



Per- and polyfluoroalkyl substances (PFAS) in Canadian municipal wastewater and biosolids: Recent patterns and time trends 2009 to 2021

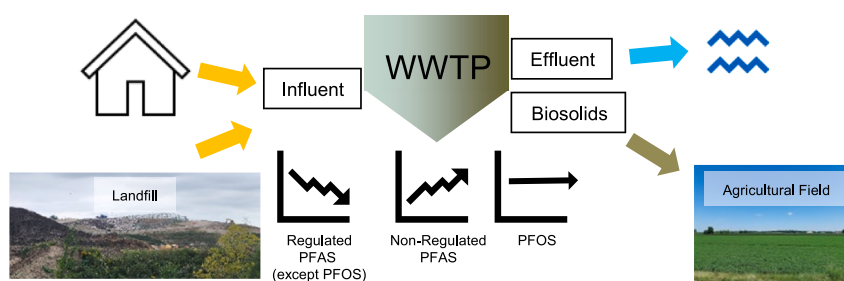
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HIGHLIGHTS

- PFAS were generally higher at WWTPs that receive landfill leachate.
- Short-chain PFAS generally increased over time in wastewater and biosolids.
- Except for PFOS, long-chain PFAS generally decreased over time.
- PFOS did not change with time indicating slow response to phase-outs/regulations.

GRAPHICAL ABSTRACT



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ABSTRACT

The concentrations of per- and polyfluoroalkyl substances (PFAS) were determined in raw influent, final effluent, and treated biosolids at Canadian wastewater treatment plants (WWTPs) to evaluate the fate of PFAS through liquid and solids trains of typical treatment process types used in Canada and to assess time trends of PFAS in wastewater between 2009 and 2021. Data for 42 PFAS in samples collected from 27 WWTP across Canada were used to assess current concentrations and 48 WWTPs were included in the time trends analysis. Although regulated and phased-out of production by industry since the early 2000s and late 2000s/early 2010s, respectively, perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and other long-chain PFAS continue to be widely detected in Canadian wastewater and biosolids. Short-chain PFAS that are not currently regulated in Canada were also widely detected. In general, elevated concentrations of several PFAS were observed at WWTPs that receive landfill leachate. Except for PFOS, concentrations of long-chain perfluoroalkyl carboxylates (PFCAs) and perfluoroalkane sulfonates (PFSAs) generally decreased over time in influent, effluent, and biosolids, which is attributable to industrial production phase-outs and regulations. Concentrations of PFOS did not decrease over time in wastewater media. This indicates that regulatory action and industrial phase-outs of PFOS are slow to be reflected in wastewater. Concentrations of short-chain PFCAs in wastewater influent and effluent consistently increased between 2009 and 2021, which reflect the use of short-chain PFAS as replacements for phased-out and regulated longer-chained PFAS. Short-chain PFAS were infrequently detected in biosolids. Continued periodic monitoring of PFAS in wastewater matrices in Canada and throughout the world is recommended to track the effectiveness of regulatory actions, particularly activities to address the broad class of PFAS.

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) have garnered much public interest in recent years and attention continues to grow. This is due in part to findings of widespread health risks associated with even low-level PFAS exposures (Cousins et al., 2022; Fenton et al., 2021). Municipal wastewater effluent discharges and land application of treated biosolids have been identified as important pathways of per- and polyfluoroalkyl substances (PFAS) to aquatic and terrestrial environments, respectively (Elmoznino et al., 2018; Gottschall et al., 2017; Johnson, 2022). Municipal wastewater treatment plants (WWTPs) are not designed to remove chemical substances such as PFAS (Metcalf and Eddy Inc, 2003). Previous research has shown only partial removal and, in some cases, apparent formation of PFAS during some wastewater treatment processes, which was attributed to transformation of unmeasured PFAS precursors (Gobelius et al., 2023; Guerra et al., 2014; Lakshminarasimman et al., 2021; Lenka et al., 2021; Moneta et al., 2023).

Individual PFAS have been subjected to various industrial production phase-outs and regulatory actions beginning in the early 2000s (ECCC and HC, 2023a; ITRC, 2022). For example, perfluorohexanesulfonate (PFHxS), perfluorooctanesulfonate (PFOS), and perfluorodecane sulfonate (PFDS) and related precursors were phased-out of production in the early 2000s, and perfluorooctanoate (PFOA) and related precursors were phased-out of production in the late 2000s/early 2010s by North American industry (Buck et al., 2011; ITRC, 2022). The 3M Company, which has been a major producer of PFAS in North America, has announced that it will exit all PFAS manufacturing and discontinue use of PFAS in their products by the end of 2025 (3M Company, 2022). PFOS, perfluorooctanesulfonamide (FOSA), PFOA, and PFHxS as well as their salts and related compounds have been listed in the Stockholm Convention on Persistent Organic Pollutants (ITRC, 2022; UN, 2022). In Canada, three subgroups of PFAS, namely PFOS, PFOA, and long-chain perfluoroalkyl carboxylates (PFCAs), as well as their salts and precursors have been regulated under the *Prohibition of Certain Toxic Substances Regulations, 2012* (PCTSR) in Canada, with a limited number of exemptions, since 2008 (PFOS) and 2016 (PFOA and long-chain PFCAs) (EC, 2006, 2012; EC and HC, 2012; ECCC and HC, 2023a). In April 2021, the Government of Canada published a notice of intent to move forward with activities to address the broad class of PFAS (Government of Canada, 2021). In May 2023, a draft State of PFAS report and a Risk Management Scope for PFAS were published (ECCC and HC, 2023a, 2023b). The draft report proposed to conclude that the broad class of PFAS meets the criteria for toxic to the environment and human health under the *Canadian Environmental Protection Act, 1999* (ECCC and HC, 2023a).

A few studies have recently evaluated the time trends of PFAS in wastewater. Cookson and Detwiler (2022) performed a meta-analysis of the time trends of eight PFAS in effluents of WWTPs in 21 countries using previously published data. They found that despite shifts in the manufacturing of PFOA and PFOS, concentrations of these two substances did not decrease significantly between 2004 and 2020 in most countries (Cookson and Detwiler, 2022), which they hypothesized was due to their global persistence, the recirculation of historically manufactured and released PFAS, and/or lack of enforcement of regulations. In comparison, concentrations of short-chained PFAS increased over time, reflecting their increasing use by industry. Cookson and Detwiler (2022) only included two years of data (2009 and 2010) collected from Canadian WWTPs and their results from other countries could have been affected by intra-country variability. In contrast, PFOA, PFOS, perfluoroheptanoate (PFHpA), perfluorononanoate (PFNA), and perfluorodecanoate (PFDA) generally decreased between 2012 and 2021 in effluent from a WWTP in Nevada, USA (Thompson et al., 2022). In an Australian WWTP, concentrations of most of the PFAS evaluated decreased between 2010 and 2020 in influent, with the exception of some short-chain substances (Gallen et al., 2022). These previous studies

have mostly focused on WWTP effluent, with the exception of the study by Gallen et al. (2022) who assessed influent. Therefore, there is a lack of information on the time trends of PFAS in both influent and biosolids. Furthermore, there is, to our knowledge, no information on the current status and time trends of PFAS concentrations in Canadian wastewater. This information is needed to assess the impact of regulatory actions in Canada.

The first objective of this study was to assess concentrations of 42 PFAS in raw influent, final effluent, and treated biosolids collected from 27 representative Canadian WWTPs in 2018, 2019, and 2021. The second objective was to evaluate PFAS concentration changes during wastewater treatment for five treatment process types. The third objective was to evaluate whether PFAS concentrations have changed in wastewater matrices over time by comparing data for recent samples with those collected between 2009 and 2015 for influent and effluent and between 2009 and 2016 for biosolids. The results of this study provide data that are critical for measuring the effectiveness of risk management actions on PFAS in Canada and to guide future measurement and management of PFAS in the Canadian environment and throughout the world.

2. Methods

2.1. Sample collection

Twenty-seven WWTPs were included in the 2018 to 2021 sampling campaigns for PFAS (Table S1.1 of Supplementary Information (SI) 1). Influent and effluent samples were collected from all WWTPs. Biosolids were collected from all WWTPs that generate them, as noted in Table S1.1. These WWTPs were selected to represent typical treatment systems and geographic variations in Canada. Of the WWTPs included in the 2018 to 2021 monitoring, eight were previously monitored between 2009 and 2011 and nine were previously monitored between 2013 and 2016 (Table S1.1). The WWTPs are participating in this program on the condition of anonymity; therefore, they are described only by process type and flow (size) in Table S1.1.

Raw influent, final effluent, and treated biosolids were sampled on three consecutive weekdays (Table S1.1). Twenty-four-hour equal volume composite samples of influent and effluent (prior to April 2015: 400 mL every 30 min; April 2015 to date: 200 mL every 15 min) were collected at most plants (Table S1.1). However, grab samples were necessary for influent and/or effluent at some plants because the flow characteristics and access were not amenable to composite sampler installation (Table S1.1). Influent and effluent samples were collected concurrently with no compensation for the hydraulic retention time (HRT) of the processes. Biosolids samples were collected as grabs. The sludge collection and treatment processes inherently composite the solids due to the retention time in clarifiers and digesters. Process temperature was measured on each sampling day. The measured average daily flows (m^3/d) and process temperatures for each plant are listed in Table S1.1.

Refrigerated autosamplers (HACH Company, Loveland, CO, USA) were used for all composite sample collection. The samples were collected into 18 L stainless steel canisters that had been cleaned with Contrad 70 detergent (Decon Laboratories, Inc., Bryn Mawr, PA, USA), and rinsed sequentially with methanol (reagent grade, Caledon Laboratories, Georgetown, Canada) and deionized water prior to use. Grab samples of bulk biosolids were collected into dedicated 10 L stainless steel pails that had undergone the same cleaning procedure. Bulk raw influent, final effluent, and biosolids samples were subdivided into Nalgene™ High Density Polyethylene bottles (Thermo Fisher Scientific, Waltham, MA, USA). Samples were packed in coolers with natural ice and shipped by overnight courier to the laboratories or stored at 4 °C prior to arrival at the laboratories.

Some of the data collected prior to 2018 have been previously published; specifically PFAS concentrations in influent, effluent, and

biosolids collected between 2009 and 2011 have been reported in [Guerra et al. \(2014\)](#) and PFAS measured in biosolids collected in 2015 and 2016 have been reported in [Lakshminarasimman et al. \(2021\)](#). The samples were collected by the same team and temporal trend analyses were conducted on data generated by the same analytical laboratory to optimize consistency over time.

2.2. Analytical methods

Chemical and instrumental analysis as well as quality assurance and quality control (QA/QC) methods and results are described in SI 2. Perfluoroethylcyclohexane sulfonate (PFECCHS) and perfluorobutanesulfonamide (FBSA) were analyzed at Environment and Climate Change Canada (ECCC) in the laboratory of Dr. Amila De Silva (Table S1.2). All other PFAS were analyzed by SGS AXYS Analytical Services Limited (SGS AXYS, Table S1.2). SGS AXYS is accredited by the Canadian Association for Laboratory Accreditation Inc. (CALA). The methods used by SGS AXYS for PFAS analysis described here were recently used as the basis of draft EPA Method 1633 for measurement of PFAS in aqueous, solid, biosolids, and tissue samples ([USEPA, 2022](#)). SGS AXYS has participated in numerous round robins and intercalibration studies where its proficiency in PFAS analysis was demonstrated.

For the SGS AXYS methods, prior to 2018 influent and effluent samples were analyzed according to in-house method MLA-060 and biosolids were analyzed according to in-house method MLA-041. Samples collected in 2018 and later were analyzed with SGS AXYS in-house method MLA-110, which is an update of MLA-060 and MLA-041. The methods used identical sample cleanup/preconcentration with weak anion exchange (WAX) solid phase extraction (SPE). As detailed in SI 2, spiked matrix and blank data showed that the methods performed with similar degrees of accuracy, precision, and blank performance. A major difference between MLA-060 and MLA-110 for influent and effluent samples was that prior to 2018, samples were filtered; samples collected between 2009 and 2011 were filtered through a 0.45 μm Nylon filter and samples collected in 2015 were filtered using a 0.5 μm glass fiber filter. Samples collected in 2018 and later were not filtered. Additional differences between the MLA-060/MLA-041 and the MLA-110 methods for both aqueous and biosolids samples included the use of a larger suite of isotopically labeled standards in MLA-110, the instrument used for analysis (high-performance liquid chromatography (HPLC) for MLA-060/MLA-041 versus ultra-high performance liquid chromatography (UHPLC) for MLA-110), the analytical column, and treatment of calibration standards. MLA-060, MLA-041, and MLA-110 are accredited to ISO 17025 standards by the Canadian Association for Laboratory Accreditation Inc. (CALA) and SGS AXYS routinely participates in inter-laboratory comparison studies. PFAS analysis at ECCC also used WAX SPE as described previously ([MacInnis et al., 2019](#); [Propp et al., 2021](#)). Samples were centrifuged prior to extraction and the liquid fraction was analyzed for PFAS. Like SGS AXYS method MLA-110, analysis was performed using UHPLC.

The influent, effluent, and biosolid samples were analyzed for conventional wastewater parameters at ECCC's National Laboratory for Environmental Testing (NLET) according to standard methods ([American Public Health Association, 2012](#)), as described in SI 2. Conventional wastewater parameter results are presented in SI 2.

The raw data for this report may be accessed at [Government of Canada \(2023\)](#).

2.3. Data analysis

For assessment of PFAS concentrations in wastewater influent, effluent, and biosolids between WWTPs, data are presented separately for the following periods: 2009–2011, 2013–2016, 2018–2019, and 2021. The reasoning behind these time divisions is as follows. Samples collected during both 2009–2011 and 2013–2016 were analyzed using SGS AXYS methods MLA-060 and MLA-041 for aqueous and biosolids

samples, respectively. There was a version change between these two time periods that included minor changes to QA/QC (e.g., the surrogate standards used to quantify FOSA was $^{13}\text{C}_4$ -PFOS in 2009–2011 but changed to $^{13}\text{C}_8$ -FOSA in 2013–2016). Except for PFECCHS and FBSA, samples collected during 2018–19 and 2021 were analyzed for PFAS using MLA-110 and there was a version change between the two periods, with additional PFAS included in the 2021 version. PFECCHS and FBSA were analyzed in samples collected in 2019 at ECCC.

Statistical analysis methods were selected for their ability to handle censored measurements, and were described previously ([Helsel, 2012](#)). Statistical analysis was conducted using R Version 4.2.2. Statistical differences between WWTPs in PFAS concentrations in influent and biosolids were assessed using the non-parametric Kruskal-Wallis test. Statistical differences between WWTPs in PFAS removals were also assessed using the Kruskal-Wallis test. This test was implemented with the *kruskal.test* function of the *stats* package ([R Core Team and contributors worldwide, 2018](#)). Given that significant differences between WWTPs were identified, unplanned multiple comparisons were performed with the Dunn's test for pairwise multiple comparisons of ranked data using the *dunn.test* function of the *rstatix* package ([Kassambara, 2023](#)) to determine which WWTPs differed from each other ([Helsel, 2012](#); [Helsel et al., 2020](#); [Quinn and Keough, 2002](#)). The *p*-values in the Dunn's test were corrected for false discovery rate using Bonferroni's formula, as recommended by [Helsel \(2012\)](#).

Removal of PFAS from wastewater treatment was calculated as $(\text{Influent} - \text{Effluent}) / \text{Influent}$ expressed as a percentage using concentrations in paired influent and effluent samples collected on the same day. Only the measured PFAS were considered as there was no information available on unmeasured precursors, transformation, or breakdown substances. If the substance was detected in influent but not in effluent, the detection limit concentration in effluent was used to estimate a removal value and the resulting calculation represented the lower bound of percent removal for the data point, with the upper bound being 100%. If the substance was detected in effluent but not in influent, the detection limit concentration in influent was used to estimate a negative removal (i.e., formation) value and the resulting calculation represented the upper bound of percent removal for the data point. Removal was not calculated when a substance was not detected in both influent and effluent.

Given the presence of multiple reporting limits, the influent, effluent and biosolids data were ranked prior to conducting the Kruskal-Wallis and Dunn's tests through calculation of U-scores as described by [Helsel \(2012\)](#) using the *Usc* function of the *NADA2* package ([Julian and Helsel, 2023](#)). The percent removal datasets contained both left and right interval censored data (i.e., there were percent removal values calculated for situations when the analyte was detected in effluent and not influent and vice versa). Therefore, the *Usci* function of the *NADA2* package, which incorporates multiply censored datasets ([Julian and Helsel, 2023](#)) was used to rank the percent removal data prior to conducting the Kruskal-Wallis and Dunn's tests.

The time trends of PFAS concentrations in influent, effluent, and biosolids were evaluated across all WWTP to provide an indication of the overall time trends of PFAS in Canadian WWTPs. At each WWTP and sampling event, the median of PFAS concentrations measured on the three consecutive days was used in the regression. The significance of the regressions was determined using Kendall's tau correlation coefficient and the trend line was estimated with Akritas-Theil-Sen nonparametric regression on log-normalized concentrations, assuming a log-linear model, as recommended by [Helsel \(2012\)](#). The *ATS* function of the *NADA2* package was used for this analysis ([Julian and Helsel, 2023](#)).

The sum of concentrations of short- and long-chain PFCAs and short- and long-chain perfluoroalkane sulfonates (PFSAs) were calculated to summarize overall trends and patterns. Consistent with [OECD \(2013\)](#) and [ITRC \(2022\)](#), long-chain included PFCAs with eight or more carbons (seven or more perfluorinated carbons) and PFSAs with six or more carbons (six or more perfluorinated carbons). Short-chain included

PFCAs with seven or fewer carbons (six or fewer perfluorinated carbons) and PFSA with five or fewer carbons (five or fewer perfluorinated carbons). The concentrations were summed on a molar-basis and non-detected concentrations were assumed to be zero for these calculations. All other concentration data are presented on a mass basis. The tables and figures in the Supplementary Information present non-detect concentrations and their impact on the calculation of median concentrations.

3. Results and discussion

3.1. Recent (2018 to 2021) PFAS measurements in wastewater matrices

3.1.1. Influent

PFAS with the highest maximum concentrations in influent between 2018 and 2021 corresponded to 6:2 fluorotelomersulfonate (6:2 FTS), 5:3 perfluorooctanoate (5:3 FTCA), and perfluorohexanoate (PFHxA), followed by PFOA, perfluoropentanoate (PFPeA), perfluorobutanoate (PFBA), perfluorobutanesulfonate (PFBS), PFHxS, and PFOS (Table S1.20). Except for PFOS and PFOA, these PFAS are currently unregulated under the PCTSR in Canada. The most frequently detected PFAS with greater than ~90 % detection frequency in influent were PFPeA, PFHxA, PFOA, PFOS, PFECHS, and FBSA (Table S1.20). PFECHS was detected in 100 % of influent samples at concentrations ranging from 0.072 to 1.7 ng/L. PFECHS is not commonly measured in influent and our results were initially surprising because PFECHS is thought to be used primarily as an erosion inhibitor in aircraft hydraulic fluids (De Silva et al., 2011; ITRC, 2022; Stefanac et al., 2018) that are unlikely to be released to municipal WWTPs. PFECHS was not detected in influent of 30 WWTPs in China (Lu et al., 2021). We suspect that this chemical has other uses in Canada because many applications of PFECHS have been identified in granted patents such as for printer inks (MPART Human Health Workgroup, 2020).

Significant differences ($p < 0.01$) in PFAS concentrations in influent were observed between WWTPs for all compounds. In general, higher concentrations of PFAS were observed in the influent of WWTPs that

receive landfill leachate such as plants TB, BF, HG, and MH (Figs. 1 and S2.1). Consistent with this finding, O'Connor et al. (2022) found that landfill leachates contained higher concentrations of PFAS compared to several other types of effluent. Plant A also receives landfill leachate but contained relatively low concentrations of PFAS except for 6:2 FTS; the maximum concentration of 6:2 FTS (1060 ng/L) at Plant A was the highest of any of the WWTPs (Fig. S2.1), which provides evidence of a specific industrial source at this location.

Short-chain PFCAs, particularly PFBA, PFPeA, and PFHxA, were consistently dominant in WWTP influent, making up between 21 and 73 % of Σ_{42} PFAS on a molar basis based on medians (Fig. 2). Long-chain PFASs (primarily PFOS) and PFCAs (primarily PFOA) made up between 2.9 and 39 % and 2.4 and 22 % of Σ_{42} PFAS. In addition, 6:2 FTS and 5:3 FTCA were dominant at select WWTPs. For example, the currently used PFAS replacement chemical 6:2 FTS (ITRC, 2022; USEPA, 2021a) was dominant at P (median = 72 %). In addition, 5:3 FTCA made up a large proportion of Σ_{42} PFAS concentrations in influent at MH (median = 47 %). As discussed above, MH receives landfill leachate. 5:3 FTCA is a degradation product of 6:2 fluorotelomer substances (Hamid et al., 2020; Harding-Marjanovic et al., 2015; Zhang et al., 2021) that have many uses such as in carpets, textiles, and food packaging (Capozzi et al., 2023; ITRC, 2022; Schellenberger et al., 2019; Schwartz-Narbonne et al., 2023). In addition, 5:3 FTCA is a dominant constituent of landfill leachates (Capozzi et al., 2023; Coffin et al., 2023; Lang et al., 2017), and was shown to be released from carpet in model anaerobic landfill reactors (ITRC, 2022; Lang et al., 2016). Studies that have evaluated the transformation of several 6:2 fluorotelomer based substances indicate that 6:2 FTS and 5:3 FTCA likely undergo further transformation to short-chain PFCAs at varying rates (Hamid et al., 2020; Maldonado et al., 2022; Wang et al., 2012; Weber et al., 2022). 6:2 FTS and 5:3 FTCA have been observed previously in WWTP influent in other countries (Gallen et al., 2022; Gobelius et al., 2023; Helmer et al., 2022; Kim et al., 2022; Schaefer et al., 2023).

Other than the substances described above, emerging PFAS such as the perfluoropolyether acids: 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoate (HFPO-DA also known as GenX) and

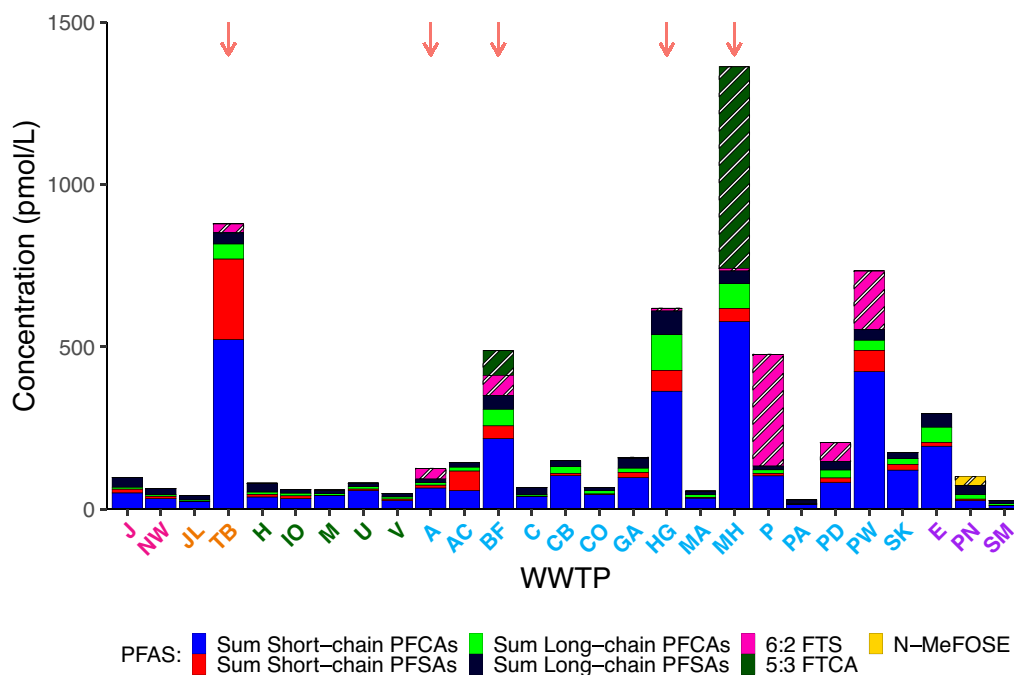


Fig. 1. Median concentrations (pmol/L) of the sum of short- and long-chain PFCAs and short- and long-chain PFSA as well as three dominant PFAA precursors, 6:2 FTS, 5:3 FTCA, and N-MeFOSE, in influent at the WWTPs evaluated between 2018 and 2021. PFCAs and PFSA are indicated with solid colours while the precursors are indicated with patterns. The WWTP colours indicate treatment type with pink, orange, green, blue, and purple showing facultative lagoons, aerated lagoons, primary, secondary, and advanced treatment types, respectively. Arrows indicate WWTPs that receive landfill leachate.

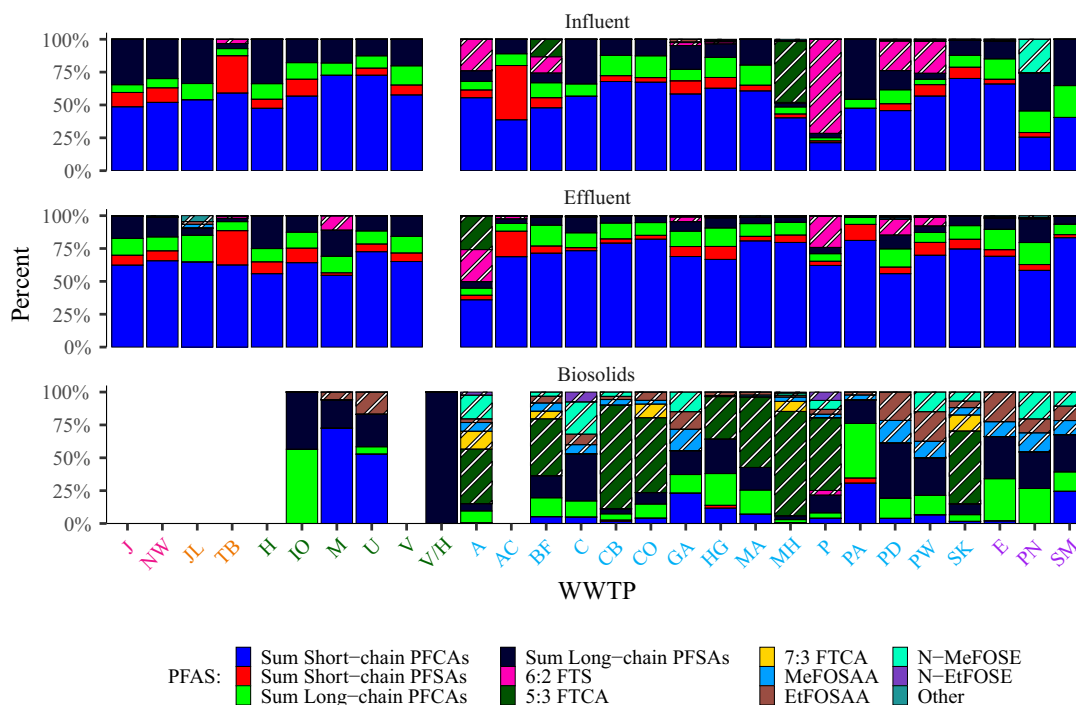


Fig. 2. Median percent contribution of PFAS compounds to Σ_{42} PFAS on a molar basis in influent, effluent, and biosolids at the WWTPs evaluated between 2018 and 2021. PFCAs and PFSAs are indicated with solid colours while all other PFAS or PFAS groups are indicated with patterns. The WWTPs colours indicate treatment type with pink, orange, green, blue, and purple showing facultative lagoons, aerated lagoons, primary, secondary, and advanced treatment types, respectively. 5:3 FTCA and 7:3 FTCA were only measured in samples collected in 2021 and hence not included in the proportions for WWTPs JL, TB, H, V, V/H, C, GA, PD, E, PN, and SM. Biosolids were not collected from lagoons J, NW, JL, and TB. Biosolids for V and H are blended and indicated by the site “V/H”.

dodecafluoro-3H-4,8-dioxanonanoate (ADONA), as well as the two components of F-53B, 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate (9Cl-PF3ONS) and 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate (11Cl-PF3OUdS), were not detected in wastewater influent (Table S1.20).

3.1.2. Effluent

Similar to influent, PFAS with the highest maximum concentrations in effluent between 2018 and 2021 were 6:2 FTS, PFHxA, PFOA, followed by PFPeA, PFBA, and PFBS (Table S1.21), which (except for PFOA) are considered short-chain perfluoroalkyl acids (PFAAs) or their precursors (ITRC, 2022; Wang et al., 2012, 2011) and are currently unregulated under the PCTSR in Canada. The detection frequency of short-chain PFCAs (specifically PFBA, PFPeA, PFHxA, and PFHpA) as well as PFBS, PFHxS, PFOA, PFOS, PFECs, and FBSA was >90 %. Similar to influent, several emerging PFAS such as the per- and poly-fluoroether carboxylates (including HFPO-DA and ADONA) and ether sulfonates (e.g., 9Cl-PF3ONS and 11Cl-PF3OUdS) were not detected in effluent samples.

The median percent contribution of long-chain PFSAs (primarily PFOS) to Σ_{42} PFAS in effluent was less compared to influent and vice versa for short-chain PFCAs (Fig. 2). Such increasing concentrations of short-chain PFAS that coincide with diminishing PFOS through WWTPs have been previously observed and attributed to the fact that wastewater may contain more short-chain compared to long-chain precursors (Kim et al., 2022). In addition, PFOS sorbs to solids to a greater extent than the short-chain chemicals during wastewater treatment (Coggan et al., 2019; Guerra et al., 2014). The relative proportion of 6:2 FTS and 5:3 FTCA also changed in effluent compared to influent, likely because these substances, which are not fully fluorinated, are transformed to substances including PFAAs, as discussed in Section 3.2. In addition, 5:3 FTCA may partition to solids during wastewater treatment to a greater extent than 6:2 FTS (Fig. 2) (Coggan et al., 2019; Schaefer et al., 2023).

Similar to influent, PFECs was detected in 100 % of effluent samples at concentrations ranging from 0.092 to 1.4 ng/L. In Nordic countries, similar or lower concentrations (0.12 to 0.35 ng/L) of PFECs were observed but this substance was only detected in 36 % of wastewater effluent samples (Aro et al., 2021).

The concentrations of PFAS in effluent are dependent on influent concentrations as well as transformation and partitioning to solids through wastewater treatment, as discussed in Section 3.2.

3.1.3. Biosolids

PFAS with the highest maximum concentrations in biosolids between 2018 and 2021 were the short-chain precursor 5:3 FTCA as well as PFBA and PFOS (Table S1.22). The most frequently detected PFAS in biosolids with detection frequency >60 % were long-chain PFCAs, PFOS, FOSA, the long-chain intermediate transformation products *N*-methylperfluorooctanesulfonamidoacetic acid (MeFOSAA) and *N*-ethylperfluorooctanesulfonamidoacetic acid (EtFOSAA), PFHxA, and 5:3 FTCA. Relatively high detection frequencies of the long-chain PFAS in biosolids compared to influent and effluent are likely a result of their greater tendency than short-chain PFAS to sorb to solids (Ebrahimi et al., 2021; Gobelius et al., 2023; Guerra et al., 2014; Helmer et al., 2022).

Significant differences ($p < 0.01$) in PFAS concentrations in biosolids were observed between WWTPs for all compounds. Patterns varied between chemical, treatment type, and WWTP (Figs. 3 and S2.2). For the majority of the PFAS evaluated, higher concentrations were generally observed in WWTPs that use anaerobic and aerobic sludge digestion compared to dewatering and alkaline stabilization. The generally elevated PFAS concentrations in biosolids treated using anaerobic and aerobic digestion could be due to transformation of unmeasured precursors, which has been shown under aerobic conditions but could also be occurring under anaerobic conditions (Lakshminarasimman et al., 2021). Any chemicals not degraded during aerobic and anaerobic digestion will instead become concentrated during treatment because

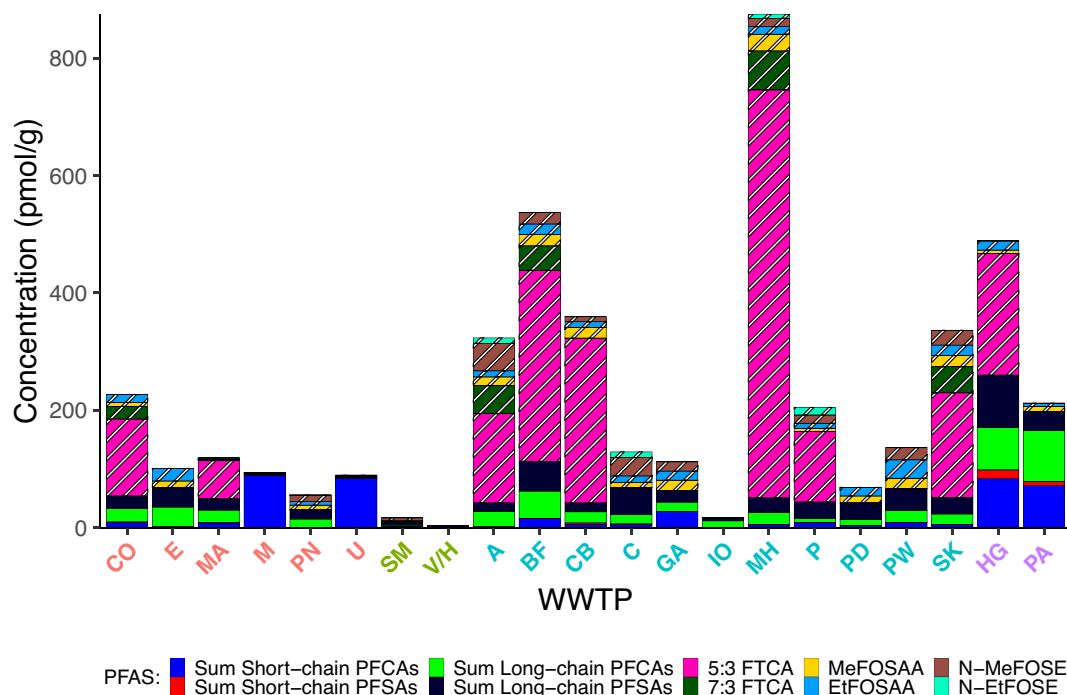


Fig. 3. Median concentrations (pmol/g) of the sum of short- and long-chain PFCAs and short- and long-chain PFASs as well as six dominant PFAA precursors, 5:3 FTCA, 7:3 FTCA, MeFOSAA, EtFOSAA, N – MeFOSE, and N – EtFOSE, in biosolids at the WWTPs evaluated between 2018 and 2021. PFCAs and PFASs are indicated with solid colours while the precursors are indicated with patterns. The WWTPs colours indicate solids treatment type with orange, green, blue, and purple showing dewatering, alkaline stabilization, anaerobic digestion, and aerobic digestion, respectively.

approximately 35 to 50 % and 56 to 66 % of volatile solids in the sludge are reduced during aerobic and anaerobic digestion, respectively (Lakshminarasimman et al., 2021; Metcalf and Eddy Inc, 2003), which is not accounted for in Figs. 3 and S2.2. Alkaline treatment involves the addition of an alkaline material to sludge for pathogen control (Metcalf and Eddy Inc, 2003) and is typically associated with reduced contaminant concentrations as a result of dilution through increased biosolids volume (Hydromantis Inc. et al., 2010a; Kim et al., 2013). However, formation of PFAS could be occurring during alkaline stabilization due to elevated pH levels (Lakshminarasimman et al., 2021). In addition, sorption of PFAS to biosolids could be affected by alkaline stabilization; Ebrahimi et al. (2021) found that sorption of PFAS to biosolids increased at elevated calcium concentrations but decreased with increasing pH. Dewatering, which is a physical operation used to reduce the moisture content of sludge (Metcalf and Eddy Inc, 2003), is not typically associated with effective removal of contaminants compared to other sludge treatment types (Guerra et al., 2015; Hydromantis Inc. et al., 2010b). We hypothesize that the extent of formation occurring during dewatering is less than other treatment types due to the absence of chemical or biological transformation. In addition to the factors discussed above, the concentrations of PFAS in biosolids are dependent on the type of wastewater treatment that preceded the biosolids treatment, the blend of primary versus waste biological sludge, and the transformation of PFAS precursors during both wastewater and solids treatment.

Most WWTPs with biosolids collected between 2018 and 2021 as part of our study contained PFOS concentrations below the proposed Canadian Food Inspection Agency (CFIA) standard of 50 ng/g (Fig. 4). The CFIA proposed standard aligns with the Michigan Department of Environment, Great Lakes, and Energy (EGLE) Interim Strategy Thresholds for PFOS concentrations in biosolids (EGLE, 2022). The only WWTP that contained PFOS concentrations >50 ng/g was HG. However, the median PFOS concentration at HG (41 ng/g) was below the proposed CFIA standard. In addition, PFOS concentrations in only three samples that were collected from HG in 2019 exceeded 50 ng/g and the samples collected in 2021 contained PFOS that were below the proposed

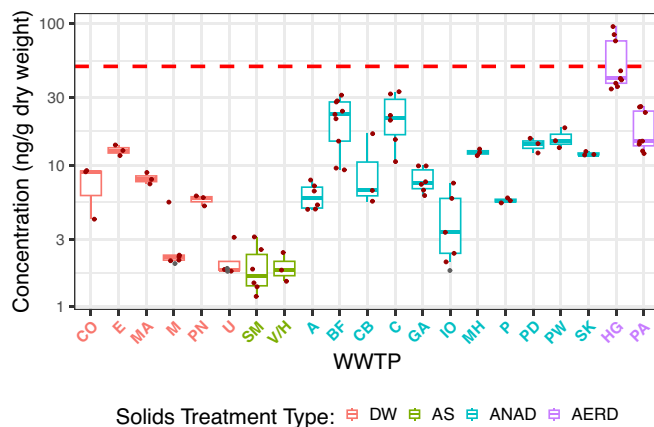


Fig. 4. Concentrations of PFOS in biosolids at the WWTPs evaluated between 2018 and 2021. DW = dewatering, AS = alkaline stabilization, ANAD = anaerobic digestion, AERD = aerobic digestion. Box plots shown if the detection frequency was >50 % for a given chemical/WWTP. The line within the boxes indicates median, the boxes indicate 25th and 75th percentiles, and the whiskers below and above the boxes indicate 10th and 90th percentiles. Dots indicate individual data points; red dots = detected concentrations, grey dots = concentrations below detection and plotted at the detection limit. The red dashed line is the Canadian Food Inspection Agency proposed interim standard of 50 ng/g dry weight for PFOS for domestic and imported biosolids intended for use as commercial fertilizers (CFIA, 2023). Note the log scale.

standard.

The dominant PFAS in biosolids varied widely between WWTPs (Fig. 2). For the majority of WWTPs, long-chain PFASs (mostly PFOS) and 5:3 FTCA were dominant. For other WWTPs, the relative proportion of PFAS was variable. In general, the patterns of PFAS in biosolids differed from those in influent and effluent, with higher contributions of the long-chain PFAS likely due to greater sorption to solids. In addition,

PFAS precursors, particularly 5:3 FTCA, were present at higher proportions in biosolids than in influent and effluent. Similarly, Schaefer et al. (2023) found that the majority of PFAS quantified in biosolids collected from 38 American WWTPs were precursors, with 5:3 FTCA and 7:3 FTCA dominating (7:3 FTCA had a median percent contribution ranging from 0 to 15 % in our study). Aro et al. (2021) also found that PFCA precursors including 5:3 FTCA dominated the PFAS profiles in biosolids samples collected from seven countries in northern Europe. 5:3 FTCA is likely formed by degradation of currently used PFAS during solids treatment and can then be further transformed to short-chain PFCAAs such as PFBA, PFPeA, and PFHxA (Schaefer et al., 2023; Weber et al., 2022; Zhang et al., 2021).

As with influent and effluent, several emerging PFAS, such as per- and polyfluoroether carboxylates (including HFPO-DA and ADONA) and ether sulfonates (e.g., 9Cl-PF3ONS and 11Cl-PF3OUds) were not detected in biosolids.

3.2. Changes in PFAS during wastewater treatment

The change of a substance in wastewater during treatment depends on both the characteristics of the substance and the type of treatment process. As shown in Table S1.23, both removal and formation of PFAS through WWTPs were occurring. Formation is attributable to transformation of PFAS precursors during wastewater treatment resulting in a higher concentration of some PFAS in effluent compared to influent (Guerra et al., 2014; Helmer et al., 2022; Moneta et al., 2023; Schaefer et al., 2023). The extent of PFAS removal is the balance of two competing processes: the amount of partitioning to solids and transformation of precursors (Gobelius et al., 2023; Kim et al., 2022; Schaefer et al., 2023).

Percent removal of two representative PFAS, PFOS and PFOA, measured between 2018 and 2021 across WWTPs are presented in Fig. 5. The percent removal of 16 frequently detected PFAS are presented in Fig. S2.3 by WWTP for 2018–2021. Removal and formation patterns varied highly within and between WWTPs. Guerra et al. (2014) previously found that formation (calculated as the inverse of removal presented in this study) values of PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFBS, and PFHxS were statistically ($p < 0.05$) different between treatment types with rank order from high to low formation as follows:

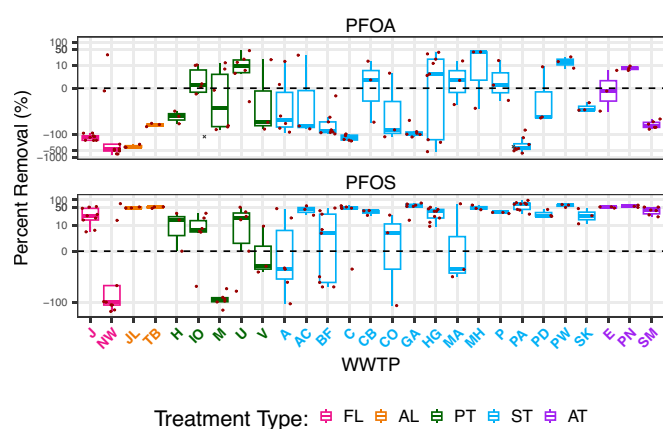


Fig. 5. Removal of two representative PFAS, PFOS and PFOA, at the WWTPs evaluated between 2018 and 2021. FL = facultative lagoon, AL = aerated lagoon, PT = primary treatment, ST = secondary treatment, AT = advanced treatment. The line within the boxes indicates median, the boxes indicate 25th and 75th percentiles, and the whiskers below and above the boxes indicate 10th and 90th percentiles. Dots indicate individual data points; red dots = removals calculated using detected concentrations and grey “x” = PFAS detected in effluent but not in influent, the detection limit concentration in influent was used to estimate a removal value, and the resulting calculation represents the upper bound of percent removal. Note the log scale.

advanced treatment > aerated/facultative lagoons > secondary treatment > primary treatment. In this study, significant differences ($p < 0.05$) in PFAS removal and formation between treatment types were observed for PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS, PFOS, MeFOSAA, and EtFOSAA. However, only patterns of short-chain PFPeA and PFHxA had evidence of greater removal at primary WWTPs compared to other treatment types (Fig. S2.3). There was considerable variation both within and between treatment types, indicating that the extent of removal and formation depends highly on factors beyond general treatment type (Fig. 5).

3.3. PFAS time trends in wastewater

The concentrations of long-chain PFCAAs decreased over time (Fig. 6), in many cases significantly ($p < 0.05$) (Figs. S2.4, S2.5, and S2.6), in influent, effluent, and biosolids, especially when detected consistently. The general decreasing time trends for the long-chain PFCAAs in influent, effluent, and biosolids reflect industrial production phase-outs and regulations.

The concentrations of long-chain PFASAs, which consist primarily of PFOS, increased significantly ($p = 0.04$) with time in wastewater influent (Figs. 6 and S2.4). These results were unexpected because PFOS was phased-out of production by North American industry in the early 2000s (ITRC, 2022) and is subject to prohibition under the PCTSR in Canada, as discussed above. The increasing concentrations of PFOS in Canadian wastewater influent differed from what has been previously observed in wastewater influent collected from an Australian WWTP (Gallen et al., 2022), where concentrations of PFOS decreased over this time period. We hypothesize that the time trends of PFOS in influent observed in this study were affected by the samples being filtered prior to 2018 but analyzed as whole water samples between 2018 and 2021. Therefore, the concentrations measured prior to 2018 in influent samples reflect the dissolved and not particulate phases and may be underestimated. In the years when filtering occurred (2009 to 2015), the concentrations of total suspended solids (TSS) in the influent samples ranged from 6.0 mg/L to 522 mg/L with a median of 138 mg/L. Cookson and Detwiler (2022) found that measured concentrations of PFAS adsorbed to suspended particulate matter were mostly between 0.01 and 1 times the concentrations of PFAS in the dissolved phase at different stages of treatment at 30 WWTPs in five countries. Similarly, in 12 American WWTPs, influent solids accounted for 1.2 to 30 % (mean = 7.4 %) of quantifiable PFAS entering the treatment plants (Schaefer et al., 2023). Filtering would have less of an effect on short- compared to long-chain PFAS and precursors because short-chain PFAS are often not detected in suspended particulate matter and they are typically found predominantly in the dissolved phase (Cookson and Detwiler, 2022; Elmoznino et al., 2018; Schaefer et al., 2023). Sorption of PFAS from the dissolved phase onto the filter was also likely occurring for aqueous samples collected prior to 2018, although its impact on the interpretation of results was likely minimal. For example, Chandramouli et al. (2015) found PFAS sorption of <15 % to the glass fiber filters that were used for samples collected in 2015. For the nylon filters that were used for samples collected between 2009 and 2011, approximately 20 %, 25 %, 30 %, and 30 % of FOSA, PFOS, PFUnA, and PFDoA, respectively, sorbed onto the filters but sorption was <15 % for the other PFAS evaluated (Chandramouli et al., 2015).

Long-chain PFSA and PFOS concentrations did not change significantly ($p > 0.05$) with time in either effluent or biosolids (Figs. 6, S2.5, and S2.6). Biosolids were analyzed as whole samples throughout the sampling period and effluent contained TSS concentrations of <5.0 mg/L to 182 mg/L with a median of 8.0 mg/L during the years where filtering occurred, which is approximately an order of magnitude less than found in influent. Therefore, it is unlikely that the time trends of PFAS in biosolids and effluent would be affected by filtering. This suggests that while the apparent increase of PFOS concentrations in influent was related to changes to the filtering protocol, the response time of

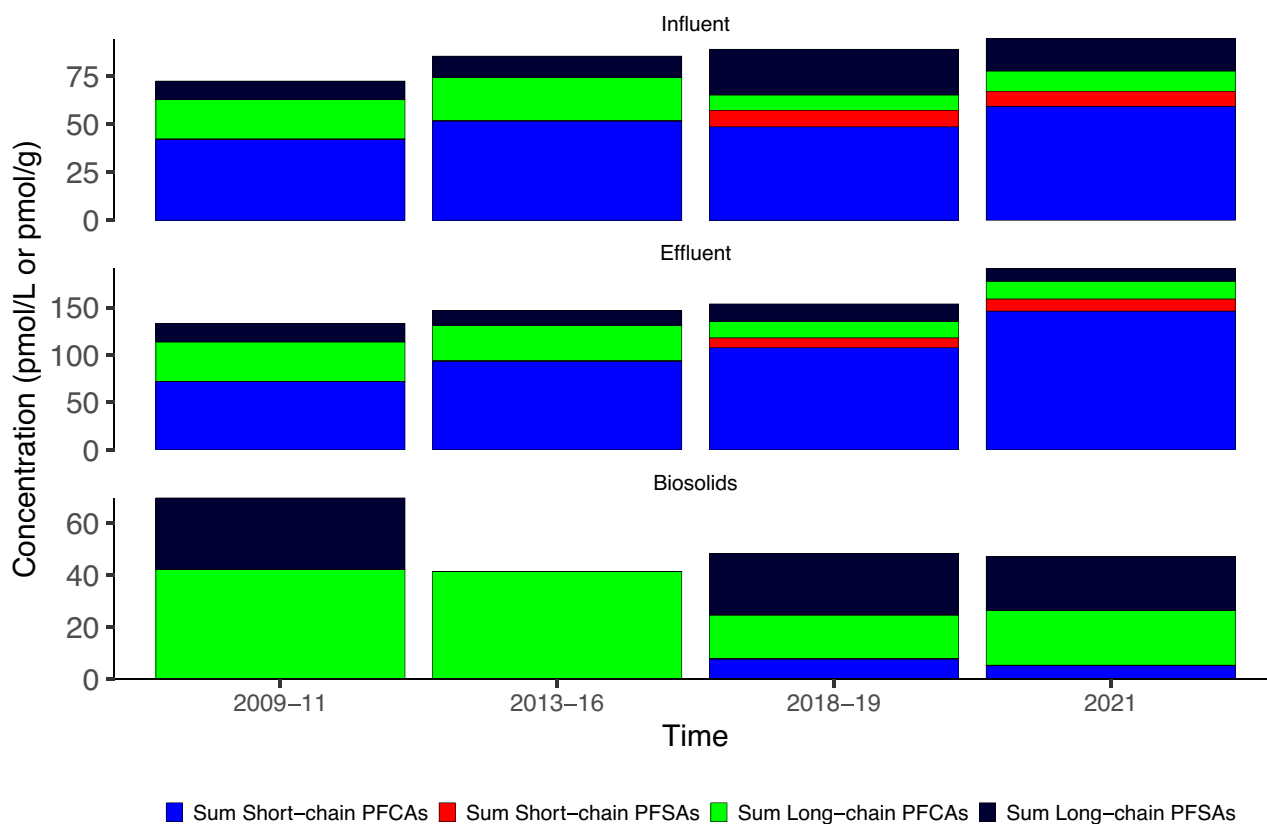


Fig. 6. Median concentrations of the sum of short- and long-chain PFCA and short- and long-chain PFSA in influent and effluent (pmol/L) and biosolids (pmol/g) across four time periods.

PFOS to industrial phase-outs and regulations is slower than other regulated PFAS. This corresponds with Cookson and Detwiler (2022) who found that PFOS did not change significantly between 2004 and 2020 in wastewater effluent from most countries but contradicts Thompson et al. (2022) who found that PFOS concentrations decreased between 2012 and 2021 in effluent from a WWTP in Nevada, USA. In addition, PFOS concentrations in Ontario source drinking water samples (including water collected from lakes, rivers, and groundwater) were significantly reduced in samples collected between 2012 and 2019 compared to samples collected between 2005 and 2007 (Kleywegt et al., 2020). In Canadian surface water, PFOS concentrations also decreased significantly between 2013 and 2020 (Lalonde and Garron, 2022). The absence of decreasing PFOS concentrations in Canadian WWTPs could be occurring because of continued presence of PFOS or its precursors in household products that are still in-use or because of the limited number of exemptions under the PCTSR. In addition, wastewater matrices are more complex compared to other media, which could lead to more variability in data and relatively low power to detect trends.

PFHxS is another substance classified as a long-chain PFSA and is of interest because it was listed in Annex A under the Stockholm Convention in 2022 and was phased-out of industrial production in the early 2000s. The concentrations of PFHxS decreased significantly ($p < 0.05$) in wastewater effluent but did not change significantly ($p > 0.05$) with time in either influent or biosolids.

Concentrations of short-chain PFCA in wastewater influent and effluent showed consistent increases that were in most cases significant ($p < 0.05$) between 2009 and 2021 (Figs. 6, S2.4, and S2.5). Such increasing patterns reflect the use of short-chain PFAS as replacements for phased-out and regulated longer-chained PFAS (Brendel et al., 2018; ITRC, 2022; Sheriff et al., 2020). PFBA and PFPeA also increased between 2013 and 2020 in Canadian surface water (Lalonde and Garron, 2022). Short-chain PFAS were not consistently detected in biosolids and did not change significantly with time in this media (Fig. S2.6).

Short-chain PFSA (predominantly PFBS) were not commonly detected prior to 2018, after which time their detection frequency and concentrations generally increased in influent and effluent (Fig. 6). PFBS has not been regulated in Canada and has been used as a replacement for long-chain PFAS, particularly for PFOS (ITRC, 2022; USEPA, 2021b). In comparison, PFBS concentrations in effluent increased across 17 countries between 2004 and 2020 (Cookson and Detwiler, 2022).

4. Implications

The occurrence and removal of PFAS in Canadian WWTPs evaluated here are summarized in Table S1.24. The results of this study show that PFAS display a variety of behaviours through wastewater treatment processes. Although regulated and phased-out of production by industry since the early 2000s and late 2000s/early2010s, respectively (ITRC, 2022), PFOS as well as PFOA and other long-chain PFSA and PFCA are widely detected in Canadian wastewater and biosolids. Currently unregulated short-chain PFAS are also widely detected, particularly in influent and effluent due to their relatively high solubility. The short-chain intermediate transformation product 5:3 FTCA as well as the regulated long-chain PFAS and their precursors were often detected in biosolids, likely due to enhanced sorption because of their larger size compared to the short-chain PFAS. Transformation of PFAS through wastewater and solids treatment plays a major role in the fate of PFAS in WWTPs, as evident from the negative and poor removal of most PFAS. This indicates that the source of PFAS differs considerably depending on the WWTP.

The results of this study illustrate how sources of PFAS to WWTPs vary throughout Canada and between countries. For example, although the currently unregulated short-chain precursor 6:2 FTS and intermediate transformation product 5:3 FTCA were seldom detected in wastewater influent and effluent in Canada, elevated concentrations were found at WWTPs where they were detected. As a second example,

PFECBS was detected in 100 % of influent and effluent samples analyzed in this current study. However, this substance was not detected in influent of 30 WWTPs in China (Lu et al., 2021) or in 36 % of effluent samples collected from seven countries in northern Europe. Third, several emerging PFAS were not detected in Canadian influent, effluent or biosolids analyzed in this study. Some of these chemicals, such as GenX, have received a lot of publicity due to elevated concentrations found near manufacturing facilities (Hupp Williamson, 2018). These substances were not detected in influent, effluent, or biosolids at other municipal WWTPs in the United States (Kim et al., 2022; Schaefer et al., 2023) or in effluent and sludge from WWTPs in seven countries in northern Europe (Aro et al., 2021). These substances are not on the Government of Canada's Domestic Substances List and have never been listed for use in Canada. However, these PFAS have been found in the wastewater of industries that are known to produce or use these substances as well as in downstream surface water (Munoz et al., 2019; USEPA, 2021a) and at some industrially impacted WWTPs (Helmer et al., 2022).

Most WWTPs with biosolids collected between 2018 and 2021 contained PFOS concentrations below the proposed CFIA standard of 50 ng/g. The use of biosolids as a fertilizer has many benefits, such as reduced landfill wastes, enhanced soil health, improved nutrient recycling, reduction of costly fertilizer use, strengthened farm economies, and improved carbon sequestration which helps combat climate change. Given that our samples were collected from a large cross-section of municipal WWTPs, the results of our study indicate that biosolids are generally suitable for application to agricultural fields with respect to PFAS when they are not impacted by industrial sources of this class of chemicals.

Time trends varied between PFAS. PFOA and long-chain PFCAs decreased in wastewater media over time. The results for PFOS were surprising; although this chemical was phased-out by industry by 2002 and regulated in Canada in 2008, concentrations in wastewater matrices indicate that the response time of PFOS to the industrial phase-outs and regulations have been slow. This could be because of the continued presence of PFOS or its precursors in household products that are still in-use or due to the complexity of wastewater matrices compared to other media leading to more variability in data and relatively low power to detect trends. Short-chain PFAS generally increased over time in influent, effluent, and biosolids, which reflects the increasing use of these substances and their precursors (Brendel et al., 2018; ITRC, 2022; Sheriff et al., 2020).

Although we quantified 42 PFAS in this study, this is a small number of the total substances in the PFAS class (OECD, 2021). Phosphate-ester surfactants such as fluorotelomer phosphate diesters made up a substantial fraction of PFAS in the particulate phase of wastewater and biosolids collected from WWTPs in the United States and Nordic countries (Aro et al., 2021; Schaefer et al., 2023) but were not measured in this current study. Further work is needed to expand the PFAS routinely targeted in wastewater monitoring programs and/or to apply techniques such as extractable organofluorine or non-target analysis (Aro et al., 2021; Schaefer et al., 2023).

Wastewater treatment processes in Canada were not designed to remove PFAS (Metcalf and Eddy Inc, 2003) and any risk management would be most effective on upstream sources. Continued periodic monitoring of PFAS in wastewater matrices is recommended to track the effectiveness of the Government of Canada's intent to move forward with activities to address the broad class of PFAS and to assess the impact of 3M's decision to phase-out all PFAS by 2025.

CRedit authorship contribution statement

Sarah B. Gewurtz: Conceptualization, Methodology, Formal analysis, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Alexandra S. Auyeung:** Conceptualization, Methodology, Formal analysis, Data curation, Writing – review & editing,

Visualization. **Amila O. De Silva:** Conceptualization, Methodology, Validation, Investigation, Resources, Data curation, Writing – review & editing, Project administration, Funding acquisition. **Steven Teslic:** Methodology, Validation, Investigation, Data curation, Writing - review & editing, Project administration. **Shirley Anne Smyth:** Conceptualization, Methodology, Validation, Investigation, Resources, Data curation, Writing – review & editing, Supervision, Project administration, Funding acquisition.

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.

Data availability

Data used in the article are available at the following link: <https://open.canada.ca/data/en/dataset/c6bbdf52-e5e4-43db-b1be-813bb4651ba3>.

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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.2023.168638>.

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