



Perfluorinated compounds in the Pearl River and Yangtze River of China

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Abstract

A total of 14 perfluorinated compounds (PFCs) were quantified in river water samples collected from tributaries of the Pearl River (Guangzhou Province, south China) and the Yangtze River (central China). Among the PFCs analyzed, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) were the two compounds with the highest concentrations. PFOS concentrations ranged from 0.90 to 99 ng/l and <0.01–14 ng/l in samples from the Pearl River and Yangtze River, respectively; whereas those for PFOA ranged from 0.85 to 13 ng/l and 2.0–260 ng/l. Lower concentrations were measured for perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctanesulfoamide (PFOSA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorononaic acid (PFNA), perfluorodecanoic acid (PFDA), and perfluoroundecanoic acid (PFUnDA). Concentrations of several perfluorocarboxylic acids, including perfluorododecanoic acid (PFDoDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA) and perfluorooctadecanoic acid (PFOcDA) were lower than the limits of quantification in all the samples analyzed. The highest concentrations of most PFCs were observed in water samples from the Yangtze River near Shanghai, the major industrial and financial centre in China. In addition, sampling locations in the lower reaches of the Yangtze River with a reduced flow rate might serve as a final sink for contaminants from the upstream river runoffs. Generally, PFOS was the dominant PFC found in samples from the Pearl River, while PFOA was the predominant PFC in water from the Yangtze River. Specifically, a considerable amount of PFBS (22.9–26.1% of total PFC analyzed) was measured in water collected near Nanjing, which indicates the presence of potential sources of PFBS in this part of China. Completely different PFC composition profiles were observed for samples from the Pearl River and the Yangtze River. This indicates the presence of dissimilar sources in these two regions.

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1. Introduction

Perfluorinated compounds (PFCs) are a group of emerging chemicals of concern in the 21st century. The abilities to repel both water and oil, together with their chemical and thermal stabilities, have made PFCs very useful in many commercial applications (Kissa, 2001). The widespread application, environmental persistence and bioaccumulative potential of PFCs result in the global occurrence of these substances in air (Martin et al., 2002; Stock et al., 2004); water (Saito et al., 2003; Schultz et al., 2004; So et al., 2004; Yamashita et al., 2004); sediment and sludge (Higgins et al., 2005); as well as various wildlife species inhabiting not only locations in close proximity to pollution sources, but also in remote areas (Houde et al., 2006, and references therein). Among the PFCs, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), regarded as the terminal degradation end-products, are the two chemicals that have frequently been detected in environmental samples, and very often occur at the highest concentrations.

Potential sources of PFCs in the aquatic environment include the application of PFC-based products such as aqueous film forming foams or the direct release to the environment during manufacturing processes (Poulsen et al., 2005; Prevedouros et al., 2006). PFCs can also be formed from indirect conversion of their precursor compounds. For example, conversion of *N*-ethyl perfluorooctane sulfonaminoethanol (*N*-EtFOSE) and *N*-ethyl perfluorooctane sulfonamide (*N*-EtFOSA) to PFOS has been observed in liver microsomes of rats (Xu et al., 2004) and rainbow trout (Tomy et al., 2004), respectively. Fluorotelomer alcohols were also suggested to be the precursor compounds of various perfluorocarboxylic acids (PFCAs) (Dinglasan et al., 2004; Ellis et al., 2004). The intentional and unintentional discharges, and the subsequent transformations, may have resulted in the occurrence of various PFCs in groundwater (Schultz et al., 2004); coastal surface water (Saito et al., 2003); drinking water (Harada et al., 2003); as well as open ocean waters (Yamashita et al., 2005). The occurrence of PFCs in open ocean waters indicates that understanding the pollution sources and the water movement patterns would be important to explain the transports of PFCs from coastal regions to the open ocean.

The extent of PFC pollution in the aquatic environment has previously been monitored in the United States (Hansen et al., 2002; Boulanger et al., 2004; Schultz et al., 2004), Canada (Moody et al., 2002) and Japan (Saito et al., 2003; Taniyasu et al., 2003; Yamashita et al., 2004). A recent study reported that ranges of concentrations of PFOS in coastal seawaters of Hong Kong and the Pearl River Delta (PRD) were 0.09–3.1 and 0.02–12 ng/l, respectively, while those for PFOA were 0.73–5.5 and 0.24–16 ng/l, respectively (So et al., 2004).

The rapid industrial development in China in the past decade has transformed China into one of the world's large

est economies. Specifically, a large number of private manufacturing operations in the PRD and the Yangtze River Delta (YRD) have transformed these regions into two of the "world's factories". The Yangtze River, one of the largest rivers in the world, extends from Qinghai-Tibet Plateau out to the East China Sea. The water quality of the Yangtze River has been adversely affected by intense industrial and urban activities (Shen et al., 2006). The manufacturing processes associated with industries, such as electronic or electric products, plastic goods and textiles, are expected to be potential sources of PFCs. As part of a continuous study, concentrations of PFCs were monitored in six tributaries of the Pearl River in Guangdong Province, south China, entering the PRD, in an attempt to locate possible pollution sources within the delta, and study their contribution to PFC contamination in the open ocean of the South China Sea. In addition, PFCs were measured in water samples from four sections along the Yangtze River, including Chongqing, Yichang, Nanjing and Shanghai, where the river eventually discharges into the East China Sea. This study was conducted to provide information on the baseline concentrations of PFCs in several major Chinese rivers. In addition, chemical composition profiles of PFCs measured in this study can also be used as fingerprints for source identification of PFCs in the open ocean environment.

2. Materials and methods

2.1. Chemicals and standards

The potassium salt of PFOS was purchased from Tokyo Chemical Industries (Portland, OR). Potassium salts of perfluorohexanesulfonate (PFHxS), perfluorobutanesulfonate (PFBS), and perfluorooctanesulfonamide (PFOSA) were provided by the 3M Company. Perfluorononanoic acid (PFNA) was purchased from Avocado Research Chemicals Ltd. (Lancashire, UK). PFOA was from Strem Chemicals Industries (Newburyport, MA). Perfluorohexanoic acid (PFHxA) was purchased from Wako Pure Chemical Industries Ltd. (Tokyo, Japan). Perfluoroheptanoic acid (PFHpA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnDA), and perfluorododecanoic acid (PFDoDA) were purchased from Fluorochem Ltd. (Derbyshire, UK). Perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA) and perfluorooctadecanoic acid (PFOcDA) were from SynQuest Lab Inc. (Alachua, FL). Purities of all the analytical standards were $\geq 95\%$. Oasis[®] weak anion exchange (WAX; 6 cc, 150 mg, 30 μ m) solid phase extraction (SPE) cartridges were purchased from Waters (Milford, MA). Milli-Q water was used throughout the whole experiment. Methanol (residual pesticide and PCB analytical grade), ammonium acetate (97%), ammonium solution (25%) and acetic acid (99.9%) were from Wako Pure Chemical Industries (Tokyo, Japan).

2.2. Sample collection

Samples of water were collected in November, 2004 from six locations situated along tributaries of the Pearl River in Guangzhou city, China. Among these, four were from the West River [near Jiujiang (JJ)], the North River [near Longjiang (LJ) and Lanshi (LS)], and the Pearl River [near Yuancun (YC)]. The other two sets of samples were collected near Xintang (XT) and Dongguan (DG) in January, 2005 (Fig. 1a). Additionally, river water samples were collected from four sampling areas near Chongqing (CQ), Yichang (YG), Nanjing (NJ) and Shanghai (SH), along the Yangtze River which enters the East China Sea near Shanghai. Each sampling area was further divided into two or three sub-areas in such a way that PFCs in the water samples could reflect the general contamination status of the upstream, middle stream and downstream portions of the Yangtze River (Fig. 1b).

Three liters of surface water were collected from each location by using a stainless steel bucket which was pre-cleaned by rinsing with methanol, Milli-Q water, and then water from the specific location. Water samples were stored in three 1 l polypropylene (PP) bottles with narrow mouths and screw caps. Whenever possible, the samples were extracted within 24 h of collection. Otherwise, water sam-

ples were stored at 4 ± 2 °C before extraction. Disposable PP laboratory ware, instead of glassware, was used to prevent the binding of the analyte to glass surfaces. All Teflon[®]-containing laboratory materials were avoided during the experimental and sampling procedures to prevent possible contamination of the samples. The above procedures provided sufficiently small detection limits for the quantification of the predominant PFCs at the observed concentrations.

2.3. Sample extraction

Duplicate water samples were analyzed from each sampling location. All samples of river water were extracted using Oasis WAX cartridge (0.2 g, 6 cm³). The cartridge was firstly pre-conditioned by passing through the cartridge in the sequence of 4 ml of 0.1% ammonium/methanol, 4 ml methanol and 4 ml water at a rate of 2 drops/s. Depending on the concentrations of the water samples, 300 ml to 1 l samples were passed through the pre-conditioned cartridges at a rate of 1 drop/s. The cartridges were prevented from drying at all times during sample loading. They were then washed by 4 ml of 25 mM acetate buffer solution (pH 4) and discarded. The water remained in the cartridges was completely removed by using vacuum pump

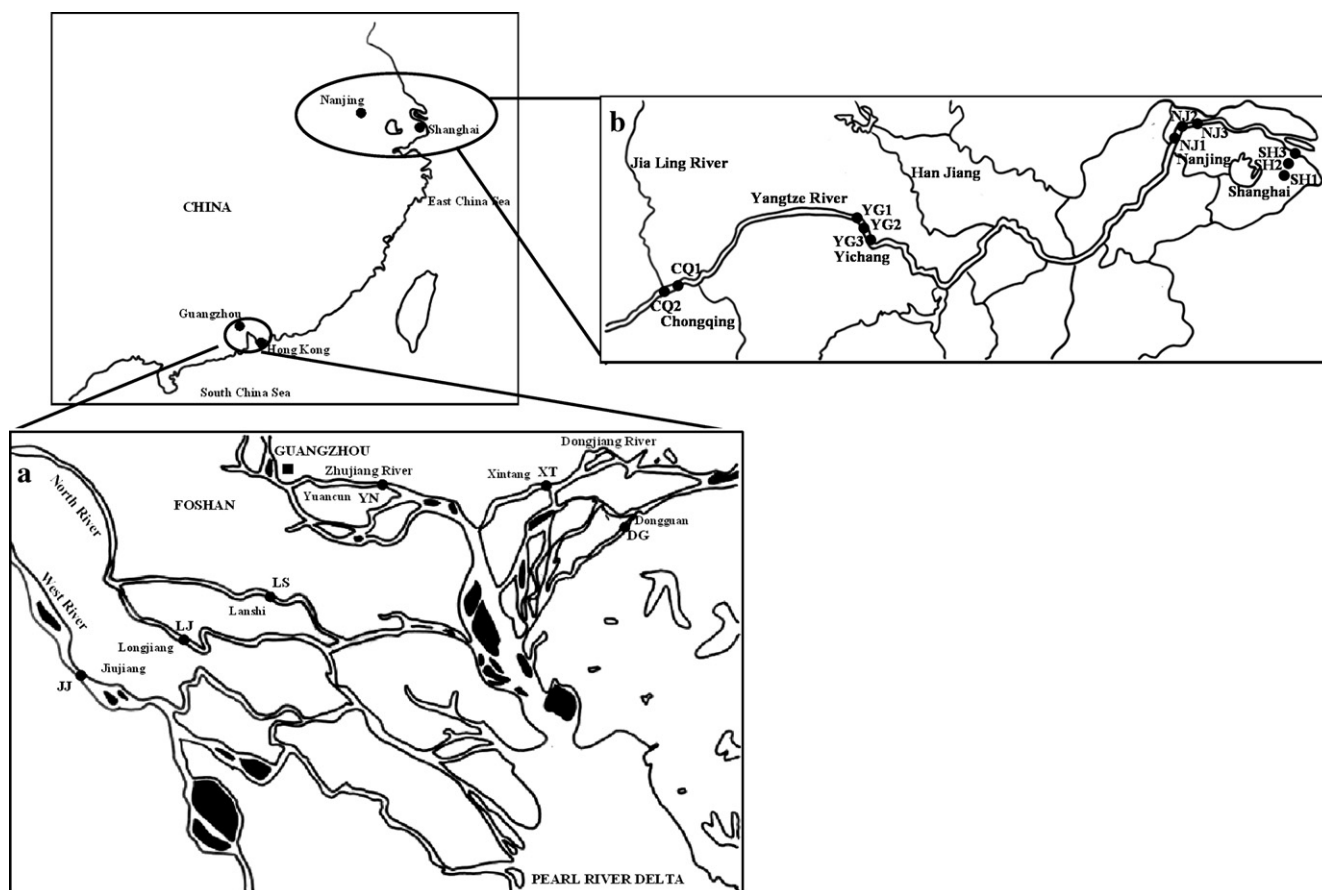


Fig. 1. Sampling locations of water from six tributaries of the Pearl River in Guangzhou and four locations along the Yangtze River (JJ: Jiujiang; LJ: Longjiang; LS: Lanshi; YC: Yuancun; XT: Xintang; DG: Dongguan; CQ: Chongqing; YG: Yichang; NJ: Nanjing; SH: Shanghai).

because water remaining in the cartridges would affect the concentration efficiency at a later process and, more importantly, affect the recovery of PFOSA (data not shown). The target analytes were eluted into two fractions. The first fraction (F1) and second fraction (F2) were eluted by 4 ml methanol and 4 ml of 0.1% ammonium/methanol, respectively. The eluant was concentrated to 0.5 ml under a stream of high purity nitrogen.

2.4. Instrumental analysis

Concentrations of PFCs in river water samples were analyzed by the use of high-performance liquid chromatography with tandem mass spectrometry (HPLC–MS/MS). Separation of the analytes was performed by an Agilent HP1100 liquid chromatograph (Agilent, Palo Alto, CA) interfaced with a Micromass Quattro Ultima Pt mass spectrometer (Waters Corp., Milford, MA) operated in electrospray negative mode. A 10 μ l aliquot of extract was injected onto a Keystone Betaasil C₁₈ column (2.1 mm i.d. \times 50 mm length, 5 μ m, 100 Å pore size, endcapped) with 2 mM ammonium acetate and methanol as the mobile phases starting at 10% methanol at a flow rate of 300 μ l/min. The gradient was increased to 100% methanol at 10 min before reverting to the original conditions at 13 min. The desolvation gas flow and temperature were kept at 610 l/h and 450 °C, respectively. The collision energies, cone voltages and MS/MS parameters for the instrument were optimized for individual analytes, and were reported elsewhere (Taniyasu et al., 2005).

2.5. Data analysis

Each ion of interest in the chromatogram was selected and integrated. Concentrations of target analytes were quantified by using external calibration curves, constructed using external standards of six different concentrations (2, 10, 50, 200, 1000, 10000 ng/l). Standard calibration curves exhibited excellent linearity (correlation coefficient >0.99). Final extracts with concentrations fell outside the ranges of calibration curve were diluted with methanol to an appropriate factor and re-injected again.

2.6. Statistical analysis

A Spearman rank correlation analysis was used to assess the correlations among PFCs in river water samples from the Pearl River and the Yangtze River. Statistical significance was accepted at $p < 0.05$.

3. Results and discussion

3.1. Quality assurance and control

The quantification of PFCs in the laboratory was influenced by the presence of fluoropolymer in various laboratory appliances. For example, PFOA and PFNA were

used as processing aids in the manufacture of polytetrafluoroethylene (PTFE), which existed in some laboratory equipment (Poulsen et al., 2005). Methods available to check and minimize possible sources of contamination have been described in detail previously (Yamashita et al., 2004). Other important precautions to minimize background interferences and allow the least limits of detection that were applied have been discussed (Schultz et al., 2003).

In order to ensure the accuracy of the sampling, extraction and analytical procedures, travel blanks, extraction procedural blanks, and procedural recoveries were conducted for each set of the samples analyzed. Travel blanks were used to check for possible sources of contamination during transportation. They were prepared by pre-filling individual 1 l PP bottles with 1 l of water, transported to the field and exposed to the same condition as the real water samples, which were then brought back to the laboratory for analysis. For each travel blank, 1 l of water was extracted, and the final volume of extract was reduced to 0.5 ml. The concentrations of various PFCs in these blank samples are summarized (Table 1). Only a small amount of PFHxA (<0.005–0.04 ng/l) and PFOA (<0.03–0.04 ng/l) were detected in the travel blanks. These concentrations were considered to be insignificant relative to the concentrations in the samples. Procedural blanks were used to check for possible sources of contamination during extraction procedures. They were prepared following the same procedures as the real samples except that Milli-Q water was used instead. Due to variation in the contamination levels in the water samples from the Pearl River and the Yangtze River, different volumes of water samples, and thus the corresponding volumes of the procedural blanks, were extracted, resulting in two sets of procedural blank values. In general, only trace concentrations of PFOA were detected (Table 1). Concentrations of the other target analytes in the blank samples were lower than the limits of quantification (LOQs). The LOQs were evaluated based on several criteria, including (i) the smallest concentration of standard on the calibration curve that could be accurately measured within $\pm 20\%$ of its theoretical value; (ii) a signal-to-noise ratio of equal to or greater than 10; (iii) concentration factor; and (iv) sample volume. Generally, the LOQs were sufficient to enable the analysis of PFCs in Chinese river water samples, which typically occur at small concentrations. The LOQs were 0.005 ng/l for PFBS, PFHxS, PFOS, PFOSA, PFHxA, PFHpA, PFNA, PFDA, PFTeDA, PFHxDA and PFOcDA; 0.025 ng/l for PFUnDA and PFDoDA, and 0.03 ng/l for PFOA, when 1 l of water sample was extracted and the final volume was reduced to 0.5 ml.

The results of a recovery test conducted by spiking a mixture of external standards (100 ng/ml, 10 μ l) into water, and then extracted following the same procedures used for real samples are shown (Table 1). Sufficient recoveries were achieved for all the PFCs with the mean recoveries of over 88%, and all reported data were not corrected for recover-

Table 1
Recoveries (%), travel blanks and procedural blanks (ng/l) for individual PFCs

| Target analyte | Travel blank (ng/l) (<i>n</i> = 4) | | Procedural blank (ng/l) | | | | Recovery (%) (<i>n</i> = 4) | |
|------------------------------------|-------------------------------------|-------------------|--|-------------------|---|-------------------|------------------------------|------|
| | Range | Mean ^a | Samples from the Pearl River (<i>n</i> = 3) | | Samples along the Yangtze River (<i>n</i> = 3) | | Range | Mean |
| | | | Range | Mean ^a | Range | Mean ^a | | |
| <i>Perfluorosulfonyl compounds</i> | | | | | | | | |
| PFBS | <0.005 | n.d. ^b | <0.03–<0.13 | n.d. ^b | <0.005 | n.d. ^b | 89.1–103 | 94.1 |
| PFHxS | <0.005 | n.d. ^b | <0.13–<0.67 | n.d. ^b | <0.005 | n.d. ^b | 84.2–101 | 90.3 |
| PFOS | <0.005 | n.d. ^b | <0.13–<0.67 | n.d. ^b | <0.005 | n.d. ^b | 93.7–98.6 | 95.3 |
| PFOSA | <0.005 | n.d. ^b | <0.03 | n.d. ^b | <0.005 | n.d. ^b | 82.7–94.0 | 88.4 |
| <i>Perfluorocarboxyl compounds</i> | | | | | | | | |
| PFHxA | <0.005–0.04 | 0.02 | <0.13–<0.67 | n.d. ^b | <0.005 | n.d. ^b | 87.9–104 | 96.5 |
| PFHpA | <0.005 | n.d. ^b | <0.13–<0.67 | n.d. ^b | <0.005 | n.d. ^b | 94.6–96.0 | 95.4 |
| PFOA | <0.03–0.04 | n.d. ^b | <0.13–<0.67 | n.d. ^b | 0.02–0.04 | 0.03 | 94.0–105 | 99.1 |
| PFNA | <0.005 | n.d. ^b | <0.13–<0.67 | n.d. ^b | <0.005 | n.d. ^b | 80.3–103 | 92.3 |
| PFDA | <0.005 | n.d. ^b | <0.13–<0.67 | n.d. ^b | <0.005 | n.d. ^b | 92.8–108 | 97.5 |
| PFUnDA | <0.025 | n.d. ^b | <0.13–<0.67 | n.d. ^b | <0.025 | n.d. ^b | 91.3–103 | 96.8 |
| PFDoDA | <0.025 | n.d. ^b | <0.03–<0.13 | n.d. ^b | <0.025 | n.d. ^b | 89.1–113 | 98.1 |
| PFTeDA | <0.005 | n.d. ^b | <0.13–<0.67 | n.d. ^b | <0.005 | n.d. ^b | 87.2–89.3 | 88.4 |
| PFHxDA | <0.005 | n.d. ^b | <0.13–<0.67 | n.d. ^b | <0.005 | n.d. ^b | 87.0–92.3 | 90.0 |
| PFOcDA | <0.005 | n.d. ^b | <0.03–<0.13 | n.d. ^b | <0.005 | n.d. ^b | 90.5–100 | 95.2 |

^a Target analytes with concentrations lower than the LOQ were treated as zero when calculating the mean value.

^b n.d. represents “not determined”.

ies. Reliability of the above method was further verified through participation in the First and Second Worldwide PFC Interlaboratory Studies, and our laboratory reported acceptable results on both occasions.

3.2. PFC concentrations in tributaries of the Pearl River within Guangzhou area

Concentrations of perfluoroalkyl compounds in river water samples are summarized (Table 2). A total of 14 PFCs were measured in these samples, however, concentrations of PFHxS and several PFCAs, including PFDoDA, PFTeDA, PFHxDA and PFOcDA, were all lower than their respective LOQs. Therefore, results for these chemicals will not be discussed in the present study. PFOS, PFOSA, and PFOA were detected in all the samples analyzed. Among these chemicals, PFOS and PFOA occurred at the highest concentrations. Concentrations of PFOS ranged from 0.90 to 99 ng/l, whereas those for PFOA ranged from 0.85 to 13 ng/l. Lower concentrations, ranging from 0.073 to 0.34 ng/l, were measured for PFOSA. PFBS, PFHxA, PFNA, PFDA and PFUnDA were quantified (higher than LOQs) in the samples at a lesser frequency. The maximum concentrations for these chemicals, in the same sequence, were 3.4, 2.2, 3.1, 0.57 and 0.40 ng/l, respectively (Table 2).

Total concentrations of perfluoroalkyl sulfonates (PFASs) and PFCAs in the water samples were compared among locations (Fig. 2). The highest PFAS concentrations were measured in samples from the location DG, followed by locations XT and YC; whereas samples from YC contained the highest amount of PFCAs, followed by those from locations XT and DG. The different contributions

of PFAS and PFOA to the total PFCs analyzed in the samples indicated that the sources of PFCs were different among cities. Among the PFCs, PFOS and PFOA generally accounted for 88–100% and 50–87%, respectively, of the total concentrations of PFASs and PFCAs analyzed. The predominance of PFOS and PFOA may not only be due to the direct discharge of these compounds to the environment during manufacturing processes or uses of related products (Lehmeler, 2005; Prevedouros et al., 2006), but also the possibility of degradation of other precursor compounds to these chemicals, which are regarded as the terminal degradation end-products that are persistent and bioaccumulative (Ellis et al., 2004; Tomy et al., 2004; Xu et al., 2004).

Water samples from location DG contained the highest concentrations of PFOS (99 and 89 ng/l); and those from location XT contained the highest concentrations of PFBS (3.4 ng/l), PFDA (0.57 and 0.45 ng/l), and PFHxA (2.2 and 1.9 ng/l). The highest concentrations of PFOSA (0.33 and 0.34 ng/l), PFOA (13 ng/l), PFHpA (4.1 and 4.0 ng/l), and PFNA (3.1 and 3.0 ng/l) were measured in samples from location YC. Location JJ was shown to be the least contaminated area. Water samples collected around this area contained the least concentrations of PFOS (0.90 and 1.1 ng/l), and PFOA (0.85 and 0.86 ng/l). In addition, most of the PFCAs in these samples were lower than the LOQs and thus could not be quantified (Table 2). The higher concentrations of PFCs in samples from locations XT and DG could be due to the discharge of domestic and industrial wastewater from the nearby industrialized areas into the small tributaries of Dongjiang River, one of the major tributaries of the Pearl River. Economic reforms and the open-door policy since 1978 have led to

Table 2
Concentrations (ng/l) of PFCs in water samples from tributaries of the Pearl River in Guangzhou and along the Yangtze River (S1 and S2 represent sample 1 and sample 2, respectively)

| Sampling location | Concentrations (ng/l) (<i>n</i> = 2) | | | | | | | | | | | | | | | | | | | |
|--|---------------------------------------|--------|--------|--------|------|-------|--------|--------|---------------------------|-------|-------|-------|------|------|--------|--------|-------|--------|--------|--------|
| | Perfluoroalkyl sulfonates | | | | | | | | Perfluorocarboxylic acids | | | | | | | | | | | |
| | PFBS | | PFHxS | | PFOS | | PFOSA | | PFHxA | | PFHpA | | PFOA | | PFNA | | PFDA | | PFUnDA | |
| | S1 | S2 | S1 | S2 | S1 | S2 | S1 | S2 | S1 | S2 | S1 | S2 | S1 | S2 | S1 | S2 | S1 | S2 | S1 | S2 |
| <i>Tributaries of the Pearl River in Guangzhou</i> | | | | | | | | | | | | | | | | | | | | |
| JJ | <0.03 | <0.03 | <0.13 | <0.13 | 0.90 | 1.1 | 0.13 | 0.13 | <0.13 | <0.13 | 0.23 | 0.27 | 0.85 | 0.86 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| LJ | <0.03 | <0.03 | <0.13 | <0.13 | 2.3 | 2.3 | 0.097 | 0.092 | <0.13 | <0.13 | <0.13 | <0.13 | 0.89 | 0.96 | 0.14 | 0.14 | <0.13 | <0.13 | <0.13 | <0.13 |
| LS | <0.03 | <0.03 | <0.13 | <0.13 | 2.5 | 5.5 | 0.073 | 0.077 | 0.29 | 0.35 | 0.42 | 0.45 | 1.3 | 1.2 | 0.24 | 0.22 | 0.21 | 0.22 | <0.13 | <0.13 |
| YC | <0.03 | <0.03 | <0.13 | <0.13 | 12 | 12 | 0.33 | 0.34 | 1.0 | 0.97 | 4.1 | 4.0 | 13 | 13 | 3.1 | 3.0 | 0.44 | 0.41 | 0.40 | 0.36 |
| XT | 3.4 | 3.4 | <0.13 | <0.13 | 24 | 26 | 0.19 | 0.12 | 2.2 | 1.9 | 1.6 | 1.5 | 5.6 | 5.0 | 1.1 | 0.94 | 0.57 | 0.45 | 0.26 | 0.20 |
| DG | <0.13 | <0.13 | <0.67 | <0.67 | 99 | 89 | 0.092 | 0.12 | 0.89 | <0.67 | <0.67 | 1.1 | 4.4 | 4.3 | 0.77 | <0.67 | <0.67 | <0.67 | <0.67 | <0.67 |
| <i>Sampling points along the Yangtze River</i> | | | | | | | | | | | | | | | | | | | | |
| <i>Chongqing</i> | | | | | | | | | | | | | | | | | | | | |
| CQ1 | <0.01 | <0.01 | <0.01 | <0.01 | 0.35 | 0.39 | 0.0077 | 0.0098 | 0.30 | 0.39 | 0.31 | 0.33 | 35 | 32 | <0.01 | <0.01 | 0.043 | 0.043 | <0.05 | <0.05 |
| CQ2 | <0.01 | <0.01 | <0.01 | <0.01 | 0.15 | <0.01 | 0.0065 | 0.0061 | 0.32 | 0.30 | 0.22 | 0.27 | 28 | 23 | <0.01 | <0.01 | <0.01 | <0.01 | <0.05 | <0.05 |
| <i>Yichang</i> | | | | | | | | | | | | | | | | | | | | |
| YG1 | <0.005 | <0.005 | <0.005 | <0.005 | 0.61 | 0.39 | <0.005 | <0.005 | 0.16 | 0.17 | 0.074 | 0.079 | 4.1 | 4.3 | <0.005 | <0.005 | 0.030 | 0.019 | <0.025 | <0.025 |
| YG2 | <0.005 | <0.005 | <0.005 | <0.005 | 0.29 | 0.29 | <0.005 | <0.005 | 0.19 | 0.18 | 0.089 | 0.085 | 4.3 | 4.1 | <0.005 | <0.005 | 0.014 | 0.017 | <0.025 | <0.025 |
| YG3 | <0.005 | <0.005 | <0.005 | <0.005 | 0.59 | 0.82 | 0.007 | <0.005 | <0.005 | 0.18 | 0.093 | 0.11 | 4.9 | 5.3 | 0.12 | <0.005 | 0.054 | 0.026 | 0.081 | <0.025 |
| <i>Nanjing</i> | | | | | | | | | | | | | | | | | | | | |
| NJ1 | 1.1 | 1.1 | <0.005 | <0.005 | 0.38 | 0.37 | 0.013 | 0.0097 | 0.18 | 0.19 | 0.28 | 0.28 | 2.1 | 2.0 | 0.17 | 0.18 | 0.045 | 0.054 | 0.030 | 0.027 |
| NJ2 | 1.2 | 1.1 | <0.005 | <0.005 | 0.33 | 0.34 | 0.0087 | 0.0079 | 0.16 | 0.23 | 0.39 | 0.29 | 2.1 | 2.3 | 0.17 | 0.15 | 0.036 | <0.005 | 0.026 | 0.036 |
| NJ3 | 0.97 | 1.2 | <0.005 | <0.005 | 0.33 | 0.39 | 0.010 | <0.005 | 0.15 | 0.20 | 0.33 | 0.29 | 2.4 | 2.6 | 0.15 | 0.17 | 0.034 | 0.043 | 0.030 | 0.028 |
| <i>Shanghai</i> | | | | | | | | | | | | | | | | | | | | |
| SH1 | 2.1 | 2.1 | <0.01 | <0.01 | 0.62 | 0.69 | <0.005 | 0.0085 | 0.39 | 0.40 | 0.65 | 0.55 | 22 | 27 | 0.50 | 0.48 | 0.17 | 0.11 | 0.10 | <0.05 |
| SH2 | 2.1 | 2.0 | <0.01 | <0.01 | 1.7 | 1.8 | 0.020 | 0.026 | 0.72 | 0.78 | 1.1 | 1.2 | 33 | 35 | 1.0 | 1.2 | 0.39 | 0.43 | 0.44 | 0.46 |
| SH3 | 0.96 | 0.98 | 0.40 | 0.36 | 14 | 12 | 0.053 | 0.044 | 5.3 | 5.0 | 8.7 | 9.2 | 260 | 230 | 10 | 9.0 | 3.8 | 3.3 | 3.0 | 2.4 |

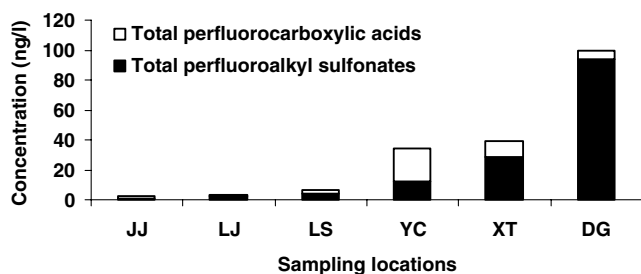


Fig. 2. Comparison of total concentrations of PFASs and PFCAs in river water samples among locations of the Pearl River in Guangzhou (JJ: Jiujiang; LJ: Longjiang; LS: Lanshi; YC: Yuancun; XT: Xintang; DG: Dongguan).

rapid economic development in China. Guangdong was the first province to be selected for the economic reform. Dongguan, one of the cities of Guangdong, has experienced rapid growth of industries with an average annual industrial growth rate of 37% between 1985 and 1992 (Yeh and Li, 1999). This has led to the establishment of many new industries from 1990 onwards (Yeung, 2001). For example, the industrial output for plastic products, electrical equipment, and telecommunication equipment has increased at rates from 1.94% to 6.44%, 3.99–8.29%, and 0.54–17.17%, respectively, during the year 1980–1997 (Yeung, 2001). Many of these industries could potentially involve the use of various PFCs during their manufacturing processes, and thus could lead to the release of these compounds into the environment. Zhujiang River, another major tributary of the Pearl River, receives domestic wastes and industrial effluents from the highly urbanized and densely populated areas of Guangzhou. This may contribute to the presence of PFCs in water samples near location YC. The total concentrations of PFASs (12 ng/l) and PFCAs (22 ng/l) in the water samples from Guangzhou, however, were comparatively lower than concentrations of total organochlorine pesticides (23–62 ng/l) and polycyclic aromatic hydrocarbons (PAH) (990–2900 ng/l) (Luo et al., 2004). Water samples from location JJ were collected along the Xijiang River. The Xijiang River, situated on the southwest of the PRD, runs through less developed areas. This may account for the comparatively lower PFC concentrations in samples from location JJ. The total concentrations of PFASs (1.1 ng/l), and PFCAs (1.1 ng/l) were lower than those of total PAH concentrations (22–140 ng/l) in the same river system (Deng et al., 2006). This river system, in fact, is not only the major source of water supply for agricultural and industrial activities, but also serves as the main drinking water supply for a population of about 4.5 million people. Concentrations of PFOS (0.90 and 1.1 ng/l) and PFOA (0.85 and 0.86 ng/l) in the samples were lower than the lifetime drinking water health advisory for PFOS (1000 ng/l) (Hansen et al., 2002) and PFOA (150000 ng/l) (Poulsen et al., 2005). This indicates that concentrations of PFOS and PFOA measured in water samples collected from the Pearl River do not pose any sig-

nificant adverse health effect to humans at this point in time.

3.3. PFC concentrations in water samples collected along the Yangtze River

Concentrations of PFCs in water collected along the Yangtze River are summarized (Table 2). Long-chained PFCAs, including PFDoDA, PFTeDA, PFHxDA, and PFOcDA were not detected in water samples from any locations along the Yangtze River. PFOS, PFHxA, PFHpA, PFOA, and PFDA were detected in most of the samples analyzed. PFOS and PFOA occurred at the highest concentrations. Concentrations of PFOS ranged from <0.01 to 14 ng/l, whereas those for PFOA ranged from 2.0 to 260 ng/l. Lower concentrations of PFHxA, PFHpA, and PFDA were measured in the water with concentrations ranging from <0.005 to 5.3 ng/l for PFHxA, 0.074–9.2 ng/l for PFHpA, and <0.005–3.8 ng/l for PFDA (Table 2).

Our results indicate that Shanghai, the largest city situated in the YRD, is the most heavily contaminated area. Water samples from location SH3 contained the highest concentrations of most of the PFCs analyzed except for PFBS. The highest concentrations of PFOSA, PFHxS, PFOS, PFHxA, PFHpA, PFOA, PFNA, PFDA, and PFOcDA were 0.053, 0.40, 14, 5.3, 9.2, 260, 10, 3.8, and 3.0 ng/l. The concentrations of PFCAs were all higher than the maximum concentrations measured in the water samples from tributaries of the Pearl River within Guangzhou Province. The second highest concentrations of all the compounds were again detected in water from the Shanghai region at sampling point SH2, locating upstream from point SH3. The highest concentrations, in the same sequence as above, were 0.026, <0.01, 1.8, 0.78, 1.2, 35, 1.2, 0.43, and 0.46 ng/l, respectively. The higher PFAS and PFCA concentrations in the downstream areas at station SH3 than SH2 indicated the presence of potential discharges of PFCs into the environment, at which the discharge volumes probably overwhelmed the dilution effect at the downstream sites. In addition, location SH3, situated at the lower reach of the river, could serve as a final sink for the contaminants from the upstream river runoffs (Yang et al., 2005). In general, significant amounts of PFOA were found in the water samples collected along the Yangtze River. A decreasing gradient in PFOA concentrations was observed from upper reaches of the Yangtze River at Chongqing (locations CQ1 and CQ2), along Yichang (locations YG1, YG2, YG3) and downstream to Nanjing (NJ1, NJ2, NJ3) at the lower reaches (Table 2). This observation could probably be the results of dilution effects with greater volume of river water at the downstream sections. Chongqing, the principal commercial and industrial centre of southwestern China, is the second most contaminated region after Shanghai. The major manufacturing industries at Chongqing include iron and steel, machinery, motor vehicles, cotton and silk textiles, and processed food. PFOA concentrations at location CQ1

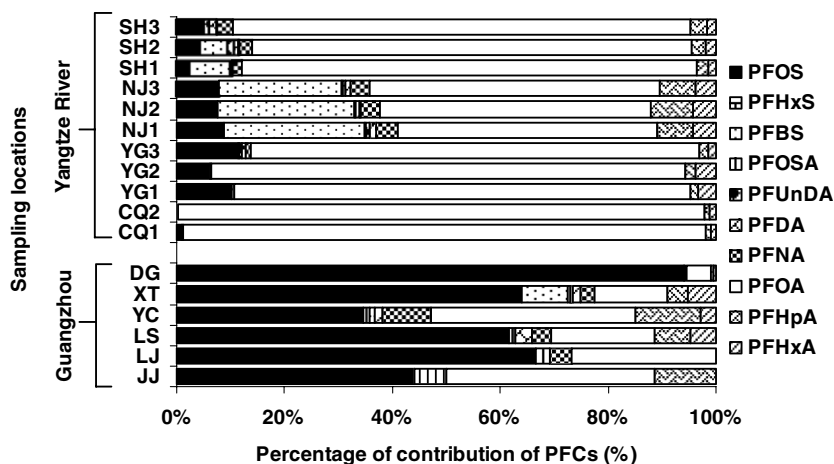


Fig. 3. Composition profile of various PFCs in river water samples from tributaries of the Pearl River in Guangzhou and along the Yangtze River (JJ: Jiujiang; LJ: Longjiang; LS: Lanshi; YC: Yuancun; XT: Xintang; DG: Dongguan; CQ: Chongqing; YG: Yichang; NJ: Nanjing; SH: Shanghai).

(35, 32 ng/l) and CQ2 (28, 23 ng/l) were comparable to those detected in Shanghai. Slightly lower concentrations of PFOS (0.35, 0.39 ng/l), PFHxA (0.30, 0.39 ng/l), and PFHpA (0.31, 0.34 ng/l) were detected in water samples from location CQ1.

3.4. Composition profile of various PFCs

The profiles of relative concentrations of 10 PFCs are shown in Fig. 3. The samples from tributaries of the Pearl River in Guangzhou exhibited completely different profiles or relative concentrations of PFCs compared to those from Yangtze River. However, the patterns were less variable among sampling locations within Guangzhou and along the Yangtze River. Generally, PFOS was the dominant chemical in water samples from locations DG, XT, LS and LJ in Guangzhou, contributing 94.1%, 63.9%, 61.5% and 66.6%, respectively, of the total PFCs analyzed. The relative contributions of PFOA in these samples were smaller and their contributions, in the same sequence, were 4.4%, 13.4%, 19.1% and 26.7%, respectively. Relatively large proportions of the total concentrations of PFCs were contributed by PFOA in water collected along the Yangtze River. PFOA contributed up to 98% of the total PFC composition in the samples from CQ. The contributions of PFOA for the other locations (YG, NJ and SH) ranged from 48.1% to 87.8%. The difference in composition patterns indicated that the potential sources of PFCs were quite different between the tributaries of the Pearl River in Guangzhou and the Yangtze River. Greater PFOS contributions in samples from Guangzhou implied a predominance in the use of perfluorosulfonyl substances; whereas perfluorocarboxyl compounds were predominantly used in the YRD region. A considerable portion of PFCs was contributed by PFBS (22.9–26.1%) in water from location NJ, while concentrations of PFBS were relatively lower in water from other locations. This result indicates the existence of potential sources of PFBS near NJ.

3.5. Correlations among various PFCs

The correlations among various PFCs from all the sampling locations were examined (Table 3). Statistically significant correlations were found among PFOS and other compounds including PFOSA, PFNA and PFHpA. The positive correlations suggested the possibility of a common pollution source for these chemicals in the Chinese environment. Significant positive correlations were also observed for most of the perfluorocarbonyl compounds (Table 3). These findings are in agreement with the hypothesis that telomer alcohols degraded to other PFCAs. For example, PFCAs with different carbon chain lengths, including PFNA, PFHpA, PFHxA, PFPeA, PFBA, were detected following the atmospheric oxidation of telomer alcohols (FTOHs) by chlorine atoms (Ellis et al., 2004). A recent study also showed that atmospheric oxidation of FTOHs could be one of the major pathways leading to the formation of PFCAs in remote areas (Hurley et al., 2004). Their positive correlations suggested the possibility of common sources of these compounds in water samples in Guangzhou and along the Yangtze River.

3.6. Comparison of PFC concentrations in Chinese rivers with other studies

Comparison of PFC concentrations in water samples from Guangzhou and the Yangtze River with those from other countries are summarized (Table 4). Concentrations of PFOS and PFOA in water samples from Guangzhou and along the Yangtze River were either comparable to or higher than those measured in coastal seawaters in Hong Kong and the PRD region (So et al., 2004). PFOS concentrations in samples from most of the locations, except for XT and DG, fell within the ranges measured for coastal water samples from Hong Kong (0.09–3.1 ng/l) and the PRD (0.02–12 ng/l). The highest PFOS concentrations from Guangzhou was detected at locations DG (99 ng/l)

Table 3
Correlation coefficient of Spearman rank correlation analysis of perfluorosulfonic acids and perfluorocarboxylic acids

| Target analytes | r_s | P value |
|-----------------|--------|--------------------|
| PFOS:PFHxS | 0.306 | 0.232 |
| PFOS:PFBS | 0.044 | 0.867 |
| PFOS:PFOSA | 0.751 | 0.001 ^b |
| PFOS:PFDA | 0.417 | 0.096 |
| PFOS:PFNA | 0.682 | 0.003 ^b |
| PFOS:PFOA | 0.098 | 0.708 |
| PFOS:PFHpA | 0.561 | 0.019 ^a |
| PFOS:PFHxA | 0.478 | 0.052 |
| PFHxS:PFBS | 0.114 | 0.662 |
| PFHxS:PFOSA | 0.102 | 0.696 |
| PFHxS:PFDA | 0.411 | 0.101 |
| PFHxS:PFNA | 0.413 | 0.099 |
| PFHxS:PFOA | 0.408 | 0.104 |
| PFHxS:PFHpA | 0.408 | 0.104 |
| PFHxS:PFHxA | 0.408 | 0.104 |
| PFBS:PFOSA | 0.001 | 0.998 |
| PFBS:PFDA | 0.515 | 0.034 ^a |
| PFBS:PFNA | 0.554 | 0.021 ^a |
| PFBS:PFOA | 0.232 | 0.371 |
| PFBS:PFHpA | 0.520 | 0.032 ^a |
| PFBS:PFHxA | 0.423 | 0.091 |
| PFOSA:PFDA | 0.221 | 0.394 |
| PFOSA:PFNA | 0.498 | 0.042 ^a |
| PFOSA:PFOA | −0.096 | 0.715 |
| PFOSA:PFHpA | 0.508 | 0.037 ^a |
| PFOSA:PFHxA | 0.389 | 0.123 |
| PFDA:PFNA | 0.743 | 0.001 ^b |
| PFDA:PFOA | 0.506 | 0.038 ^a |
| PFDA:PFHpA | 0.747 | 0.001 ^b |
| PFDA:PFHxA | 0.705 | 0.002 ^b |
| PFNA:PFOA | 0.375 | 0.138 |
| PFNA:PFHpA | 0.869 | 0.000 ^b |
| PFNA:PFHxA | 0.770 | 0.000 ^b |
| PFOA:PFHpA | 0.537 | 0.026 ^a |
| PFOA:PFHxA | 0.717 | 0.001 ^b |
| PFHpA:PFHxA | 0.911 | 0.000 ^b |

^a Correlation is significant at the 0.05 level.

^b Correlation is significant at the 0.01 level.

and was about 8 times higher than the maximum concentrations measured in the PRD region (12 ng/l) (So et al., 2004), but was comparatively lower than the maximum concentrations measured in waters from Lake Ontario (121 ng/l) (Boulanger et al., 2004), Tama River (157 ng/l) (Saito et al., 2003), and Tennessee River (144 ng/l) (Hansen et al., 2002). The concentration was also lower than the maximum concentrations (651 ng/l) observed at Lake Shihwa in south Korea, where the area is heavily influenced by the industrial effluent from the Shihwa industrial complex (Rostkowski et al., 2006); and were lower than the highest concentrations detected in surface waters of the Etobicoke Creek (2200000 ng/l) following an accidental release of fire-retardant foam (Moody et al., 2002).

PFOA concentrations in tributaries of the Pearl River in Guangzhou and most of the samples collected along the Yangtze River were comparable to those found in Hong Kong and the PRD. Only samples from locations CQ and SH contained PFOA concentrations higher than the maximum concentrations measured in water samples from Hong Kong (5.5 ng/l) and the PRD region (16 ng/l). In the present study, the maximum PFOA concentrations was measured in water samples at location SH3 (260 ng/l) in Shanghai. This concentration was approximately 2 times lower than the maximum concentration (598 ng/l) from Tennessee River in the United States, where the water quality was affected by the wastewater discharges from a fluorochemical manufacturing facility (Hansen et al., 2002). The PFOA concentration at SH3 was greater than the highest level measured in surface waters of Tokyo Bay (192 ng/l), known to be one of the most polluted areas in Japan (Yamashita et al., 2004). This level was also found to be higher than the maximum concentration measured in waters from the Great Lakes (70 ng/l) (Boulanger et al., 2004) and Lake Shihwa from south Korea (62 ng/l) (Rostkowski et al., 2006).

The levels of PFOS and PFOA in the samples from China are much lower than the maximum levels quantified in water samples from the Tyndall Air Force Base and the Naval Air

Table 4
Global comparison of PFOS and PFOA concentrations in water samples from Guangzhou and along the Yangtze River with those from other countries

| Location | Sample type | Concentration (ng/l) | | References |
|----------------------------|-------------------------------|----------------------------|----------------------------|--------------------------|
| | | PFOS | PFOA | |
| Guangzhou, China | Surface river water | 0.90–99 | 0.85–13 | Present study |
| Yangtze River, China | Surface river water | <0.01–14 | 2.0–260 | Present study |
| Lake Ontario (Great Lakes) | Freshwater | 15–121 | 15–70 | Boulanger et al. (2004) |
| Tama River, Japan | Surface freshwater | 0.7–157 | n.a. ^a | Saito et al. (2003) |
| Tennessee River, US | Downstream surface freshwater | 74.8–144 | 140–598 | Hansen et al. (2002) |
| Hong Kong | Surface seawater | 0.09–3.1 | 0.73–5.5 | So et al. (2004) |
| Pearl River Delta, China | Surface water | 0.02–12 | 0.24–16 | So et al. (2004) |
| Lake Shihwa, south Korea | Surface freshwater | 2.24–651 | 0.9–62 | Rostkowski et al. (2006) |
| Etobicoke Creek, Canada | Freshwater | n.d. ^a –2210000 | n.d. ^a –10600 | Moody et al. (2002) |
| Tokyo Bay, Japan | Surface freshwater | 12.7–25.4 | 154–192 | Yamashita et al. (2004) |
| Tyndall Air Force Base | Freshwater | 147000–2300000 | n.d. ^a –116000 | Schultz et al. (2004) |
| Naval Air Station Fallon | Freshwater | n.d. ^a –380000 | n.d. ^a –6570000 | Schultz et al. (2004) |

^a n.a. and n.d. represent “not analyzed” and “not detected”, respectively.

Station Fallon in the United States. The maximum PFOS and PFOA in waters from the Tyndall Air Force Base were 2 300 000 ng/l and 1 16 000 ng/l, respectively, whereas those from the Naval Air Station Fallon were 380 000 ng/l and 6 570 000 ng/l, respectively. Such high PFC concentrations were the consequence of the use of aqueous film-forming foams associated with fire-fighting training activities at these sites in the past (Schultz et al., 2004).

In general, PFC concentrations in waters from Guangzhou and the Yangtze River were either comparable to or higher than those recorded in Hong Kong and the PRD, but were found to be lower as compared to those from other countries. The only exception is the comparatively higher PFOA concentration in Shanghai indicating the severity of PFC contamination in certain areas in China.

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References

- Boulanger, B., Vargo, J., Schnoor, J.L., Hornbuckle, K.C., 2004. Detection of perfluorooctane surfactants in Great Lakes water. *Environ. Sci. Technol.* 38, 4064–4070.
- Deng, H., Peng, P., Huang, W., Song, J., 2006. Distribution and loadings of polycyclic aromatic hydrocarbons in the Xijiang River in Guangdong, South China. *Chemosphere* 64, 1401–1411.
- Dinglasan, M.J.A., Ye, Y., Edwards, E.A., Mabury, S.A., 2004. Fluorotelomer alcohol biodegradation yields poly- and perfluorinated acids. *Environ. Sci. Technol.* 38, 2857–2864.
- Ellis, D.A., Martin, J.W., Silva, A.O.D., Mabury, S.A., Hurley, M.D., Andersen, M.P.S., Wallington, T.J., 2004. Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* 38, 3316–3321.
- Hansen, K.J., Johnson, H.O., Eldridge, J.S., Butenhoff, J.L., Dick, L.A., 2002. Quantitative characterization of trace levels of PFOS and PFOA in the Tennessee River. *Environ. Sci. Technol.* 36, 1681–1685.
- Harada, K., Saito, N., Sasaki, K., Inoue, K., Koizumi, A., 2003. Perfluorooctane sulfonate contamination of drinking water in the Tama River, Japan: estimated effects on resident serum levels. *Bull. Environ. Contam. Toxicol.* 17, 31–36.
- Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environ. Sci. Technol.* 39, 3946–3956.
- Houde, M., Martin, J.W., Letcher, R.J., Solomon, K.R., Muir, D.C.G., 2006. Biological monitoring of polyfluoroalkyl substances: a review. *Environ. Sci. Technol.* 40, 3463–3473.
- Hurley, M.D., Ball, J.C., Wallington, T.J., Andersen, M.P.S., Ellis, D.A., Martin, J.W., Mabury, S.A., 2004. Atmospheric chemistry of 4:2 fluorotelomer alcohol: products and mechanisms of CI atom initiated oxidation. *J. Phys. Chem. A* 108, 5635–5642.
- Kissa, E., 2001. Fluorinated surfactants and repellents, second ed. Marcel Dekker, New York.
- Lehmeler, H.J., 2005. Synthesis of environmentally relevant fluorinated surfactants – a review. *Chemosphere* 58, 1471–1496.
- Luo, X., Mai, B., Yang, Q., Fu, J., Sheng, G., Wang, Z., 2004. Polycyclic aromatic hydrocarbons (PAHs) and organochlorine pesticides in water columns from the Pearl River and the Macao harbor in the Pearl River Delta in south China. *Mar. Pollut. Bull.* 48, 1102–1115.
- Martin, J.W., Muir, D.C.G., Moody, C.A., Ellis, D.A., Kwan, W.C., Solomon, K.R., Mabury, S.A., 2002. Collection of airborne fluorinated organics and analysis by gas chromatography/chemical ionization mass spectrometry. *Anal. Chem.* 74, 584–590.
- Moody, C.A., Martin, J.W., Kwan, W.C., Muir, D.C.G., Mabury, S.A., 2002. Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into Etobicoke Creek. *Environ. Sci. Technol.* 36, 545–551.
- Poulsen, P.B., Jensen, A.A., Wallström, E., 2005. More environmentally friendly alternatives to PFOS-compounds and PFOA, Environmental Protection Agency, Danish Ministry of the Environment.
- Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* 40, 32–44.
- Rostkowski, P., Yamashita, N., So, I.M.K., Taniyasu, S., Lam, P.K.S., Falandysz, J., Lee, K.T., Kim, S.K., Khim, J.S., Im, S.H., Newsted, J.L., Jones, P.D., Kannan, K., Giesy, J.P., 2006. Perfluorinated compounds in streams of the Shihwa industrial zone and lake Shihwa, South Korea. *Environ. Toxicol. Chem.* 25, 2374–2380.
- Saito, N., Sasaki, K., Nakatome, K., Harada, K., Yoshinaga, T., Koizumi, A., 2003. Perfluorooctane sulfonate concentrations in surface water in Japan. *Arch. Environ. Contam. Toxicol.* 45, 149–158.
- Schultz, M.M., Barofsky, D.F., Field, J.A., 2003. Fluorinated alkyl surfactants. *Environ. Eng. Sci.* 20, 487–501.
- Schultz, M.M., Barofsky, D.F., Field, J.A., 2004. Quantitative determination of fluorotelomer sulfonates in groundwater by LC MS/MS. *Environ. Sci. Technol.* 38, 1828–1835.
- Shen, M., Yu, Y., Zheng, G.J., Yu, H., Lam, P.K.S., Feng, J., Wei, Z., 2006. Polychlorinated biphenyls and polybrominated diethyl ethers in surface sediments from the Yangtze River Delta. *Mar. Pollut. Bull.* 52, 1299–1304.
- So, M.K., Taniyasu, S., Yamashita, N., Giesy, J.P., Zheng, J., Fang, Z., Im, S.H., Lam, P.K.S., 2004. Perfluorinated compounds in coastal waters of Hong Kong, South China, and Korea. *Environ. Sci. Technol.* 38, 4056–4063.
- Stock, N.L., Lau, F.K., Ellis, D.A., Martin, J.W., Muir, D.C.G., Mabury, S.A., 2004. Polyfluorinated telomer alcohols and sulfonamides in the north American troposphere. *Environ. Sci. Technol.* 38, 991–996.
- Taniyasu, S., Kannan, K., Horii, Y., Hanari, N., Yamashita, N., 2003. A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan. *Environ. Sci. Technol.* 37, 2634–2639.
- Taniyasu, S., Kannan, K., So, M.K., Gulkowska, A., Sinclair, E., Okazawa, T., Yamashita, N., 2005. Analysis of fluorotelomer alcohols, fluorotelomer acids, and short- and long-chain perfluorinated acids in water and biota. *J. Chromatogr. A* 1093, 89–97.
- Tomy, G.T., Tittlemier, S.A., Palace, V.P., Budakowski, W.R., Braekvelt, E., Brinkworth, L., Friesen, K., 2004. Biotransformation of *N*-ethyl perfluorooctanesulfonamide by rainbow trout (*Oncorhynchus mykiss*) liver microsomes. *Environ. Sci. Technol.* 38, 758–762.
- Xu, L., Krenitsky, D.M., Seacat, A.M., Butenhoff, J.L., Anders, M.W., 2004. Biotransformation of *N*-ethyl-*N*-(2-hydroxyethyl)perfluorooctanesulfonamide by rat liver microsomes, cytosol, and slices and by expressed rat and human cytochromes P450. *Chem. Res. Toxicol.* 17, 767–775.
- Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Okazawa, T., Petrick, G., Gamo, T., 2004. Analysis of perfluorinated acids at parts-per-quadrillion levels in seawater using liquid chromatography–tandem mass spectrometry. *Environ. Sci. Technol.* 38, 5522–5528.

- Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Petrick, G., Gamo, T., 2005. A global survey of perfluorinated acids in oceans. *Mar. Pollut. Bull.* 51, 658–668.
- Yang, R.Q., Jiang, G.B., Zhou, Q.F., Yuan, C.G., Shi, J.B., 2005. Occurrence and distribution of organochlorine pesticides (HCH and DDT) in sediments collected from East China Sea. *Environ. Int.* 31, 799–804.
- Yeh, A.G., Li, X., 1999. Economic development and agricultural land loss in the Pearl River Delta, China. *Habitat Int.* 23, 373–390.
- Yeung, G., 2001. *Foreign investment and socio-economic development in China: the case of Dongguan*, New York, Palgrave.