

## Per- and polyfluoroalkyl substances fate and transport at a wastewater treatment plant with a collocated sewage sludge incinerator

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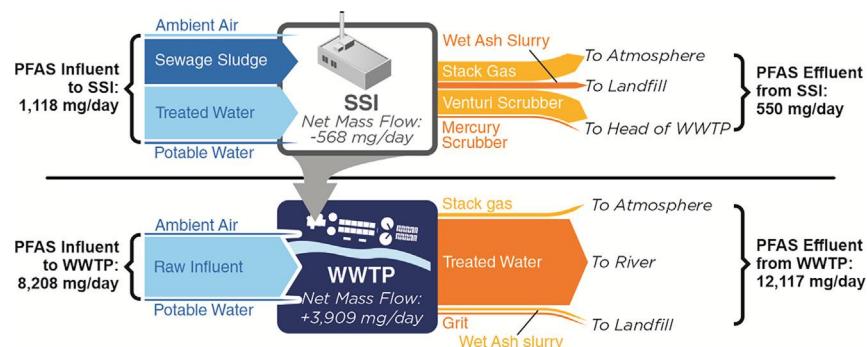
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### HIGHLIGHTS

- The fate and transport of PFAS at WWTPs operating SSIs is an important data gap.
- Study measured PFAS and IF at all influents/effluents of a WWTP operating an SSI.
- Statistical analyses characterized concentrations and mass flows at the WWTP/SSI.
- Most PFAS mass discharged in aqueous effluent; small contributions to air/landfill.
- The SSI may inadequately destroy PFAS, as the observed thermal removal was 51 %.

### GRAPHICAL ABSTRACT



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### ABSTRACT

This study aims to understand the fate and transport of per- and polyfluoroalkyl substances (PFAS) and inorganic fluoride (IF) at an undisclosed municipal wastewater treatment plant (WWTP) operating a sewage sludge incinerator (SSI). A robust statistical analysis characterized concentrations and mass flows at all WWTP and SSI primary influents/effluents, including thermal-treatment derived airborne emissions. WWTP-level net mass flows (NMFs) of total PFAS were not statistically different from zero. SSI-level NMFs indicate that PFAS, and specifically perfluoroalkyl acids (PFAAs), are being broken down. The NMF of perfluoroalkyl sulfonic acids (PFSAs;  $-274 \pm 34$  mg/day) was statistically significant. The observed breakdown primarily occurred in the sewage sludge. However, the total PFAS destruction and removal efficiency of 51 % indicates the SSI may inadequately remove PFAS. The statistically significant IF source (NMF =  $16 \pm 4.2$  kg/day) compared to the sink of PFAS as fluoride (NMF =  $-0.00036$  kg/day) suggests that other fluorine-containing substances are breaking down in the SSI. WWTP PFAS mass discharges were primarily to the aquatic environment (>99 %), with <0.5 % emitted to the atmosphere/landfill. Emission rates for formerly phased-out PFOS and PFOA were compared to previously reported levels. Given the environmental persistence of these compounds, the observed decreases in PFOS and PFOA discharge rates from prior reports implies regional/local differences in emissions or possibly their accumulation elsewhere. PFAS were observed in stack gas emissions, but modestly contributed to NMFs and showed negligible contribution to ambient air concentrations observed downwind.

**Abbreviations:** ASE, accelerated solvent extraction; AWOS, Automatic Weather Observing Station; DoD/DOE QSM 5.3, Department of Defense/Department of Energy Quality Systems Manual Version 5.3; DRE, destruction and removal efficiency; GC/MS, gas chromatography/mass spectrometry; HF, hydrogen fluoride; IC, ion chromatography; IF, inorganic fluoride; ISC-PRIME, Industrial Source Complex – Plume Rise Model Enhancements; ISE, ion selective electrode; LC/MS/MS, liquid chromatography tandem mass spectrometry; MDL, measurement detection limit; NC, negative control; NMF, net mass flow; PCI, positive chemical ionization mode; PIC, products of incomplete combustion; PFAA, perfluoroalkyl acid; PFAS, per- and polyfluoroalkyl substances; PFCA, perfluoroalkyl carboxylic acid; PFSA, perfluoroalkyl sulfonic acids; SPE, solid phase extraction; SSI, sewage sludge incinerator; TF, total fluorine; WWTP, wastewater treatment plant.

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## 1. Introduction

Nearly 15,000 wastewater treatment plants (WWTPs), serving 238.2 million people, and processing 25 billion gallons/day of liquid raw influent (i.e., municipal wastewater, landfill leachate, and industrial waste (Stoiber et al., 2020)) were in operation in the United States in 2012 (EPA, 2016a). Given per- and polyfluoroalkyl substances (PFAS) have been used in diverse industrial and consumer applications since 1940, with over 600 PFAS in current commercial use in the United States (EPA, 2020), WWTP raw influents often contain elevated levels of PFAS. Furthermore, previous studies have found higher concentrations of PFAS in treated wastewater effluent as compared to the raw influent (Eriksson et al., 2017; Gallen et al., 2018; Kim Lazcano et al., 2019; Loganathan et al., 2007; Schultz et al., 2006; Venkatesan and Halden, 2013; Wang et al., 2018), likely due to the wastewater treatment's biological and physical processes converting precursor compounds to terminal PFAS (Stoiber et al., 2020; Schultz et al., 2006; Arvaniti and Stasinakis, 2015). It has been reported that WWTPs discharge PFAS into aquatic environments through the direct release of treated water, the atmosphere via aeration tank treatment and other processes (Stoiber et al., 2020; Vierke et al., 2011), and soil and groundwater through the leaching of landfilled biosolids. One byproduct of the wastewater treatment process, sewage sludge, can be either landfilled with other solid wastes, spread on agricultural fields as a fertilizer, or incinerated.

While various factors influence PFAS sorption potential, generally longer chain PFAS more readily adsorb to solids, and hence show greater accumulation in sewage sludge, while shorter chain PFAS partition to liquids, providing greater accumulation in treated water effluent (Coggan et al., 2019). Further, higher partitioning of perfluoroalkyl sulfonic acids (PFSAs) as compared to perfluoroalkyl carboxylic acids (PFCAs) to sewage sludge has previously been observed (Coggan et al., 2019; Higgins et al., 2005). Millions of tons of sewage sludge per year are applied on agricultural fields in the United States (NEBRA, 2007), and studies (Blaine et al., 2013; Ghisi et al., 2019; Sepulvado et al., 2011; Wang et al., 2020a) have found that PFAS can bioaccumulate in plants during this process. With the potential of PFAS-laden sewage sludge contaminating crops, the State of Maine has temporarily banned the practice (Burns, 2019) until further testing can be conducted.

Sewage sludge incinerators (SSIs) are currently in operation at approximately 200 WWTPs in the United States, in which over one million tons of WWTP processed sludge are incinerated annually (NEBRA, 2007). Previously reported studies have shown that waste incineration of fluorotelomer based polymers mineralized PFAS to inorganic fluoride at high temperatures ( $>870^{\circ}\text{C}$ ) (Aleksandrov et al., 2019; Taylor et al., 2014). However, more research is required regarding the incomplete combustion and ash byproduct from sewage sludge incineration to fully understand the fate and transport of PFAS during thermal treatment (Stoiber et al., 2020; EPA, 2019). Laboratory studies have found that the required incineration temperature to degrade a given PFAS compound increases with increasing perfluoroalkyl chain lengths (Rayne and Forest, 2009), with 99 % of PFAS degrading at  $600^{\circ}\text{C}$  (Taylor and Yamada, 2003) and higher destruction requiring temperatures exceeding  $1000^{\circ}\text{C}$  and residence times  $>2$  seconds (Taylor et al., 2014). Few field studies have investigated PFAS incineration at full-scale operating facilities (Stoiber et al., 2020). One study found that concentrations declined two to 10-fold from pre-incineration sewage sludge to post-incineration wet ash slurry (Loganathan et al., 2007). Another study found that leachates from wet ash slurry landfills had significantly lower PFAS levels than from solid waste landfills, and the lower ash leachate concentrations correlated to higher incineration temperatures (Solo-Gabriele et al., 2020). Elevated PFOA concentrations have also been measured onsite as compared to upwind of municipal solid waste incinerators (Wang et al., 2020b). However, to fully understand the fate and transport of PFAS during thermal treatment, specifically at SSIs, full-scale field studies that quantify mass flows of all applicable effluents, including stack gas emissions and wet ash slurry, are needed. Further, while mineralization of PFAS is dependent on incineration operating conditions, such as temperature and residence time (Aleksandrov et al., 2019; Taylor et al., 2014), it is

not well understood whether current incineration processes generate products of incomplete combustion (PICs) or completely mineralize PFAS compounds (Tsang et al., 1998). Further research in analytical methods capable of capturing and characterizing PICs potentially formed during thermal destruction processes is needed. Given the current state of the science, it is important to measure fluoride coincidentally with PFAS to better understand if incineration is generating PICs or fully mineralizing PFAS. To the best of our knowledge, there are no published studies regarding the fate and transport of PFAS and fluoride through all primary influents and effluents of an SSI (Winchell et al., 2020), which represents an important data gap (Stoiber et al., 2020).

To address this gap, this study measured up to 30 different PFAS and inorganic fluoride (IF) in the influents and effluents of a full-scale WWTP operating a fluidized bed SSI. We aim to improve the understanding of the fate and transport of these compounds at both the level of the WWTP, which is inclusive of the SSI, and through the SSI alone. Herein, we (1) report concentrations of PFAS and IF at all influents and effluents streams, (2) estimate net mass flows (NMFs) from the WWTP and SSI, (3) investigate the efficacy with which PFAS are destroyed in the SSI under typical operating conditions, (4) estimate PFAS emission rates in all effluent streams, and (5) estimate stack gas contributions to downwind ambient air PFAS concentrations to understand thermal treatment's potential contribution to ambient air.

## 2. Materials and methods

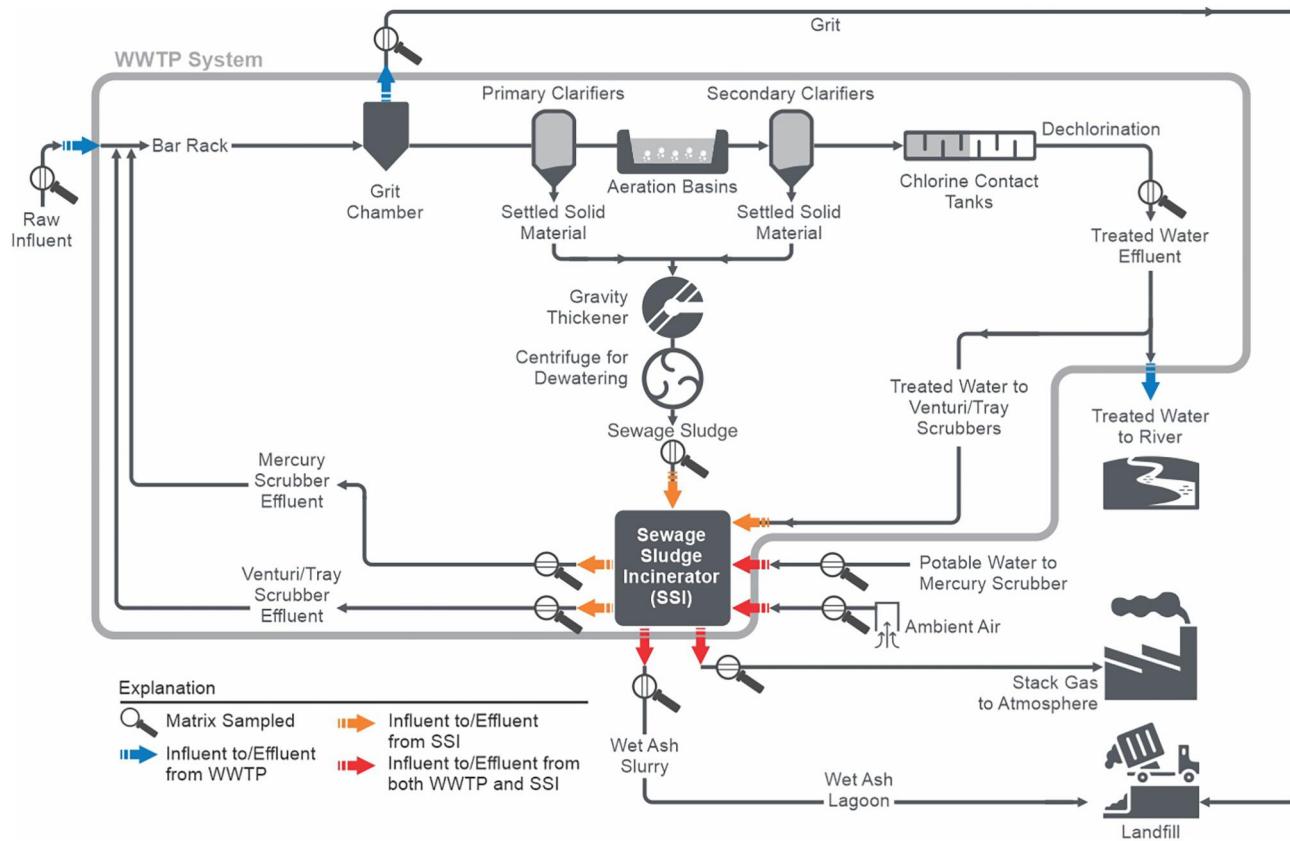
### 2.1. Study design and sampling approach

The two-day field study occurred on August 28–29, 2019, at an undisclosed U.S. WWTP (Fig. S1) operating a fluidized bed SSI. The SSI actively processed and incinerated approximately 160,000 kg of sewage sludge under its typical operating conditions ( $830^{\circ}\text{C}$  internal temperature and  $\sim 8$  s residence time) during the entirety of the study. Municipal waste incineration is typically operated at temperatures  $>810^{\circ}\text{C}$  and residence time of  $>2$  s. A schematic of the WWTP's treatment process along with the ten influent and effluent matrices which were assayed are shown in Fig. 1. The sampling schedules, flow rates, and other details for each matrix are provided in Table S1.

Discrete stack gas samples were collected in the morning and afternoon on both days of the study. The SSI airborne effluent was assayed for total fluorine (TF; Modified EPA Method 18 (EPA, U. S, n.d.)), hydrogen fluoride (HF; EPA Method 26A (EPA, U. S, n.d.)), and 30 PFAS compounds (Modified EPA Method 0010 (EPA, 1986), adapted for PFAS analysis). Table S2 lists every compound measured from the stack and each of the other nine matrices. One field blank train was also prepared and collected for each of the sampling methods described above. A detailed description of the stack gas sampling approach is provided in the supplemental information (SI; Text S1).

Grab sampling was performed for each of the eight solid and aqueous matrices. Three sewage sludge, potable water, treated water, venturi scrubber water, mercury scrubber water, and wet ash slurry sampling events occurred approximately at the beginning, middle, and end of each stack gas run, for a total of 12 sampling events per matrix. Excluding potable water, each of these matrices was expected to be temporally correlated to one another and the stack gas. One raw influent and grit sampling event occurred at the beginning and end of each day. No temporal correlation was expected between either the raw influent or grit with any other sampled matrix. Identical field samples were collected during each sampling event to allow for both duplicate measurements of a given compound class and the assay for various compound classes, i.e., both target PFAS and IF. One negative quality control sample on each day for each matrix and compound class was also collected. Additional discrete samples of aqueous matrices were collected for use as positive controls.

Collocated ambient air samplers were positioned both north ( $\sim 275$  m) and south ( $\sim 450$  m) of the SSI (Fig. S1) and operated at approximately  $12\text{ m}^3/\text{h}$  for 24 h both days. The custom high-volume sampling method was based on a modification of EPA Method TO-13A (EPA, 1999) and similar



**Fig. 1.** Flow diagram of the WWTP and SSI treatment process from initial waste input (raw influent; upper left) to the final discharge location (river, atmosphere, landfill; lower right) of the various effluents. Both the larger WWTP system (grey outer box) and the incorporated SSI system (dark grey square) are illustrated along with the various material influent and effluent streams (colored arrows). Arrow colors indicate if the influent/effluent is to/from the WWTP (blue), SSI (orange), or both (red) systems. Magnifying glass symbols indicate matrices sampled in the study.

to methods previously described (Piekorz et al., 2007; Wong et al., 2018). Each sampler was loaded with a 102 mm diameter quartz fiber filter (Whatman) atop a PUF/XAD/PUF “sandwich” (Sigma-Aldrich) for collection and analysis of 24 ionic (Tables S2, S4-S5) and seven neutral (Table S2-S3) PFAS, respectively. A total of eight discrete field samples were collected along with two field blanks and a trip blank.

## 2.2. Sample extraction and analysis

The sample extraction and analysis methodology for each matrix are briefly described here. Additional details are provided in the SI (Text S2).

### 2.2.1. Aqueous and solid matrices

Extraction and analysis of the aqueous and solid matrices were performed for target PFAS and IF. The wet ash samples were biphasic, consisting of an aqueous layer overlying a small amount ( $\sim 0.5$  to  $\sim 1$  g) of wet solid material. The aqueous and solid phases were separated and analyzed independently for target PFAS, whereas only the aqueous fraction was assayed for IF. The measured concentrations for all solid matrices are reported on a dry weight basis.

Target ionic PFAS analysis in all the sample matrices was performed using isotope dilution liquid chromatography tandem mass spectrometry (LC/MS/MS). Target PFAS (18 PFAS analytes, Table S2) in potable water samples were extracted and analyzed following EPA Method 537.1 (Shoemaker and Tettenhorst, n.d.). Non-potable water samples were analyzed for 27 PFAS analytes (Table S2) using weak anion exchange solid phase extraction (SPE) cartridges following an extraction method compliant with the U.S. Department of Defense/Department of Energy Quality Systems Manual Version 5.3 (DoD/DOE QSM 5.3) Table B-15 criteria

(DoD and DOE, 2009). Solid (grit and sewage sludge) matrix samples were analyzed for 28 PFAS analytes (Table S2) using solvent extraction followed by ENVI-Carb™ clean-up procedure compliant with DoD/DOE QSM 5.3 Table B-15 criteria (DoD and DOE, 2009).

IF was measured in the aqueous matrices by ion chromatography (IC) with conductivity detection. Due to the presence of coeluting chromatographic interferences, positive bias was suspected in the sewage sludge extracts' measured fluoride concentrations; therefore, reanalysis of the sewage sludge was performed with a potentially more selective technique using an ion selective electrode (ISE; Text S2).

### 2.2.2. Stack gas matrix

Stack gas was assayed for 30 target ionic PFAS, HF, and TF (Table S2). The PFAS collected on the MM0010 sampling trains were extracted with alkaline methanol and analyzed by isotope dilution LC/MS/MS using modified EPA Method 537 (EPA, 2009). Analysis of HF in the Method 26A trains was performed by IC following EPA Method 9056A (EPA, 2007). An aliquot of methanol from each of the six impingers in the modified Method 18 sampling train was combined into a single, composited sample, after which the fluorinated species in this composite were converted to free fluoride using EPA Method 5050 (bomb combustion) followed by fluoride analysis by EPA Method 9056A (EPA, 2007).

### 2.2.3. Ambient air matrix

Neutral PFAS collected on PUF/XAD/PUF were extracted using accelerated solvent extraction (ASE) with ethyl acetate followed by analysis using gas chromatography/mass spectrometry (GC/MS) in positive chemical ionization mode (PCI) with methane as the reagent gas.

Ionic PFAS (Table S4 and S5) collected on QFFs were extracted by fortifying the filters with extraction internal standards and serially extracted twice using methanol and cleaned using Supelclean™ Envi-Carb™ SPE cartridges (Millipore Sigma, Burlington, MA). Extracts were concentrated to dryness under nitrogen and reconstituted with 50:50 methanol/water (V/V) and fortified with injection internal standards for analysis by isotope dilution LC/MS/MS.

### 2.3. Dispersion modeling

Site meteorological data assessment and ambient dispersion modeling was performed to predict 24-h incinerator stack concentration contributions at the two ambient air monitoring locations. A Met One model 034B weather station sited adjacent to the WWTP stack and Automatic Weather Observing Station (AWOS) data from a Regional Airport, located approximately 1 mile southeast of the WWTP, were the sources of meteorological data. The Industrial Source Complex – Plume Rise Model Enhancements (ISC-PRIME) ambient dispersion model (Schulman et al., 2000) was applied to estimate the 24-h average dilution of a unit emission from the SSI stack at both ambient air monitoring locations for both days of the study. Applying the model predicted dilutions to the measured stack gas concentrations provided an estimate of the incinerator's contribution to the downwind ambient air concentrations. Further details on the dispersion modeling are provided in the SI (Text S3).

### 2.4. Data analysis

For each sampling matrix and compound, concentration and mass flow central tendencies were calculated as the average negative control (NC) corrected measurement from all unique sampling events performed over both study days. For sampling events containing duplicate measurements, the duplicate concentrations were averaged prior to the event level averaging. Any measurement qualified as a non-detect was zero substituted and included in the calculation. This conservative approach, as opposed to substitution of one half the measurement detection limit (MDL) for non-detects, for example, or omitting non-detects from calculations altogether, prevented biasing results high and protected against false positive results. Furthermore, to minimize bias, all numerical results were retained and included, even those less than applicable MDLs, so long as qualitative identification criteria were met. The NC correction was made by subtracting the maximum NC from the averaged value. All negative NC corrected central tendency concentrations were set to zero. Per matrix PFAS class (PFCAs, PFSAs, precursors/intermediates, new alternatives, and total PFAS) central tendencies were then derived as the sum of all individual NC corrected compound values for PFAS belonging to a specific class.

The concentration central tendency ( $C$ ) for each matrix ( $m$ ) and compound ( $p$ ) was derived as:

$$C(m, p) = \frac{1}{n} \sum_{i=1}^n (c_i - NC), \quad (1)$$

where  $c_i$  is the concentration of an individual sampling event,  $NC$  is the maximum negative control (Tables S11 – S21), and  $n$  is the number of unique events aggregated across both study days for the given matrix and compound. The NC corrected mass flow central tendency ( $MF$ ) was derived as:

$$MF(m, p) = \frac{1}{n} \sum_{i=1}^n f_i (c_i - NC), \quad (2)$$

where  $f$  is the averaged flow rate (Table S1) for the matrix,  $m$ . The per compound net mass flow ( $NMF$ ) was calculated at both the WWTP and SSI levels as the difference between sums of  $MF$ s in the effluent and influent matrices:

$$NMF(p) = \sum_{e=1}^E (MF)_e - \sum_{i=1}^I (MF)_i, \quad (3)$$

where  $e$  and  $i$  represent an effluent or influent matrix, respectively. Fig. 1 and Table S1 identify the influents to and effluents from both the WWTP and SSI. At the SSI level only, PFAS-specific destruction and removal efficiencies (DREs) were calculated as:

$$DRE(p) = 100 \times \left( 1 - \left( \frac{\sum_{e=1}^E (MF)_e}{\sum_{i=1}^I (MF)_i} \right) \right) \quad (4)$$

Uncertainty of the central tendencies ( $C$  and  $MF$ ) and  $NMF$  were estimated as the standard error based on the concentration, matrix flow rate, and covariance between the two. For the  $NMF$  uncertainties, covariances between daily averages were also considered. Hypothesis testing was applied to derive 95 % confidence intervals for the  $NMF$  point estimates. Both unadjusted and adjusted  $p$ -values were derived, where the latter was calculated following the Holm-Bonferroni method (Holm, 1979). Further details on the central tendencies, uncertainties, and hypothesis testing are provided in the SI (Text S4).

## 3. Results and discussion

### 3.1. PFAS concentrations

Individual and total PFAS concentrations (Eq. (1), Fig. S2, Tables S11–S21) in the raw influent ( $117 \pm 39$  ng/L; study average  $\pm$  uncertainty) were within the range of measured concentrations at other WWTPs reported in the literature (Schultz et al., 2006; Coggan et al., 2019; Nguyen et al., 2019), and comprised mostly of perfluoroalkyl acids (PFAAs; 88 %), with considerable concentrations of short-chain compounds as well as PFOA and PFOS. Of the precursors/intermediates and new alternatives, 6:2 FTS and HFPO-DA accounted for over 10 % of the total PFAS concentration.

The WWTP separates and processes the raw influent into grit, sewage sludge, and treated water. The grit contained traces of PFAS ( $1.3 \pm 2.5$  ng/g), namely PFBA, PFHxA, and PFOA. Sewage sludge concentrations were  $>20$  times higher ( $31 \pm 3.7$  ng/g), where PFAS tend to accumulate through sorption, with long-chain PFAS generally partitioning to the sludge more readily (Coggan et al., 2019). PFOS, a long-chain PFSA, represented 48 % of the total PFAS concentrations in the sewage sludge, followed by PFHxA (18 %) and PFPeA (12 %) (two short-chain PFCAs). While these short-chained compounds provided a large absolute percentage of the total PFAS in the sewage sludge, concentrations in the treated water were greater than that in the raw influent for both, indicating PFHxA and PFPeA primarily remained bound in the liquid phase (plus additional transformation). Total PFAS concentration in the treated water ( $167 \pm 83$  ng/L) was greater than but not statistically different than in the raw influent. This concentration increase was primarily attributed to increases in PFBA ( $19.6 \pm 29.8$  ng/L to  $72.0 \pm 75.9$  ng/L) and to a lesser extent HFPO-DA ( $7.5 \pm 2.5$  ng/L to  $18.6 \pm 6.9$  ng/L), suggesting their formation during wastewater treatment, as previously observed (Eriksson et al., 2017; Gallen et al., 2018; Loganathan et al., 2007; Schultz et al., 2006; Venkatesan and Halden, 2013; Wang et al., 2018; Kim Lazcano et al., 2020; Sun et al., 2016). The long-chain PFCAs and all PFSAs, however, exhibited lower concentrations in the treated water, which may be attributable to their sorption to sewage sludge (Coggan et al., 2019).

An intercomparison of SSI matrix concentrations shows that total PFAS concentrations of treated water ( $167 \pm 83$  ng/L), which is admitted to the venturi/tray scrubber and contributes approximately 99 % of the wet ash slurry volume, were within the measurement uncertainties of both the venturi/tray scrubber ( $86.9 \pm 17.9$  ng/L) and wet ash slurry ( $136 \pm 44.7$  ng/L), as expected. All applicable individual PFAS from the potable water measured below both state (Cordner et al., 2019; Legislature, 2020) and 2016 U.S. EPA (EPA, 2016b) advisory levels, however, both PFOA and PFOS measured above the updated 2022 U.S. EPA interim lifetime health advisory levels (EPA, 2022). The potable water total PFAS influent ( $9.9 \pm 0.6$  ng/L) was not statistically different than the mercury scrubber

effluent ( $13.2 \pm 3.6$  ng/L) across like-measured compounds. These results are discussed in more detail in the SI (Text S5).

The total sum ionic PFAS (Table S20) measured in ambient air across both days of the study and from both sampling locations averaged  $56.2 \pm 34.8$  pg/m<sup>3</sup>, with the largest contributions from PFOA ( $26.3 \pm 31.9$  pg/m<sup>3</sup>) and PFBA ( $22.5 \pm 6.6$  pg/m<sup>3</sup>). The limited number of previous studies regarding PFAS in WWTP ambient air have shown that compared to non-contaminated reference sites the PFAS concentrations on WWTP sites were 1.5 to 15 times higher (Hamid, 2016). However, results here were more similar to previously reported reference sites than onsite WWTPs. Across like measured compounds, the average PFCA concentration observed here (50.1 pg/m<sup>3</sup>) was similar to that measured at a distant reference site (59.1 pg/m<sup>3</sup>) located approximately 600 m from an Ontario, Canada WWTP (Ahrens et al., 2011) and lower than that at near reference sites (70.4–134 pg/m<sup>3</sup>), primary clarifiers (95.7–208 pg/m<sup>3</sup>), aeration tanks (202–237 pg/m<sup>3</sup>), and secondary clarifiers (106–121 pg/m<sup>3</sup>). Similarly, PFOS (2.15 pg/m<sup>3</sup>) was most similar to the distant reference site (3.05 pg/m<sup>3</sup>) and lower than those at near reference sites (4.68–34.2 pg/m<sup>3</sup>), primary clarifiers (42.7–120 pg/m<sup>3</sup>), aeration tanks (126–171 pg/m<sup>3</sup>), and secondary clarifiers (93.9–108 pg/m<sup>3</sup>). The total sum neutral PFAS (Table S21) measured in the ambient air averaged  $780.3 \pm 488.2$  pg/m<sup>3</sup>, primarily from 6:2 FTOH (89 %) and 8:2 FTOH (7 %). The dominance of 6:2 FTOH followed by 8:2 FTOH has been observed at various Ontario, Canada WWTPs (Vierke et al., 2011; Ahrens et al., 2011; Shoeib et al., 2016). Conversely, two WWTPs in northern Germany (Weinberg et al., 2011) observed 8:2 FTOH >6:2 FTOH, which is typical to that observed in ambient urban air not influenced by WWTPs (Piekorz et al., 2007; Barber et al., 2007; Jahnke et al., 2007; Shoeib et al., 2006). Shoeib et al. (2016) provided possible explanations for the higher 6:2 FTOH levels observed at the Canadian WWTPs, including higher 6:2 FTOH levels in the raw influent (FTOH was not measured in the liquid matrices in this study), differences in the compounds' chemical properties, and transition from long- to short-chain PFAS in industrial practices. As primary sources of atmospheric FTOHs are manufacturing facilities and/or other commercial product usage, the higher 6:2 FTOH compared to 8:2 FTOH observed here could be due to nearby industries' transition to short-chain PFAS. Like the ionic compounds, the neutral PFAS concentrations were most similar to previously observed reference sites nearby WWTP features (442–1095 pg/m<sup>3</sup>) and lower than those by primary clarifiers (9354–22,677 pg/m<sup>3</sup>), aeration tanks (4334–11,541 pg/m<sup>3</sup>), and secondary clarifiers (1414–1909 pg/m<sup>3</sup>) (Ahrens et al., 2011).

### 3.2. Inorganic fluoride concentrations

IF concentrations at the WWTP (Eq. (1), Tables S11–S19, Fig. S3) were most notably observed in the wet ash slurry ( $30.2 \pm 7.82$  mg/L), with measured concentrations >20 times greater than the next closest aqueous matrix. This large disparity could indicate mineralization of fluorinated compounds during thermal treatment of the sewage sludge, but nonetheless was unanticipated and is not fully explainable within the scope of this study.

The potable water IF concentration ( $0.64 \pm 0.06$  mg/L) was consistent with that from fluoridation of the public water supply (Health and Human Services Federal Panel on Community Water F, 2015). The elevated concentration in the raw influent ( $1.06 \pm 0.07$  mg/L) suggests contributions from additional sources beyond potable water fluoridation. The raw influent consisted of residential wastewater (65.4 %) mostly comprised of potable water, stormwater (19.2 %), and industrial wastewater (15.4 %). IF in the treated water ( $0.82 \pm 0.19$  mg/L) was not statistically different than in the raw influent, coinciding with previous research indicating that conventional wastewater treatment does not remove fluorides (Gehr and Leduc, 1992; Tafu et al., 2016).

### 3.3. Stack gas PFAS emission contributions to downwind ambient air concentrations

On Day One, the stack gas plume was estimated to contribute 0.15 pg/m<sup>3</sup> (0.17 %) to the total ionic PFAS (83.6 pg/m<sup>3</sup>) measured at the North

sampling site (Fig. S4, Table S22). Changing meteorological conditions on Day Two resulted in an estimated plume contribution of 0.27 pg/m<sup>3</sup> (0.83 %) to the total PFAS (32.7 pg/m<sup>3</sup>) observed at the South location. The estimated concentration contributions from the plume at the downwind sites for both days and for every PFAS compound were less than both the uncertainty in the daily averaged ambient concentrations and the ambient air analysis MDLs (Table S22). Further, when considering the daily location of maximum downwind plume impact within the modeled domain, all concentration contributions were still below the MDLs. These results indicate the plume's contribution to ambient air concentrations within the modeled domain were negligible on both study days.

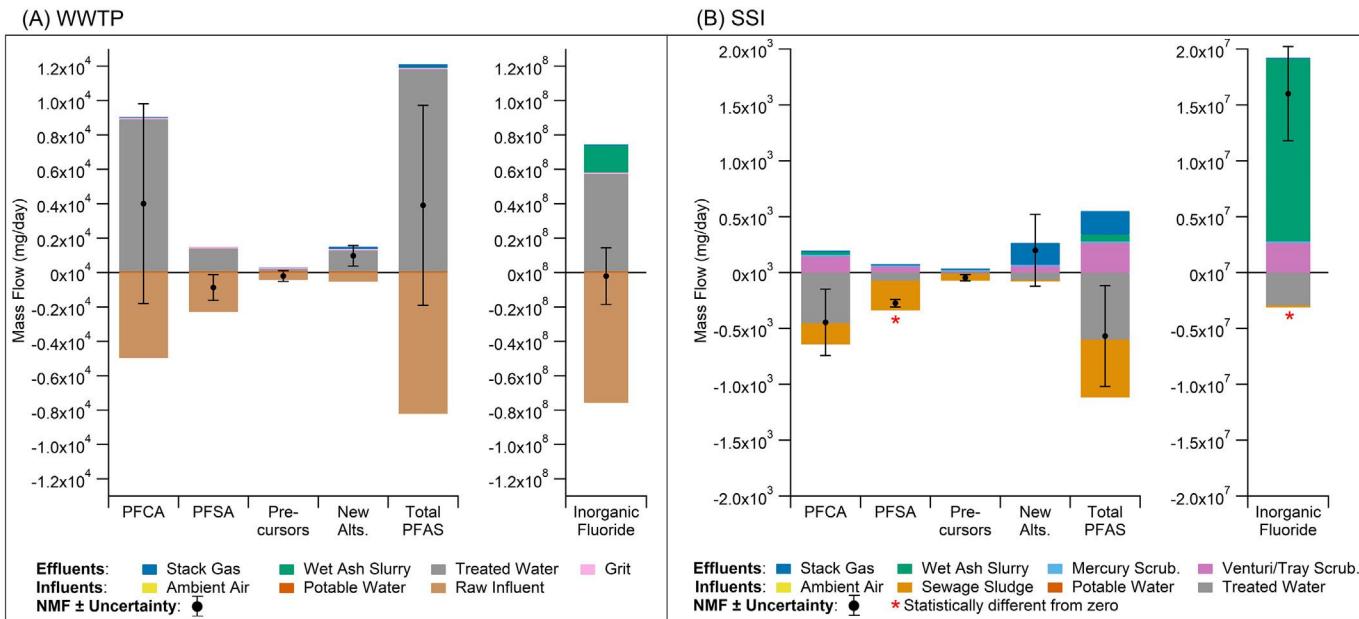
Neutral PFAS concentrations (Table S23) exhibited similar spatial and temporal trends as the ionic PFAS. While neutral PFAS were not measured in the stack gas, given the dispersion results and observed ambient concentrations on both days, the stack's influence on downwind ambient air concentrations appears to be minimal compared to other potential sources. Concentrations of 6:2 FTOH and 8:2 FTOH, particularly at the North site, are greater than that previously measured at rural and urban locations (Barber et al., 2007) and more similar to monitoring nearby WWTP features (e.g., aeration tanks, clarifiers) (Ahrens et al., 2011). This suggests a potential onsite source, other than the stack plume, of these neutral PFAS. These results are discussed in more detail in the SI (Text S6).

### 3.4. PFAS mass flow at the WWTP, including the SSI

PFAS mass flows (Eq. (2); Figs. 2, S5, and S6; Tables S11–S20) at the WWTP were driven primarily by the raw influent and treated water effluent. Both PFCA ( $4004 \pm 5808$  mg/day) and total PFAS ( $3909 \pm 5815$  mg/day) NMFs were positive (Eq. (3), Fig. 2, Table 1), consistent with previous studies (Eriksson et al., 2017; Houtz et al., 2016) showing that transformation of unmeasured PFAS precursor species, such as fluorotelomers, to target terminal PFAS is likely occurring during wastewater treatment. The NMF of PFCAs was driven largely by the formation of PFBA ( $3872 \pm 5778$  mg/day), with 1 to 2 orders of magnitude lower net positive contributions from PFPeA, PFHxA, and PFDA (Figs. S5–S6, Table 1). The remainder of the PFCAs behaved more similarly to the PFSAs, which exhibited a negative NMF ( $-872 \pm 748$  mg/day), demonstrating partial loss during water treatment, as previously observed (Lenka et al., 2021; Wang et al., 2020c). This sink, particularly for the longer chained terminal PFAS, could be at least in part due to sorption onto the sewage sludge and transformation prior to incineration (Coggan et al., 2019; Lenka et al., 2021; Sun et al., 2012; Zhou et al., 2019). Primary contributors to the loss of PFSAs included PFBS, PFHxS, and PFOS (Table 1). Across the PFAAs (PFCAs and PFSAs), the influent mass flows of even chain-length PFAS were larger than odd chain-length PFAS, e.g., PFBA > PFPeA, PFBS > PFPeS, etc. Such a pattern is consistent with that observed previously during wastewater treatment (Loganathan et al., 2007; Sinclair and Kannan, 2006).

Among the measured PFAS precursors/intermediates, NEtFOSAA, which is an aerobic biotransformation intermediate of N-EtFOSE (Mejia Avendaño and Liu, 2015) and an immediate precursor of PFOS, appears to be formed during wastewater treatment. Conversely, the fluorotelomer sulfonates (e.g., 6:2 FTS) are being broken down, potentially into PFCAs (e.g., PFHxA) due to aerobic biotransformation in the activated sludge (Wang et al., 2011). Primarily due to the loss of 6:2 FTS during wastewater treatment, the NMF of the precursor species is negative ( $-198 \pm 315$  mg/day). Among the new alternatives, only HFPO-DA was measured to an appreciable extent, with a positive NMF ( $976 \pm 596$  mg/day), suggesting it was formed and released during treatment of the raw influent. However, HFPO-DAs NMF was not statistically significantly different than zero at the 95 % confidence level, and while studies have found that conventional wastewater treatment does not adequately remove HFPO-DA (Vakili et al., 2021), to the authors' knowledge there has been no prior research supporting or observing HFPO-DAs formation during treatment.

The qualitative trends in formation and removal noted above notwithstanding, none of the PFAS classes, total PFAS, or the individual species



**Fig. 2.** Study average mass flows for each PFAS class and IF at the level of the WWTP (A), which is inclusive of the SSI, and the SSI alone (B). Each colour indicates a separate influent and effluent source. Influent are shown as negatives and effluent as positives on the y-axes. The black circles represent the NMF for a given pollutant group, i.e., the sum of all effluents minus the sum of all influents. A positive (negative) NMF indicates the WWTP or SSI is a source (sink) of the PFAS class or IF. The black error bars represent the NMF uncertainty. Red asterisks (\*) denote NMFs that are statistically different from zero at the 95 % confidence interval. Note that the IF y-axes are scaled 10<sup>4</sup> times larger than the PFAS class y-axes for both subplots (A) and (B).

exhibited NMFs that were statistically significantly different from zero at the 95 % confidence level (Tables 1, S24, and S25). Therefore, based on the observed variability in flow rates and PFAS concentrations over the duration of this field study, it is not possible to draw definitive conclusions regarding the net production or breakdown of PFAS during the water treatment process.

### 3.5. PFAS mass flow and DREs at the SSI

SSI NMFs for PFCA ( $-446 \pm 297$  mg/day) and all individual PFCA species were negative, except for PFTeDA, whose NMF was negligible ( $< 0.2$  mg/day; Table 1). The negative NMF was driven by the loss of PFBA from the treated water introduced into the venturi/tray scrubber, along with losses of PFPeA, PFHxA, and PFOA from both the treated water influent and the sewage sludge. Exclusive of PFTeDA, SSI DREs ranged from 16 to 99 % (Table 1). Such suggests that PFCAs are mineralizing to some extent in the SSI, offering an explanation as to the observed negative NMFs of PFHxA, PFOA, PFNA, PFUnA and other longer-chain PFCAs at the level of the WWTP, which includes thermal treatment in the SSI. Net loss of the PFCAs was also the major contributor to the negative NMF for total PFAS ( $-568 \pm 452$  mg/day, 51 % DRE). While the NMFs of PFCA and total PFAS were not statistically significant (Tables 1 and S24), NMFs for two individual PFCAs, PFHxA ( $-99 \pm 12$  mg/day, 53 % DRE) and PFDA ( $-9.7 \pm 2.5$  mg/day, 87 % DRE), were statistically significant (Tables 1 and S26, Fig. S6). Excluding PFBA, PFCAs with higher DREs were those with significant contributions from sewage sludge. Given long-chain PFAS generally partition to sewage sludge more readily (Coggan et al., 2019), this explains why higher DREs were observed for some of the longer-chained homologs.

Among the precursor/intermediate species, statistically significant NMFs of NMefOSAA ( $-35 \pm 6$  mg/day, 96 % DRE) and NefFOSAA ( $-27 \pm 5$  mg/day, 96 % DRE) suggest they are breaking down, primarily in the sewage sludge, during incineration (Tables 1 and S26, Fig. S6). These losses drove the observed negative NMF for the precursor/intermediate family ( $-46 \pm 28$  mg/day, 65 % DRE). Conversely, there is evidence that 6:2 FTS ( $14 \pm 25$  mg/day) was formed in the SSI, albeit its NMF was

not statistically significant (Tables 1 and S26, Fig. S6). Other unmeasured precursors/intermediates, e.g., 6:2 FTAA, 6:2 FTAB, 6:2 FTSAS, may be transforming to 6:2 FTS during thermal treatment (Xiao et al., 2021).

While the SSI also appears to be a net source of the new alternatives (Table 1), and specifically HFPO-DA ( $198 \pm 321$  mg/day), these results should be observed with caution. The positive NMF for HFPO-DA, and the class of new alternatives taken together, was driven almost entirely by stack gas emissions of HFPO-DA (Table S19; mass flow =  $196 \pm 331$  mg/day, concentration =  $488 \pm 827$  ng/m<sup>3</sup>). However, a potential mechanism for HFPO-DAs formation is unknown, as it is unexpected to survive thermal treatment (Alinezhad et al., 2022; EPA, 2021; Sasi et al., 2021; Xiao et al., 2020) and contributions from the potential vaporization of treated and potable water introduced at the scrubbers cannot fully account for that observed in the stack gas. The variability in the observed stack gas concentrations, potentially due in part to the application of the substantial maximum negative control correction, may have confounded these results and contributed to the lack of statistical significance for the NMFs of new alternatives as a class and HFPO-DA specifically.

The one PFAS class that showed a statistically significant negative NMF from the SSI was the PFSAs ( $-274 \pm 34$  mg/day, 81 % DRE; Tables 1 and S24). The loss of PFOS, the majority of which was introduced into the SSI in the sewage sludge, was primarily responsible and its NMF ( $-274 \pm 30$  mg/day, 91 % DRE) was also statistically significant (Tables 1 and S26, Fig. S6). Conversely, PFBS and PFHxS showed little net change, as neither were substantially observed in the sewage sludge, and the other PFSAs were modest contributors with mass flows of  $<0.3$  mg/day.

As this is the first study, to the authors' knowledge, to assess the DRE of PFAS in an SSI, direct comparison to results reported elsewhere in the literature is not possible. Theoretical considerations suggest that temperatures of at least 1000 °C and potentially  $>1400$  °C may be required to fully mineralize PFAS, including the CF<sub>4</sub> that may be formed during thermal treatment of PFAS (Tsang et al., 1998; Ryan and Gullet, 2020; Winchell et al., 2020). Previous bench-scale work (Taylor et al., 2014; Yamada et al., 2005) demonstrated 99.9 % destruction of fluorotelomer-based polymers (based on measurements of PFOA) at 1000 °C and field-scale work at facilities equipped with thermal oxidizers or secondary combustors at  $>1000$  °C

Table 1

Matrix aggregated mass flows and statistical confidence<sup>a</sup> at the Wastewater Treatment Plant (WWTP) and Sewage Sludge Incinerator (SSI) levels, and SSI destruction and removal efficiencies (DREs).

Compound	WWTP Level (mg/day $\pm 1\sigma$ ) <sup>b</sup>			SSI Level (mg/day $\pm 1\sigma$ ) <sup>b</sup>			SSI DRE (%) <sup>d</sup>
	Influent <sup>c</sup>	Effluent <sup>c</sup>	NMF <sup>d</sup>	Influent <sup>c</sup>	Effluent <sup>c</sup>	NMF <sup>d</sup>	
PFBA †	1284 $\pm$ 1966	5156 $\pm$ 5434	3872 $\pm$ 5778	259 $\pm$ 273	17 $\pm$ 18	-242 $\pm$ 271	93
PFPeA †	416 $\pm$ 476	572 $\pm$ 411	156 $\pm$ 629	90 $\pm$ 31	34 $\pm$ 14	-55 $\pm$ 30	62
PFHxA	1620 $\pm$ 661	1904 $\pm$ 123	284 $\pm$ 672	186 $\pm$ 21	88 $\pm$ 14	<b>-99 <math>\pm</math> 12</b>	53
PFHpA	393 $\pm$ 65	331 $\pm$ 30	-62 $\pm$ 72	17 $\pm$ 3.4	14 $\pm$ 2.7	-2.7 $\pm$ 1.9	16
PFOA	1097 $\pm$ 54	859 $\pm$ 133	-237 $\pm$ 143	60 $\pm$ 16	38 $\pm$ 9.1	-22 $\pm$ 9.2	37
PFNA	107 $\pm$ 26	89 $\pm$ 7.6	-17 $\pm$ 27	4.5 $\pm$ 0.90	3.0 $\pm$ 0.62	-1.5 $\pm$ 0.51	32
PFDA	39 $\pm$ 16	59 $\pm$ 19	20 $\pm$ 24	11 $\pm$ 2.6	1.4 $\pm$ 0.30	<b>-9.7 <math>\pm</math> 2.5</b>	87
PFUnA	0.45 $\pm$ 6.8	0.037 $\pm$ 0.090	-0.41 $\pm$ 6.8	6.5 $\pm$ 5.0	0.037 $\pm$ 0.090	-6.4 $\pm$ 5.0	99
PFDoA	4.9 $\pm$ 8.2	0.057 $\pm$ 0.065	-4.9 $\pm$ 8.2	8.3 $\pm$ 3.6	0.057 $\pm$ 0.065	-8.2 $\pm$ 3.5	99
PFTrDA	2.0 $\pm$ 6.0	0.047 $\pm$ 0.088	-2.0 $\pm$ 6.0	0.056 $\pm$ 3.6	0.047 $\pm$ 0.088	-0.0089 $\pm$ 3.6	16
PFTeDA	3.7 $\pm$ 6.1	0.062 $\pm$ 0.071	-3.7 $\pm$ 6.1	3.8E-5 $\pm$ 1.5E-5	0.17 $\pm$ 0.82	0.17 $\pm$ 0.82	< 0
<b><math>\Sigma</math>PFCA</b>	<b>4966 <math>\pm</math> 1868</b>	<b>8970 <math>\pm</math> 5500</b>	<b>4004 <math>\pm</math> 5808</b>	<b>642 <math>\pm</math> 301</b>	<b>196 <math>\pm</math> 37</b>	<b>-446 <math>\pm</math> 297</b>	<b>69</b>
PFBS	853 $\pm$ 758	416 $\pm$ 29	-437 $\pm$ 759	21 $\pm$ 5.5	20 $\pm$ 4.8	-1.6 $\pm$ 2.3	7.4
PFPeS †	0	0.31 $\pm$ 0.15	0.31 $\pm$ 0.15	0	0.31 $\pm$ 0.15	0.31 $\pm$ 0.15	N/A
PFHxS	341 $\pm$ 114	275 $\pm$ 16	-66 $\pm$ 115	15 $\pm$ 8.0	16 $\pm$ 5.1	0.86 $\pm$ 8.9	< 0
PFHpS †	3.5 $\pm$ 21	0.0094 $\pm$ 0.040	-3.5 $\pm$ 21	0	0.0094 $\pm$ 0.040	0.0094 $\pm$ 0.040	N/A
PFOS	1086 $\pm$ 610	720 $\pm$ 64	-366 $\pm$ 614	302 $\pm$ 30	28 $\pm$ 6.4	<b>-274 <math>\pm</math> 30</b>	91
PFNS †	0	0.0048 $\pm$ 0.0096	0.0048 $\pm$ 0.0096	0	0.0048 $\pm$ 0.0096	0.0048 $\pm$ 0.0096	N/A
PFDS †	6.6E-7 $\pm$ 1.8E-6	0.021 $\pm$ 0.12	0.021 $\pm$ 0.12	6.6E-7 $\pm$ 1.8E-6	0.021 $\pm$ 0.12	0.021 $\pm$ 0.12	< 0
PFDoS §	0	0.035 $\pm$ 0.055	0.035 $\pm$ 0.055	0	0.035 $\pm$ 0.055	0.035 $\pm$ 0.055	N/A
<b><math>\Sigma</math>PFSA</b>	<b>2283 <math>\pm</math> 741</b>	<b>1411 <math>\pm</math> 100</b>	<b>-872 <math>\pm</math> 748</b>	<b>338 <math>\pm</math> 34</b>	<b>64 <math>\pm</math> 15</b>	<b>-274 <math>\pm</math> 34</b>	<b>81</b>
NMeFOSAA	17 $\pm$ 20	61 $\pm$ 11	44 $\pm$ 23	36 $\pm$ 6.2	1.3 $\pm$ 0.69	<b>-35 <math>\pm</math> 5.8</b>	96
NEtFOSAA	16 $\pm$ 18	17 $\pm$ 5.2	1.7 $\pm$ 19	28 $\pm$ 4.5	1.1 $\pm$ 1.4	<b>-27 <math>\pm</math> 4.7</b>	96
PFOSA †	3.4E-4 $\pm$ 1.2E-4	0.10 $\pm$ 0.17	0.10 $\pm$ 0.17	3.4E-4 $\pm$ 1.2E-4	0.10 $\pm$ 0.17	0.10 $\pm$ 0.17	< 0
4:2 FTS †	0	0.032 $\pm$ 0.029	0.032 $\pm$ 0.029	0	0.032 $\pm$ 0.029	0.032 $\pm$ 0.029	N/A
6:2 FTS †	387 $\pm$ 301	153 $\pm$ 79	-234 $\pm$ 311	7.0 $\pm$ 3.8	21 $\pm$ 24	14 $\pm$ 25	< 0
8:2 FTS †	11 $\pm$ 14	1.1 $\pm$ 2.1	-9.6 $\pm$ 14	0.021 $\pm$ 0.058	1.2 $\pm$ 1.3	1.2 $\pm$ 1.3	< 0
10:2 FTS §	0	0.10 $\pm$ 0.15	0.10 $\pm$ 0.15	0	0.10 $\pm$ 0.15	0.10 $\pm$ 0.15	N/A
<b><math>\Sigma</math>Precursors/intermediates</b>	<b>430 <math>\pm</math> 306</b>	<b>232 <math>\pm</math> 78</b>	<b>-198 <math>\pm</math> 315</b>	<b>71 <math>\pm</math> 8.9</b>	<b>25 <math>\pm</math> 24</b>	<b>-46 <math>\pm</math> 28</b>	<b>65</b>
HPO-DA †	528 $\pm$ 99	1503 $\pm$ 588	976 $\pm$ 596	67 $\pm$ 25	265 $\pm$ 340	198 $\pm$ 321	< 0
Adona †	0	0.043 $\pm$ 0.045	0.043 $\pm$ 0.045	0	0.043 $\pm$ 0.045	0.043 $\pm$ 0.045	N/A
11CI-PF3OUdS †	0	0.040 $\pm$ 0.030	0.040 $\pm$ 0.030	0	0.040 $\pm$ 0.030	0.040 $\pm$ 0.030	N/A
9CI-PF3ONS †	0	0.0055 $\pm$ 0.014	0.006 $\pm$ 0.014	0	0.0055 $\pm$ 0.014	0.0055 $\pm$ 0.014	N/A
<b><math>\Sigma</math>New Alts.</b>	<b>528 <math>\pm</math> 99</b>	<b>1503 <math>\pm</math> 588</b>	<b>976 <math>\pm</math> 596</b>	<b>67 <math>\pm</math> 25</b>	<b>265 <math>\pm</math> 340</b>	<b>199 <math>\pm</math> 321</b>	<b>&lt; 0</b>
<b><math>\Sigma</math>PFAS</b>	<b>8208 <math>\pm</math> 1735</b>	<b>12,117 <math>\pm</math> 5551</b>	<b>3909 <math>\pm</math> 5815</b>	<b>1118 <math>\pm</math> 332</b>	<b>550 <math>\pm</math> 376</b>	<b>-568 <math>\pm</math> 452</b>	<b>51</b>
Inorganic Fluoride	7.6E+7 $\pm$ 4.8E+6	7.4E+7 $\pm$ 1.6E+7	-2.1E+6 $\pm$ 1.7E+7	3.1E+6 $\pm$ 7.1E+5	1.9E+7 $\pm$ 4.5E+6	<b>1.6E+7 <math>\pm</math> 4.2E+6</b>	< 0

<sup>a</sup>Bold red text indicates NMF point estimates statistically significantly different from 0 at the 95 % confidence level (unadjusted  $p$ -values  $<0.05$ ). The per compound and compound class 95 % confidence intervals and  $p$ -values are provided in Tables S24, S25, and S26.

<sup>b</sup> $\sigma$  = standard deviation.

<sup>c</sup>Matrix influents to and effluents from both the WWTP and SSI are identified in Fig. 1 and Table S1.

<sup>d</sup>NMF and SSI DRE equations are provided in Section 2.4 (Eqs. (3) and (4), respectively).

† Compound not measured in potable water.

§ Compound only measured in stack gas.

‡ Compound not measured in ambient air.

(Ryan and Gullet, 2020; Focus Environmental Inc., 2020). The single most comparable study is that of Loganathan et al. (2007), which reported PFAS concentrations in sewage sludge 2 to 10 times higher than in ash following incineration, suggesting their removal. Results of the present work were similar, with total PFAS mass flows in sewage sludge 7 times higher than the wet ash slurry and 2 times higher than the combination of wet ash slurry and stack gas. However, the SSI-level NMFs and DREs presented here consider all SSI influent (sewage sludge, treated water, potable water, and ambient air) and effluent (wet ash slurry, stack gas, venturi/tray scrubber, and mercury scrubber) matrices, rather than just the influents thermally treated in the fluidized bed incinerator (sewage sludge) and the thermal treatment effluent byproducts (wet ash slurry and stack gas). The matrices that do not undergo thermal treatment (treated water, potable water) were also considered as influents, as they contribute to the PFAS observed in the thermally

treated byproduct effluents. For example, the treated water influent is expected to contribute to both the stack gas (via water vaporization at the venturi/tray scrubber), the wet ash slurry (approximately 99 % of the volume of wet ash slurry was treated water), and venturi/tray scrubber effluents. Excluding the treated water influent and venturi/tray scrubber effluent would therefore bias the NMF and DRE results low. Considering all SSI matrices provides the most holistic and unbiased NMF and DRE estimates of the entire SSI system processes. With that said, excluding PFBA, compounds that exhibited a large DRE were those with substantial contributions from the sewage sludge, which indicates, as expected, that the majority of PFAS removal through the SSI were from the sewage sludge incineration.

The DRE results provide evidence for the removal of several individual PFAS species (PFHxA, PFDA, PFOS, NMeFOSAA, and NEtFOSAA) in the

SSI. Such is based on hypothesis testing in which *p*-values were unadjusted for multiple tests being completed simultaneously. Following application of the relevant adjustments to control for false positives, these results were not statistically significant, therefore caution is suggested in their interpretation. Overall, this study found that PFAS removal through the SSI system varies between DREs <0 up to 99 % for individual PFAS compounds. The total PFAS DRE was 51 %. The only PFAS class with a statistically significant NMF was PFSA, which had a DRE of 81 %. Such suggests that an SSI may inadequately remove PFAS and that process optimization, such as updating incinerator temperature and/or residence time or replacing PFAS-laden treated water introduced to the venturi/tray scrubber with PFAS-free water, is required to achieve consistent and higher removal efficiencies.

### 3.6. PFAS mass discharges to the environment

The population-normalized WWTP effluent mass flows of PFAS (Table S27) allow for comparison of emission rates to those reported elsewhere. The total PFAS discharge rate ( $97 \pm 45 \mu\text{g}/\text{day}/\text{person}$ ) was within the range of that reported by Loganathan et al. (2007) at two southeastern U.S. WWTPs in the summer (37 to 872  $\mu\text{g}/\text{day}/\text{person}$ ), by Campo et al. (2014) at 16 WWTPs in Spain (33 to 148  $\mu\text{g}/\text{day}/\text{person}$ ), and by Kim et al. (2012) at 15 WWTPs in Korea (44  $\mu\text{g}/\text{day}/\text{person}$ ). Agreement with the latter study improves following exclusion of PFBA ( $42 \pm 44 \mu\text{g}/\text{day}/\text{person}$ ) and HFPO-DA ( $11 \pm 2.7 \mu\text{g}/\text{day}/\text{person}$ ), which were unmeasured by Kim et al. (2012). Given PFOS and PFOA have been phased out from U.S. commerce over the past two decades (Company, 2000; EPA, 2000), discharge rate comparisons between the Loganathan et al. (2007) study and the current study can provide a qualitative assessment of the environmental change of these PFAS over this time. The discharge rate of PFOS from the current study ( $5.8 \pm 0.52 \mu\text{g}/\text{day}/\text{person}$ ) is approximately 36 times lower than that from Loganathan et al. (2007) (206  $\mu\text{g}/\text{day}/\text{person}$ ). Similarly, the discharge rate of PFOA from the current study ( $6.9 \pm 1.1 \mu\text{g}/\text{day}/\text{person}$ ) is approximately 19 times lower than that from Loganathan et al. (2007) (132  $\mu\text{g}/\text{day}/\text{person}$ ). Since PFOS and PFOA do not environmentally degrade (Post et al., 2012), the observed discharge reductions could be due to the compounds accumulating in other matrices (Ghisi et al., 2019). Given PFOS has a higher tendency to accumulate than PFOA (Cui et al., 2009), the larger decrease observed for PFOS corroborates this hypothesis. Alternatively, regional/local differences in emissions of these compounds could explain the observed differences.

The majority ( $> 99\% ; 96.2 \pm 44.7 \mu\text{g}/\text{day}/\text{person}$ ) of total PFAS was discharged to the aquatic environment (via treated water to the adjacent river), with  $\sim 0.4\%$  and  $\sim 0.2\%$  emitted to the atmosphere (through stack gas emissions) and terrestrial (via landfilling of the wet ash slurry and grit) environments, respectively. In general, discharges to treated water dominated those to air or land for the individual PFAS species with discharges  $> 1 \mu\text{g}/\text{day}/\text{person}$ , with the exceptions being 6:2 FTS and HFPO-DA ( $\sim 2\%$  to landfills and  $\sim 4\%$  to the air, respectively). The contribution of 6:2 FTS to the landfill (via wet ash slurry) potentially resulted from the transformation of other unmeasured precursors during thermal treatment (Xiao et al., 2021), whereas the contribution of HFPO-DA to air (via stack gas) should be observed with caution for the reasons discussed in Section 3.5. Consistent with the results of the dispersion modeling, airborne emissions of target PFAS from the SSI were modest compared to those to the aquatic environment.

### 3.7. Inorganic fluoride mass flow at the WWTP and SSI

The NMF of fluoride at the WWTP level was nearly zero ( $-2.1 \pm 17 \text{ kg}/\text{day}$ ) and driven by a small difference between the raw influent and the sum of the treated water and wet ash slurry effluents. At the SSI level, the overall NMF of fluoride was  $16 \pm 4.2 \text{ kg}/\text{day}$  and statistically significant at the 95 % confidence interval. The total influent mass flow was driven primarily by treated water (94 %) and sewage sludge (5.6 %),

whereas the major effluent sources were wet ash slurry (86 %) and venturi/tray scrubber water (14 %). While a small effluent source, the fluoride emissions from the stack gas produced interesting results. The mass emission rate of IF from the stack gas was  $0.0041 \pm 0.0030 \text{ kg}/\text{day}$  and total PFAS as fluoride was  $0.00013 \text{ kg}/\text{day}$ , whereas the mass emission rate of TF from the stack was  $> 1000$  times larger at  $5.08 \pm 10.2 \text{ kg}/\text{day}$  (Table S19). The observed TF mass flow being substantially larger than the sum of IF and total PFAS as fluoride could be due to a combination of multiple factors. We offer three possible explanations: (1) the IF measurements were biased low (see Section 2.2.1 and Text S2), (2) this was an analytical artifact of the TF field measurements given they were highly variable and included only one measurement larger than the substantial maximum NC correction, and/or (3) there may have been a significant gas-phase emission of PFAS products of incomplete combustion and/or other fluorine containing chemicals. Note, TF was only measured in the stack gas matrix as access to a total fluoride method for the solid/aqueous matrices was not commercially available at the time of the study.

The large statistically significant positive NMF of fluoride from the SSI ( $16 \pm 4.2 \text{ kg}/\text{day}$ ) was unanticipated. While the NMF of total PFAS at the SSI was not statistically significantly different from zero, the result was  $-0.00057 \pm 0.00045 \text{ kg}/\text{day}$ , indicating PFAS were potentially being mineralized. On a fluoride basis, this NMF was  $-0.00036 \text{ kg}/\text{day}$ , meaning the IF NMF was approximately 44,000 times larger than the loss of all target PFAS as fluoride, indicating other mechanisms must be responsible for the large IF NMF. While the data produced in this study do not provide insights into the possible mechanism(s), we provide two possible explanations. The first being that previously uncharacterized PFAS or other fluorine-containing compounds (e.g., pharmaceuticals, pesticides, and herbicides) may have been present in the influent to the SSI and thermally degraded to IF. While common PFAS compounds were well characterized by the methodologies used in this study, the total universe of PFAS compounds characterized is a small percentage, lending this as a possibility. For this to be practical, however, the mass of the previously uncharacterized PFAS would need to exceed the fluence for the known PFAS compounds. Alternatively, only water soluble, extractable IF was measured in these matrices. Fluorine atoms covalently bound in other compounds and water insoluble IF salts (e.g.,  $\text{CaF}_2$ ) were not measured. Therefore, a second possible explanation is that IF present in the influent to the SSI but otherwise sequestered as an insoluble IF salt or other IF bound to organic matter prevented the fluoride from being analyzed in the influent by the analytical methodologies used in this study. The thermal treatment by the SSI may have liberated the fluoride, thus providing a form that is amenable to IC or ISE and therefore analyzed in the effluent. Additional effort is recommended to understand the fluoride mass balance through the SSI.

## 4. Conclusion

During a two-day field study at a WWTP operating an SSI, PFAS and IF concentrations and mass flows from all primary influents/effluents were characterized. PFAS concentrations were within the range of that observed at other WWTPs, with total PFAS in the treated water effluent exceeding that in the raw influent. However, while PFAS NMF was positive at the WWTP level as observed in previous studies, the robust hypothesis testing found that no statistically significant net production or breakdown of PFAS occurred. The NMF of fluoride at the WWTP level was nearly zero.

At the SSI level, DREs for individual PFAS varied between <0 up to 99 %, with five compounds (PFHxA, PFDA, PFOS, NMeFOSAA, and NEtFOSAA) and one class (PFSA) having a statistically significant negative NMF. Each of these compounds had significant influent contributions from sewage sludge, the primary matrix in which destruction is expected through the SSI. Nonetheless, the total PFAS DRE was 51 % and not statistically significant, suggesting the entire SSI system may inadequately remove PFAS and might require process optimization to achieve consistent and higher removal efficiencies. Such optimizations could include updating

incinerator temperature, incinerator residence time, and/or replacing PFAS-laden treated water introduced to the venturi/tray scrubber with PFAS-free water. IF was primarily observed in the wet ash slurry, and the statistically significant positive NMF indicate other uncharacterized PFAS or fluorine-containing compounds were potentially breaking down, or unextractable/unmeasurable organically bound IF present in the influents potentially released measurable IF in the effluent after thermal treatment. Additional effort is recommended to understand the fluoride mass balance through the SSI.

Nearly all environmental discharges of PFAS from the WWTP went to the adjacent river, with <0.5 % being landfilled or emitted to the atmosphere. Consistent with these results, dispersion modeling showed the stack gas plume's contribution to ambient air PFAS concentrations within the modeled domain were negligible on both study days.

## 5. Future research needs

While the present study is, to the authors' best knowledge, the most thorough assessment of PFAS at the various inflows and outflows of a WWTP/SSI, inclusive of the gas phase emissions released from the SSI, future studies can expand on the matrices sampled and compounds measured. While the bar rack effluent is likely a small source of PFAS and IF to the overall WWTP system, future assays of this matrix can nonetheless provide a more complete account of the fate and transport of these pollutants. The volatilization of PFAS can also be quantified from the aeration tanks, clarifiers, and wet ash slurry lagoons to further characterize WWTP features' (alongside the incinerator stack gas) influence on downwind ambient air concentrations. Further, future research performing high resolution mass spectral techniques can identify many additional PFAS not included in the standard targeted analysis performed here, which measured between 18 and 30 target PFAS per matrix.

The DREs reported here represent the losses of a given target PFAS or PFAS class, without respect to the potential for species to be partially broken down into unmeasured products of incomplete combustion. Future research measuring full mineralization can provide a more complete understanding of the breakdown of PFAS during incineration. Further, only water-soluble fluoride, a subset of inorganic fluoride, was measured in the solid and aqueous matrices as access to a total fluoride method at the time of the study was not commercially available. Therefore, additional research could provide a more complete understanding of the fluoride mass balance through the WWTP and SSI.

Conclusions regarding the net production or loss of some PFAS families could not be drawn given elevated background levels, concentration variability, and the limited study period. Future extended studies utilizing more sensitive analytical methods could provide more definitive conclusions. Lastly, care should be taken to avoid extrapolation of these results to different seasons, other publicly-owned treatment works, or incineration of AFFF and other PFAS-containing matrices.

## CRediT authorship contribution statement

**Brannon A. Seay:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **Kavitha Dasu:** Conceptualization, Methodology, Validation, Data curation, Writing – original draft, Visualization, Supervision. **Ian C. MacGregor:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization, Supervision, Project administration. **Matthew P. Austin:** Conceptualization, Methodology, Software, Validation, Formal analysis, Data curation, Writing – original draft. **Robert T. Krile:** Conceptualization, Methodology, Validation, Formal analysis, Writing – original draft. **Aaron J. Frank:** Conceptualization, Methodology, Validation, Writing – original draft. **George A. Fenton:** Methodology, Software, Formal analysis, Writing – original draft. **Derik R. Heiss:** Investigation, Writing – original draft. **Rhett J. Williamson:** Investigation, Writing – original draft. **Stephanie Buehler:** Conceptualization, Writing – original draft.

## Data availability

Data will be made available on request.

## 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.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.162357>.

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