OCCRRENCE OF PERFLUORINATED ORGANIC COMPOUNDS IN WASTE WATER TREATMENT PLANT SAMPLES FROM KENTUCKY AND GEORGIA, USA

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Introduction

Fluorinated Organic Compounds (FOCs) are emerging environmental pollutants in the global ecosystem[1-9]. Particularly, perfluorooctane sulfonyl fluoride (POSF) based compounds have been widely used in variety of industrial applications and domestic products[3]. Earlier studies have reported FOC residues in environmental (air, water), biological (fish[2], crustaceans, oysters[4], mink, otters[5], marine mammals[6], birds[7,8], humans[1]), and fast food[9], samples from various parts of the world as well as in remote pristine environment such as Arctic and Antarctic[2]. Detailed studies on the sources and sinks of FOC contamination are essential in order to prevent further contamination and protect wildlife and humans from possible health effects.

The discharge of municipal wastewater effluents is one of the important routes of introducing organic chemicals that are used in domestic and industrial activities into aquatic environments. Very limited information is available on the FOC levels in waste water treatment samples including prior to treatment, at various stages of treatment, and after treatment. In this study, we measured FOC concentrations in sewage samples collected from waste water treatment plants (WWTPs) in western Kentucky (Plant A) and coastal Georgia (Plant B). The Plant A and the Plant B process over 19.7 and 75.8 million liters of sewage samples/day respectively. Major sources of waste water for the WWTPs were from domestic and commercial district. The objective of this study was to determine concentrations, composition and seasonal variation of various perfluorinated compounds in influent, oxidation ditch, return activated sludge (RAS), before chlorination, after chlorination and dried solids. Although initial waste water processing methods are similar in both WWTPs, Plant B incinerate the sludge, therefore, sludge sample before burning and incinerated sludge ash were collected and analyzed. The target analytes include, Perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluoroocatane sulfonate (PFOS), perfluoroocatane sulfonylamide (PFOSA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFunDA) and perfluorododecanoic acid (PFDoA) were detected and quantified.

Materials and Methods

Wide mouth (250 mL), low density polyethylene (LDPE), Nalgene bottles (Part #: 2103-0008; Nalge Nunc International, NY, USA) were used to collect the samples. Sampling was done during winter; spring, summer and fall of 2005. Wastewaters were extracted according to a method previously described[10]. 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 cc) 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[11], with some modifications. Briefly, 100 mg of air-dried sludge was spiked with 10 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. 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 cc) 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.

Separation of analytes was done using an Agilent 1100 high performance liquid chromatograph (HPLC). 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. Quantitation of each analyte 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. All procedural blank peak areas 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. LOQs for wastewater and sludge were 0.5 ng/L and 2.5 ng/g dry weight, respectively.

Results and Discussion

Among the various FOCs measured, PFOA concentration was the greatest in both Plant A and Plant B during all seasons measured (Table 1a and 1b). This provides evidence that PFOA was constantly released into receiving waters. Relatively higher concentrations of PFOA were found in Plant A samples than Plant B samples. The highest concentration (334 ng/L) of PFOA was found in Plant A samples (after chlorination process) collected

Table 1a. PFOA and PFOS concentrations in various samples collected at Plant A during various seasons.

Samples	Unit	Winter		Spring		Summer		Fall	
		PFOA	PFOS	PFOA	PFOS	PFOA	PFOS	PFOA	PFOS
INFL	ng/L	83	8.1	184	11	100	16	22	7.0
OxD	ng/L	163	41	254	19	185	15	76	9.9
OD-S	ng/gdw	33	120	62	154	117	217	36	124
B-Cln	ng/L	187	23	211	12	83	11	110	11
A-Cln	ng/L	NA	NA	334	13	NA	NA	NA	NA
Effl	ng/L	155	14	183	8.0	122	13	149	28
RAS L	ng/L	173	47	334	25	158	13	82	12
RAS	ng/gdw	86	176	62	133	151	990	178	640
Dry-S	ng/gdw	219	95	16	110	20	43	8.3	8.2

INFL=Influent; OxD= Oxidation Ditch; ODS= Oxidation Ditch Solids;

B-Cln= Before chlorination; A-Cln= After chlorination; Effl= Effluent; RAS L= Return Activated Sludge Liquid;

RAS= Return Activated Sludge Solids; Dry-S= Dry solids for landfill.

during spring. The concentrations of PFOA determined here are comparable to those measured in WWTPs samples from New York State and Cleveland, OH[12,13]. Considering the effluent PFOA concentrations, Plant A contained comparatively higher concentrations than Plant B effluents. Plant B incinerates the solid sewage prior to disposal in to a landfill. We measured PFOA concentrations in sewage cake before and after incineration. It is interesting to note that PFOA concentrations significantly reduced after incineration process. PFOS was also measured in almost all samples analyzed. PFOS concentration varied with different sample types. The concentration varied from 7 ng/L to 47 ng/L in liquid samples. In solids, the concentration varied from 8.2 ng/g dry wt. to 990 ng/g dry wt. In general, Plant A samples contained relatively higher PFOS concentration than samples from Plant B.

Table 1b. PFOA and PFOS concentrations in various samples collected at Plant B during various seasons (Sampling was not done at this Plant during the Winter 2005).

Samples	Unit	Spring		Summer		Fall	
		PFOA	PFOS	PFOA	PFOS	PFOA	PFOS
Influent	ng/L	30	7.9	50	7.8	2.0	2.5
Primary	ng/L	33	5.4	37	7.6	1.0	3.1
A-Supernat.	ng/L	141	20	54	7.2	7.3	2.3
MLSS	ng/gdw	33	36	49	40	10	<2.5
RAS Supernt	ng/L	227	22	47	7.1	8.8	7.9
RAS	ng/gdw	NA	NA	27	54	56	70
Effluent	ng/L	102	13	52	9.3	6.7	1.8
Ash Basin L	ng/L	108	18	82	22	7.3	2.3
B-incineratn.	ng/gdw	64	38	130	61	47	77.2
A-incineratn.	ng/gdw	35	50	10	35	7.0	<2.5

A-Supernat= Aeration Supernatant; MLSS= Mixed Liquid Suspension Solid;
RAS= Return Activated Sludge; Ash Basin L= Ash Basin Water;
B-incineratn= Before incineration of solids; A-incineratn= After incineration.

PFHxS concentration was slightly lower concentration than PFOS in almost all samples. This suggests that domestic waste introduces low ng/L concentrations of PFHS. PFNA was measured at relatively lower concentration than PFOA, PFOS, and PFHxS. PFNA concentration ranged from below detection limit to 67 ng/g dry wt. Similar to PFNA, PFDA also recorded concentrations closer to detection limit (<2.5 ng/L). PFUnDA and PFDoA were rarely detected or not detected in samples. Overall, consistent occurrence of PFOA, and PFOS in effluent waters and dry solids is of particular concern. PFOS is more bio-accumulative than PFOA. This study provides evidence that FOC concentrations and compositions vary with seasons, influent characteristics and methods of waster water treatment. PFNA concentration ranged from below detection limit to 67 ng/g sludge dry weight.

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