PARTITION AND FATE OF PERFLUOROCHEMICALS IN SEWAGE SLUDGE

Ruowei, Ma
Dept. of Civil Engineering, The University of Hong Kong, HK.

Abstract
Perfluorochemicals (PFCs) are the subject of increasingly intense environmental research. The compounds are globally distributed, environmentally persistent, bioaccumulative, and potentially harmful. In this study, contamination profiles of PFCs were determined in samples collected at various stages of wastewater treatment plant in Hong Kong. A quantitative analytical method was developed that consists of liquid solvent extraction of the analytes from sediments and sludge, cleanup via solid-phase extraction, and injection of the extracts into a Ultra-performance liquid chromatography (UPLC) system coupled to a tandem mass spectrometer (LC/MS/MS). A solid-phase extraction procedure coupled with LC/MS/MS was used to isolate, identify and quantify low concentrations of PFCs in wastewater. Several PFCs were detected in samples from WWTPs and sediment. PFOS was the predominant PFCs ranged from 3.1 to 7304.9 ng/g (dry weight) in domestic sludge. The detection of PFOS in wastewaters, despite the voluntary phase-out on the production of perfluorooctane sulfonylfluoride-based chemistries in 2002, indicates that products containing these chemicals are being released into WWTPs. Data from a survey of Kai Tak and Mai Po area sediments suggest widespread occurrence of PFCs in sediments at the low ng/g level.

Introduction
Perfluorochemicals (PFCs) are the subject of increasingly intense environmental research. The compounds are globally distributed, environmentally persistent, bioaccumulative, and potentially harmful (1). PFCs comprise a class of artificial, full fluorinated organic compounds and exhibit both hydrophobic and lipophobic characteristics. These kinds of compound have been used in a variety of consumer and industrial applications for nearly 60 years. These products include protective coatings for food contact packaging, textile, carpets, paper, coats, fabric, leather; non-stick cooking material; commercial and industrial surfactants (e.g., fire-fighting foams, electroplating baths); and insecticides (1). Among these compounds, Perfluorooctane sulfonate (PFOS) and Perfluorooctanoate (PFOA) are the two chemicals that have received the most attention in recent years. They are contaminants and have been detected in wide range in the organisms in the environment, including some remote regions, like the arctic (2). PFOA is a likely human carcinogen; it causes liver, pancreatic, testicular, and mammary gland tumors in laboratory animals. PFOS causes liver and thryoid cancer in rats (3). PFCs remain in our body for years. PFOA's half-life in our bodies is estimated at more than 4 years. PFOS's half-life is estimated at more than 8 years (4). It is also shown that some PFCs were resistant to hydrolysis, photolysis, and degradation by acids, bases, oxidants, reductants, microbes and metabolism (5).

Various researches have studied the distribution of PFCs in the biota collected from all over the world, very little is known about these compounds' sources of release into the environment. Some studies have shown the discharge of wastewater effluent is a significant source of PFCs to the environment (6-8) and some data indicate that PFCs such as perfluorooctane sulfonate (PFOS) may strongly sorb to solids (9). These evidence shows that wastewater sludge is widely suspected as a major sink of PFCs entering municipal waste streams. A recent study reported detectable PFCs concentrations in Hong Kong costal waters which was near the effluent of wastewater treatment plants (WWTPs) in Hong Kong (10), but no available data on any other environmental matrices (such as wastewater, sludge and sediment) in Hong Kong.

Hong Kong contains three major WWTPs serve 7 million population. Usage of PFCs involved consumer products are expected to be the potential sources of PFCs, such as PFOS and PFOA. Assess the levels of PFCs in WWTP samples collected at various stages of the treatment process and sediment in different location in Hong Kong will fill an important knowledge gap in understanding of the scope and extent of the potential environmental problems related to PFCs.

The major challenges to accurate and reliable analyses of PFCs include procedural blanks and lack of well-developed analytical methods. The presence of blanks in various equipment items as well as the analytical instruments themselves cause difficulty of analysis of trace level of PFCs. Therefore, the objective of this study is to developed and modified an analytical methods for the detection and quantification of PFCs in wastewater and sludge in a all-pervading way and assessing PFCs levels in sludge and wastewater samples obtained from selected municipal wastewater treatment plants in Hong Kong.

Materials and methods

Chemicals and standards

Potassium salt of perfluorobutanesulfonate (PFBuS, 97%), potassium salt of perfluorohexanesulfonate (PFHxS, 98%), potassium salt of perfluorooctanesulfonate (PFOS, 98%), perfluorobutanoic acid (PFBA, 98%), perfluoropentanoic acid (PFPeA, 97%), perfluorohexanoic acid (PFHxA, 97%), perfluoroheptanoic acid (PFHpA, 99%), perfluorooctanoic acid (PFOA, 96%), perfluorononanoic acid (PFNA, 97%), perfluorodecanoic acid (PFDA, 97%), perfluoroundecanoic acid (PFUnDA, 95%),
and perfluorododecanoic acid (PFDoA, 95%), perfluorotetradecanoic acid (PFTA, 97%), and perfluorotetradecanoate (PFTrA, 97%) were purchased from Sigma-Aldrich Co (St. Louis, MO). Sodium salt of perfluoroheptanesulfonate (PFHpS, 98%), Sodium salt of perfluorodecanesulfonate (PFDS, 98%) and N-methylperfluorooctanesulfonamide (N-MeFOSA, 98%) were purchased from Wellington Laboratories (Guelph, ON). Perfluorooctanesulfonamide (FOSA, 95%) and N-ethylperfluorooctanesulfonamide (N-EtFOSA, 98%) were purchased from Wuhan Bright Chemical Co (Wuhan, Hubei). Optima grade methanol and Optima grade water was purchased from Fisher Scientific (Pittsburgh, PA), ammonium hydroxide (32%) and glacial acetic acid (100%) were from Merck (Darmstadt, Hessen), ammonium acetate was obtained from VWR International Ltd (Poole, Dorset).

Sample collection and preparation

Sludge and sediment samples were collected from six locations in Hong Kong. Samplings were performed during the winter and the fall of 2008 in the plants in Sha Tin (Plant A) and Stanley (Plant B), and during the spring and the winter of 2008 in stonecutters island WWTP (Plant C). Plant A and Plant B WWTPs serve populations of 950,000 and 27,000 respectively, and both plants employed the activated sludge treatment process. Plant C provides a chemically enhanced primary treatment serving about 3,500,000 populations. Seawater is used to flush toilets in Hong Kong. Both Plant A and Plant C contained seawater except Plant B treated non-saline wastewater. Besides we also obtained some sediment from Kai Tak and Mai Po areas and drinking water sludge from Water Supply Department in Ma On Shan (DWS). Sampling on Kai tak channel sediments were collected in 2006. Kai Tak channel sediments were major sink of the nearby airport oil and grease pollutants. The sediments from Mai Po areas were collected from 2001 to 2005. Mai Po areas were influence by the Shenzhen River from Mainland China which contains lots of factory effluent discharge. All the samples were collected in polypropylene (PP) bottles. Prior to extraction, sediment and sludge samples were oven-dried at 105^{o}C and ground and homogenized with a solvent-rinsed blender.

Sample extraction

Wastewaters were extracted in the laboratory with slightly difference according to a method previously described (10). Briefly, wastewater samples were centrifuged to get rid of some suspend particles, and 250 mL of it were loaded on Oasis HLBs (0.5 g, 6 cm^3) (Waters Corporation). Prior to load with the water sample, the cartridge was condition and equilibrates with 6 mL methanol follow by 6 mL water. Then, 250 mL wastewater samples were loaded on the cartridge. After the sample loaded, the cartridge was wash with 6 mL water follow by 6 mL 30% methanol. Finally, the cartridge was eluted with 10 mL methanol. All of the steps were maintain a follow rate at 3 mL per min. And the elute solution was evaporate under nitrogen to 1 mL. For sediment and sludge samples, modified extraction methods were performed. 1 g of sludge or 5 g of sediment samples was transferred to a 50 mL polypropylene centrifuge tube and extracted 3 times for 10 min with basic methanol (1% NH_4OH) in a 60 ^{o}C sonication bath. Extracts were then combined and acidified with acetic acid (1% by volume) and concentrated under nitrogen to 5 mL. To remove the potential matrix interferences, each sediment and sludge extract was passed through ENVI-Carb SPE Tube (1 g, 12 mL) two times and rinsed with 2.5 mL methanol. We modify the method by let the extract pass through 2 g ENVI-Carb SPE Tube and rinsed with

different volume solution from 10ml to 2.5ml and find the 2.5ml was the suitable volume to rinse the target compound from the cartridge. Most of method in the literature was used ENVI-Carb SPE Tube in a dispersive way (11, 12). Compare to this study it present a low efficiency to get rid of the impurity in environmental solid. At last, the combine solutions were concentrated under nitrogen purging to 1 mL. The extracts were filtered using a 0.2-mm nylon filter into an auto sampler vial with polypropylene cap.

Instrumental analysis

Quantification of PFCs were performed using a Waters Acquity ultraperformance LC system, Waters BEH C_{18} column, 2.1×50×1.7 (mm inside diameter × mm length × μm particle size) equipped with a Waters Acquity TQD, a tandem quadrupole mass spectrometer. To minimize background for PFCs, we substituting in polyetheretherketone (PEEK) tubing to carry the solvents and placing the Waters PFC isolator column in-line before the sample injector port assists the analytical column in separating background PFC contaminants from the samples. A gradient mobile phase of 2 mM ammonium acetate in methanol and 2 mM ammonium acetate in water/methanol (95/5) was used. At a flow rate of 0.4 mL/min, the mobile-phase gradient was ramped from 25% to 85% methanol in 5 min, then to 100% methanol at 5.10 min, and then ramped down to 25% methanol in 7 min. The MS/MS was operated in electrospray negative ionization mode. Analyte ions were monitored using the multiple reaction monitoring (MRM) mode.

Results and discussion

Accuracy and Precision

High levels of background was a big limitation to instrumental analyses of PFCs. The background comes from the fact that PFCs are in a number of laboratory appliances and results in contamination of not only samples, but also laboratory reagents (10). This contamination can come from everything from the laboratory appliances, like the auto sampler vial caps, tubings and filters. The laboratory reagents were also a contamination cause to a high background in the analysis. The reagents used in this study were Fisher Optima LC/MS grade methanol and water. We can see different response between same blank sample of using Fisher LC/MS methanol and Optima LC/MS methanol. The response was $2.38e^5$ of PFOS in blank sample use Fisher LC/MS grade methanol and laboratory MilliQ water as mobile phase. After change the mobile phase to Fisher Optima LC/MS methanol and water. The response was decreasing to $5.83e^4$. Although some PTFE components used in the UPLC system can be replaced by PEEK or stainless steel materials, it is impractical to replace all PTFE components (13). Thus, trace levels of PFC contaminants still exist. To solve this problem, the instrument was installed a residue trap to separate the background of PFC contaminants come from the UPLC and solvent from the sample. Placing the residue trap in-line before the sample injector port defers PFC contaminants response in the analytical column. During the analysis of PFCs in environmental matrices, samples or extracts should be avoided to contact with such fluoropolymers, such as polytetrafluoroethylene (PTFE) or perfluoroalkoxy compounds. Handling equipment should preferably be made of polypropylene (PP) or polyethylene (PE) materials.

Three times the standard deviation of the background levels detected in the blanks was set as the instrument detection limit (IDL). The method detection limit (MDL) was calculated base on the IDL (14). In the absence of a background in blanks, lowest quantitative standards were used. The IDL was ranged from 0.1- 1ppb, and MDL value was 0.14-1.43 ng/g for sludge, 0.03-0.29 ng/g for sediment and 0.57-5.71 ng/L for wastewater. To determine the recovery of PFCs in water sample, 0.1ppb of PFCs mixture was spiked into Optima LC/MS water samples and extracted following the same procedures used for the wastewater samples. The average recovery of the PFCs was around 80% except PFTA and PFTrA. The PFOS recovery was more than 100% due to some systematic contamination in the experiment procedure. Extraction spike/recovery experiments were performed for Stanley aeration tank sludge to evaluate the accuracy of the method. The spikes were ranging from 50 to 200ng/g. The entire compound produces a good recovery rate from 62% to 94%. Concentrations of all target analytes were quantified by using calibration curves constructed using external standards. Additional Extraction of Stanley aeration tank sludge in different weight of 0.05g, 0.1g, 0.5g, 1g and 1.5g followed the same procedures used for sludge sample were performed to determine whether the concentrations of PFCs present in the extract accurately reflected the concentrations present on the environmental solids. The PFCs extract from 1g sludge was capable to represent 99% of analytes in the sludge. Up to 1.5g the extraction efficiency was decrease.

Concentrations in wastewater
A few PFCs were detected in wastewater samples collected from Plant A and B. The results presented are collected at a single time point in one day. PFOS was the predominant contaminant in aqueous samples (19.0 – 49.9 ng/L in Plant A, 28.8 - 29.3 ng/L in Plant B). Measured PFOS concentrations were higher than levels reported for Kentucky and Georgia (15), but similar to levels reported for New York WWTPs (7). The detection of PFOS in wastewaters, despite the voluntary phase-out on the production of perfluorooctane sulfonyl-based chemistries in 2002, indicates that products containing these chemicals are being used and released into WWTPs. WWTPs are a significant source of PFCs to natural waters (16).

PFOA was detected in both Plant A and B, but lower than the MDL. The effluent concentration of PFOA (4.1 ng/L) was higher than the influent maybe due to the breakdown of precursors such as fluorotelomer alcohols (FTOHs) in the wastewater treatment process. Perfluorocarboxylates are known to be produced as biodegradation products of FTOHs in activated sludge process (17) and biodegradation of precursor compounds during activated sludge treatment is a likely source of this increase in PFOA and PFOS in the effluents (18).

PFPeA was presented a higher concentration from influent (6.3ng/L in Plant A and 8.7ng/L in Plant B) than the effluent. PFHxA, PFHpA, PFNA and PFBuS were detected in both Plants. PFBA and PFTA were detected in Plant A and below the MDL.

Concentrations in sludge
Concentration of PFOS in sludge from Plant B was 54.4 – 157.9 ng/g. PFBA was also presented a higher concentration (30.2 – 111.4 ng/g) than other 11 types of PFCs detected in Plant B. PFOS was the predominant contaminant in sludge samples (6.2 – 7304.9 ng/g) in Plant A between different sampling date. The highest PFOS concentrations were found in samples of primary sludge collected in November 13, 2008 (7304.9 ng/g). The PFOS concentration (6.2 – 8 ng/g) was lower on October 8, compare to the other two days. PFHxA and PFTA present a higher concentration (27.8 ng/g and 34.1 ng/g) than other types of PFCs detected in three different days indicate special source of these compounds were discharged to the wastewater treatment plant. PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoA, PFTrA, PFTA and PFBuS were detected in both Plants. The concentration of PFCs presents a higher value in primary sludge than other sludge and PFHpS was dectected only in primary sludge in Plant A.

We also test the sludge get from water supply department and stonecutters island WWTP (Plant C) which provide a chemically enhanced primary treatment. 3 and 69.4 ng/g of PFOS concentration was found in two different days of Plant C. And the drinking water sludge (DWS) was also found trace amount of PFCs in it. PFHxS, PFDS, FOSA, N-MeFOSA, N-EtFOSA were not detected in this study.
Potential precursors of PFOS, including FOSAA and its N-ethyl and N-methyl derivatives, have been reported in anaerobically digested sludge (9). But N-EtFOSA, N-MeFOSA and FOSA were not detected in this study. PFOA was also a dominant pollutant detected in sludge from WWTPs (15). No significant high concentration of PFOA was detected in this study.

Concentrations in sediments
Sediment A and Sediment B were collected in Kai Tak channel in different location. Sediment B1 and Sediment B2 were collected in different depth in the same location B. 30.7 ng/g of PFOS concentration was found in sediment A higher than Sediment B (3.4 - 4.6 ng/g). And higher concentration of PFCs was found in superficial place in Sediment B from B1 than B2. Sediment 1 to Sediment 5 were collected in different year from 2001 to 2005 in Mai Po areas. PFBA, PFBuS and PFOS were detected in both sediment samples. PFOS was the predominant contaminant ranged from 2.5 to 8 ng/g and present no big variation between different years.

Acknowledgements
Thank my supervisor, Dr Kaimin Shih, for his comments advice and patience throughout my research experience.

Reference
(1) Giesy, J. P.; Kannan, K. *Environ Sci Technol.* 2002, 36, 147A-152A.

(2) Martin, J. W.; Smithwick, M. M.; Braune, B. M.; Hoekstra, P. F.; Muir, D. C. G.; Mabury, S. A. *Environ. Sci. Technol.* 2004, 38, 373-380.
(3) Key, B. D.; Howell, R. D.; Criddle, C. S. *Environ. Sci. Technol.* 1997, 31, 2445-2454.
(4) Kannan, K.; Corsolini, S.; Falandysz, J.; Oehme, G.; Focardi, S.; Giesy, J. P. *Environ. Sci. Technol.* 2002, 36, 3210-3216.
(5) Olsen et al, 2005 FLUOROS: International Symposium on Fluorinated Alky Organics in the Environment, TOX017)
(6) Boulanger, B., Vargo, J.D., Schnoor, J.L., Hornbuckle, K.C. *Environ. Sci. Technol.* 2005, 39, 5524–5530.
(7) Sinclair, E., Kannan, K. *Environ. Sci. Technol.* 2006, 40, 1408–1414.
(8) Schultz, M.M., Barofsky, D.F., Field, J.A. *Environ. Sci. Technol.* 2006, 40, 289–295.
(9) Higgins, C. P.; Field, J. A.; Criddle, C. S.; Luthy, R. G. *Environ. Sci. Technol.* 2005, 39, 3946-3956.
(10) So, M. K., Taniyasu, S ., Yamashita, N., G iesy, J. P., Zheng, J., Fang , Z., Im, S. H., Lam, P.K.S. *Environ. Sci. Technol.* 2004, 38, 4056-4063.
(11) Powley, C. R.; George, S. W.; Ryan, T. W.; Buck, R. C. *Anal Chem* 2005, 77, 6353-6358.
(12) Higgins, C. P. and Luthy, R. G. *Environ. Sci. Technol.* 2006, 40, 7251-7256.
(13) John M. Flaherty, et al. *Journal of Chromatography B*, 2005, 819, 329–338.
(14) Gomez-Taylor, M.; Kahn, H. D.; Telliard, W. A.; Ditthavong, K.; Kopylev, L.; McCarty, H.; Riddick, L.; Miller, K.; Cuddeback, J.; Rushneck, D.; Dedah, S.; Stralka, K., Technical SupportDocument for the Assessment of Detection and Quantitation Approaches; U.S. Environmental Protection Agency: Washington, DC, 2003.
(15) Bommanna G. Loganathan, Kenneth S. Sajwan, Ewan Sinclair, Kurunthachalam Senthil Kumar and Kurunthachalam Kannan. *Water Research.* 41, 4611-4620
(16) Boulanger, B., Peck, A.M., Schnoor, J.L., Hornbuckle, K.C. *Environ. Sci. Technol.* 2005b, 39, 74–79
(17) Wang, N., Szostek, B., Folsom, P.W., Sulecki, L.M., Capka, V., Buck, R.C., Berti, W.R., Gannon, J.T. *Environ. Sci. Technol.* 2005, 39, 531–538.
(18) Schultz, M.M., Higgins, C.P., Huset, C.A., Luthy, R.G., Barofsky, D.F., Field, J.A. *Environ. Sci. Technol.* 2006, 40, 7350–7357.