ΣPFAS-F loading. Long chain PFAS such as perfluorodecanoate (PFDA) and perfluorooctane sulfonate (PFOS) exhibited a wide variation in behavior ranging from substantial formation (> 75% formation) to modest removal (42% removal) in the surveyed systems while short chain perfluoropentanoate (PFPeA) mass flows increased through the three systems where they occurred. Overall, the contaminant mass balances revealed that there were significant changes in mass flows of the target PFAS through all kinds of sludge treatment systems. The results of this study on PFAS fate through sludge processing can inform future global PFAS risk management activities as well as sludge treatment considerations.

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1. Introduction

Per- and poly-fluoroalkyl substances (PFAS) are an emerging class of organic micropollutants that has garnered wide attention in the past decade (ITRC, 2020). Some of these compounds are surfactants, used for

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https://doi.org/10.1016/j.scitotenv.2020.142431
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their hydrophobic and lipophobic properties, and they consist of two distinct components: an alkyl carbon chain with multiple carbon-fluorine bonds and a hydrophilic functional group. Two of the groups within the PFAS class include perfluoroalkyl acids (PFAA) and perfluoroalkyl sulfonamides (PFASA), which differ based on the functional group attached to the alkyl backbone. >5000 compounds within the PFAS class have been reported and they have been used in water-resistant clothing, food packaging, grease and stain resistant coatings, industrial surfactants, resins, molds, plastics, metal plating and etching, coatings in semiconductors and wires, and firefighting foams (ITRC, 2020; Venkatesan and Halden, 2013). Many of these compounds are persistent, bioaccumulative, and toxic in nature (Sáez et al., 2008), and are ubiquitously detected in a variety of environmental matrices such as air, surface water, groundwater, wildlife, fish, human blood serum and breast milk (Ahrens, 2011; Kannan et al., 2004; Lindstrom et al., 2011).

Water Resource Recovery facilities (WRRFs) can play an important role in the discharge of PFAS to the environment. Conventional wastewater treatment technologies have been reported to be relatively ineffective in removing them from wastewater (Ahrens, 2011; Sinclair and Kannan, 2006). Mass balances on several full-scale WRRFs have shown an overall increase in the mass flows of shorter PFAS through secondary treatment (Chen et al., 2018; Guerra et al., 2014; Schultz et al., 2006). This has been attributed to the transformation of precursor compounds such as fluorotelomer alcohols (FTOHs) into PFAAs during treatment (Sinclair and Kannan, 2006; Schultz et al., 2006). Guerra et al. (2014) observed higher formation of PFAAs at longer hydraulic retention times and higher temperatures during biological treatment. PFAS are also known to partition to solids with the sorptive behavior influenced by the carbon chain length of the compound, the functional groups attached to the alkyl chain, and the type of sludge (Arvaniti et al., 2012, 2014; Higgins et al., 2005; Higgins and Luthy, 2006; Ochoa-Herrera and Sierra-Alvarez, 2008; and Sinclair and Kannan, 2006).

The occurrence of PFAS in WRRF biosolids can present challenges to beneficial land application programs as the contaminants could mobilize in the soil, leach into run-off, infiltrate into groundwater or be taken up by biota. Sepulvado et al. (2011) found a linear correlation between PFAS soil concentrations and biosolids application rates. PFAS were detected in soil cores taken at depths of 120 cm indicating contaminant transport from the land applied biosolids (Sepulvado et al., 2011). Lindstrom et al. (2011) observed elevated PFAS concentrations in surface water and well water in areas adjacent to a field that received biosolids from a WRRF that treated industrial wastewater. Long-term studies have shown leaching of PFAS from municipal biosolids into tile drainage and groundwater (Gottschall et al., 2010) even one year after application (Gottschall et al., 2017). Besides PFAS movement in the environment, bioaccumulation in earthworm tissues (Rich et al., 2015), lettuce and tomatoes (Blaine et al., 2013) and in radish roots, celery shoots, and pea fruits (Blaine et al., 2014) have been reported. This widespread prevalence of PFAS in matrices associated with the biosolids life-cycle demonstrates that the environmental implications of PFAS in biosolids need to be better understood.

There are gaps in our understanding of PFAS fate during sludge treatment and addressing them can aid the global PFAS risk management activities. While several studies have monitored concentrations of PFAS in biosolids (Armstrong et al., 2016), there is little information on the fate of PFAS in sludge treatment systems. Recent studies have shown that side-chain perfluoroalkyl polymers may degrade during sludge treatment to form PFAAs (Letcher et al., 2020). However, mass balance-based quantification of the change in PFAS loadings through sludge treatment systems has not been reported. The current study sought to evaluate the responses of thirteen PFAS through physical, chemical and biological sludge treatment processes using a mass balance approach. In this regard, the concentrations of thirteen PFAS were documented and their mass flows in the raw sludge and biosolids from typical sludge treatment systems in Canada were estimated.

2. Materials and methods

2.1. Sludge sampling

Grab samples of raw sludge and final stabilized biosolids were collected from the sludge treatment systems of nine WRRFs that employed either pelletization (P), alkaline stabilization (AS), aerobic (AE1, AE2) or anaerobic (AN1 to AN5) digestion, representing typical physical, chemical and biological solids treatment processes employed in Canada. The sludge sources, treatment system descriptions and operating conditions are tabulated in Table S1 in the Supplemental Information I. Samples were collected on three consecutive days within a one-month period in each of 2015 and 2016. The return streams from sludge dewatering were not sampled in this study. Solids samples were collected in pre-cleaned amber glass jars (Systems Plus, Baden, Canada) and shipped overnight on ice to the laboratory. Standard Ottawa sand (ThermoFisher Scientific, Waltham, USA) was collected in the sampling jars as equipment blanks to assess for cross contamination during sampling.

2.2. Analytical method

The analytical method characterized thirteen PFAS that consisted of nine perfluorocarboxylic acids (PFCA), three perfluorosulfonic acids (PFSA) and one perfluoroalkyl sulfonamide (PFASA). The target compounds and their chemical structures are listed in Table 1. All PFAS analysis was carried out by SGS AXYS Analytical Services, Sidney, BC, Canada (SGS AXYS) using AXYS Method MLA-041. The detailed analytical procedure (Section 2) and the reporting limits (Table S2) are presented in Supplemental Information I. The thirteen individual PFAS homologues had different reporting limits (RLs) and they also changed between samples. The median RLs of the individual PFAS were in the range of 3.09–6.82 ng/g dry weight (dw) in the raw sludges and 2.89–5.87 ng/g dw in the biosolids. The performance of MLA-041 method in relation to the NIST SRM 2781 standard biosolid reference material is summarized in Supplemental Information I (Section 3).

2.3. Quality control procedures

A summary of the findings of the quality control measures conducted as part of the analytical procedure is presented in Supplemental Information I (Tables S3 to S5). No target PFAS were detected in any of the equipment blanks, indicating that cross contamination during sampling was negligible. Similarly, no PFAS was reported in any of the laboratory blank samples. PFAS concentrations in raw materials used in the

Table 1
Target PFAS and their physico-chemical properties.

Target PFAS	Molecular formula	Molecular weight (g/mol)
Perfluoroalkyl carboxylates (PFCA)		
Perfluorobutanoate (PFBA)	$C_3F_7CO_2^-$	214.04
Perfluoropentanoate (PFPeA)	$C_4F_9CO_2^-$	264.05
Perfluorohexanoate (PFHxA)	$C_5F_{11}CO_2^-$	314.05
Perfluoroheptanoate (PFHpA)	$C_6F_{13}CO_2^-$	364.06
Perfluorooctanoate (PFOA)	$C_7F_{15}CO_2^-$	414.07
Perfluorononanoate (PFNA)	$C_8F_{17}CO_2^-$	464.08
Perfluorodecanoate (PFDA)	$C_9F_{19}CO_2^-$	514.08
Perfluoroundecanoate (PFUnA)	$C_{10}F_{21}CO_2^-$	564.09
Perfluorododecanoate (PFDoA)	$C_{11}F_{23}C_2^-$	614.1
Perfluoroalkyl sulfonates (PFSA)		
Perfluorobutane sulfonate (PFBS)	$C_4F_9O_3S^-$	300.1
Perfluorohexane sulfonate (PFHxS)	$C_6F_{13}O_3S^-$	400.11
Perfluorooctane sulfonate (PFOS)	$C_8F_{17}O_3S^-$	500.13
Perfluoroalkyl sulfonamides (PFASA)		
Perfluorooctane sulfonamide (PFOSA)	$C_8H_2F_{17}NO_2S$	499.14

analysis (e.g., methanol) were below the reporting limit, and the analytical instruments did not contain potential sources of PFAS contamination, such as Teflon tubing. The median recoveries of the eight labelled surrogates were within the acceptable limits of the analytical method. PFAS concentrations were inherently recovery-corrected as an isotope dilution method was used. Relative percent difference (RPD) in the concentration of duplicate samples was calculated to evaluate the reproducibility of the analytical method. The median RPD of all the duplicate analyses was at 6% showing high reproducibility of the concentration measurement.

2.4. PFAS mass balance and removal calculations

The measured concentrations of PFAS in raw sludge and treated biosolids provided valuable information on the levels of contamination of the materials. However, this information alone does not provide insight into PFAS fate as changes in concentrations may be due to either transformation mechanisms or changes in solids concentrations through the sludge treatment processes. Hence, contaminant mass balances were assembled and removals of PFAS were estimated to obtain insight into their fate through the different sludge treatment systems. This was achieved by initially assembling solids balances across the sludge treatment systems and then estimating PFAS mass flows based upon the measured PFAS concentrations. Monthly averages of the totals solids (TS) mass flows (kg TS/day) in and out of the sludge treatment systems were estimated for each sampling campaign based on data recorded by the WRRF. The mass flow of each PFAS compound (PFAS mg/day) was subsequently calculated as the product of the measured concentration at each sampling point and the monthly average of the solids loading.

The physico-chemical and biological activity of PFAS compounds were expected to be a function of the compound chain length. As multiple compounds with varying PFAS chain lengths were studied (carbon length from 4 to 12), a normalized, summative loading approach was employed to assess the overall contaminant mass flow through the treatment systems. The individual PFAS mass flows were converted into PFAS fluorine equivalents (PFAS-F mg/day) and the total PFAS loading (Σ PFAS-F mg/day) associated with the measured compounds was calculated as the sum of the individual PFAS loadings on an F basis.

Sludge treatment systems typically operate with extended retention times and the solids retention time (SRT) in the surveyed biological systems ranged from 15 to 43 days. In this study, the raw sludge and the biosolids samples were collected on the same day. Therefore, the raw sludge and biosolids mass flows were not paired as such to calculate removals. A Monte-Carlo simulation approach that incorporated the variability of the sampling in the data analysis was employed to estimate the changes in mass flows of the PFAS through treatment.

In the Monte-Carlo analysis, the PFAS mass flows in the raw sludge and biosolids of each treatment system were assumed to be normally distributed and this was confirmed by goodness of fit test in ProUCL Version 5.1 by the US Environmental Protection Agency. The mean and standard deviation of the PFAS-F mass flows were then estimated from the obtained data set for six sampling days. On the basis of the mean and standard deviation values (Table S8 of Supplemental Information I) and the assumption of a normal distribution of PFAS loading, 1000 mass flow values were randomly generated for the raw sludge and biosolids streams. Paired samples were then employed to estimate the removal efficiencies as per Eq. (1):

$$\%\text{Removal} = 100 * (L_{RS} - L_{BS})/L_{RS} \quad (1)$$

where, L_{RS} – PFAS-F mass flow in the raw sludge (mg PFAS-F/day) L_{BS} – PFAS-F mass flow in the biosolids (mg PFAS-F/day).

The 1000 estimated values (N) for each response were employed to develop descriptive statistics such as mean and standard error (standard deviation/$\sqrt{N}$) for the percentage removal. Paired student's *t*-tests were conducted between the raw sludge and biosolids loading at a 95% confidence level to assess the statistical significance of estimated removals. As the data set included a number of responses where the concentrations were below the reporting limits, the following strategy was used in the estimation of the means and standard deviations: i) at least two detectable concentrations out of the six samples were required to calculate a removal; ii) when either of the raw sludge or biosolids sample sets had all concentrations below the reporting limit and the other had sufficient detectable values to calculate a mean and standard deviation, the reporting limit was substituted in place of the missing concentrations to calculate the PFAS-F mass flow and further estimate the removal conservatively; iii) all other concentrations that were below the reporting limits were treated as zero in mass flow calculations.

3. Results and discussion

3.1. Occurrence and abundance of PFAS

The PFAS concentrations from the nine sludge treatment processes were initially examined to characterize their occurrence and abundance in the raw sludge and biosolids streams. The raw data describing the PFAS concentrations through the various treatment systems are included as a spreadsheet in Supplemental Information II. The data gathered for the target PFAS in the raw sludges and biosolids were composited across the studied treatment systems to characterize the overall occurrence and abundance (Table 2). The detection frequency was calculated as the ratio of the number of samples that yielded a measured concentration above the reporting limit to the total number of samples analyzed in the given matrix. Literature reports of PFAS occurrence/concentration were included in Table 2 to facilitate a comparison with the results of the current study.

Out of the thirteen target PFAS, only four were detected appreciably (> 1%) in both raw sludge and biosolids samples. When arranged in descending order of detection frequency (PFDA > PFOS > PFDoA > PFOA), the trend was the same for the raw sludge and biosolids matrices. The partitioning of PFAS to solids has been reported to increase with carbon chain length (Arvaniti et al., 2012; Higgins and Luthy, 2006). In this study, PFDA (10 carbon atoms), was the third longest compound, however, it had the highest frequency of occurrence with detection in >85% of samples of raw sludge and biosolids. PFDA also registered the highest median concentrations with values of 15 and 21 ng/g dw in the raw sludge and biosolids, respectively. In contrast, the compound with the longest carbon chain among the target contaminants, PFDoA (12 carbon atoms) was detected in only 13% of the raw sludge and 40% of the biosolids samples with similar median concentrations (~ 6 ng/g dw). The inconsistency between the observed frequency of detection and the partitioning properties suggests that PFDA, a common ingredient in floor polishes (ITRC, 2020) and/or its precursors was used more extensively in the study areas when compared to PFDoA and its precursors. On the other hand, short chain compounds (< 8 carbon atoms) such as PFBA and PFHxS that have been previously detected in Canadian wastewater influent (Guerra et al., 2014) were not detected in any of the solids samples in this study. This may have been due to their relatively low sorption tendency.

Besides the compound chain length, the functional group attached to the C—F backbone also affects the partitioning of PFAS to solids. Sulfonated PFAS have been reported to demonstrate greater sorption to solids when compared to carboxylated PFAS (Higgins and Luthy, 2006; Zhou et al., 2010). The results of this study were consistent with the expected partitioning as there was a higher occurrence of PFOS than PFOA in both the raw sludge and biosolids samples. Similar to the detection frequency results, the median concentration of PFOS in the raw sludge samples (10.6 ng/g dw) was significantly higher ($P < 0.05$) than the corresponding PFOA concentration (4.7 ng/g dw). It is also likely that the higher occurrence of PFOS was because there was more PFOS and/or its precursors in the influent wastewater

Table 2
PFAS detection and concentration in raw sludge and biosolids composited across treatment systems in this study and literature.

Sludge source	Descriptive statistic	PFAS concentrations (ng/g dry weight)												
		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFBS	PFHxS	PFOS	PFOSA
Raw sludges, This Study	Detection frequency (%)	0	0	< 1	0	4	0	86	0	13	<1	0	31	<1
	Median (Min - Max)	BRL	BRL	**3.5** (BRL-3.5)	BRL	**4.7** (BRL-4.8)	BRL	**15** (BRL-38)	BRL	**5.4** (BRL-8.7)	**9** (BRL-9)	BRL	**10.6** (BRL-27)	**3.3** (BRL-33)
Biosolids, This Study	Detection frequency (%)	0	29	21	6	25	25	88	21	40	10	0	46	15
	Median (Min - Max)	BRL	**6.2** (BRL-14)	**5.2** (BRL-8.3)	**5.0** (BRL-5.2)	**14** (BRL-23)	**6.6** (BRL-20)	**21** (BRL-53)	**5** (BRL-7)	**6** (BRL-10)	**8.8** (BRL-11)	BRL	**14** (BRL-25)	**3.8** (BRL-5.7)
Biosolids, US. Sinclair and Kannan (2006)	Min - Max	NA	NA	NA	NA	18–241	NA	<25–91	< 25–115	NA	NA	< 10–18	<10–65	NA
Biosolids, Denmark. Bossi et al. (2008)	Mean (Max – Min)	NA	NA	NA	NA	0.4 (0.7–19.7)	1.5 (0.4–8)	7.2 (1.2–32)	1.2 (0.5–4.4)	NA	NA	3.6 (0.4–10.7)	18.4 (4.8–74.1)	0.8 (0.5–3.6)
Biosolids, Spain. Navarro et al. (2011)	Mean (Min - Max)	BRL	1.46 <0.01–18.2	0.42 < 0.03–2.60	0.28 <0.01–2.04	2.85 <0.03–7.94	1.23 (<0.01–10.2)	5.41 (<0.04–24.3)	NA	NA	BRL	1.46 (<0.01–18.2)	63.99 (<0.01–268.8)	NA
Biosolids, Greece. Arvaniti et al. (2012)	Min - Max	NA	BRL – 45.2	BRL – 61.5	BRL – 16.4	BRL – 19.4	BRL – 13.5	BRL – 9.6	BRL – 4.6	BRL – 9.8	BRL	BRL −18.3	0.6–16.7	BRL – 5.7
Biosolids, Nigeria. Sindiku et al. (2013)	Median (Max – Min)	NA	NA	0.21 (BRL – 0.24)	0.014 (BRL – 0.014)	0.043 (0.019–0.42)	0.041 (0.010–0.13)	0.063 (0.022–0.57)	0.054 (0.039–0.16)	0.24 (BRL – 0.28)	0.041 (BRL − 0.14)	0.031 (BRL – 0.042)	0.28 (BRL – 0.54)	NA
Biosolids, Spain. Campo et al. (2014)	Min - Max	0.13–1880	0.13–1080	1.33–11.1	0.33–55.1	0.13–103	1.33–208	0.09–666	0.1–68.8	0.1–0.1	0.41–175	0.01–0.01	0.01–1790	0.67–0.67
Biosolids, China. Zhang et al. (2015)	Mean ± Standard Deviation	BRL	BRL	0.59 ± 0.04	0.35 ± 0.04	20.2 ± 1	BRL	2.7 ± 0.3	3.51 ± 0.17	0.76 ± 0.03	5.3 ± 0.94	NA	38.5 ± 2.8	NA
Biosolids, US. Armstrong et al. (2016)	Median (Max – Min)	NA	6.85 (1.54–27.7)	7.03 (BRL-21.1)	0.41 (BRL – 67.7)	23.5 (BRL – 601)	17.6 (BRL-218)	NA	NA	NA	NA	NA	19.3 (BRL – 68.1)	NA
Biosolids, Australia. Coggan et al., 2019	Median (Min - Max)	BRL (BRL – 4.1)	BRL (BRL – 5.2)	0.92 (BRL – 13)	BRL (BRL-4.1)	BRL (BRL-25)	BRL (BRL – 1.1)	0.6 (BRL – 26)	BRL (BRL – 1.2)	0.48 (BRL – 20)	BRL (BRL – 9.3)	BRL (BRL – 17)	4.7 (BRL – 90)	NA

NA – Compound not measured
BRL – Below reporting limit
Max – Maximum concentration
Min – Minimum concentration

supplied to the upstream process when compared to PFOA. Guerra et al. (2014) measured a broader range of PFOS concentration (2 to 1100 ng/L) when compared to a relatively narrow range of 2.2 to 150 ng/L for PFOA in the raw wastewater from 15 Canadian WRRFs. These two compounds, along with other PFAAs such as PFHxA, PFDA, PFDoA and the only perfluorosulfonamide studied, PFOSA were detected at a higher frequency and concentration in the biosolids than the raw sludges (Table 2). The results suggested that transformations of unmeasured PFAS precursors to generate the target compounds were occurring in the sludge treatment processes and this was assessed more intensively in the subsequent mass balance analyses.

Previous studies have demonstrated that the presence of precursors can dictate the biosolids quality produced by sludge treatment processes. FTOHs with general formula $F(CF_2)_nCH_2CHOH$ where n is an even number (Ellis et al., 2004) and which are manufactured as 4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH, are well known PFAS precursors. They are commonly used in industrial coating and windshield cleaning fluids (Renner et al., 2006) and hence can be present in sludges. In upstream wastewater treatment processes, FTOHs have been found to transform predominantly into the corresponding PFCAs (Dinglasan et al., 2004). This may explain why PFCAs such as PFDA, PFOA, and PFDoA were detected more frequently in the current study when compared to PFCAs with odd numbers of carbons in the chain (PFPeA, PFHpA, PFNA, PFUnA), which were not detected in the raw sludge samples. It is, however, interesting to note an increase in detection frequency of PFPeA, PFHpA, PFNA, and PFUnA at 29%, 6%, 25%, and 21%, respectively, in biosolids. This difference in occurrence between raw sludge and biosolids suggests formation of these compounds in select sludge treatment processes, which is discussed later. Thus, the occurrence of PFAS in biosolids is affected by transformations that happen in both wastewater and sludge treatment.

The concentrations of the target PFAS in this sampling campaign were compared with international literature reports to assess whether differences in usage and regulatory practices impact biosolids quality. The range of PFAS concentrations measured by Campo et al. (2014) in Spanish biosolids were much broader than the range in this study. On the other hand, the median and the maximum concentrations reported by Coggan et al. (2019) in Australian biosolids and Sindiku et al. (2013) in Nigerian biosolids were consistently lower than those observed in the current study. PFOS and PFOA are the two most widely studied PFAS and there is a sizeable body of information available in the literature for occurrence of these two compounds. While the concentrations of PFOS and PFOA in the current study were within the range of those described in the literature, they occurred less frequently (PFOS = 46% and PFOA = 25%) in the Canadian biosolids when compared to the US (Armstrong et al., 2016; Sinclair and Kannan, 2006), Nigeria (Sindiku et al., 2013), and Australia (Coggan et al., 2019) that had detection frequencies of 70–95%. The differences between the Canadian and international results may have several underlying causes as subsequently delineated.

Regional differences in usage of products containing PFAS and their precursors may lead to differences in occurrence in biosolids. Further, the configurations of the upstream wastewater treatment processes and the sludge treatment process can also be a major source of variation (Guerra et al., 2014). Also the PFAS mass load in the influent wastewater (Nguyen et al., 2019) and the WRRF performance with respect to PFAS removal can vary seasonally (Chen et al., 2018; Guerra et al., 2014) and hence the time of sampling may influence the PFAS levels in the solids. Finally, the manufacture and use of PFAS have been regulated differently over time and there may be variations in use patterns in response to regulatory actions. For instance, the manufacture, import and use of PFOA, PFOS, long-chain PFCAs, their salts, and precursors have been prohibited, with a limited number of exceptions, under the *Prohibition of Certain Toxic Substances Regulation, 2012* by the (Government of Canada, 2017). Prior to this, PFOS had been regulated since 2008 under the *Perfluorooctane sulfonate and its salts and certain other compounds Regulations* (Government of Canada, 2016). Accordingly, the contaminant levels from this sampling campaign (2015 and 2016) were likely influenced by these control measures.

3.2. Overall PFAS concentration in raw sludge and biosolids

It was hypothesized that the presence of PFAS in raw sludges and biosolids would be influenced by the characteristics of the sewershed generating the wastewater. The nine sludge treatment systems in this study served populations ranging from 10,000 to 705,000 inhabitants which translated to average raw sludge productions of 775 to 69,360 kg TS/day. Some of the sludge processing trains received only primary sludge and the surveyed WRRFs included industrial and landfill leachates in their wastewater influents (Table S1). Hence it was anticipated that municipalities of differing scales and sewershed inputs may have different PFAS levels in their raw sludge samples. To assess the hypothesis, the ΣPFAS-F concentrations (ng PFAS-F/g TS) in raw sludge and biosolids were ordered by sewershed population as shown in Fig. 1.

No discernable trends were observed between the ΣPFAS-F concentrations in the raw sludges and the population served in the sewershed (Fig. 1). The lowest ΣPFAS-F concentration in raw sludge was seen in AN2 (average = 5 ± 5 ng PFAS-F/g TS) and the highest in AN4 (27 ± 5 ng PFAS-F/g TS). Several of the treatment systems had industrial contributions to the wastewater stream including landfill leachate contributions in AN1 and AN4 (Table S-1) and in spite of these differing inputs, the ΣPFAS-F concentration did not vary extensively. Similarly, in the biosolids there was no apparent relationship between the ΣPFAS-F concentration and the population served or industrial contributions. However, the variability of the ΣPFAS-F concentrations in the composited data was higher in biosolids (RSD = 75%) when compared to raw sludge (RSD = 52%) from the nine sludge treatment systems. This was attributed to differences in the performance of the various sludge treatment systems with respect to transformations of PFAS precursors and compounds.

3.3. Contribution of PFAS compounds to ΣPFAS-F mass flows

The contribution of the individual PFAS compounds to the ΣPFAS-F mass flows in the different treatment systems was examined to assess whether the sludge source impacted the variety of PFAS entering the sludge handling system. The average contribution of the individual compounds (expressed as F) relative to the ΣPFAS-F loading in raw sludge and biosolids streams for each system is shown in Fig. 2. PFDA was the sole contributor to the ΣPFAS-F mass flows in the raw sludges for AS and AN1. The feed to these systems consisted of primary sludges predominantly (Table S1). With the exception of AN2, treatment systems fed with blended primary and waste activated sludges (WAS)

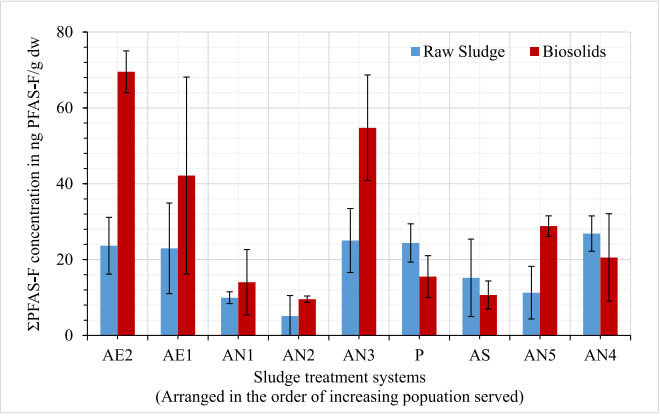

Fig. 1. ΣPFAS-F concentrations in raw sludges and biosolids from individual sludge treatment systems.

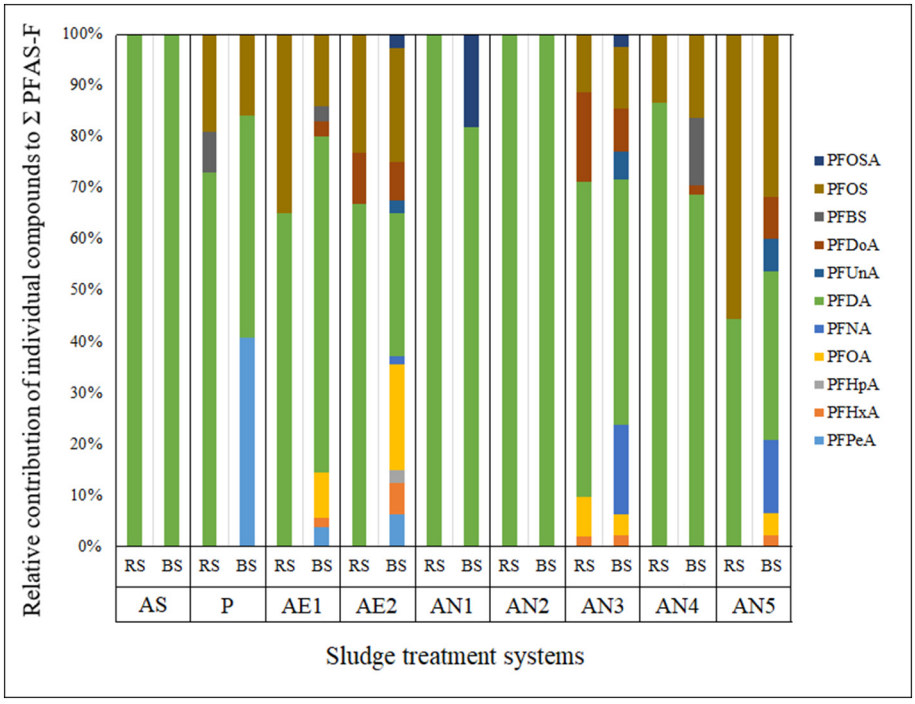

Fig. 2. Average relative contribution of individual compounds to ΣPFAS-F mass flows in raw sludge (RS) and biosolids (BS).

(AE1, AE2, AN3, AN4, and AN5), the ΣPFAS-F loading consisted of a variety of PFAS. The lack of diversity in the PFAS profile in the primary sludge may have been due to i) minimal biotransformation in the primary settler, ii) lack of input from secondary treatment where PFAAs are produced from precursors, and iii) differences in sorption characteristics of PFAS between primary and secondary sludge (Arvaniti et al., 2012). Viewed collectively, it was apparent that the source of the raw sludge impacted the type of PFAS compounds entering the sludge treatment systems and hence may influence the composition of PFAS in the product biosolids.

The contributions of individual PFAS compounds to the ΣPFAS-F mass flows in the biosolids streams were assessed to study the collective impact of the source sludge and the treatment process on the final biosolids quality. Of the two systems fed with predominantly primary sludge, the ΣPFAS-F mass flow in the biosolids from AS was entirely composed of PFDA which was consistent with the raw sludge. By contrast, in biosolids from AN1, PFOSA contributed 15% of the ΣPFAS-F mass flow. The results indicated that alkaline stabilization did not change the PFAS compositional profile while anaerobic digestion at AN1 did change the relative composition of the ΣPFAS-F mass flow. The presence of relevant precursors in the raw sludge and the nature of the sludge treatment process design may be contributing to these differences in PFAS profiles in the biosolids for the same type of raw sludge source.

In the systems with blended sludge feeds (P, AE1, AE2, AN3, AN4 and AN5), changes in ΣPFAS-F composition between the feed sludges and the product biosolids were observed. In all these cases, PFAS compounds were observed in the product biosolids that were not present in the feed sludges. The results suggest that the factors defining the PFAS composition in product biosolids are complex and appear to be influenced by feed sludge properties as well as sludge processing. It should be noted that changes in relative composition of the raw sludge and biosolids do not necessarily provide insight into the fate of a compound through treatment. For example, a decrease in the contribution of a given compound may not be due to a decrease in its mass flow but rather a change in the mass flows of other contributors. The formation and removal of PFAS compounds in the treatment systems were subsequently examined using a mass balance analysis to obtain further information on the transformations of individual compounds.

3.4. Responses of individual PFAS in sludge treatment systems

The behaviors of the individual target compounds were assessed to understand their fate through physical, chemical, and biological sludge treatments. The removal or formation of the target PFAS compounds in the various sludge treatment systems were calculated based on the observed PFAS mass flows and Monte-Carlo simulations that were conducted to facilitate an assessment of the variability of the responses. The removal efficiencies that were estimated from the mass flows of the individual and combined PFAS-F (mean ± standard error) compounds through the various solids treatment processes are presented in Table 3. All changes in mass flows in the systems were found to be statistically significant (student's pairwise *t*-test; $P < 0.05$) with the exception of the transformation of PFDA in AN2 ($P > 0.05$).

3.4.1. Alkaline stabilization

In this treatment process, the raw sludge was mixed with admixtures such as quick lime (Calcium oxide – CaO) and cement kiln dust to initiate an exothermic pH adjustment reaction, inactivate the pathogens, and stabilize the solids. This chemical treatment brings about several changes in the matrix such as increase in pH, elevated concentration of Ca^{2+}, and addition of a sorptive material. This may result in changes to the sorptive behavior of the solids or enhanced transformations of the PFAS.

The mass balances on the AS process revealed a high level of formation of PFDA (−99 ± 14%). No other formation or removal of PFAS compounds was observed. The increase in the mass flow of PFDA may have resulted from hydrolytic reactions of unmeasured precursors in the high pH environment. While the C—F bond shields against nucleophilic attack of the alkyl backbone, the remainder of the molecule might be available for transformation. Washington et al. (2015) observed abiotic hydrolysis of fluorotelomer polymers (FTP) into carboxylate homologues in deionized water and subsequently Washington and Jenkins (2015) found that base mediated hydrolysis of FTPs at pH = 12 ($t_{1/2}$ = 0.7 years) was faster than hydrolysis at circumneutral pH ($t_{1/2}$ = 55 to 89 years). In summary, a statistically significant increase in the mass flow of ΣPFAS-F, contributed entirely by PFDA-F, was observed through alkaline stabilization

Table 3
– Percent removal or formation (Mean ± Standard Error; $N = 1000$) of individual PFAS estimated from mass flows. Shading of cells highlights average % removal as per colour key.

Treatment System	PFPeA-F	PFHxA-F	PFHpA-F	PFOA-F	PFNA-F	PFDA-F	PFUnA-F	PFDoA-F	PFBS-F	PFOS-F	PFOSA-F	ΣPFAS-F
AS						-99 ± 14						-99 ± 14
P	-203 ± 4					17 ± 0.5				-7 ± 0.8		-19 ± 0.5
AE1	-27 ± 12	28 ± 0.2		-146 ± 8		-131 ± 86		9 ± 6	41 ± 3	-2 ± 6		-11 ± 2
AE2	-20 ± 0.8	-11 ± 0.5	9 ± 0.1	-278 ± 0.1	48 ± 0.07	41 ± 0.4	9 ± 0.1	24 ± 0.2		2 ± 0.4	34 ± 0.3	10 ± 0.2
AN1						32 ± 0.3		43 ± 0.1				34 ± 0.2
AN2						-264 ±47*						-264 ± 47*
AN3		32 ± 0.2		11 ± 0.4	-95 ± 3	11 ± 0.2	25 ± 0.1	31 ± 0.4		2 ± 3	38 ± 0.5	10 ± 0.1
AN4						-29 ± 0.7			71 ± 0.07	42 ± 0.05		38 ± 0.2
AN5				14 ± 0.1	-34 ± 0.3	-62 ± 11	-4 ± 2	-33 ± 2		-17 ± 4		-13 ± 0.4

Colour key for shading of cells							
Average PFAS formation				Average PFAS removal			
High	Moderate	Low	Very Low	Very Low	Low	Moderate	High
< -75%	-75% to -50%	-50% to -25%	-25% to 0%	0% to 25%	25% to 50%	50% to 75%	>75%
		PFAS concentration below reporting limit in both raw sludge and biosolids.					

*not statistically significant (P>0.05) based on Paired Student's T-test.

possibly because of enhanced transformation to PFDA from unmeasured precursors under high pH conditions.

3.4.2. Pelletization

Pelletization is a physical process where the raw sludge is thermally dried and compacted into pellets. In the current study, system P dried solids at 85–90 °C for up to 20 min. While the C—F backbone is highly resistant to thermal break down or other transformations reactions, the non-fluorinated functional groups might undergo abiotic hydrolysis (ITRC, 2020). Hydrolysis reactions of organic compounds are influenced by temperature and higher temperature results in faster hydrolysis kinetics (Tebes-Stevens et al., 2017; Washington, 1995). Thus hydrolytic transformation of PFAS enhanced by high temperature may occur in the pelletization process.

In this study, substantial formation of PFPeA (−203 ± 4%), low formation of PFOS (−7 ± 0.8%) and low removal of PFDA (17 ± 0.5%) were observed in the pelletization process (P). The formation of PFPeA and PFOS may be the result of enhanced hydrolysis of precursors at elevated temperatures. Letcher et al. (2020) reported widespread occurrence of side-chain PFAS polymers (C_8F_{17} side-chain and C_4F_9 side-chain) in Canadian biosolids including system P. The increase in mass flows of PFPeA and PFOS in system P may have resulted from abiotic hydrolysis of the ester bonds in unmeasured side chain PFAS polymers that connect five- and eight-carbon long PFAS moieties to the main polymer. The results are consistent with those of Lazcano et al. (2019) where an increase in PFHxS concentration from 19 to 42 μg/kg was observed during heat treatment (45 min 480–650 °C) of biosolids and it was postulated the formation was from precursors with a C6 perfluorinated alkyl chain. Overall, the high temperature conditions in pelletization appeared to enhance hydrolysis of sidechain PFAS polymers and resulted in an increased mass flow of ΣPFAS-F through treatment.

3.4.3. Aerobic digestion

In aerobic digestion, microbes stabilize sludges through biological mineralization in the presence of oxygen. It was anticipated that the PFAS carbon backbone with highly strong C—F bond would be recalcitrant while labile functional groups may undergo biotransformation by the microbial consortia present in these processes. In the current study the fate of individual PFAS through two full scale aerobic digesters was assessed.

When individual PFAS compounds were examined, the behavior of certain PFAS was found to be similar in both treatment systems. High levels of formation of PFOA were observed in AE1 (−146 ± 8%) and AE2 (−278 ± 0.1%) and a modest increase in mass flows of PFPeA-F (average = 20 to 30%) was observed in both AE1 and AE2. The formation of PFCAs from a wide range of precursors by various microbial inoculations is well documented in the literature. PFOA was the primary transformation product of 8:2 dipolyfluoroalkyl phosphate diester (8:2 diPAP) in soil microcosms (Liu and Liu, 2016). Hamid et al. (2020) observed slow biotransformation of 8:2 FTOH into PFCAs by microcosms in landfill leachate. Formation of PFOA and other PFCAs from fluorotelomer alcohols (Dinglasan et al., 2004; Wang et al., 2005), fluorotelomer ethoxylates (Frömel and Knepper, 2010), and polyfluoroalkyl phosphates (Lee et al., 2010) have been observed in aerobic activated sludge inoculations. Thus, the presence of these PFCAs in the biosolids from aerobic digestion likely results from their presence in feed sludges and their formation from precursors including fluorophosphates, fluorotelomer alcohols and ethoxylates.

Some PFAS compounds, notably PFDA, demonstrated different responses in the two aerobic digestion systems. A high formation of PFDA was observed in AE1 (Average = −131%) while a modest removal was observed in AE2 (Average = 41%). Similarly, for ΣPFAS-F, low levels of formation (−11 ± 2%) in AE1 and low removal (average = 10 ± 0.2%) in AE2 were observed. These differences in the behavior of the target PFAS may be due to differing operating conditions in the two systems. AE1 was operating at a relatively longer SRT (35 days) that supports the growth of slow growing microorganisms that may be responsible for the transformation of the target PFAS from the precursors. In AE2, the relatively better removal may be because of the lack of precursor transformations at a shorter SRT of 15 days. It is also possible that the upstream extended aeration treatment process in AE2, with its prolonged aeration, transformed the relevant precursors during secondary treatment preventing contaminant formation in the subsequent aerobic digestion process. Overall, the results from the two aerobic digestion systems indicate that the SRT of both the upstream process and the digester may influence the fate of PFAS and further biodegradation studies with relevant precursors are needed to understand the role of operational conditions in the transformation of PFAS during aerobic digestion.

3.4.4. Anaerobic digestion

In anaerobic digestion, the sludge is mineralized in the absence of oxygen to stabilize the solids and generate biogas. Anaerobic environments are conducive to the growth of organohalide respiring bacteria and reductive dehalogenation of chlorinated (Heidler and Halden, 2009; Smith et al., 2015) and brominated (Tokarz et al., 2008; Zhao et al., 2018) compounds such as triclosan, triclocarban, and polybrominated diphenyl ethers (PBDEs). Reductive dehalogenation reactions are thermodynamically feasible (Parsons et al., 2008) and reductive defluorination transformations are theoretically possible during anaerobic digestion. However, such metabolic pathways have not been reported in the literature. Nevertheless, depending on available electron acceptors, anaerobic environments may maintain iron

reducing, sulfur reducing, and denitrifying conditions, that could result in the transformation of labile functional groups in either the target or unmeasured PFAS compounds.

Anaerobic digestion systems with low raw sludge flows (< 5000 kg TS/day), AN1 and AN2, were examined separately. In addition to having similar solids handling capacity, these two systems were also similar in terms of their use of a two-step sludge digestion process with primary and secondary digesters. On the contrary, they were operated at somewhat different SRTs with AN1 at an average of 43 days and AN2 at 36 days. A review of Table 3 reveals that there was a low removal of the ΣPFAS-F composite parameter in AN1 (34 ± 0.2%) and this was attributed to the removals of long chain PFAS such as PFDA (32 ± 0.3%) and PFDoA (43 ± 0.1%). While defluorination reactions could be responsible for these removals, there was no concurrent increase in the levels of short chain PFAS. Hence, the removal mechanism remains unclear. In AN2, a high average formation of ΣPFAS-F (−264 ± 47%) was observed and this was due to an increase in PFDA. However, there was high variability in the data and the response was found to be not statistically significant ($P > 0.05$).

Among the three remaining anaerobic digestion systems with high raw sludge flows (AN3, AN4, and AN5 > 20,000 kg TS/day), AN3 and AN5 were located in the same city, had similar design, and upstream wastewater treatment processes that incorporated biological nutrient removal. They both were operated at similar SRTs (AN3 = 34 days and AN5 = 30 days). Both systems demonstrated low average removals of PFOA (< 15%) and low (AN5 = −34 ± 0.3%) to high (AN3 = −95 ± 3%) average formation of PFNA (Table 3). In contrast, in these systems long chained and sulfonated PFAS such as PFDA, PFUnA, PFDoA, and PFOS responded differently in the two digesters. While AN5, with relatively shorter SRT reported low to moderate levels of formation (average = −4 to −62%) of these four compounds, AN3 reported low removals (2 to 31%) (Table 3). AN4, the system with the shortest SRT in the study (18 days) showed the highest average removal of ΣPFAS-F observed in this study (38 ± 0.2%). The removal of PFAS in AN4 was due to reductions in the mass flows of sulfonated PFAS such as PFBS (71 ± 0.07%) and PFOS (42 ± 0.05). On the whole, a wide range of PFAS responses were apparent in the five anaerobic digestion systems ranging from moderate removal to high formation at the individual compound and the overall loading levels.

In order to address the variability in the PFAS response, the change in ΣPFAS-F loading through anaerobic digestion was investigated as a function of the operational SRT. The average SRT of the systems increased with AN4 (18 days) < AN5 (31 days) < AN2 (36 days) ~ AN3 (38 days) < AN1 (43 days) and there was no relation with the average ΣPFAS-F removal [AN2 (−264%) < AN5 (−13%) < AN3 (10%) < AN1 (34%) ~ AN4 (38%)]. On an individual compound level, PFDA was considered as it was the only compound that was detected in all five anaerobic digestion systems and, similarly, no consistent trend was seen [AN2 (−264%) < AN5 (−62%) < AN4 (−29%) < AN3 (11%) < AN1 (32%)]. Therefore, the observed differences between treatment systems may not be entirely due to the variation in SRT and other unknown factors pertaining to the precursor compounds or the microbial community may contribute to these variations in the transformation of PFAS during anaerobic digestion.

The interpretation of the results was challenging as there are few literature reports of transformations of PFAS compounds and precursors in anaerobic environments. Anaerobic reduction of aromatic fluoride compounds such as fluorobenzoates has been observed in sulfur reducing (Drzyzga et al., 1994) and denitrifying (Vargas et al., 2000) conditions. However, it is not known if these biochemical pathways are possible for PFAS during anaerobic digestion. To our knowledge, this is the first study to develop mass balances on PFAS through full scale anaerobic digestion systems with the goal of achieving insight into their fate in these systems. It is clear that additional studies are required to explore the transformation pathways and evaluate their kinetics in anaerobic processes.

3.4.5. Comparison of responses between treatment types

The responses of the individual PFAS compounds and the ΣPFAS-F through the four types of sludge treatment processes were compared to assess how the various unit operations could impact PFAS management in biosolids (Table 3). Pelletization and alkaline stabilization demonstrated an overall increase in the mass flow of ΣPFAS-F with very high formation of PFDA (average = −99%) during alkaline stabilization and PFPeA (average = −203%) during pelletization. In contrast, one aerobic digestion facility (AE2) and three of the five anaerobic digestion systems (AN1, AN3 and AN4) demonstrated low ΣPFAS-F removals of 10%, 34%, 10% and 38%, respectively. Thus, based on results from this study, biological sludge treatment processes could result in relatively better performance and achieve modest removals of the measured PFAS when compared to physico-chemical processes. In other words, the biological processes were less effective in converting the PFAS precursors when compared to the enhanced abiotic transformations that may be occurring in alkaline stabilization and pelletization.

When individual compounds in aerobic and anaerobic digestion were compared both consistent and inconsistent responses were observed. Removal of PFOSA was seen in both aerobic (AE2) and anaerobic (AN3) digestion at similar levels (approximately 35%). By contrast, PFOA was modestly removed during anaerobic digestion (AN3 and AN5 at <15%) but substantially formed in the two aerobic digestion facilities (>−145%). Conversely, almost half of the PFNA mass flow was removed in one of the aerobic digestion facilities (AE2), while it was substantively formed in two anaerobic digestion facilities (−95% and −34% in AN3 and AN5, respectively). The most frequently detected compound in this study (PFDA), demonstrated responses that ranged from very low removal to high formation (Table 3) in the various biological treatment processes with no definitive relation to the operational SRT. Additional information on precursors and biotransformation pathways is needed to describe the observed variations in the responses of the target PFAS in biological treatment systems.

Overall, this study revealed evidence of changes in the mass flows of selected PFAS compounds in all the treatment categories. The discussion of the results has been predicated upon reports that the C—F bond is very strong and the observed changes in mass flows were due to the transformations in the non-fluoride groups. However, future studies should investigate the total organic fluorine and evaluate if there are any defluorination reactions occurring in these systems. Apart from transformation reactions, sorption-desorption mechanisms during the process could also impact the fate of PFAS. Measuring the levels of PFAS in recycle streams could provide additional insights into the mass balance. Finally, it has been established that a variety of PFAS compounds occur in biosolids due to insufficient removal and transformations during sludge treatment.

4. Conclusion

This study examined the behavior of thirteen PFAS compounds by assembling contaminant mass balance in nine full-scale sludge treatment systems that collectively employed four different types of processing technologies. To the best of our knowledge, this is the first study to quantitatively assess the removal and formation of PFAS exclusively in full scale sludge treatment systems. Some of the major findings were:

- PFDA was the most frequently detected PFAS compound with detection in over 85% of the samples and with concentrations that ranged from BRL to 53 ng/g dw in the biosolids. PFOA and PFOS that have been regularly reported in the literature, were detected in only 25% and 46% of the biosolids samples, respectively.
- The composition of the ΣPFAS-F loading was highly dependent on the upstream wastewater treatment process and the source of the raw sludge. ΣPFAS-F loading in the sludge treatment systems with predominantly primary sludge feed were entirely composed of the long

chain PFDA, while systems with blended sludge reported a mix of short and long chain PFAS in the feed sludge.

- Contaminant mass balances that were constructed from the measured data and integrated with Monte-Carlo simulations revealed statistically significant formation and removal of individual PFAS-F and ΣPFAS-F in all four types of sludge treatment. The change in the average ΣPFAS-F mass flows ranged from −264% to 38% across the nine treatment systems.
- Physical and chemical sludge treatment processes demonstrated an increase in mass flows of ΣPFAS-F, indicating abiotic hydrolysis of PFAS precursors is enhanced by high pH or high temperature. In particular, very high formations of PFDA (average = −99%) and PFPeA (average = −203%) were observed during alkaline stabilization and pelletization, respectively.
- Several systems with biological treatment, namely aerobic (AE2) and anaerobic digestion (AN1, AN3 and AN5) had low removals (10–38%) of ΣPFAS-F, respectively. Thus, depending on the design and operations, biological sludge treatment may produce relatively better sludge quality in terms of these PFAS.
- There were significant variations in the formation and removal trends of PFAS within and among treatment categories. Notably, the average change in mass of PFDA ranged from low removal (41%) to very high formation (−264%) in all four treatment categories. The SRT of operation did not explain the variations in the behavior of PFAS in anaerobic digestion systems studied. Treated biosolids contain valuable nutrients which can be beneficially used for agriculture, land reclamation, and other purposes (CCME, 2012). A better understanding of the occurrence and fate of PFAS and other trace contaminants is needed to ensure that biosolids use is not curtailed by these substances. Future studies should focus on identifying relevant PFAS precursors and estimating the kinetics of transformation in different categories of sludge treatment to address these variabilities.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors would like to thank the participating municipalities and WRRF personnel for their assistance with sampling and providing all the treatment system process information that was very critical in analyzing the data in this study. We thank Amber Albert, Eraj Gillani, Velda Wong, and Steve Teslic for all sample collection. We would also like to acknowledge the inputs of Bharat Chandramouli and Richard Grace from SGS AXYS Analytical Services regarding method validation using reference biosolids material. This study was funded by the Chemicals Management Plan, Environment and Climate Change Canada.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.142431.

References

Ahrens, L., 2011. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. J. Environ. Monit. 13, 20–31. https://doi.org/10.1039/C0EM00373E.

Armstrong, D.L., Lozano, N., Rice, C.P., Ramirez, M., Torrents, A., 2016. Temporal trends of perfluoroalkyl substances in limed biosolids from a large municipal water resource recovery facility. J. Environ. Manag. 165, 88–95. https://doi.org/10.1016/j.jenvman.2015.09.023.

Arvaniti, O.S., Ventouri, E.I., Stasinakis, A.S., Thomaidis, N.S., 2012. Occurrence of different classes of perfluorinated compounds in Greek wastewater treatment plants and determination of their solid–water distribution coefficients. Journal of Hazardous Materials, Occurrence and fate of emerging contaminants in municipal wastewater treatment systems 239–240, 24–31. https://doi.org/10.1016/j.jhazmat.2012.02.015.

Arvaniti, O.S., Andersen, H.R., Thomaidis, N.S., Stasinakis, A.S., 2014. Sorption of Perfluorinated compounds onto different types of sewage sludge and assessment of its importance during wastewater treatment. Chemosphere 111, 405–411. https://doi.org/10.1016/j.chemosphere.2014.03.087.

Blaine, A.C., Rich, C.D., Hundal, L.S., Lau, C., Mills, M.A., Harris, K.M., Higgins, C.P., 2013. Uptake of perfluoroalkyl acids into edible crops via land applied biosolids: field and greenhouse studies. Environ. Sci. Technol. 47, 14062–14069. https://doi.org/10.1021/es403094q.

Blaine, A.C., Rich, C.D., Sedlacko, E.M., Hundal, L.S., Kumar, K., Lau, C., Mills, M.A., Harris, K.M., Higgins, C.P., 2014. Perfluoroalkyl acid distribution in various plant compartments of edible crops grown in biosolids-amended soils. Environ. Sci. Technol. 48, 7858–7865. https://doi.org/10.1021/es500016s.

Bossi, R., Strand, J., Sortkjær, O., Larsen, M.M., 2008. Perfluoroalkyl compounds in Danish wastewater treatment plants and aquatic environments. Environ. Int. 34, 443–450. https://doi.org/10.1016/j.envint.2007.10.002.

Campo, J., Masiá, A., Picó, Y., Farré, M., Barceló, D., 2014. Distribution and fate of perfluoroalkyl substances in Mediterranean Spanish sewage treatment plants. Sci. Total Environ. 472, 912–922. https://doi.org/10.1016/j.scitotenv.2013.11.056.

Canadian Council of Ministers of the Environment, 2012. Canada-wide approach for the management of wastewater biosolids. PN 1477. https://www.ccme.ca/files/Resources/waste/biosolids/pn_1477_biosolids_cw_approach_e.pdf.

Chen, S., Zhou, Y., Meng, J., Wang, T., 2018. Seasonal and annual variations in removal efficiency of perfluoroalkyl substances by different wastewater treatment processes. Environ. Pollut. 242, 2059–2067. https://doi.org/10.1016/j.envpol.2018.06.078.

Coggan, T.L., Moodie, D., Kolobaric, A., Szabo, D., Shimeta, J., Crosbie, N.D., Lee, E., Fernandes, M., Clarke, B.O., 2019. An investigation into per- and polyfluoroalkyl substances (PFAS) in nineteen Australian wastewater treatment plants (WWTPs). Heliyon 5, e02316. https://doi.org/10.1016/j.heliyon.2019.e02316.

Dinglasan, M.J.A., Ye, Y., Edwards, E.A., Mabury, S.A., 2004. Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. Environ. Sci. Technol. 38, 2857–2864. https://doi.org/10.1021/es0350177.

Drzyzga, O., Jannsen, S., Blotevogel, K.-H., 1994. Mineralization of monofluorobenzoate by a diculture under sulfate-reducing conditions. FEMS Microbiol. Lett. 116, 215–219. https://doi.org/10.1111/j.1574-6968.1994.tb06703.x.

Ellis, D.A., Martin, J.W., De Silva, A.O., Mabury, S.A., Hurley, M.D., Sulbaek Andersen, M.P., Wallington, T.J., 2004. Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. Environ. Sci. Technol. 38, 3316–3321. https://doi.org/10.1021/es049860w.

Frömel, T., Knepper, T.P., 2010. Fluorotelomer ethoxylates: sources of highly fluorinated environmental contaminants part I: biotransformation. Chemosphere 80, 1387–1392. https://doi.org/10.1016/j.chemosphere.2010.06.002.

Gottschall, N., Topp, E., Edwards, M., Russell, P., Payne, M., Kleywegt, S., Curnoe, W., Lapen, D.R., 2010. Polybrominated diphenyl ethers, perfluorinated alkylated substances, and metals in tile drainage and groundwater following applications of municipal biosolids to agricultural fields. Sci. Total Environ. 408, 873–883. https://doi.org/10.1016/j.scitotenv.2009.10.063.

Gottschall, N., Topp, E., Edwards, M., Payne, M., Kleywegt, S., Lapen, D.R., 2017. Brominated flame retardants and perfluoroalkyl acids in groundwater, tile drainage, soil, and crop grain following a high application of municipal biosolids to a field. Sci. Total Environ. 574, 1345–1359. https://doi.org/10.1016/j.scitotenv.2016.08.044.

Government of Canada (2016). Perfluorooctane Sulfonate and its Salts and Certain Other Compounds Regulations. SOR/2008-178, as repealed by SOR/2016-252, s.27. https://laws-lois.justice.gc.ca/PDF/SOR-2008-178.pdf

Government of Canada (2017). Prohibition of Certain Toxic Substances Regulation, 2012. SOR/2012-285. https://laws-lois.justice.gc.ca/PDF/SOR-2012-285.pdf

Guerra, P., Kim, M., Kinsman, L., Ng, T., Alaee, M., Smyth, S.A., 2014. Parameters affecting the formation of perfluoroalkyl acids during wastewater treatment. J. Hazard. Mater. 272, 148–154. https://doi.org/10.1016/j.jhazmat.2014.03.016.

Hamid, H., Li, L.Y., Grace, J.R., 2020. Aerobic biotransformation of fluorotelomer compounds in landfill leachate-sediment. Sci. Total Environ. 713, 136547. https://doi.org/10.1016/j.scitotenv.2020.136547.

Heidler, J., Halden, R.U., 2009. Fate of organohalogens in US wastewater treatment plants and estimated chemical releases to soils nationwide from biosolids recycling. J. Environ. Monit. 11, 2207–2215. https://doi.org/10.1039/b914324f.

Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. Environ. Sci. Technol. 40, 7251–7256. https://doi.org/10.1021/es061000n.

Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. Environ. Sci. Technol. 39, 3946–3956. https://doi.org/10.1021/es048245p.

Interstate Technology and Regulatory Council (ITRC), 2020. PFAS Technical and Regulatory Guidance Document [WWW Document]. URL. https://pfas-1.itrcweb.org/. (Accessed 7 June 2020).

Kannan, K., Corsolini, S., Falandysz, J., Fillmann, G., Kumar, K.S., Loganathan, B.G., Mohd, M.A., Olivero, J., Wouwe, N.V., Yang, J.H., Aldous, K.M., 2004. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. Environ. Sci. Technol. 38, 4489–4495. https://doi.org/10.1021/es0493446.

Lazcano, R.K., Perrede, C., Mashtare, M.L., Lee, L.S., 2019. Per- and polyfluoroalkyl substances in commercially available biosolid-based products: the effect of treatment processes. Water Environ. Res. 91, 1669–1677. https://doi.org/10.1002/wer.1174.

Lee, H., D'eon, J., Mabury, S.A., 2010. Biodegradation of polyfluoroalkyl phosphates as a source of perfluorinated acids to the environment. Environ. Sci. Technol. 44, 3305–3310. https://doi.org/10.1021/es9028183.

Letcher, R.J., Chu, S., Smyth, S.-A., 2020. Side-chain fluorinated polymer surfactants in biosolids from wastewater treatment plants. J. Hazard. Mater. 388, 122044. https://doi.org/10.1016/j.jhazmat.2020.122044.

Lindstrom, A.B., Strynar, M.J., Libelo, E.L., 2011. Polyfluorinated compounds: past, present, and future. Environ. Sci. Technol. 45, 7954–7961. https://doi.org/10.1021/es2011622.

Liu, C., Liu, J., 2016. Aerobic biotransformation of polyfluoroalkyl phosphate esters (PAPs) in soil. Environ. Pollut. 212, 230–237. https://doi.org/10.1016/j.envpol.2016.01.069.

Navarro, I., Sanz, P., Martínez, M.Á., 2011. Analysis of perfluorinated alkyl substances in Spanish sewage sludge by liquid chromatography–tandem mass spectrometry. Anal. Bioanal. Chem. 400, 1277–1286. https://doi.org/10.1007/s00216-011-4655-6.

Nguyen, H.T., Kaserzon, S.L., Thai, P.K., Vijayasarathy, S., Bräunig, J., Crosbie, N.D., Bignert, A., Mueller, J.F., 2019. Temporal trends of per- and polyfluoroalkyl substances (PFAS) in the influent of two of the largest wastewater treatment plants in Australia. Emerging Contaminants 5, 211–218. https://doi.org/10.1016/j.emcon.2019.05.006.

Ochoa-Herrera, V., Sierra-Alvarez, R., 2008. Removal of perfluorinated surfactants by sorption onto granular activated carbon, zeolite and sludge. Chemosphere 72, 1588–1593. https://doi.org/10.1016/j.chemosphere.2008.04.029.

Parsons, J.R., Sáez, M., Dolfing, J., de Voogt, P., 2008. Biodegradation of perfluorinated compounds. Rev. Environ. Contam. Toxicol. 196, 53–71. https://doi.org/10.1007/978-0-387-78444-1_2.

Renner, R., Eichenseher, T., Thrall, L., 2006. Leftovers may explain perfluorinated compound puzzle | the cloudy side of sunscreens | news briefs: boundaries of bacterial biodiversity, quick, cheap method for algae removal, PBDEs in U.S. cars, database helps green cleaning products | another danger for developing frogs. Environ. Sci. Technol. 40, 1376–1380. https://doi.org/10.1021/es0626436.

Rich, C.D., Blaine, A.C., Hundal, L., Higgins, C.P., 2015. Bioaccumulation of perfluoroalkyl acids by earthworms (Eisenia fetida) exposed to contaminated soils. Environ. Sci. Technol. 49, 881–888. https://doi.org/10.1021/es504152d.

Sáez, M., de Voogt, P., Parsons, J.R., 2008. Persistence of perfluoroalkylated substances in closed bottle tests with municipal sewage sludge. Environ. Sci. Pollut. Res. 15, 472–477. https://doi.org/10.1007/s11356-008-0020-5.

Schultz, M.M., Higgins, C.P., Huset, C.A., Luthy, R.G., Barofsky, D.F., Field, J.A., 2006. Fluorochemical mass flows in a municipal wastewater treatment facility. Environ. Sci. Technol. 40, 7350–7357. https://doi.org/10.1021/es061025m.

Sepulvado, J.G., Blaine, A.C., Hundal, L.S., Higgins, C.P., 2011. Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. Environ. Sci. Technol. 45, 8106–8112. https://doi.org/10.1021/es103903d.

Sinclair, E., Kannan, K., 2006. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. Environ. Sci. Technol. 40, 1408–1414. https://doi.org/10.1021/es051798v.

Sindiku, O., Orata, F., Weber, R., Osibanjo, O., 2013. Per- and polyfluoroalkyl substances in selected sewage sludge in Nigeria. Chemosphere 92, 329–335. https://doi.org/10.1016/j.chemosphere.2013.04.010.

Smith, B.J., Boothe, M.A., Fiddler, B.A., Lozano, T.M., Rahi, R.K., Krzmarzick, M.J., 2015. Enumeration of organohalide respirers in municipal wastewater anaerobic digesters. Microbiology Insights 8, 9–14. https://doi.org/10.4137/MBI.S31445.

Tebes-Stevens, C., Patel, J.M., Jones, W.J., Weber, E.J., 2017. Prediction of hydrolysis products of organic chemicals under environmental pH conditions. Environ. Sci. Technol. 51, 5008–5016. https://doi.org/10.1021/acs.est.6b05412.

Tokarz, J.A., Ahn, M.-Y., Leng, J., Filley, T.R., Nies, L., 2008. Reductive debromination of polybrominated diphenyl ethers in anaerobic sediment and a biomimetic system. Environ. Sci. Technol. 42, 1157–1164. https://doi.org/10.1021/es071989t.

Vargas, C., Song, B., Camps, M., Häggblom, M.M., 2000. Anaerobic degradation of fluorinated aromatic compounds. Appl. Microbiol. Biotechnol. 53, 342–347. https://doi.org/10.1007/s002530050032.

Venkatesan, A.K., Halden, R.U., 2013. National inventory of perfluoroalkyl substances in archived U.S. biosolids from the 2001 EPA national sewage sludge survey. J. Hazard. Mater. 252-253, 413–418. https://doi.org/10.1016/j.jhazmat.2013.03.016.

Wang, N., Szostek, B., Folsom, P.W., Sulecki, L.M., Capka, V., Buck, R.C., Berti, W.R., Gannon, J.T., 2005. Aerobic biotransformation of 14 C-labeled 8-2 telomer B alcohol by activated sludge from a domestic sewage treatment plant. Environ. Sci. Technol. 39, 531–538. https://doi.org/10.1021/es049466y.

Washington, J.W., 1995. Hydrolysis rates of dissolved volatile organic compounds: principles, temperature effects and literature review. Groundwater 33, 415–424. https://doi.org/10.1111/j.1745-6584.1995.tb00298.x.

Washington, J.W., Jenkins, T.M., 2015. Abiotic hydrolysis of fluorotelomer-based polymers as a source of perfluorocarboxylates at the global scale. Environ. Sci. Technol. 49, 14129–14135. https://doi.org/10.1021/acs.est.5b03686.

Washington, J.W., Jenkins, T.M., Rankin, K., Naile, J.E., 2015. Decades-scale degradation of commercial, side-chain, fluorotelomer-based polymers in soils and water. Environ. Sci. Technol. 49, 915–923. https://doi.org/10.1021/es504347u.

Zhang, C., Yan, H., Li, F., Zhou, Q., 2015. Occurrence and fate of perfluorinated acids in two wastewater treatment plants in Shanghai, China. Environ. Sci. Pollut. Res. 22, 1804–1811. https://doi.org/10.1007/s11356-013-2044-8.

Zhao, S., Rogers, M.J., Ding, C., He, J., 2018. Reductive debromination of polybrominated diphenyl ethers - microbes, processes and dehalogenases. Frontiers in Microbiology 9. doi:https://doi.org/10.3389/fmicb.2018.01292.

Zhou, Q., Deng, S., Zhang, Q., Fan, Q., Huang, J., Yu, G., 2010. Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated sludge. Chemosphere 81, 453–458. https://doi.org/10.1016/j.chemosphere.2010.08.009.