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Mass Loading and Fate of Perfluoroalkyl Surfactants in Wastewater Treatment Plants

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Wastewater treatment plants have recently been identified as a significant pathway for the introduction of perfluoroalkyl surfactants (PASs) to natural waters. In this study, we measured concentrations and fate of several PASs in six wastewater treatment plants (WWTPs) in New York State. We also monitored and measured matrix effects (ionization suppression and enhancement) by postcolumn infusion and standard additions. Concentrations of perfluorooctanoate (PFOA) in effluents of the six WWTPs ranged from 58 to 1050 ng/L. Perfluorooctanesulfonate (PFOS) was also ubiquitous in effluents of these WWTPs, albeit at much lower concentrations (3−68 ng/L). Two of these WWTPs employed identical treatment processes, with similar hydraulic retentions, but differed only in that Plant B treated domestic and commercial waste, whereas Plant A had an additional industrial influence. We found that this industrial influence resulted in significantly greater mass flows of all of the PASs analyzed. Primary treatment was found to have no effect on the mass flows of PASs. Secondary treatment by activated sludge in Plant A significantly increased ($p < 0.05$) the mass flows of PFOS, PFOA, perfluorononanoate (PFNA), perfluorodecanoate (PFDA), and perfluoroundecanoate (PFUnDA). However, in Plant B, only the mass flow of PFOA was significantly increased. The observed increase in mass flow of several PASs may have resulted from biodegradation of precursor compounds such as fluorotelomer alcohols, which is supported by significant correlations in the mass flow of PFOA/PFNA and PFDA/PFUnDA. Furthermore, the masses of PFDA and PFUnDA were significantly correlated only after the secondary treatment. In Plant A, concentrations of odd-number PFCAs were greater than those of even-number PFCAs, and concentration decreased with increasing chain length (from C8 to C12). A different pattern was observed in sludge samples, in which the dominance of PFOA decreased, and PFDA and PFUnDA increased, suggesting preferential partitioning of longer-chain PFCAs to sludge.

Introduction

Perfluoroalkyl surfactants (PASs), particularly perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), are persistent environmental contaminants; they are globally distributed and are found even in remote rural locations (*1*, *2*). PASs are characterized by a completely fluorinated alkyl chain with a hydrophilic headgroup. The strong carbon−fluorine bonds make PASs resistant to physical and metabolic degradation. PFOS is the stable end product of the degradation of most perfluorooctanesulfonylfluoride (POSF)-based perfluorochemicals. Although the production of POSF-based fluorochemicals is now being regulated, these compounds have been manufactured for use in a number of industrial and commercial products for over 40 years (*3*). Perfluorohexanesulfonate (PFHS), in addition to being measured as a residual of POSF-based fluorochemicals, has been produced for use in firefighting foams and carpet treatments (*4*). Perfluorocarboxylic acids (PFCAs), such as perfluorooctanoic acid (PFOA), are used as wetting agents in the production of fluoropolymers (e.g., poly(tetrafluoroethylene)) (*4*), and are also formed from biodegradation of precursor fluorotelomer alcohols (*5*). The oxidation pathway of telomer alcohols has been shown to proceed via telomer aldehyde and telomer acid intermediates. Telomer alcohols are widely used as surfactants and in the production of commercial and industrial materials (*6*).

The U.S. Environmental Protection Agency, together with the manufacturers and users of perfluorochemicals, is investigating the sources and exposure pathways of PASs in the environment, and an appeal has been made for researchers to aid in this investigation (*3*, *7*). Industrial and commercial wastewaters have been implicated as a likely source of PASs to the environment (*8*−*11*). Contaminated wastewaters, when directed to municipal wastewater treatment plants (WWTPs), may alter the composition and profiles of PASs in the wastewater treatment process. The ionic nature of PASs makes them highly mobile in an aqueous system, and there is a potential for these compounds to be efficiently transferred from domestic, commercial, or industrial discharge to natural waters.

To date, a few studies have reported the occurrence of PASs in wastewaters. In 1999, the 3M Company measured PFOS and PFOA in the effluent of six WWTPs (*11*). Both PFOS and PFOA were measured in the effluent of a WWTP in Iowa City, IA (*12*). Wastewaters generated by the cleaning of perfluoroalkyl surfactant-treated products and cosmetics are believed to be a possible commercial or domestic source of PASs to municipal WWTPs. However, PASs may also enter wastewater systems through industrial discharge. For example perfluoroalkyl surfactants have a number of industrial uses in specialty surfactants, additives, and coatings. The relative significance of domestic, commercial, and industrial influences on PAS contamination to wastewater treatment streams is unclear.

The distribution and fate of PASs during the wastewater treatment processes is not well documented. The fully fluorinated nature of PFOS and PFOA prevents their aerobic decomposition (*13*). However, biotransformation of the more highly substituted perfluorooctyl surfactants has been shown to occur during the wastewater treatment process. Specifically, there is evidence that 2-(*N*-ethyl-perfluorooctanesulfonamido)ethanol (N-EtFOSE alcohol) and 2-(*N*-ethyl perfluorooctane sulfonamido) acetic acid (N-EtFOSAA) are biotransformed to PFOS during activated sludge treatment (*12*, *14*). Telomer alcohols have also been shown to biotransform into PFCAs during activated sludge treatment (*15*). These precursor compounds form an additional source of PFCAs and sulfonates in the WWTP effluents. The occurrence of

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PASs in sludge from several WWTPs suggests a partioning of these compounds from the waste stream to solids during the treatment process (*9*). However, the distribution of PASs within the aqueous and solid phases of a waste stream has not been investigated.

The objectives of this study were to assess the influence of industrial sources of wastewater, and to determine the behavior of PFOS, PFOA, and their perfluorinated analogues in wastewater streams. To accomplish this, we measured PASs in effluent wastewaters of six WWTPs in New York State. Two of these WWTPs, Plant A and Plant B, employed identical activated sludge treatment processes and differed only in that Plant B was influenced by domestic and commercial discharge, whereas Plant A had an additional industrial discharge. For these two WWTPs, we collected influent, primary, and effluent wastewaters. Daily hydraulic flows were recorded for these plants, and the mass flow of PASs was calculated at each stage of the treatment. Finally, we measured these compounds in combined primary and waste-activated-sludge samples (combined sludge).

Materials and Methods

Standards and Reagents. Potassium salts of perfluorohexane sulfonate (PFHS), perfluorobutane sulfonate (PFBS), and perfluorooctane sulfonamide (PFOSA) were a gift from the 3M Company (St. Paul, MN). The potassium salt of perfluorooctane sulfonate (PFOS) was purchased from Tokyo Chemical Industries (Portland, OR). Perfluorononanoic acid (PFNA) was purchased from Avocado Research Chemicals, Ltd (Heysham, Lancashire, UK). Perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), and perfluorododecanoic acid (PFDoDA) were purchased from Fluorochem Ltd (Glossop, Derbyshire, UK). Perfluorotetradecanoic acid (PFTDA), perfluorohexadecanoic acid (PFHxDA), and perfluorooctadecanoic acid (PFOcDA) were purchased from SynQuest Lab, Inc (Alachua, FL). Perfluorooctanoic acid (PFOA) was purchased from Strem Chemicals, Inc (Newburyport, MA). 1,2 ^{13}C-labeled PFOA was obtained from Perkin-Elmer (Boston, MA). 2-Perfluorooctylethanoic acid (8:2 FTCA) and unsaturated 8:2 FTUCA were purchased from Asahi Glass Co. Ltd (Tokyo, Japan). All of the analytical standards were of ≥95% purity.

Sampling Sites. Influent, primary-treated, and effluent waters were collected from two WWTPs, referred to in this study as Plant A and Plant B. Both plants serve a moderately populated city (approximately 100 000) in New York State. Plants A and B were designed to treat daily flows of wastewater up to 35 and 25 million gallons per day (MGD), respectively. The two plants employed an identical treatment process (Figure S1, Supporting Information). Effluent wastewaters were also collected from four additional WWTPs, hereafter referred as Plants C, D, E, and F, located in New York State. These plants treated much smaller flows of wastewater than Plants A and B, and they served smaller populations. Plants C, D, and F treated domestic and commercial wastewaters at an average daily flow of 0.8, 0.4, and 1.5 MGD, respectively. Plant E treated 40% domestic waste and 60% waste from a dairy industry with a daily flow of 1.17 MGD. These plants all employed biological secondary treatment; however, Plant F operated trickling filter rather than conventional activated sludge treatment.

Wastewater and Combined Sludge Samples. Wastewaters were collected from Plants A and B during two study periods. During the first study period, wastewater samples were collected on seven dates from June 30 to October 13, 2004. During the second study period, wastewater samples were collected daily from May 22 to 26, 2005. Wastewater samples consisted of 24-h composite samples taken from raw wastewater entering the plant (influent), after primary clarification (primary), and from water leaving the plant following activated sludge treatment (effluent). These wastewater samples were collected in 500-mL polypropylene bottles, and stored at 4 °C prior to analysis. Sludge samples were collected during the second study period. Combined sludge liquors were collected in 500-mL polypropylene bottles. This liquor was air-dried and the sludge was ground with a mortar and pestle. This sludge was transferred to a 50-mL polypropylene vial and was stored at −20 °C until analysis.

Effluent wastewaters were collected from Plants C, D, E, and F from May 4 to 24, 2004. Grab samples were taken from water leaving the plant (effluent). These wastewater samples were collected in 500-mL polypropylene bottles and were stored at 4 °C prior to analysis. Samples were analyzed within two weeks from the time of collection.

Sample Extraction. Wastewaters were extracted according to a method previously described (*8*). Briefly, wastewater samples were allowed to settle, and an aliquot of 200 mL was carefully decanted into a polypropylene bottle. Each sample was spiked with 5 ng of perfluorobutane sulfonate (PFBS) and 5 ng of ^{13}C perfluorooctanoic acid (^{13}C PFOA) as internal standards. These were then passed through Oasis HLB (60 mg, 3 cm^3) cartridges (Waters Corporation, Milford, MA) preconditioned with methanol and Milli-Q water. A flow rate of 1 drop/sec was maintained through the cartridges. The cartridges were then washed with 20% methanol in water, and were dried completely under vacuum. The target compounds were eluted in 5 mL of methanol into a polypropylene tube and were concentrated under nitrogen to a final volume of 1 mL. These extracts were filtered using a 0.2-μm nylon filter into an autosampler vial with polypropylene cap.

Air-dried sludge samples were extracted according to a method recently developed (*9*), with some modifications. Briefly, 100 mg of air-dried sludge was spiked with 5 ng of PFBS and 5 ng of ^{13}C−PFOA as internal standards. The sludge was sonicated at 60 °C for 20 min in 7.5 mL of 1% acetic acid. The supernatant was removed by centrifugation at 3500 rpm for 10 min. The remaining pellet was resuspended in 1.7 mL of methanol/1% acetic acid (90:10), and was sonicated at 60 °C for 20 min. The supernatant was separated by centrifugation, and the two extractions were combined. This procedure was repeated three times to produce 27.6 mL of extract. A further 7.5 mL of 1% acetic acid was added to the extract to a final volume of 35.1 mL. The extract was passed through an Oasis HLB (60 mg, 3 cm^3) cartridge preconditioned with methanol and 1% acetic acid. A wash step of 20% methanol was applied and the cartridge was dried completely under vacuum. The target compounds were eluted in 5 mL of methanol, which was concentrated to 1 mL. The extracts were filtered using a 0.2-μm nylon filter into an autosampler vial with polypropylene cap. A portion (100 mg) of each air-dried sludge sample was placed in an oven at 100 °C for 24 h, for the calculation of moisture content.

Instrumental Analysis. Separation of PASs was performed using an Agilent 1100 high-performance liquid chromatograph (HPLC). Aliquots of 10 μL of the extracts were injected onto a 50 × 2 mm (5-μm) Keystone Betasil C_{18} column. A gradient mobile phase of methanol and 2 mM ammonium acetate was used. At a flow rate of 300 μL/min, the mobile phase gradient was ramped from 10% to 25% methanol in 7 min, then to 100% methanol at 10 min, held at 100% methanol for 2 min, and then ramped down to 10% methanol. For quantitative analysis, the HPLC was interfaced with an Applied Biosystems API 2000 tandem mass spectrometer (MS/MS). The MS/MS was operated in electrospray negative ionization mode. Analyte ions were monitored using multiple reaction monitoring (MRM) mode. Ion transitions monitored for quantitation of each analyte, together with optimized MS parameters, are shown in the Supporting Information (Table S1).

TABLE 1. Concentrations (ng/L) of PASs Measured in Effluent Waters of Six Activated Sludge Wastewater Treatment Plants in New York State

	n	max flow capacity (MGD)	sources[a]	PFOS[c,d]	PFHS[d]	PFOA[d]	PFNA[e]	PFDA[d]	PFUnDA[d]	8:2 FTCA[d]	8:2 FTUCA[d]
Plant A	12	35	D, C, I	9−68 (31)	5−39 (13)	142−398 (239)	35−376 (107)	18−47 (34)	5−10 (8)	<2.5−7 (3)	<2.5−29 (4)
Plant B	12	25	D, C	4−10 (6)	<2.5−8 (5)	66−202 (135)	4−11 (6)	<2.5−3 (3)	<2.5	<2.5−6 (2)	<2.5−4 (1)
Plant C	3	0.8	D, C	3−5 (4)	2−3 (2)	435−851 (663)	<10	<2.5	4−6 (5)	<2.5	<2.5
Plant D	6	0.4	D, C	7−11 (9)	2−4 (3)	361−1050 (697)	<10	6−13 (10)	<2.5	<2.5	<2.5
Plant E	8	1.2	D, I[b]	4−7 (5)	3−8 (6)	132−196 (165)	<10	<2.5	<2.5	<2.5	<2.5
Plant F	4	1.5	D, C	8−10 (9)	6−12 (7)	58−78 (67)	<10	<2.5	<2.5	<2.5	<2.5

[a] Wastewater sources are categorized as domestic (D), commercial (C), and industrial (I). [b] Industrial influence to Plant E is from a single dairy industry. [c] Values reported as minimum−maximum (mean). When value is <LOQ, mean is calculated using half the LOQ. [d] LOQ was 2.5 ng/L. [e] LOQ was 5 ng/L for Plant A and B and 10 ng/L for Plants C, D, E, and F.

Quantitation. Quantitation was performed using a quadratic regression fit analysis weighted $1/x$ of a single unextracted calibration curve. Seven-point calibration curves were produced from 0.1 to 100 ng/mL concentrations. The coefficient of determination (r^2) for each calibration was >0.99. Quality control standards were measured after every 10 samples to check for instrumental drift. Analysis was stopped and a new calibration curve was run if the quality control standard was not measured at ±30% of its theoretical value. PFOA was consistently found in procedural blanks and methanol injections performed between samples. This background PFOA has been shown to be continuously leached from the HPLC system and concentrated on the head of the LC column during column equilibration periods (*16*). However, since this background PFOA signal was consistent it was subtracted from the calibration curves and samples. PFOA contamination may also be introduced from fluoropolymer-containing vial caps (*3*). All procedural blank peak areas ($n = 10$) were less than half the determined limit of quantitation (LOQ) for each analyte. The LOQ was estimated as three times the lowest concentration point on the calibration curve that is accurately measured within ±30% of its theoretical value. Mean recoveries of PFBS, PFHS, PFOS, PFOSA, ^{13}C−PFOA, PFOA, PFDA, and telomer acids from all wastewaters (influent, primary, and effluent) were within ±30% of their matrix spike concentrations. Mean recoveries of PFUnDA, PFDoDA, PFTDA, PFHxDA, and PFOcDA from wastewaters ranged from 25% to 75%. PFNA recoveries ranged from 95% to 179%. Mean recoveries of all analytes from sludge were within ±30% of their matrix spike concentrations with some exceptions. PFDoDA, PFTDA, PFHxDA, PFOcDA, and PFOSA recoveries ranged from 37% to 65%.

Matrix Effects. Matrix components present in sample extracts have potential to cause ionization suppression or enhancement of PASs within the electrospray source. We have measured these matrix effects using standard addition and characterized the ionization behavior of PASs during chromatography using postcolumn infusion technique. We determined that ionization suppression occurs during a chromatographic period when non- or less-volatile matrix components elute. Some of the long-chain PFCAs that elute during this period were affected by ionization suppression. We determined that matrix effects, although present, did not significantly affect the mass flow analysis of PASs reported in this study. Details of the matrix effect studies are reported in the Supporting Information.

Statistical Analyses. Differences in concentrations and masses of PASs between WWTPs were determined using *t*-tests or ANOVA with Bonferroni post-hoc analysis. All analyses were performed using the statistical software SPSS 11.0.

Results and Discussion

PASs in Wastewaters. Care must be taken when comparing concentrations of PASs measured in the waste streams of different WWTPs. WWTPs operate a variety of treatment processes, and the effects of different combinations of these processes on PAS levels are not clear. Furthermore, specific sampling strategies also have an impact on such comparisons. PAS concentrations measured in Plants A and B represent average concentrations over a 24-h period. However, PAS concentrations measured in Plants C, D, E, and F represent PAS levels at a single time point, and could have been acquired at high- or low-flow periods.

PFOA was the dominant PAS and was measured in all six WWTPs (Table 1); this provides evidence that PFOA is constantly released into receiving waters. The highest concentrations of PFOA were measured in Plants C and D, which treated domestic and commercial wastewaters, and had no industrial influence. The concentrations of PFOA determined here are comparable to those measured in a WWTP in Cleveland, OH, in a study conducted by 3M in 1999 (*11*) (Table S2). This suggests that PFOA can occur at hundreds of ng/L concentrations in wastewaters without influence from fluorochemical manufacture or industry. Commercial wastewaters include a wide range of sources such as hospitals, shopping malls, and office buildings. However, such wastewaters are mainly generated from sanitation, and PFOA may enter these wastewaters following the cleaning of fluorochemical-treated products. Much lower concentrations of PFOA (22 ± 2.1 ng/L) were reported in effluents of a WWTP in Iowa City, IA (*12*) than were found in our study. The lower concentrations of PFOA may reflect the absence of a commercial influence to the waste stream at that site. Wastewaters treated by Plant E in our study also contained no commercial influence, but PFOA was measured at 7-fold greater concentrations than were found for the Iowa City plant. Of the waste treated by Plant E, 60% came from a dairy industry, and this could be the source of the additional PFOA.

PFOS was also measured in effluent waters of all six WWTPs (Table 1). Concentrations of PFOS were greatest in the effluents of Plant A; however, in the other five WWTPs, PFOS concentrations were similar and showed little variation. The greater concentrations found in Plant A suggest that the industrial influence to this plant provides an additional source of PFOS. Plant E, which has no commercial influence, contained concentrations of PFOS similar to those of Plants B, C, D, and F. This suggests that domestic waste is responsible for the consistent, but low, concentrations of PFOS. PFOS concentrations in the effluent waters of Plant A were from 1.5- to 161-fold lower than those in the four WWTPs with known fluorochemical exposure (*11*), and they were 2- to 14-fold lower than those in the two WWTPs with no known sources. The multi-city study was conducted in 1999, before POSF-based fluorochemicals were phased out of production, and the lower concentrations measured in our study may reflect a trend of decreasing PFOS discharges.

PFHS was found at slightly lower concentrations than PFOS in all effluent waters. This suggests that domestic waste introduces low ng/L concentrations of PFHS; the

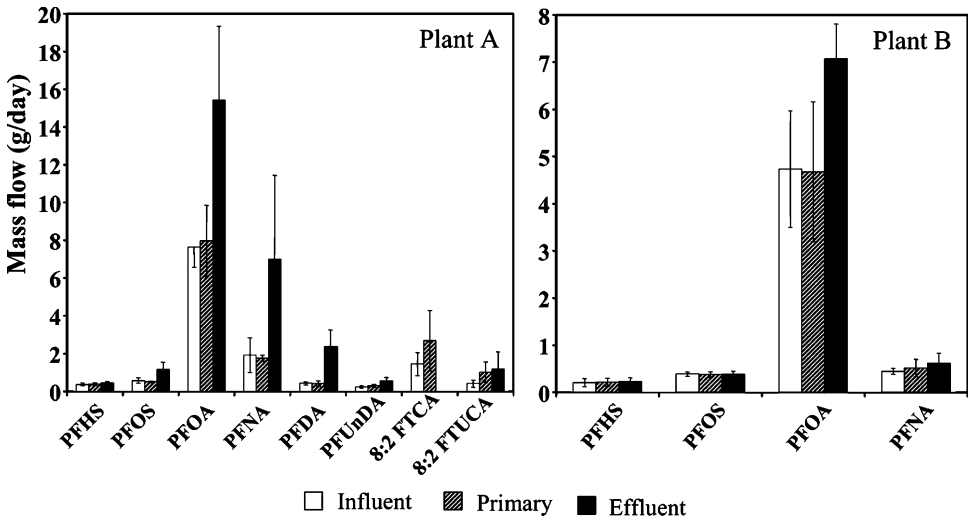

FIGURE 1. Mass flows of PASs (g/day) measured in influent, primary, and effluent waters in two wastewater treatment plants from May 22−26, 2005. Concentrations of PFDA, PFUnDA, 8:2 FTCA, and 8:2 FTUCA in Plant B samples were below limit of detection.

industrial influence to the wastewaters of Plant A provides an additional source of PFHS.

PFNA was measured at >5 ng/L (LOQ) in all effluent waters of Plant A. In Plant B, PFNA was measured at 18- fold lower concentrations than in Plant A. In the remaining WWTPs, PFNA was not found at >10 ng/L. The lower LOQ reported for PFNA in Plant A and B was a result of instrument method improvements. The high concentration of PFNA found in Plant A suggests that this plant has an industrial source enriched in either PFNA or a precursor to this compound. PFDA was measured in all effluent waters of Plants A and D. Concentrations in Plant A were 3-fold greater than those in Plant D. PFDA was not measured at >2.5 ng/L (LOQ) in any of the other WWTPs. PFUnDA was measured at >2.5 ng/L in all effluent waters of Plants A and C, but not in the other WWTPs. 8:2 FTCA and 8:2 FTUCA were measured in the effluent of Plant A at >2.5 ng/L, in 16% and 50% of the samples, respectively. These compounds were only measured at >2.5 ng/L in 16% of the samples from Plant B, and in none of the other WWTPs. PFOSA, PFDoDA, PFTDA, PFHxDA, and PFOcDA were not found in any wastewaters and are therefore excluded from further discussion.

Mass Flows During Treatment. During the second study period, daily mass flows were calculated for PASs in influent, primary, and effluent waters of Plants A and B, using recorded daily hydraulic flows (Table S3). Conversion of concentrations to mass flows allowed the normalization of the levels of PASs and corrected for the effects of precipitation. This was important, as it rained every day during the second study period with daily rainfall ranging from 0.04 to 0.41 inches.

In Plant A, PFOA was the dominant PAS entering the WWTP (Figure 1). A pattern of decreasing mass loads of PFCAs with increasing chain length (from C8 to C12) was observed. We observed an even > odd carbon PFCA pair pattern, in which PFOA > PFNA and PFDA > PFUnDA. This pattern may suggest a telomer alcohol source of PFCAs. There is some evidence to suggest that telomer alcohols, although only manufactured as even-carbon chains, may biodegrade to form even and odd PFCAs (*15*). In biota from the Canadian Arctic, a pattern of odd > even PFCA pairs was observed and the authors concluded that these were a result of the biodegradation of telomer alcohols (*17*). The different ratio of odd and even PFCAs found in biota may be a result of differential bioaccumulation and excretion.

In Plant A, no statistically significant change in the mass flow of any of the PASs was observed following primary treatment (Table S5; Figure 2). However, following secondary

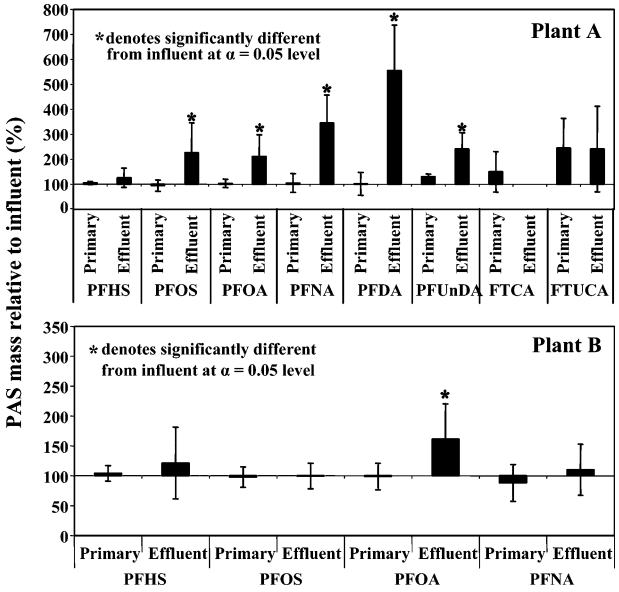

FIGURE 2. Effect of primary and secondary treatment on PAS mass balance at Plants A and B from May 22−26, 2005. Concentrations of PFDA, PFUnDA, 8:2 FTCA, and 8:2 FTUCA in Plant B samples were below limit of detection.

treatment, the mass flow of PFOS, PFOA, PFNA, PFDA, and PFUnDA was statistically significantly increased. Mass flows of PFOS, PFOA, and PFUnDA were similarly increased, by 227 ± 119%, 211 ± 87%, and 241 ± 66%, respectively. A more pronounced increase in the mass flow of PFNA (345 ± 112%) was observed. PFDA was most affected by secondary treatment, which resulted in a 556 ±182% increase in mass flow. A pattern of even > odd PFCA pairs was observed in effluent waters, similar to that seen in influent waters. 8:2 FTCA was found in influent and primary waters, but not in effluent waters. The observed removal of 8:2 FTCA may result from aerobic oxidation during secondary treatment. The mass flow of 8:2 FTUCA was not significantly changed by either primary or secondary treatment.

PFOS and PFOA are known to be nonbiodegradable by an activated sludge process (*13*). As fully fluorinated homologues, PFHS, PFNA, PFDA, and PFUnDA are expected to be equally nonbiodegradable. Therefore, a reduction in mass flow following activated sludge treatment was neither expected nor observed. The measured increase in the mass flow of PFOS, PFOA, PFNA, PFDA, and PFUnDA, following

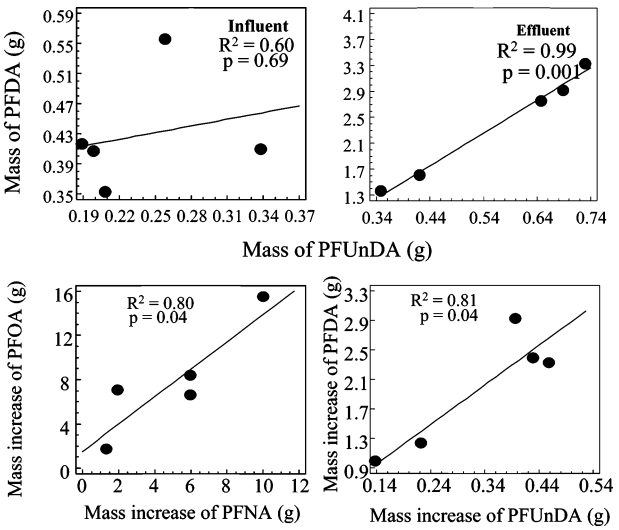

FIGURE 3. Correlations of PFDA and PFUnDA measured in influent and effluent wastewaters of Plant A (top two panels) and correlation between mass flow increases in PASs following wastewater treatment (bottom two panels).

secondary treatment, suggests an additional source of these compounds within the wastewater stream. Biodegradation of precursor compounds during activated sludge treatment is a likely source of these PASs. Specifically, POSF-based perfluorochemicals, such as *N*-EtFOSE alcohol, can biodegrade to PFOS. 8:2 FTOH may biodegrade to form PFOA and possibly to PFNA; similarly, biodegradation of 10:2 FTOH may lead to the formation of PFDA and PFUnDA (*15*, *17*).

Mass flows of PFDA and PFUnDA were not significantly correlated in influent wastewater; however, following secondary treatment, these compounds became statistically significantly correlated (Figure 3). We also found statistically significant, positive correlation between the mass flow increases of PFDA and PFNA following the secondary treatment (Figure 3). Our results suggest that these compounds are formed from the decomposition of a single precursor compound during secondary treatment.

PFNA and PFOA were not significantly positively correlated in either influent or effluent waters. However, we found significant positive association between the mass flows of PFNA and PFOA generated following secondary treatment (Figure 3). This suggests that PFOA and PFNA are not introduced to the waste stream from the same sources; however, they are generated together during secondary treatment as a result of decomposition of precursors.

Similarly to Plant A, no significant changes in the mass flow of PFHS, PFOS, PFOA, or PFNA were observed following primary treatment in Plant B (Figure 2). However, only the mass flow of PFOA was significantly increased following secondary treatment. This observed increase in the mass flow of PFOA, by 161 ± 59%, was similar, but slightly less than, that observed in Plant A. These results suggests that fluorotelomer precursors are present in Plant B wastewaters, but not at levels that result in measurable formation of PFNA, PFDA, PFUnDA, or telomer acids.

The influence of matrix effects on these observed changes in mass flow was determined by correction of each PAS concentration for the ionization suppression/enhancement experienced in each matrix. Specifically, we divided each PAS concentration by the average matrix effect measured by standard additions for that analyte within the corresponding matrix (Figure S2). Ideally, every sample would be corrected using a standard addition from the same sample; however this would generate large number samples and would be a daunting task. In Plant A, the observed increases in mass flow for each PAS became less pronounced following the correction for matrix effects (Table S5). However, the overall significance of the mass flow increases was unaffected by the correction. In Plant B, the mass flow increase of PFOA became more pronounced, and remained significant. Overall, the observed increases in mass flow of these PASs, following secondary treatment, cannot be solely explained by the influence of matrix effects.

Mass flows of PFHS, PFOS, and PFOA were significantly greater in all wastewaters of Plant A than in those of Plant B (Table 2). PFNA was significantly greater in primary and effluent waters of Plant A, and the difference approached significance for the influent waters. These results suggest that although PFHS, PFOS, PFOA, and PFNA are introduced to WWTPs through a combination of domestic and commercial sources, industrial sources introduce significant masses of PASs. In Plant B, PFDA was only measured in effluent waters, and at significantly smaller concentrations than in Plant A. PFUnDA was only measured in the wastewaters of Plant A. This suggests that industrial discharge is a significant source of PFDA and PFUnDA to wastewaters.

Overall, these results provide evidence to suggest that precursors are present in the wastewater stream and are biodegraded during secondary treatment to PFCAs. Analysis of telomer alcohols in wastewaters is needed to confirm this finding; accordingly, development of a reliable analytical method for telomer alcohols in wastewaters is warranted. In this study, we analyzed telomer acid intermediates, but they were not consistently present at quantifiable concentrations.

PASs in Sludge. PFOA was the dominant PAS found in sludge from Plant A (Table 3). PFNA was not measured at concentrations <25 ng/g, dry wt, whereas concentrations of PFDA and PFUnDA were consistently >25 ng/g (LOQ). This pattern is distinct from that observed in the wastewater, where the PFNA concentration was approximately 3-fold greater than that of PFDA, and 10-fold greater than that of PFUnDA. Lower concentrations of PFNA than PFDA or PFUnDA were previously reported in aerobically digested sludge, anaerobically digested sludge, and domestic sludge reference material (*9*). The observed dominance of PFOA measured in wastewater was reduced in sludge. Concentrations of PFOA in effluent waters were 5.8- and 25-fold greater than those of PFDA and PFUnDA, respectively. However, concentrations of PFOA in sludge were 2.9- and 3.3-fold greater than those of PFDA and PFUnDA, respectively. These results suggest preferential partitioning of PFCAs to sludge, which increases with increasing carbon-chain length.

Concentrations of PFDA and PFUnDA were highly correlated in sludge samples from Plant A ($R^2 = 0.93$, $p = 0.001$), further suggesting that these compounds are introduced through the decomposition of a telomer precursor. PFOS was measured in sludge samples at concentrations ranging from 26 to 65 ng/g dry wt. PFHS was measured in one sludge sample at a concentration >10 ng/g (LOQ). Neither 8:2 FTCA nor 8:2 FTUCA was measured at a concentration of >25 ng/g in any sludge sample.

In Plant B, patterns of PASs in sludge were similar to those seen in Plant A. PFOA was the predominant PAS measured. Although measured in the waste stream, PFNA was not measured at >25 ng/g in any sludge sample. PFDA, found at concentrations lower than those of PFNA in the waste stream, was measured in 80% of the sludge samples. Again, this suggests a greater partitioning of PFDA to sludge than that for PFNA, due to increased chain length. PFOS was measured at >25 ng/g in 80% of the sludge samples.

Significantly greater concentrations of PFOA were measured in sludge from Plant A than in that from Plant B ($p = 0.04$). Concentrations of PFDA were not markedly higher in the sludge from Plant A than in that from Plant B, although the difference approached significance ($p = 0.08$). PFUnDA

TABLE 2. Comparison of PAS Mass Flows in Wastewater Treatment Plants A and B in New York State

sample	plant	PFHS	PFOS	PFOA	PFNA	PFDA[c]	PFUnDA[d]
influent	Plant A/Plant B[a]	1.8	1.5	1.6	4.3	N/A	N/A
	significance (p)[b]	0.011*	0.028*	0.004*	0.085	N/A	N/A
primary	Plant A/Plant B	1.8	1.4	1.7	3.4	N/A	N/A
	significance (p)	0.008*	0.003*	0.016*	0.001*	N/A	N/A
effluent	Plant A/Plant B	2.0	3.1	2.2	11	8.7	N/A
	significance (p)	0.002*	0.009*	0.002*	0.032*	0.005*	N/A

[a] Plant A/Plant B represents how much greater the mass flow was in Plant A than in Plant B. [b] *Denotes significance at $\alpha = 0.05$. [c] PFDA was only measured at >LOQ in the effluent of Plant B. [d] PFUnDA was not measured at >LOQ in Plant B wastewater.

TABLE 3. Concentrations of PASs (ng/g, oven dry wt) in Combined Sludge Samples from Wastewater Treatment Plants A and B[a]

	oven-dry/air-dry	PFHS[b]	PFOS	PFOA	PFDA[c]	PFUnDA
			Plant A, $n = 5$			
median	0.10	<10	28	134	46	40
mean[d]	0.12	<10	37	144	52	60
SD	0.04		17	63	26	35
range	0.09−0.18	<10−18	26−65	69−241	25−91	35−115
			Plant B, $n = 5$			
median	0.11	<10	32	80	30	<25
mean	0.14	<10	25	70	27	<25
SD	0.08		12	29	12	
range	0.08−0.29	<10	<10−34	18−89	<25−39	<25

[a] PFOSA, PFNA, PFDoDA, PFTDA, PFHxDA, PFOcDA, 8:2 FTCA, and 8:2 FTUCA were not measured at >25 ng/g (LOQ) in any samples. [b] LOQ for PFOS, PFHS, and PFOA was 10 ng/g. [c] LOQ for PFDA and PFUnDA was 25 ng/g. [d] Concentrations of half the LOQ were estimated for the determination of mean values.

was measured in all sludge samples from Plant A at concentrations >25 ng/g, but in none of the samples from Plant B. Unlike in wastewater, there was no significant difference between PFOS concentrations in sludge from Plants A and B. PFHS, PFOSA, PFDoDA, PFTDA, PFHxDA, PFOcDA, and telomer acids were not measured in any sludge sample.

In sludge extracts from both plants, PFDA experienced ionization enhancement: 144 ± 28% for Plant A and 135 ± 8% for Plant B. Correction of the PFDA concentrations for ionization enhancement did not affect the significance of the comparisons or correlations discussed. The remaining PASs measured in sludge were relatively unaffected by ionization suppression and enhancement.

On the basis of the PAS concentrations measured in the effluent waters of Plants B, C, D, and F, the results of this study suggest that for every million gallons of domestic and commercial waste treated, a New York State WWTP will discharge 17 ± 10 mg of PFHS, 27 ± 10 mg of PFOS, and 1.3 ± 1.2 g of PFOA. While domestic waste appears to provide a consistent source of PFOS, commercial waste introduces higher and more variable levels of PFOA. Sanitation discharge following the cleaning of fluorochemical-treated products, and the use of personal care products such as shampoos and conditioners are the likely sources of PFOA in domestic and commercial wastes. Industrial discharge was shown to provide an additional source of PFOS, PFHS, and PFOA, as well as introducing measurable mass flows of PFNA, PFDA, and PFUnDA. Precursors, such as POSF-based perfluorochemicals and fluorotelomer alcohols, are most likely introduced to the waste steam from these industrial sources. Following activated sludge treatment, these precursors biodegrade and produce additional mass flows of PASs, including PFCAs. In this study, special attention has been paid to matrix effects. Greater matrix suppression of PASs should occur in influent and primary wastes than in effluent waters. The increase in mass flow of PASs in effluent waters, relative to influent and primary waters, is observed following correction for measured matrix effects. Overall, the consistent discharge of PFOS and PFOA into receiving waters is of particular concern. Although lower levels of PFOS than PFOA are discharged, PFOS is significantly more bioaccumulative than PFOA (*18*). This study provides further evidence that PASs are not removed from wastewater by conventional treatment. An effective strategy for reducing their contamination of the environment should include the removal of PASs and their precursors from domestic, commercial, and industrial sources.

Supporting Information Available

Additional Materials and Methods section, matrix effect results, generalized wastewater treatment flow scheme, ionization supression/enhancement of PASs in various WWTP matrices, chromatographic analysis data, mass spectrometric parameters, concentration results from other studies, weather conditions and hydraulic flow rates for the tested WWTPs, measured mass flows of PAS, significance of primary and secondary treatments on PAS mass flows, and supplementary references. This material is available free of charge via the Internet at http://pubs.acs.org.

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