Perfluorochemicals in wastewater treatment plants and sediments in Hong Kong

*Ruowei Ma and Kaimin Shih**

Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, Hong Kong SAR, China

* Corresponding author. Tel: +852-28591973; fax: +852-25595337.

E-mail address: kshih@hku.hk

ABSTRACT

The study reported in this paper examined the concentrations of nineteen perfluorochemicals (PFCs), including perfluoroalkyl sulfonates, carboxylates, and sulfonamides in samples collected from Hong Kong wastewater treatment plants (WWTPs) and sediments. The study was the first to use an external isolator column to assist in the quantification of PFCs in environmental samples without having to make internal modifications to a liquid chromatography system. Perfluorooctanesulfonate was found to be the dominant PFC pollutant in Hong Kong, and the WWTP sludge was the major sink of PFCs discharged from the urban areas. Compared to discharge influenced by industrial activities, much less perfluorooctanoate was found in waste streams. The significantly lower level of perfluorodecanesulfonate in WWTP sludge reflects the important influence of consumer products on PFC distribution. The dominance of even-chain length perfluoroalkyl carboxylates in all of the WWTP sludge samples investigated further suggests the strong aerobic degradation of fluorotelomer alcohols in WWTPs.

Capsule

WWTP sludge is the major sink for PFCs discharged from the urban areas and has a distinctive compound distribution corresponding to its source.

Keywords

Perfluorochemical, sludge, sediment, WWTP, LC/MS/MS

1. Introduction

Perfluorochemicals (PFCs) have been the subject of increasingly intense environmental research. These compounds are globally distributed, environmentally persistent, bioaccumulative, and potentially harmful (Giesy et al., 2002). PFCs comprise a class of artificial, fully fluorinated organic compounds, and may exhibit both hydrophobic and lipophobic characteristics. As demonstrated by the attachment of the three types of functional groups shown in Fig. 1, these compounds have been used in a variety of consumer and industrial applications for nearly 60 years (OECD, 2002). The products in which they are utilized include protective coatings for food contact packaging, textiles, carpets, paper, coats, fabrics, leather, non-stick cooking material, commercial and industrial surfactants (e.g., fire-fighting foams, electroplating baths), and insecticides (Giesy et al., 2002). Among the chemical compounds used in such products, perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) are the two that have received the most attention in recent years. They have been widely detected in organisms in many environments, including some remote regions such as the Arctic (Martin et al., 2004). PFOA is likely to be a human carcinogen; it causes liver, pancreatic, testicular, and mammary gland tumors in laboratory animals. PFOS causes

liver and thryoid cancer in rats (Key et al., 1997). PFOA and PFOS are persistent, with half-lives in the human body estimated at more than 4 years and more than 8 years, respectively (Kannan et al., 2002). It has also been shown that some PFCs are resistant to hydrolysis, photolysis, and degradation by acids, bases, oxidants, reductants, microbes, and metabolism (Olsen et al., 2005).

Many studies have reported the distribution of PFCs in biota collected from all over the world, but there is less information available about these compounds' sources and levels in environmental matrices. Studies have shown that the discharge of wastewater effluent is a significant source of PFCs to the environment (Boulanger et al., 2005a, b, Schultz et al., 2006a, Sinclair and Kannan, 2006). However, available data indicate that some compounds, such as PFOS, may strongly sorb to environmental solids (Higgins et al., 2005), while others, such as *N*-ethyl perfluorooctane sulfonamidoethanol (*N*-EtFOSE), may be stripped into the atmosphere (Rhoads et al., 2008). A recent study reported detectable PFC concentrations in Hong Kong coastal waters near the effluent outlets of local wastewater treatment plants (WWTPs) (So et al., 2004). Hong Kong is a city with a population of 7 million people on a land area of 1,108 km^2. It is one of the most densely populated areas in the world, and the use of PFC-containing products may be one of the main sources of PFCs discharged into the regional environment. Assessing the levels of PFCs in WWTP samples and in natural sediments collected in Hong Kong will facilitate the understanding of the impact of releasing PFC pollutants from urban areas, a question that has been less addressed in environmental PFC studies.

Most environmental PFC studies require the use of liquid chromatography tandem mass spectrometry (LC/MS/MS) to ensure reliable species identification and quantification. However, two of the major challenges in analyzing environmental PFCs are quality procedural blanks and the lack of a well-developed analytical protocol. The presence of PFCs in various laboratory wares, solvents, and analytical instruments themselves leads to significant difficulties in analyzing trace levels of PFCs. To lower the detection limits of PFCs for wastewater samples, Schultz and coworkers (Schultz et al., 2006a) used the large volume injection method by injecting 500 µL samples into a liquid chromatography (LC) system rather than using the regular system volume of 10 µL. However, this method requires that the LC system be modified, including the accommodation of a 500 µL sample loop which sometimes exceeds the instrumental system volume limit and may not be widely applicable as a standard method for all LC/MS/MS systems. Some studies (Flaherty et al., 2005, Higgins et al., 2005, Washington et al., 2008) have involved the installation of guard columns and/or the use of polyetheretherketone (PEEK) tubing as a substitute to minimize background contamination in carrying solvents used for analyzing PFC samples. Apart from these improvements to analytical instruments, Alzaga et al. (2005) analyzed perfluoroalkyl carboxylates (PFCAs) in harbor sediments by acid extraction using a pressurized liquid extraction method (acetone–methanol 1:3 mixture), subsequent derivatization to alkyl esters, concentration of the volatile derivatives, and analysis by gas chromatography negative ion chemical ionization mass spectrometry (GC/NCI/MS). Although the procedural blanks were reported to be below the method LOQ (0.5–0.8 ng/g), the major drawbacks of this method are its excessive operational procedures and the incompatibility of the extraction solvent mixture for short-chain length PFCs. A “matrix effect-free” extraction method for the determination of various PFCs in soil, sediment,

and sludge was demonstrated by Powley et al. (2005). Due to its straightforward handling process and reliable results, this method became the basis for many PFC extraction and quantification studies. Nevertheless, certain sample preparation details may need further refinement to ensure it is suitable for working with a wide variety of analytical instruments.

The objectives of the study reported in this paper were to provide a more refined PFC quantification method for sludge and sediments and to investigate their levels in Hong Kong WWTPs and sediments. The quantification method used included the modified solid sample preparation procedure based on the work of Powley et al. (2005) and the adoption of an external isolator column in measurement by LC/MS/MS. The aim was to achieve low detection limits and a higher degree of adaptability in quantifying PFC concentrations in WWTP and sediment samples in a variety of laboratory LC/MS/MS systems with minimum instrumental modification. The resulting PFC concentrations determined for wastewater, sludge, and sediment in Hong Kong reveal how a typical urban area is influenced by persistent PFC pollutants.

2. Materials and methods

2.1. Chemicals and standards

The majority of PFC standards used in this study were purchased from Sigma-Aldrich Co. (St. Louis, MO), which include the potassium salts perfluorobutanesulfonate (PFBuS, 97%), perfluorohexanesulfonate (PFHxS, 98%), and 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%), perfluorododecanoic acid (PFDoA, 95%), perfluorotetradecanoic acid (PFTA, 97%), and perfluorotetradecanoate (PFTrA, 97%).

The sodium salts perfluoroheptanesulfonate (PFHpS, 98%) and perfluorodecanesulfonate (PFDS, 98%), and N-methylperfluorooctanesulfonamide (N-MeFOSA, 98%) were obtained 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 were purchased from Fisher Scientific (Pittsburgh, PA) and used to make 30% aqueous methanol in the sample preparation process. Ammonium hydroxide (32%) and glacial acetic acid (99.8%) were obtained from Merck (Darmstadt, Hesse) and used to prepare a methanol solution with 1% ammonium hydroxide and 1% glacial acetic acid. The ammonium acetate used for preparing the mobile phase in the LC/MS/MS analysis was obtained from VWR International Ltd (Poole, Dorset). Oasis HLB cartridges (0.5 g, 12 mL) used for extraction and ENVI-Carb SPE tubes (1 g) used for sample cleanup were purchased from Waters Corp. (Milford, MA) and Supelco Inc. (Bellefonte, PA), respectively.

2.2. Sample collection and preparation

The locations from which our wastewater, sludge, and sediment samples were collected in Hong Kong are shown in Fig. 2. Both wastewater and sludge samplings were carried out during the winter and fall of 2008 at two WWTPs (Plant A and Plant B) and during the spring and winter of 2008 at the other WWTP (Plant C). Plant A and Plant B serve

148 respective populations of 950,000 and 27,000 and perform secondary treatment using
149 the activated sludge method. Plant C employs a chemically enhanced primary treatment
150 and serves a population of 3,500,000. The treatment processes of these WWTPs are
151 schematically shown in the Supplementary Information available online. In addition to
152 wastewater and its sludge, sediments from two areas in Hong Kong and sludge
153 generated during the local drinking water treatment process were also collected to
154 compare their PFC levels with the samples taken from wastewater sources. Samples of
155 Kai Tak channel sediments (sediments A, B, and C), which were suspected to be the
156 major sink of previous airport oil and grease pollutants, were collected in 2006. Five
157 natural sediments (sediments 1-5) collected from 2001 to 2005 from Mai Po, a protected
158 wetland area in Hong Kong, were also used for comparison. In addition, since the
159 majority of Hong Kong's drinking water supply is sourced from surface water in
160 southern mainland China, sludge samples (DWS) were collected from the drinking
161 water treatment facility to evaluate the PFC inputs from this type of source. All the
162 above samples were collected in polypropylene (PP) bottles. Prior to extraction, the
163 sediment and sludge samples were dried at 105^{o}C overnight and ground before being
164 homogenized by a solvent-rinsed blender.
165

166 **2.3. Sample extraction**

167 To bring them within quantifiable ranges for LC/MS/MS, the PFCs in the wastewater
168 samples were extracted in the laboratory based on a slightly modified version of the
169 method reported by So et al. (2004). Because we expected higher PFC concentrations in
170 wastewater than in seawater, larger Oasis HLB extraction cartridges (0.5 g) were used
171 rather than the 0.2 g cartridges used in the previous study. The sample preparation
172 process was started by preconditioning the Oasis HLB cartridges with 6 mL of Optima

grade methanol followed by 6 mL of Optima grade water (Fig. 3). The wastewater collected was first centrifuged to remove suspended particles and a 250 mL aliquot of water sample was loaded into an Oasis HLB cartridge. The loaded cartridge was then washed using 6 mL of Optima grade water followed by 6 mL of 30% methanol. Finally, the cartridge was eluted with 10 mL of Optima grade methanol to extract the targeted PFC compounds. All of the abovementioned steps were undertaken at a flow rate of 3 mL per min. and the methanol solution derived was purged under nitrogen to 1 mL.

For the sediment and sludge samples, a modified version of the method proposed by Powley et al. (2005) was used to extract PFCs (Fig. 4). The homogenized and 105^{o}C-dried sludge or sediment (1 g for sludge and 5 g for sediment) was transferred to a 50 mL polypropylene centrifuge tube and extracted for 10 min. with 10 mL of basic methanol (1% NH_4OH) in a 60^{o}C sonication bath in a process repeated three times. The supernatant were then combined and acidified with acetic acid (1% by volume) and concentrated under nitrogen purging to 5 mL. To remove potential matrix interference, two 1 g ENVI-Carb SPE tubes were used for each solution cleanup, followed by 2.5 mL of methanol for cartridge rinsing. The methanol solution collected was then concentrated under nitrogen purging to 1 mL. During the sample preparation process, laboratory wares made of materials such as fluoropolymers, polytetrafluoroethylene, and perfluoroalkoxy were completely avoided. The plastic wares used to handle the samples were made of either polypropylene (PP) or polyethylene (PE).

2.4. Instrumental analysis

Due to its superiority in PFC analysis, LC/MS/MS is the preferred method for analyzing PFCs in natural samples. The PFCs in the samples were quantified using a Waters

198 Acquity ultra-performance LC/MS/MS system (UPLC/MS/MS) equipped with a 50 mm
199 × 2.1 mm Waters BEH C18 column (1.7-µm particle size) and tandem quadrupole mass
200 spectrometers (Waters Corp., Milford, MA). As it has been widely found that the
201 interference from standard LC systems and solvents during the quantification of PFCs at
202 low concentrations (such as in many environmental samples) is significant, a preventive
203 strategy should be adopted when carrying out such an analysis. In this study, the Teflon
204 tubes used for transferring the solvents and samples in the UPLC system were replaced
205 by polyetheretherketone (PEEK) tubes and an in-line PFC isolator column (Waters
206 Corp., Milford, MA) was utilized to assist the analytical column in separating the
207 background PFC contaminants from the samples (Fig. 5). In this way, the background
208 contaminants would be retained and eluted after the target analytes from samples, and to
209 the best of our knowledge, this paper is the first to report on the use of this technique to
210 quantify PFCs in environmental matrices.
211
212 To improve the resolution and increase the sensitivity of detection, a gradient mobile
213 phase of 2 mM ammonium acetate in methanol and 2 mM ammonium acetate in
214 water/methanol (95/5) was used. At a flow rate of 0.4 mL/min, the mobile-phase
215 gradient was ramped from 25% to 85% methanol in 5 min., then to 100% methanol at 5-
216 10 min., and finally ramped down to 25% methanol in 7 min. The MS/MS was operated
217 in electrospray negative ionization mode due to the PFC properties whereby hydrogen
218 ions are easily lost. Analyte ions were monitored using the multiple reaction monitoring
219 (MRM) mode; their monitored transitions are listed in Table 1.
220
221 **2.5 Detection limits and recovery**

The limit of detection (LOD) is the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value) within a stated confidence limit (American Chemical Society, 1980). A number of different "detection limits" are commonly used, including the instrument detection limit (IDL), the method detection limit (MDL) and the limit of quantification (LOQ). The LOD is defined as 3 times the standard deviation of the blank, whereas the LOQ is defined as 10 times the standard deviation of the blank. Even when the same terminology is used, different LODs can be derived for the same substance according to nuances in what definition is used and what type of noise contributes to the measurement and calibration (Long and Winefordner, 1983). In this study, the instrument detection limit (IDL) was set at three times the standard deviation of the background levels detected in the blanks, and the method detection limit (MDL) was calculated based on the IDL according to U.S. EPA guidance (Gomez-Taylor et al., 2003). Detectable responses that were below the IDL were reported as non-detected (n.d.). Responses that were below the calculated MDL but above the IDL were reported as less than the corresponding MDL. The IDL and MDL values (for wastewater, sludge, and sediment) of the PFCs analyzed in this study are listed in Table 1.

To determine the extraction recoveries of PFCs from water samples, 0.1 ppb of PFC mixture was spiked into Optima grade water and extracted following the processes shown in Fig. 3 for quantification. Most compounds extracted by this method were recovered at more than 75%, with the exception of long-chain length ($m>8$) perfluoroalkyl carboxylates (Table 1). The sorption experiments performed by Higgins and Luthy (2006) suggest that perfluoroalkyl carboxylates with longer CF_2 chains may possess stronger sorptivity. Therefore, the lower recoveries of long-chain length

perfluoroalkyl carboxylates may indicate their stronger sorption to the packing material of HLB cartridges. Thus, it is worth noting that this now widely used HLB cartridge extraction method is not an optimal method for analyzing long-chain length perfluoroalkyl carboxylates. The unusually high recovery of PFOS reported in Table 1 is again due to systematic contamination during compound extraction and/or the elution procedure.

For sludge sample, to evaluate their recoveries through extraction protocol, the Plant B aeration tank sludge (Plant B ATS) was spiked with the 19 PFCs under study at concentrations of 50, 100, 150, and 200 ng/g follow the same extration and cleanup method mentioned above. The results are listed in Table 1. The compound recoveries from sludge were generally higher than 70%, but in common with the wastewater samples, the long-chain length perfluoroalkyl carboxylates, such as PFDoA, PFTrA, and PFTA, were all observed to have lower recoveries. However, although these recoveries were obtained through spike experiments on water and sludge, the PFC concentrations reported here were not corrected for their extraction recoveries and the original values obtained through our measurements are shown. Applying recovery correction factors would have had a larger impact on long-chain length perfluoroalkyl carboxylates (PFCAs), but would have had a minimal effect on most of the analytes assessed in this study.

3. Results and Discussion

3.1. Effect of the in-line isolator column

The background contamination of PFCs during LC/MS/MS quantification can be caused by a number of instrumental parts and laboratory reagents, such as tubings, filters, internal tube connections, pump heads, plungers, and the solvents used. The preferred solvents used in this study were found to be Fisher Optima LC/MS grade methanol and water. By using PFOS for comparison through measurements made with the unmodified system, as shown in Fig. 6(a), the background signal was eluted out between 4.2-4.7 mins. and reached a peak of around 2.38×10^5 counts when Fisher LC/MS grade methanol and MilliQ water were used as the mobile phase. With the use of Fisher Optima LC/MS grade methanol and water under the same instrumental conditions, the background signal eluted during the same period reached a much lower peak of around 5.83×10^4 counts (Fig. 6(b)). The significant background PFC interference caused by solvents in attempting to quantify trace concentrations of PFCs in environmental samples can thus be observed.

Although certain PFC-containing components used in the LC/MS/MS system can be replaced by PEEK or stainless steel materials, it is impractical to replace all PFC-containing components of the instrument (Flaherty et al., 2005). Excessive and non-standardized modifications of the LC/MS/MS system will also limit the scope of application of analytical methods developed. Moreover, improvements made to system performance may not be reliable and consistent after each internal modification, particularly when they are implemented in different LC/MS/MS brands and models. To resolve the issue of interfering background PFCs without making significant modifications to the LC/MS/MS system, we simply replaced the Teflon solvent transferring tubes with PEEK tubes and installed an in-line PFC isolator column. The in-line PFC isolator column used between sample injection and solvent supply can delay

297 the response of PFC contaminants from solvents. Fig. 6(c) illustrates how the in-line
298 PFC isolator column was used to delay the background PFOS signal, which was eluted
299 out between 5.2-5.7 min. In comparison with the eluted period of 4.2-4.7 min. without a
300 PFC isolator column as illustrated in Fig. 6(b), the background PFOS signal was
301 significantly delayed and the separation of background and sample signals was thus
302 achieved. Fig. 6(d) shows the sample signal of 0.1 ppb PFOS eluted at 4.5- 4.9 min.,
303 whereas the background peak was delayed to the period 5.2-5.7 min. Further
304 confirmation can be observed in Fig. 6(c), in which there is no visible signal in the 4.5-
305 4.9 min. period, representing a successful attempt to create a sample blank for
306 measurement.
307
308
309 **3.2. PFC concentrations in wastewater**
310 Several types of PFCs were found in the wastewater samples collected. PFOS was the
311 predominant compound, ranging in concentration from 19.0 to 49.9 ng/L as shown in
312 Table 2. The PFOS concentrations detected were generally higher than the levels
313 reported from wastewater treatment facilities in Kentucky and Georgia (Loganathan et
314 al., 2007), but were similar to the levels reported for New York WWTPs (Sinclair and
315 Kannan, 2006). Despite the voluntary phasing out of the production of perfluorooctane
316 sulfonyl-based chemistries in 2002, the detection of PFOS in Hong Kong WWTPs
317 indicates that products containing PFCs are still releasing PFCs into the Pearl River
318 Delta region (in southern China) and that WWTPs are a main source of PFOS in the
319 area. PFOA, another PFC commonly found in aqueous environments, was only detected
320 in trace concentrations in the Hong Kong wastewater samples we examined. Higher
321 PFOA levels in aqueous environments have previously been reported due to the impact

of industrial discharge (Lin et al., 2009). The results of our study provide further evidence that PFOA discharges from urban sources are relatively minor.

Previous studies have reported that perfluoroalkyl carboxylates are produced as biodegradation products of fluorotelomer alcohols (FTOHs) in the activated sludge process (Wang et al., 2005). Therefore, the biodegradation of precursor compounds during activated sludge treatment is also a likely source of perfluoroalkyl carboxylates in effluents (Schultz et al., 2006a, b). Another study (Loganathan et al., 2007) has even observed higher PFOA and PFOS concentrations in effluent than in influent and suggested that both compounds can also be generated through the degradation of their precursors in the treatment processes of both rural and urban WWTPs. The PFCs detected in wastewater samples in this study were mostly short-chain length perfluoroalkyl carboxylates, and some of them (PFBA, PFHxA, PFOA, and PFNA) were observed to have very similar effluent concentrations, if not slightly higher, compared to their influents. This observation supports the previous suggestion of degradation process in WWTPs, and indicates certain precursors, potentially FTOHs, may contribute the discharge of perfluoroalkyl carboxylates from urban WWTPs.

3.3. Sludge extraction

Sludge and sediments were extracted following the protocol illustrated in Fig. 4. Most previous studies have used dispersed ENVI-Carb powder to cleanup samples extracted from sediments or sludge (Powley et al., 2005, Higgins and Luthy, 2006). In this study, a preliminary test was carried out by dispersing 1 g of ENVI-Carb in 5 mL of sample solution derived by extracting 1 g of Plant A aeration tank sludge (Plant A ATS (Jan)). A comparison was made by loading the same amount of sample solution into the ENVI-

Carb SPE syringe tube to pass through 1 g of packed ENVI-Carb powder. The colors of the derived solutions after these two cleanup methods are shown in Fig. 7, suggesting that the method of passing the extraction solution through an SPE tube (packed tube method) provides for better impurity removal. Based on the same ratio of treated solution to ENVI-Carb powder used, the packed tube method was the more efficient one and thus was adopted in this study for extracting PFCs from sludge and sediments. In addition, to further enhance the cleanup effect and method of recovery, two 1 g ENVI-Carb SPE tubes were used in sequence for cleaning up each derived solution, followed by 2.5 mL of methanol for cartridge rinsing. The final combined solutions were eventually purged under nitrogen to 1 mL for UPLC/MS/MS analysis. This sample cleanup method was used in the sludge/sediment extraction protocol mentioned in Section 2.5, and the protocol recovery results are listed in Table 1.

In developing an extraction protocol for solid samples, determining the optimal solid to extraction solution ratio used to extract the targeted compounds effectively is crucial. Incomplete extraction will lead to a high degree of variation in recovery, but excessive extraction solution will lead to unnecessary effort in concentrating the solution for analysis. Extraction tests using same amounts of totally 30 mL methanol solution (1% NH_4OH) and different amounts of Plant B aeration tank sludge (Plant B ATS) were carried out to determine the optimal solid to extraction solution ratio for the sludge sample extraction protocol. As shown by the measured PFOS concentrations in Fig. 8, the optimal solid to extraction solution ratio was determined to be 1 g of sludge, which yielded results consistent with those in which less mass of solid were used. Extraction of 1.5 g of sludge was incomplete due to the insufficient amount of extraction solution as reflected by the decrease of observed PFOS concentration. In the complete extraction

process following the protocol shown in Fig 4, sediment extraction was carried out using a solid amount 5 times the weight of sludge (5 g), in comparison with the 10 times more solid amount used in a previous study (Higgins et al., 2005).

3.4. Concentrations of PFCs in sludge and sediments

Prior to the phasing out of PFOS and other perfluorooctane sulfonyl fluoride-based chemicals by 3M in 2002, a total concentration of perfluoroalkylsulfonyl-based chemicals of higher than 3000 ng/g could be detected in U.S. domestic WWTP sludge, with PFOS as the dominant compound (Higgins et al., 2005). The PFC concentrations measured in our sludge samples, which represented a type of urban source in the post phase-out period, showed the same PFOS dominance, though at much lower levels (Table 3). Most of the total concentrations of perfluoroalkylsulfonyl-based chemicals in the sludge of present study were less than 100 ng/g, although the inhomogeneity of samples may sometimes lead to greater PFOS level observed in the sludge, such as the primary sludge sample collected at Plant A in November (7304.9 ng/g).

Perfluorodecanesulfonate (PFDS) is another dominant perfluoroalkyl sulfonate that has commonly been found in U.S. domestic wastewater sludge (Higgins et al., 2005; Schultz et al., 2006b). However, none of the sludge samples collected in this study showed detectable concentrations of PFDS. Previous studies have not provided evidence showing that PFDS can be generated during the wastewater treatment process, and very little is known about the use and occurrence of PFDS (Schultz et al., 2006a, b). Gewurtz et al. (2007) recently observed that PFDS is a major compound that contributes to an increase in indoor PFCs following the installation of carpet. Coincidentally, carpets are rarely found on floors in Hong Kong due to the humid tropical climate.

Therefore, carpets or their impregnating products are likely to be an important source of PFDS release into domestic WWTPs.

The extant literature reports that PFOA is used in the manufacturing of fluoropolymers (such as Teflon®) and semiconductors (Washburn et al., 2005; Lin et al., 2009; Tang et al., 2006), and in the photolithographic processes (Tang et al., 2007). It may also occur as an impurity in these products and later be released into the environment, such as from coated non-stick kitchenware and electronic products. The abovementioned manufacturing activities are not undertaken in Hong Kong, perhaps explaining why PFOA was not present in significant quantities in the wastewater and sludge samples investigated. Although PFOA was commonly detected in the samples, the levels observed (a few ng/L in wastewater and several ng/g in sludge) may represent the typical release of PFOA from an urban area solely influenced by consumer product impurities. In addition, the mean concentrations of even-chain length PFCAs (e.g., PFBA, PFHxA, PFOA) were higher than those of odd-chain length PFCAs (e.g., PFPeA, PFHpA, PFNA) for all 13 sludge samples. Martin et al. (2004) investigated 8 PFCAs in arctic mammals and observed that the concentrations of odd-chain length PFCAs exceeded the concentrations of even-chain length PFCAs, suggesting that odd-chain length PFCAs are more abundant in the environment. In a study quantifying 6 PFCAs in 13 WWTP sludge samples, Higgins et al. (2005) found no clear trend in the dominance of either odd-numbered or even-numbered PFCAs, although even-chain length PFCAs were detected more frequently. Given the wider range of PFCAs investigated in this study (11 in total), our results strongly suggest the dominance of even-chain length PFCAs in WWTP sludge in Hong Kong. This dominance of even-chain length PFCAs is consistent with the results of a study that shows biodegrading FTOHs under aerobic

422 conditions produces mainly even-chain length PFCAs (Dinglasan et al., 2004).
423 Therefore, it is possible that the aerobic biodegradation of FTOHs contributed to the
424 even-chain length PFCAs observed in the sludge examined in this study.
425
426 Table 4 reports the low PFC levels observed in sludge precipitated from drinking water
427 treatment (DWS) in Hong Kong. These results represent the low PFC levels in Hong
428 Kong water resources and provide a good contrast with the higher levels observed in the
429 WWTP samples. The largest concentration was from PFOS, which is a common
430 background contaminant. The potential sources of the PFOS observed and other trace-
431 level PFCs may be treatment chemicals, piping materials, pumping facilities, or source
432 contamination from the impact of waste streams. Sediments 1-5 were collected from a
433 protected wetland area in Hong Kong and should represent an environment in which
434 there has been minimal anthropogenic impact. The PFC levels of these samples, which
435 were collected from 2001-2005, were similar or even lower than those detected in
436 drinking water sludge (Table 4). Data for the 3 sediment samples collected from the Kai
437 Tak channel, which were suspected to have suffered from industrial oil and grease
438 pollution due to previous use of the area as an airport, indicate two PFC distribution
439 scenarios (Table 4). Sediments B and C had low PFOS levels and only trace amounts of
440 other PFCs, results similar to those for the sediment 1-5 and DWS samples. In contrast,
441 sediment A had higher PFOS and PFCA levels than the other sediment samples, and
442 this result is evidence of an additional anthropogenic release of PFCs in the area, which
443 may be due to the industrial activities that previously took place at the site. Similar to
444 the observation for WWTP sludge, the concentrations of even-chain length PFCAs were
445 also noticeably higher than those of odd-chain length in sediment A, which may again
446 indicate the contribution of FTOH aerobic degradation in the sediment.

4. Conclusion

A modified analytical method consisting of liquid solvent extraction, clean up via ENVI-Carb, and injection of the solution derived into an ultra-performance liquid chromatography (UPLC) system coupled to a tandem mass spectrometer (LC/MS/MS) was used to quantify perfluorochemicals (PFCs) in sediments and wastewater sludge. The significantly higher PFC levels measured in Hong Kong WWTP sludge in comparison with those detected in local sediments suggest that the municipal waste stream from urban areas plays a role in PFC discharge. The study also shows that the WWTP sludge is a sink of PFCs on a global scale, despite the voluntary phasing out of perfluorooctane sulfonyl-related chemistry production in the U.S. in 2002. The dominant PFC compound found in most of the Hong Kong wastewater, sludge, and sediment samples we examined in this study was PFOS. In comparison with industrial discharges, much lower PFOA levels were observed in the WWTPs of urban environment, such as Hong Kong. PFDS, which is commonly found in WWTP sludge in the U.S. and is thought to be released by carpet-related products, was not detected in the Hong Kong samples we examined, indicating that certain observed PFCs in the environment may largely be attributable to one particular category of consumer products. All of the WWTP sludge samples investigated showed the dominance of even-chain length PFCAs, giving further support to the aerobic degradation of FTOHs as proposed by other PFC studies on WWTPs. As a final point, this study has successfully adopted an external isolator column in PFC measurement by LC/MS/MS, which is a simple and adaptable approach in detecting trace-level PFCs in environmental samples.

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Supplementary information

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Table 1. Monitored PFC transitions, extraction method recoveries, and analytical detection limits.

Analyte	Transition monitored (m/z)	% Recovery (RSD, n=4) of PFCs in water	% Recovery (RSD, n=4) of PFCs in sludge	IDL (ppb)	MDL of water (ng/L)	MDL of sludge (ng/g)	MDL of sediment (ng/g)
PFBuS	299 > 80	88 (2)	89 (2)	0.1	0.57	0.14	0.03
PFHxS	399 > 80	80 (4)	83 (4)	0.1	0.57	0.14	0.03
PFHpS	449 > 80	86 (1)	90 (5)	0.1	0.57	0.14	0.03
PFOS	499 > 80	105 (3)	82 (4)	0.5	2.86	0.71	0.14
PFDS	599 > 80	92 (2)	76 (2)	0.1	0.57	0.14	0.03
PFBA	213 > 169	86 (1)	89 (5)	0.5	2.86	0.71	0.14
PFPeA	263 > 219	78 (2)	90 (2)	0.1	0.57	0.14	0.03
PFHxA	313 > 269	91 (2)	65 (3)	0.1	0.57	0.14	0.03
PFHpA	363 > 319	89 (2)	80 (3)	0.1	0.57	0.14	0.03
PFOA	413 > 369	87 (3)	83 (5)	0.5	2.86	0.71	0.14
PFNA	463 > 419	92 (4)	94 (3)	0.1	0.57	0.14	0.03
PFDA	513 > 469	75 (8)	89 (7)	0.1	0.57	0.14	0.03
PFUnDA	563 > 519	63 (4)	81 (3)	0.1	0.57	0.14	0.03
PFDoA	613 > 569	60 (2)	72 (6)	0.1	0.57	0.14	0.03
PFTrA	663 > 619	25 (1)	66 (3)	0.1	0.57	0.14	0.03
PFTA	713 > 669	21 (1)	62 (5)	0.1	0.57	0.14	0.03
FOSA	498 > 78	88 (2)	88 (3)	0.1	0.57	0.14	0.03
N-MeFOSA	512 > 169	81 (2)	73 (4)	1	5.71	1.43	0.29
N-EtFOSA	526 > 169	85 (3)	75 (3)	0.1	0.57	0.14	0.03

RSD, relative standard deviation; IDL, instrument detection limit; MDL, method detection limit.

Table 2. Concentrations of PFCs analyzed in Hong Kong wastewater (ng/L)

Sample	PFBuS	PFHpS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoA	PFTrA	PFTA
Plant A Influent (Nov)	1.1 (13)	n.d.	49.9 (14)	n.d.	6.3 (12)	1 (20)	**	**	**	n.d.	n.d.	n.d.	n.d.	**
Plant A Effluent (Nov)	1.5 (10)	n.d.	19 (13)	**	**	1.2 (16)	**	4.1 (16)	**	n.d.	n.d.	n.d.	n.d.	**
Plant B Influent (Oct)	2.8 (10)	n.d.	29.4 (4)	n.d.	8.7 (6)	1 (3)	**	**	**	n.d.	n.d.	n.d.	n.d.	n.d.
Plant B Effluent (Oct)	1.3 (13)	n.d.	28.8 (9)	n.d.	**	0.7 (3)	**	**	0.6 (4)	n.d.	n.d.	n.d.	n.d.	n.d.

All samples were collected in 2008. Values in parentheses are % relative standard deviations (RSDs; n=4). n.d.: not detected; **: concentrations below the MDL, but above the IDL. PFHxS, PFDS, FOSA, N-EtFOSA, N-MeFOSA were also analyzed but not detected.

Table 3. Concentrations of PFCs analyzed in Hong Kong WWTP sludge (ng/g)

Sample	PFBuS	PFHpS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoA	PFTrA	PFTA
Plant A ATS (Jan)	4 (1)	n.d.	46.2 (24)	n.d.	6.3 (1)	4.5 (1)	3.6 (2)	5.5 (1)	23 (4)	15.2 (6)	7.8 (7)	n.d.	19 (3)	46 (6)
Plant A ATS (Oct)	0.7 (3)	n.d.	7.2 (12)	n.d.	4.3 (13)	5.6 (10)	1.8 (9)	1.8 (9)	0.8 (4)	1.7 (17)	2.3 (12)	n.d.	1.1 (1)	0.8 (2)
Plant A RS (Oct)	0.6 (4)	n.d.	6.2 (15)	n.d.	6.9 (9)	16.5 (5)	2.1 (6)	2.1 (5)	9.5 (9)	3 (5)	2.8 (6)	n.d.	1.8 (1)	1.9 (11)
Plant A DS (Oct)	1.8 (2)	n.d.	8 (10)	n.d.	8.1 (4)	27.8 (12)	2.6 (9)	1.6 (2)	2 (3)	2.9 (3)	2.9 (7)	n.d.	4 (3)	4.3 (2)
Plant A PS (Nov)	6.4 (2)	106.6 (5)	7304.9 (12)	10.3 (2)	10.1 (7)	7.6 (5)	3.7 (5)	15.7 (10)	n.d.	0.4 (10)	0.7 (5)	0.6 (3)	0.4 (10)	**
Plant A TS (Nov)	1.7 (9)	n.d.	116 (7)	8.3 (2)	0.7 (10)	0.9 (5)	0.4 (6)	1.3 (1)	0.9 (20)	1.9 (15)	1.2 (8)	0.6 (5)	1.3 (14)	0.2(15)
Plant A DS (Nov)	3 (1)	n.d.	23.4 (6)	3.1 (2)	3.6 (3)	5.5 (4)	4 (3)	1.4 (1)	0.5 (15)	0.6 (1)	0.8 (5)	0.9 (4)	0.5 (1)	0.2 (10)
Plant B ATS (Jan)	1.2 (2)	n.d.	60.6 (10)	63.6 (3)	3.2 (22)	4.8 (3)	0.6 (2)	2.4 (4)	2.5 (7)	7.4 (14)	2.2 (13)	5.7 (2)	3.3 (5)	4.4 (20)
Plant B FSS (Oct)	4.5 (5)	n.d.	61.4 (5)	37.1 (5)	2.3 (7)	4.1 (3)	1.3 (1)	3.6 (3)	2.9 (12)	7.5 (2)	3.1 (1)	8.6 (3)	2.2 (11)	1.9 (2)
Plant B RS (Oct)	5.1(5)	n.d.	101 (3)	111.4 (7)	2.2 (7)	3 (2)	1.2 (1)	3.1 (11)	2.2 (3)	7.9 (2)	2.7 (12)	7.1 (5)	2.2 (13)	1.5(3)
Plant B DS (Oct)	5.3 (5)	n.d.	157.9 (10)	30.2 (5)	0.5 (4)	1.4 (1)	n.d.	2.8 (3)	1.8 (11)	8.3 (1)	5.4 (3)	7.1 (5)	1.8 (4)	1.8 (2)
Plant C DS (Apr)	1.2 (7)	n.d.	3.1 (25)	10.2 (6)	4.4 (19)	0.3 (16)	n.d.	**	**	0.3 (9)	n.d.	n.d.	0.2 (17)	0.2 (8)
Plant C DS (Dec)	2.1 (4)	n.d.	69.4 (10)	14.1 (5)	5.7 (2)	0.3 (10)	n.d.	**	0.9 (9)	0.6 (8)	0.4 (9)	0.6 (2)	0.3 (2)	0.4 (6)

All samples were collected in 2008. Values in parentheses are % relative standard deviations (RSDs; n=4). ATS: aeration tank sludge; RS: returned sludge; PS: primary sludge; TS: thickened sludge; DS, dewatered sludge; FSS, final sedimentation sludge; n.d.: not detected; **: concentrations below the MDL, but above the IDL. PFHxS, PFDS, FOSA, N-EtFOSA, N-MeFOSA were also analyzed but not detected.

Table 4. Concentrations of PFCs analyzed in Hong Kong drinking water sludge and sediments (ng/g)

Sample	PFBuS	PFHpS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoA	PFTrA	PFTA
DWS (Jun, 2008)	1.4 (16)	n.d.	6.6 (11)	n.d.	0.5 (15)	0.6 (22)	0.6 (20)	**	0.8 (17)	0.6 (22)	1.1 (20)	n.d.	0.9 (15)	0.5 (15)
Sediment 1 (2001)	1 (5)	n.d.	6.5 (10)	0.6 (1)	0.4 (6)	0.4 (5)	n.d.	**	0.1 (2)	n.d.	n.d.	n.d.	n.d.	n.d.
Sediment 2 (2002)	1.3 (5)	n.d.	3.7 (5)	0.4 (4)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1 (10)	n.d.	n.d.
Sediment 3 (2003)	1.3 (4)	n.d.	5 (3)	0.4 (5)	n.d.	0.1 (2)	0.1 (3)	n.d.	0.1 (4)	n.d.	n.d.	0.1 (15)	n.d.	1.3 (4)
Sediment 4 (2004)	1.1 (6)	n.d.	2.6 (7)	0.4 (5)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1 (3)	n.d.	1.1 (2)
Sediment 5 (2005)	1 (8)	n.d.	8.3 (6)	0.6 (10)	n.d.	0.1 (5)	n.d.	**	n.d.	n.d.	n.d.	0.1 (5)	n.d.	1 (7)
Sediment A (2006)	7.2 (1)	n.d.	30.7 (12)	6.6 (5)	4.2 (1)	4.9 (1)	1.2 (2)	2.9 (1)	0.2 (4)	0.9 (6)	0.6 (5)	4.2 (7)	5.1 (3)	9 (6)
Sediment B (2006)	1 (3)	n.d.	4.6 (6)	n.d.	0.8 (6)	1.9 (10)	0.9 (9)	2.1 (9)	0.6 (4)	0.5 (8)	0.8 (6)	n.d.	2.8 (1)	4 (2)
Sediment C (2006)	0.4 (4)	n.d.	3.4 (7)	n.d.	0.1 (9)	0.1 (5)	0.1 (6)	0.2 (5)	0.1 (9)	0.1 (5)	0.3 (6)	n.d.	0.4 (1)	0.3 (11)

Values in parentheses are % relative standard deviations (RSDs; n=4). n.d.: not detected; **: concentrations below the MDL, but above the IDL. PFHxS, PFDS, FOSA, N-EtFOSA, N-MeFOSA were also analyzed but not detected.

Figure Captions

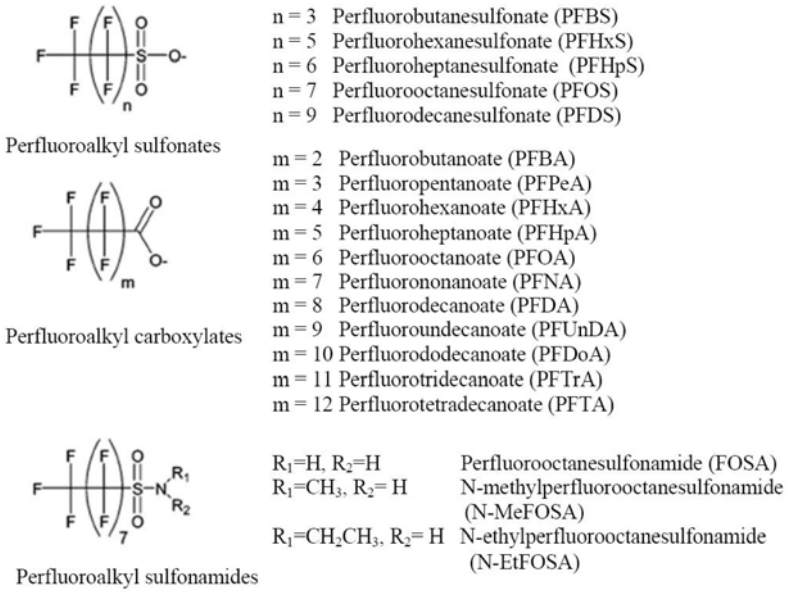

Fig. 1. The perfluorochemicals (PFCs) investigated in this study. Three types of functional groups with variable CF_2 chain length were included: perfluoroalkyl sulfonates, perfluoroalkyl carboxylates, and perfluoroalkyl sulfonamides.

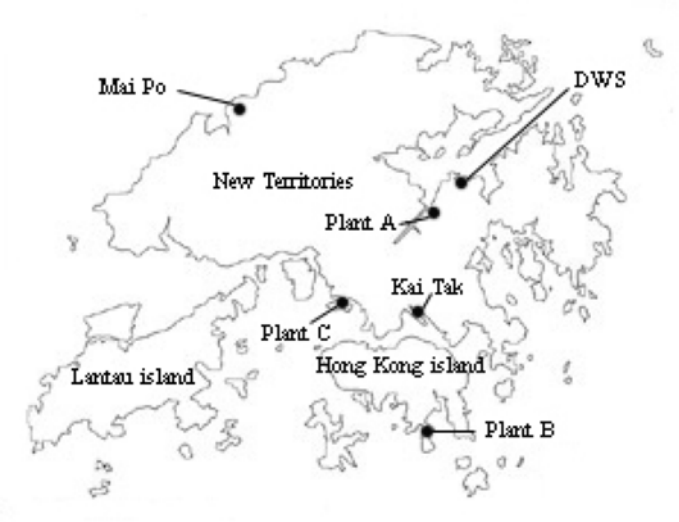

Fig. 2. Water treatment plants and sediment samples collected in this study. Plants A, B, and C are wastewater treatment plants (WWTPs) and DWS is a drinking water treatment plant. All water treatment plant sampling activities were carried out in 2008. Five sediment samples were collected from Mai Po (sediments 1-5) during 2001-2005, and three sediment samples were collected from Kai Tak (sediments A, B, and C) in 2006.

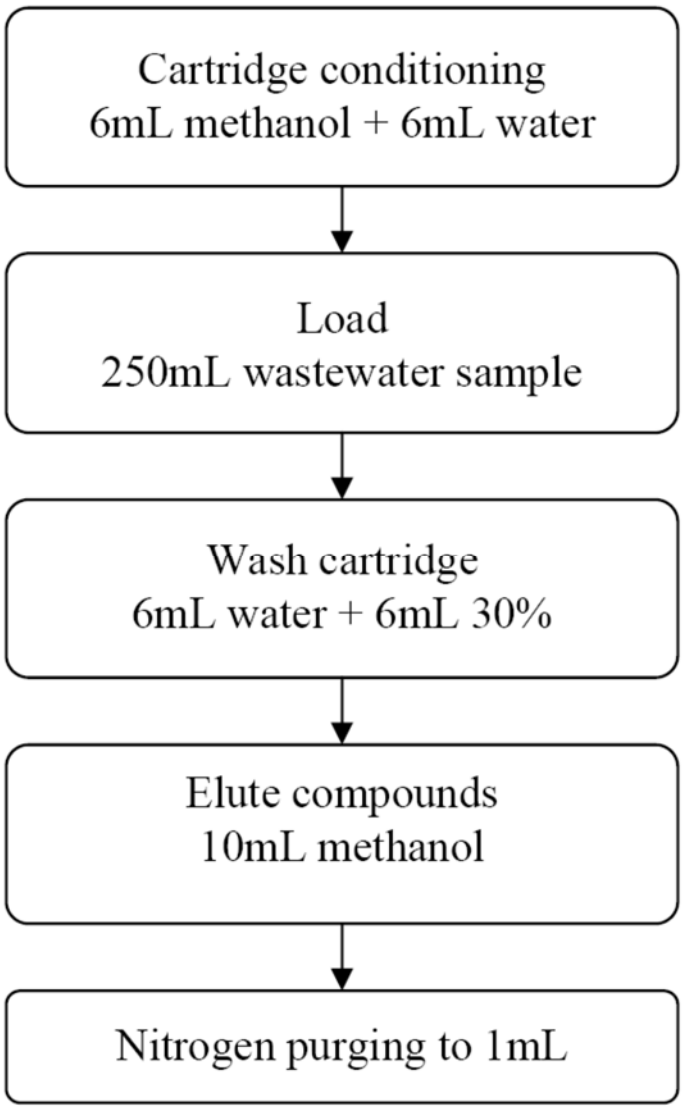

Fig. 3. Extraction of PFCs from wastewater samples. The procedure consists of Oasis HLB cartridge conditioning, sample loading, cartridge washing, target compound elution, and analyte concentration.

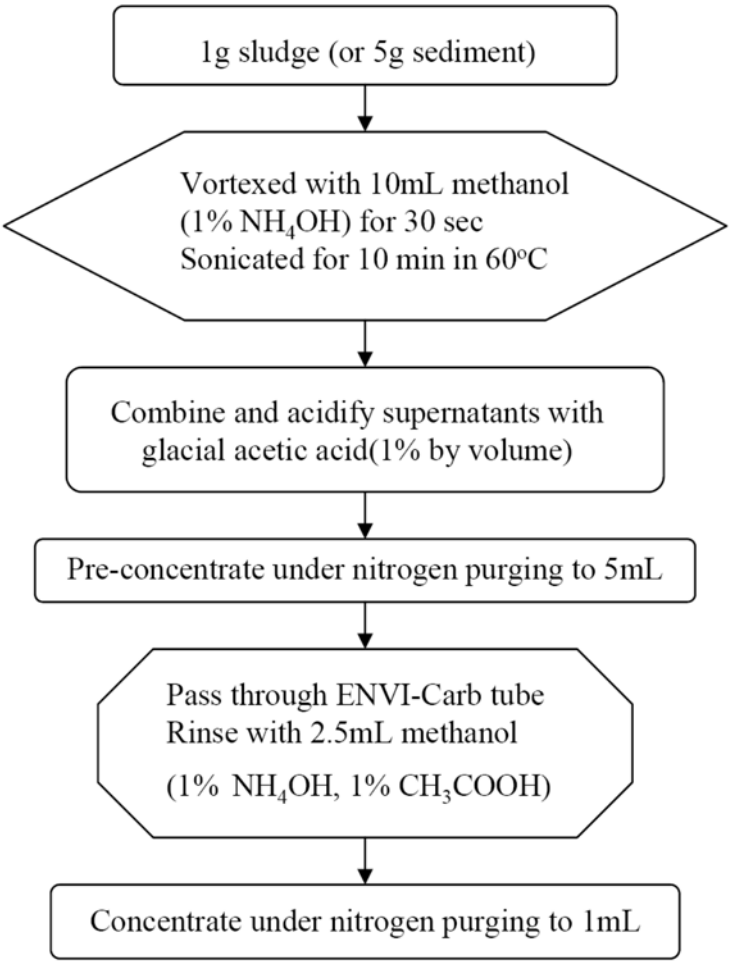

Fig. 4. Extraction of PFCs from sludge or sediment samples. The procedure consists of methanol extraction, supernatant acidification and pre-concentration, ENVI-Carb cleanup, and analyte concentration. The process shown in the hexagonal box was repeated three times, while the process represented in the octagonal box was repeated twice.

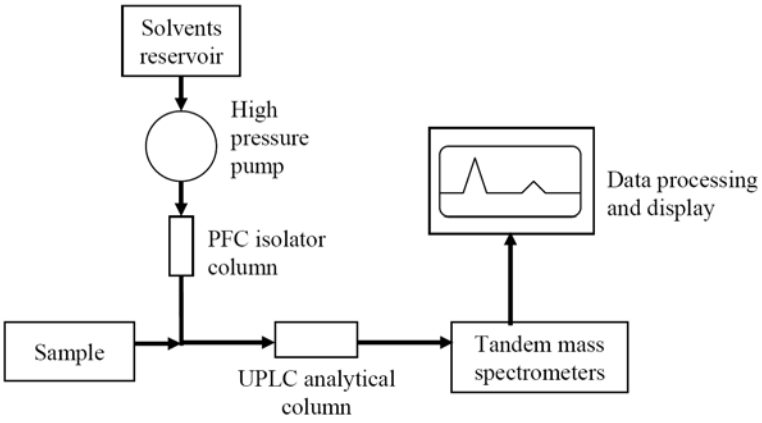

Fig. 5. Schematic diagram of the UPLC/MS/MS system used in this study. In addition to a standard LC/MS/MS system, an external Waters® PFC isolator column was used before injection into the UPLC analytical column to delay the contaminant responses of the solvents.

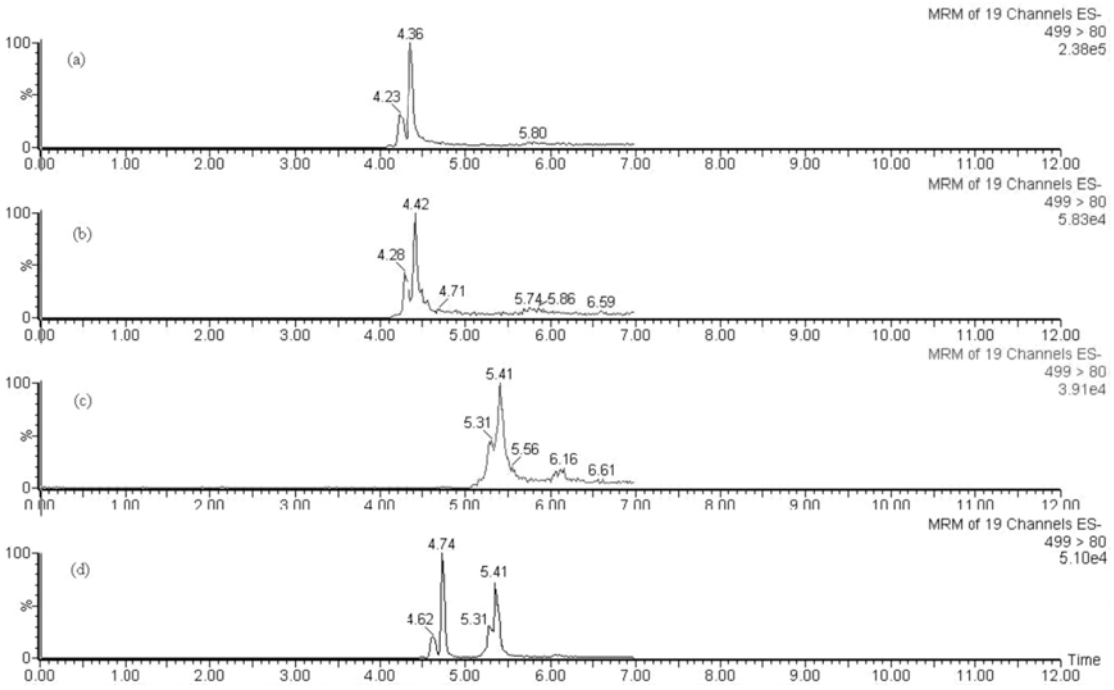

Fig. 6. Sample signal improvement due to better solvents and the PFC isolator column. The PFOS signal obtained from a blank sample using Fisher LC/MS grade methanol and laboratory MilliQ water (a); using Fisher Optima LC/MS grade methanol and water (b); and condition (b) together with the aid of the PFC isolator column (c). A standard solution of 0.1 ppb PFOS analyzed with the condition (c) can be observed with the contaminant-separated signal at the eluted period of 4.5- 4.9 min (d).

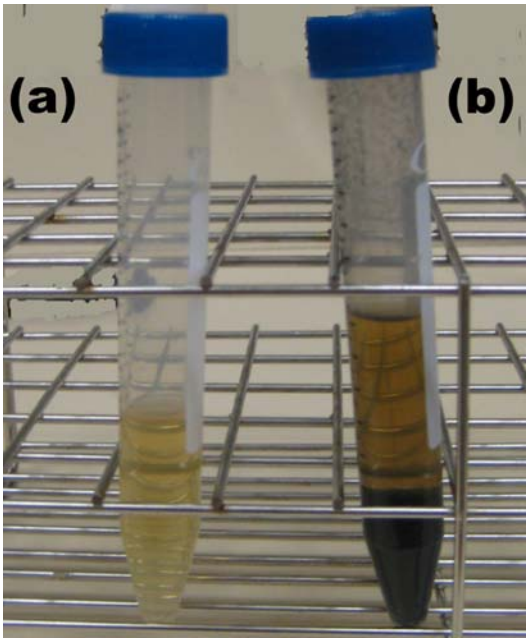

Fig. 7. Comparing the results of ENVI-Carb sample cleanup using the packed tube method (a) and using the powder dispersing method (b). The observable color difference of the extracts after the cleanup processes suggests that the method of passing the extraction solution through an ENVI-Carb packed tube provides for better impurity removal.

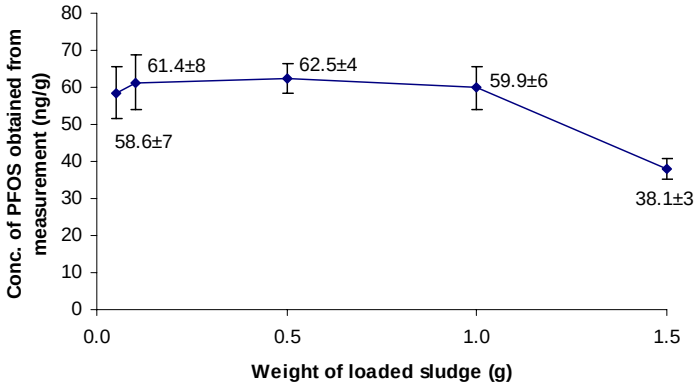

Fig. 8. Determination of optimal sludge solid to extraction solution ratio for the extraction method used in this study. Extraction tests using different amounts (0.05, 0.1, 0.5, 1.0, and 1.5 g) of Plant B aeration tank sludge (Plant B ATS) were carried out to monitor the PFOS concentrations obtained. The optimal solid to extraction solution ratio was thus determined to be 1 g sludge to 30 mL methanol solution (1% NH_4OH).

Supplementary Information for

Perfluorochemicals in wastewater treatment plants and sediments in Hong Kong

*Ruowei Ma and Kaimin Shih**

Department of Civil Engineering, The University of Hong Kong, Pokfulam Road,

Hong Kong, Hong Kong SAR, China

3 figures (Figure S1 – S3)

* Corresponding author. Tel: +852-28591973; fax: +852-25595337.

E-mail address: kshih@hku.hk

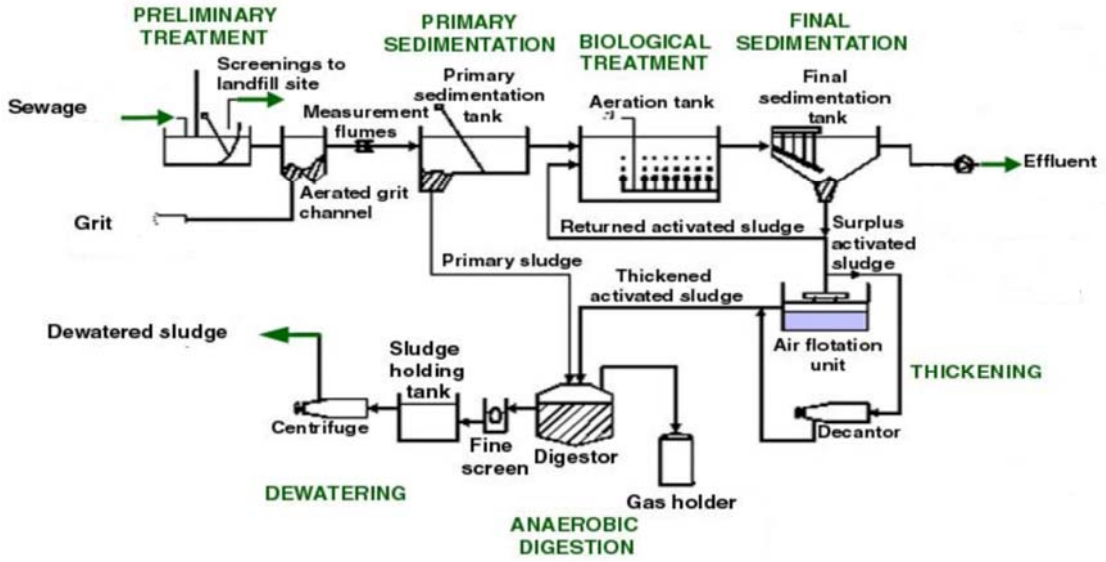

Figure S1. Schematic diagram of treatment processes (secondary treatment with activated sludge method) used by the WWTP Plant A in this study.

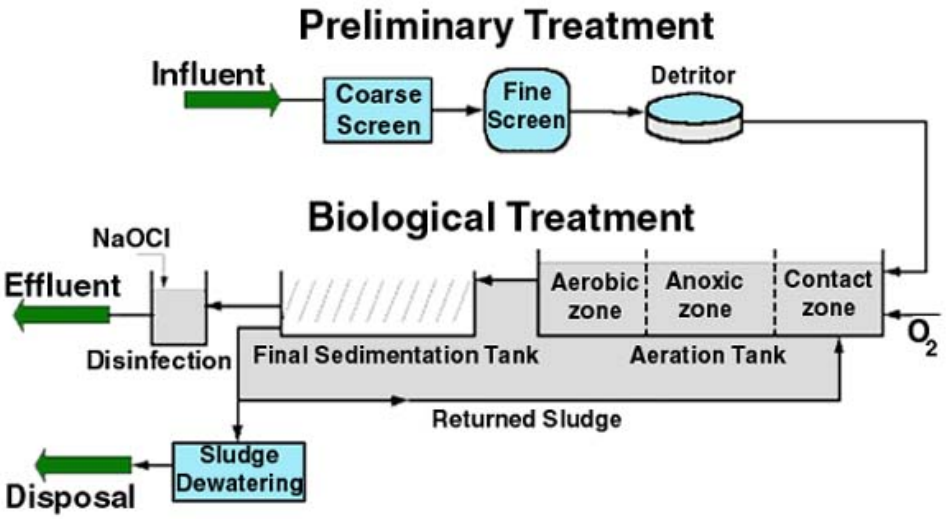

Figure S2. Schematic diagram of treatment processes (secondary treatment with activated sludge method) used by the WWTP Plant B in this study.

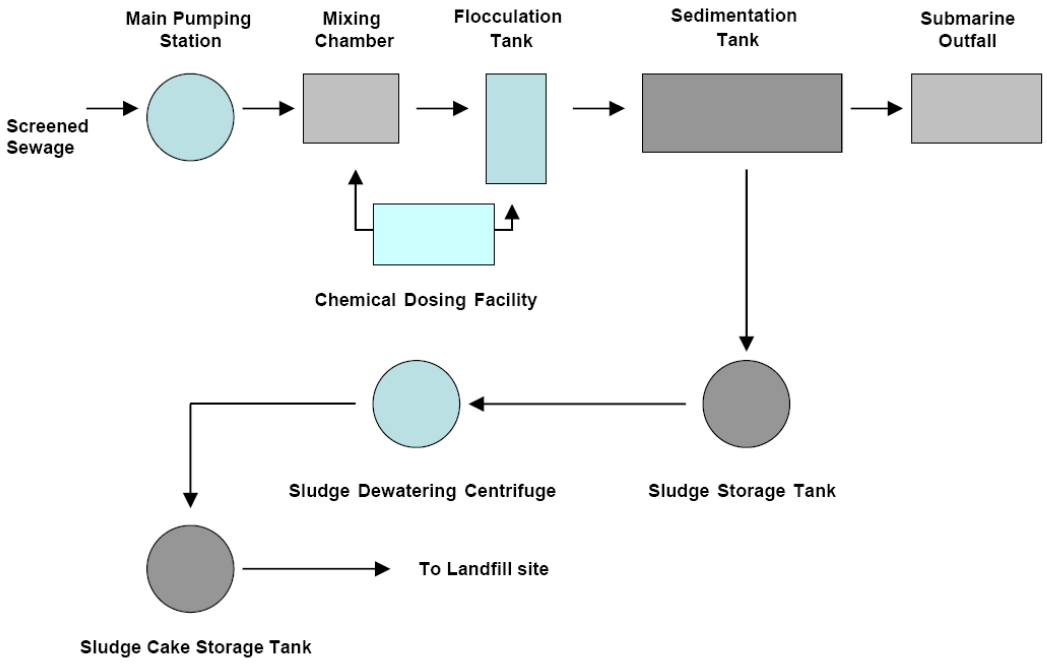

Figure S3. Schematic diagram of treatment processes (chemically enhanced primary treatment) used by the WWTP Plant C in this study.