



Spatial distribution of perfluoroalkyl acids in the Pearl River of Southern China



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HIGHLIGHTS

- We present the spatial distribution of PFAAs in the tributaries of Pearl River.
- The increase of PFBS and the dramatic decrease of PFOS were observed.
- PFOA was relatively constant in comparison to that measured 8 years ago.
- This work shows the effects of global phase-out of PFOS based chemicals.

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ABSTRACT

An intensive campaign was conducted in September 2012 to collect surface water samples along the tributaries of the Pearl River in southern China. Thirteen perfluoroalkyl acids (PFAAs), including perfluorocarboxylates (PFCAs, C4–C11) and perfluorosulfonates (PFSAs, C4, C6–C8, and C10), were determined using high-performance liquid chromatography/negative electrospray ionization–tandem mass spectrometry (HPLC/(–)ESI–MS/MS). The concentrations of total PFAAs (Σ PFAAs) ranged from 3.0 to 52 ng L^{–1}, with an average of 19 ± 12 ng L^{–1}. The highest concentrations of Σ PFAAs were detected in the surface water of the Dong Jiang tributary (17–52 ng L^{–1}), followed by the main stream (13–26 ng L^{–1}) and the Sha Wan stream (3.0–4.5 ng L^{–1}). Perfluorooctanoate (PFOA), perfluorobutane sulfonate (PFBS), and perfluorooctane sulfonate (PFOS) were the three most abundant PFAAs and on average accounted for 20%, 24%, and 19% of Σ PFAAs, respectively. PFBS was the most abundant PFAA in the Dong Jiang tributary, and PFOA was the highest PFAA in the samples from the main stream of the Pearl River. A correlation was found between PFBS and PFOA, which suggests that both of these PFAAs originate from common source(s) in the region. Nevertheless, the slope of PFBS/PFOA was different in the different tributaries sampled, which indicates a spatial difference in the source profiles of the PFAAs.

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1. Introduction

Perfluorinated alkyl substances (PFASs) have been widely produced during anthropogenic processes over the last 60 years (OECD, 2002; Ahrens, 2011) and are used as fluoropolymer additives and surface coatings for textiles, furniture, and paper products (Paul et al., 2009). Currently, PFASs are ubiquitous organic compounds in various environments, i.e., atmosphere, aquatic bodies, soil, and organisms (Houde et al., 2006; Busch et al.,

2010a; Goosey and Harrad, 2012; Zhao et al., 2012). In the past decades, the occurrence, transport, and fate of PFASs in the environment have been studied due to their environmental persistence, bioaccumulation, and potential adverse effects on the health of humans and wildlife (Houde et al., 2005; Pan and You, 2010; Bao et al., 2011; Müller et al., 2012; Zhao et al., 2012).

Perfluoroalkyl acids (PFAAs), including perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFSAs), are the most important forms of PFASs in the environment. Previous studies have reported that PFAAs can be detected in water samples, including tap water (Jin et al., 2009; Llorca et al., 2012), lake water (Delinsky et al., 2010; Zhou et al., 2012), river water (So et al., 2007; Wang et al., 2012), and sea water (Yamashita et al., 2005; Ahrens et al.,

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2010). The direct source of PFAAs in an aquatic environment includes air deposition, precipitation, discharge from water treatment processes (Ahrens et al., 2009a), release during a PFAA-related manufacturing process (Paul et al., 2009), leaching of landfills (Busch et al., 2010b), and contaminated runoff (Cai et al., 2012). Public concerns that have focused on the pollution of PFAAs have led to the phase-out of some PFAA species, such as perfluorooctane sulfonate (PFOS). The European Union started to phase out PFOS in 2008, and this compound was later included in the list of Persistent Organic Pollutants (POPs) of the Stockholm Convention in 2009.

China plays an important role in global production. On an annual basis, a large amount of PFAAs are manufactured (e.g., 200 t PFOSF in 2006; Ministry of Environmental Protection of China, 2008), and the contamination of PFAAs in aquatic systems has been observed (So et al., 2007; Jin et al., 2009; Bao et al., 2012; Sun et al., 2012). The Pearl River is the third longest river in China, and its tributaries run through four provinces of southern China. The Pearl River Delta (PRD) region is located in Guangdong Province and is one of the fastest developing regions of China. In the past decades, industries related to the manufacture, application, and disposal of PFASs have been emerging in this region, which has resulted in the aquatic system being highly contaminated (So et al., 2007; Bao et al., 2010; Zhang et al., 2011).

The objectives of this study were (1) to investigate the concentrations and distribution of PFAAs in the surface water of the Pearl River, (2) to compare the results with previous studies, and (3) to understand the contamination and the sources of PFAAs in the tributaries of the Pearl River.

2. Materials and methods

2.1. Sampling

The sampling of surface water was conducted along the tributaries of the Pearl River in September 2012. Nineteen samples were collected in the main stream (MS, 10 samples denoted W7–W16), the Dong Jiang tributary (DJ, means East River, 6 samples denoted

W1–W6), and the Sha Wan stream (SW, 3 samples denoted W17–W19; see Fig. 1). The six DJ samples were collected from three sub-tributaries: the North sub-tributary (W1 and W2), the Dan Shui stream (W3 and W4), and the South sub-tributary (W5 and W6). Five hundred milliliters of surface water were collected in glass bottles, which were pre-cleaned by rinsing with Milli-Q water (18 M Ω , Millipore) and methanol in the laboratory. The glass bottles were prebaked in the oven before sampling to remove any organic contamination. The water samples were stored at 4 °C in the dark. The samples were filtrated using glass fiber filters (\varnothing 47 mm, 0.45 μ m, Whatman, UK) before extraction.

2.2. Chemicals and standards

Thirteen PFAAs, including PFCAs (C4–C11) and PFSAs (C4, C6–C8 and C10), were analyzed (see Table 1). Nine mass-labeled PFSAs were used as the internal standard (IS) mixture, i.e., 13 C-labeled ionic PFSAs and 18 O-labeled perfluorohexane sulfonate (PFHxS). 2H-perfluoro-[1,2- 13 C $_2$]-2-decenoic acid (8:2 FTUCA) was used as the injection standard (InjS; Table 1). Methanol (SupraSolv) and ammonium hydroxide (25%, Suprapur) were purchased from Merck (Darmstadt, Germany). The methanol was distilled in a glass apparatus before use, and the Milli-Q water was pre-cleaned through cartridges (see Section 2.3) to remove any residual PFAAs in the water.

2.3. Extraction and analysis

The filtrates were solid-phase extracted (SPE) using glass funnels and SPE cartridges. Oasis WAX cartridges (150 mg, 6 cm 3 , 30 mm, Waters) were used for SPE. The pretreatment of the cartridges is described elsewhere (Zhao et al., 2012). After being spiked with 1 ng IS (50 pg μ L $^{-1}$, 20 μ L), the filtrate was loaded onto the cartridge at a rate of 2 drops per second. The cartridge was then washed with 10 mL of Milli-Q water to remove the salt and dried by a vacuum pump to achieve a better recovery. The dried cartridges were eluted using 10 mL of methanol with 0.1% ammonium hydroxide. The elutes were reduced to 150 μ L under a gentle stream of nitrogen (>99.999%). Before being injected into the



Fig. 1. Map of the sampling locations in the tributaries of the Pearl River.

Table 1

Analytes, acronym, precursor, and product ion for HPLC–MS/MS detection, method detection limit (MDL), and recoveries of internal standard in the water samples.

Analyte	Acronym	Precursor/ product ion (<i>m/z</i>)	MDL (ng L ⁻¹)	Internal standard	Acronym	Precursor/ product ion (<i>m/z</i>)	Recovery (%)
Perfluorobutane sulfonate	PFBS	298.877/79.8	0.03	Perfluoro- <i>n</i> -(1,2,3,4- ¹³ C ₄)butanoic acid	[¹³ C ₄]-PFBA	216.823/171.8	61 ± 22
Perfluorohexane sulfonate	PFHxS	398.894/79.8	0.03	Perfluoro-1-hexane[¹⁸ O ₂]sulfonate	[¹⁸ O ₂]-PFHxS	402.981/83.9	78 ± 25
Perfluoroheptane sulfonate	PFHpS	449.034/79.3	0.07	Perfluoro-1-[1,2,3,4- ¹³ C ₄]octanesulfonate	[¹³ C ₄]-PFOS	502.899/79.5	51 ± 21
Perfluorooctane sulfonate	PFOS	498.971/79.7	0.07	Perfluoro- <i>n</i> -(1,2- ¹³ C ₂)hexanoic acid	[¹³ C ₂]-PFHxA	314.891/269.9	75 ± 20
Perfluorodecane sulfonate	PFDS	598.896/79.5	0.05	Perfluoro- <i>n</i> -[1,2,3,4- ¹³ C ₄]octanoic acid	[¹³ C ₄]-PFOA	416.978/371.8	73 ± 20
Perfluorobutanoic acid	PFBA	112.900/168.7	0.14	Perfluoro- <i>n</i> -[1,2,3,4,5- ¹³ C ₅]nonanoic acid	[¹³ C ₅]-PFNA	467.907/423.0	64 ± 25
Perfluoropentanoic acid	PFPA	262.825/218.9	0.05	Perfluoro- <i>n</i> -[1,2- ¹³ C ₂]decanoic acid	[¹³ C ₂]-PFDA	514.944/469.8	60 ± 23
Perfluorohexanoic acid	PFHxA	312.934/268.8	0.09	Perfluoro- <i>n</i> -[1,2- ¹³ C ₂]undecanoic acid	[¹³ C ₂]-PFUnDA	564.959/519.8	76 ± 20
Perfluoroheptanoic acid	PFHpA	862.980/818.9		Perfluoro- <i>n</i> -[1,2- ¹³ C ₂]dodecanoic acid	[¹³ C ₂]-PFDoDA	614.913/569.9	65 ± 22
Perfluorooctanoic acid	PFOA	412.987/368.9	0.07	2H-perfluoro-[1,2- ¹³ C ₂]-2-decenoic acid	8:2 FTUCA*	589.015/418.7	60 ± 20
Perfluorononanoic acid	PFNA	462.908/418.9	0.03				
Perfluorodecanoic acid	PFDA	512.876/469.0	0.02				
Perfluoroundecanoic acid	PFUnDA	562.865/519.0	0.02				

instrument, 1 ng (50 μL, 20 pg μL⁻¹) of mass-labeled 8:2 FTUCA as the InjS was spiked into the vials.

The instrumental analysis was performed using a high-performance liquid chromatography–negative electrospray ionization–tandem mass spectrometry system (HPLC–(-)ESI–MS/MS) with an HP1100 HPLC system (Agilent, Germany) coupled to an API 3000 triple-quadrupole mass spectrometer (Applied Biosystems/MDS SCIEX). The instrumental setup is described elsewhere (Ahrens et al., 2009b).

2.4. Quality assurance and quality control

The method detection limit (MDL), recovery of each spiked sample, matrix spike recoveries, field blank, and duplicate samples were measured. The results are shown in Table 1. The MDLs were calculated at a signal-to-noise ratio (S/N) of 10, which ranged from 0.02 ng L⁻¹ (for both PFDA and PFUnDA) to 0.14 ng L⁻¹ for PFBA. The overall recoveries varied from 51 ± 21% for [¹³C₄]-PFOS to 78 ± 20% for [¹⁸O₂]-PFHxS. The concentrations were corrected by the recoveries of IS in every sample.

3. Results and discussion

Thirteen PFAAs were measured in the 19 surface water samples of Pearl River (Table 2 and Fig. 2). PFBA, PFPA, PFHxA, PFHpA, PFOA, PFBS, and PFOS were detected in all of the samples. PFNA, PFDA, PFHxS, and PFDS were detectable in 18 of the 19 samples, whereas PFHpS and PFUnDA were measured in 16 and 11 samples, respectively. The concentration of the total PFAA concentration (ΣPFAAs) was ranged from 3.0 to 52 ng L⁻¹, with an average of 19 ± 12 ng L⁻¹. PFBS, PFOA, and PFOS were the most abundant PFAAs in the samples and accounted for 24%, 20%, and 19% of the ΣPFAAs (see Fig. 3).

3.1. Spatial distribution

The spatial distribution of the PFAA concentrations is shown in Table 3. The highest concentrations of ΣPFAAs were measured in the DJ samples, which exhibited an average of 29 ± 16 ng L⁻¹, followed by the MS samples (18 ± 4.2 ng L⁻¹) and the SW samples (3.9 ± 0.83 ng L⁻¹). DJ has three sub-tributaries running through

Table 2Concentration of PFAAs (ng L⁻¹) in the surface water samples of the Pearl River Delta.

Sample	PFBA	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFBS	PFHxS	PFHpS	PFOS	PFDS	ΣPFAAs
W1	1.2	1.3	0.84	0.55	2.6	0.58	0.35	0.09	7.2	0.20	0.08	3.9	<MDL	18
W2	2.50	1.25	1.08	0.74	3.4	0.59	0.31	0.07	7.5	0.32	0.09	3.8	<MDL	22
W3	2.60	1.31	1.13	0.75	2.8	0.59	0.36	<MDL	5.3	0.35	0.05	3.9	<MDL	19
W4	1.43	1.31	0.95	0.58	2.4	0.63	0.30	0.07	5.3	0.17	0.05	4.1	<MDL	17
W5	1.00	1.14	2.33	1.45	5.4	1.4	0.29	0.08	16	0.81	14	1.4	0.03	46
W6	3.34	2.06	2.58	1.30	5.5	1.0	0.64	0.10	23	1.0	1.0	11	<MDL	52
W7	1.26	0.93	0.87	0.61	2.4	0.54	0.24	0.07	4.5	0.20	0.09	2.9	<MDL	15
W8	1.60	0.96	0.83	0.66	2.4	0.53	0.25	<MDL	3.5	0.23	0.06	2.4	<MDL	13
W9	1.24	1.02	0.90	0.86	3.2	0.69	0.31	0.07	4.5	0.33	0.05	2.9	<MDL	16
W10	1.56	1.21	1.22	0.96	8.7	0.62	0.36	<MDL	3.3	0.39	0.06	3.2	<MDL	22
W11	1.95	1.58	1.18	0.93	4.9	0.76	0.34	<MDL	3.4	0.47	<MDL	3.4	<MDL	19
W12	2.39	1.84	1.41	1.01	5.9	1.0	0.50	0.10	4.7	0.65	0.06	4.5	<MDL	24
W13	2.29	1.93	1.47	0.81	7.2	0.81	0.37	0.08	6.2	0.44	0.09	4.0	<MDL	26
W14	2.09	1.49	1.17	0.80	3.3	0.70	0.31	0.09	2.1	0.40	0.05	3.4	<MDL	16
W15	1.80	0.98	1.03	0.71	3.0	0.68	0.31	<MDL	2.6	0.47	0.06	3.0	<MDL	15
W16	2.12	1.73	1.15	0.89	4.8	0.75	0.30	0.09	2.6	0.43	0.06	3.0	<MDL	18
W17	0.44	0.46	0.20	0.30	0.87	0.17	0.08	<MDL	0.91	0.07	<MDL	1.0	<MDL	4.5
W18	0.46	0.40	0.17	0.30	0.71	<MDL	<MDL	<MDL	0.42	<MDL	<MDL	0.52	<MDL	3.0
W19	0.20	0.37	0.22	0.23	0.85	0.21	0.09	<MDL	0.48	0.05	0.05	1.6	<MDL	4.3

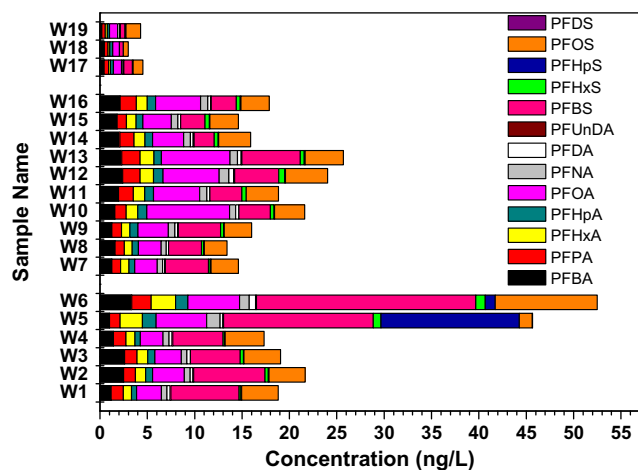


Fig. 2. Concentration of PFAAs measured in the surface water samples of the Pearl River.

the city of Dongguan, which is one of the most industrialized cities in the PRD region. A large number of industries have been built in the past three decades, and many of these, e.g., clothing, electronics, furniture, paper, and paper package making, are possible sources of PFAAs (Yearbook Dongguan, 2011). In 2010, the industrial production in Dongguan increased by 20%, and more than 60% of this increase was due to electronics, clothing, furniture manufacturing, production of packaging materials, and chemical production (Yearbook Dongguan, 2011). The industries in Dongguan are considered the major sources of PFAA in the DJ samples. The highest and the second highest concentrations of Σ PFAAs were detected in W6 (52 ng L⁻¹) and W5 (46 ng L⁻¹), respectively. These two samples were collected from the south sub-tributary of DJ, where the electronic and clothing industries were located. In 2010, the production value of both of these industries exhibited increases of 29.50% and 17.14%, respectively, in the town closest to this sub-tributary (Yearbook Dongguan, 2011). The concentrations of Σ PFAAs in these two samples were more than twofold higher than those measured in the other DJ samples, which exhibited an average of 19 ng L⁻¹. The highest concentrations of PFHpA (1.5 ng L⁻¹), PFNA (1.4 ng L⁻¹), and PFHpS (15 ng L⁻¹) were measured in W5, and the three most abundant PFAAs in this sample were PFBS (35%), PFHpS (32%), and PFOA (12%). The highest concentrations of PFBA (3.3 ng L⁻¹), PFPA (2.1 ng L⁻¹), PFHxA (2.6 ng L⁻¹), PFDA (0.64 ng L⁻¹), PFBS (23 ng L⁻¹), PFHxS (1.0 ng L⁻¹), and PFOS (11 ng L⁻¹) were detected in W6. With the exception of W5, PFBS (28–44%) and PFOS (18–24%) were the two most abundant PFAA species in the DJ samples. Based on previous results in the same region (So et al., 2007), the concentration of PFBS has increased in the past years, whereas the concentrations of PFOS has markedly decreased (see Table 4). A recent study also showed a higher PFBS concentration in the river sediment of the Pearl River compared with the Yangtze River (Bao et al., 2011). This

difference could be due to the global phase-out of PFOS and the use of PFBS as a substitute for PFOS-based products. PFBS is also related to the increasing production of n-methyl perfluorobutanesulfonamidoethanol (MeFBSE) and its related products with four perfluorinated carbons (D'Eon et al., 2006).

The MS samples were collected along more than 100 km of the course of the Pearl River, and the concentration of Σ PFAAs in these samples ranged from 13 ng L⁻¹ to 26 ng L⁻¹. Higher Σ PFAAs concentrations were detected in the river course in Guangzhou city (i.e., samples W10 through W13, range of 19–26 ng L⁻¹) compared with the upstream MS (15–18 ng L⁻¹) and downstream MS samples (13–16 ng L⁻¹). The highest concentrations of Σ PFAAs were measured in W13 and W12 (26 and 24 ng L⁻¹, respectively). The locations of these samples are close to downtown Guangzhou, and two municipal waste water treatment plants (WWTPs) are located nearby. Since 2008, most of the industries have moved out of Guangzhou (Yearbook Guangzhou, 2011). The waste water discharge in this urban area could be the major source for PFAAs in the MS of the Pearl River. Guangzhou is a growing megacity in China with a population of more than 15 million. Each day, 4.65×10^6 t of domestic waste water is treated in Guangzhou, and more than 90% is treated in municipal WWTPs (Yearbook Guangzhou, 2011). WWTPs could be major point sources of PFAAs because the treatment processes cannot efficiently remove PFAAs (Ahrens et al., 2009a; Bao et al., 2010; Chen et al., 2012). Moreover, wet deposition in the region could also be another possible source due to the frequent precipitation in the region during the summer months (Liu et al., 2009). PFOA, PFBS, and PFOS were the three most abundant PFAAs in the MS samples. In the urban MS samples, PFOA was the most abundant PFAA (25–40%) with a concentration range of 4.9–8.7 ng L⁻¹, which is higher than that obtained in the upstream (3.0–4.8 ng L⁻¹) and downstream MS samples (2.4–3.2 ng L⁻¹). The downstream MS samples (W7–W9) were collected after the confluence of MS and the sub-tributaries of DJ, and the concentration of Σ PFAAs was in the range of 14–16 ng L⁻¹, which is lower than that obtained in the urban MS and DJ samples. PFBS was the most abundant PFAA (26–31%) in the downstream MS samples, which may imply the strong influence of DJ after confluence.

The lowest concentrations were measured in the SW samples. The concentration of Σ PFAAs in these samples ranged from 3.0 to 4.5 ng L⁻¹, which is much lower than that obtained in the MS and DJ samples. These results were consistent with those obtained in a previous study, which showed that this tributary was less polluted by PFAAs (So et al., 2007). This tributary runs through a less-developed area with a lower industry and population density. PFOS and PFOA were the major PFAAs in the SW samples and accounted for 17–35% and 19–24% of the total PFAA concentrations, respectively (see Fig. 3).

3.2. Source identification

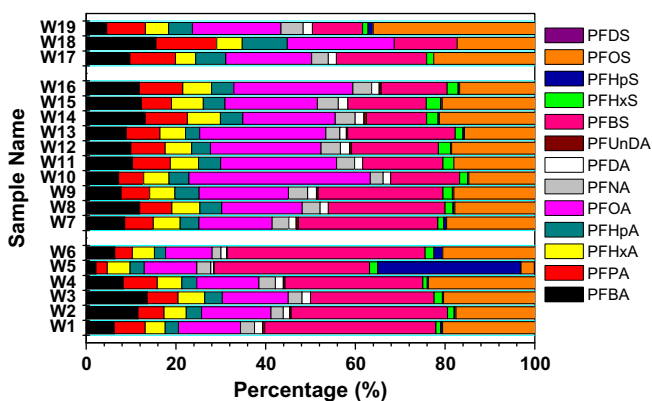
The sources of PFAAs in a river can be many. Point sources include the waste water discharge of industries and WWTPs, whereas landfill leachate, dry or wet atmospheric deposition, and

Table 3
Range and mean concentration of Σ PFAAs and dominant PFAA in the tributaries of the Pearl River.

Location	Sub-tributary	Sample	Mean of Σ PFAAs (ng L ⁻¹)	Range (ng L ⁻¹)	Predominant PFAA (ng L ⁻¹)
Dong Jiang (DJ)	North	2	20 ± 2.0	19–22	PFBS(7.4)
	Dan Shui	2	18 ± 1.2	17–19	PFBS(5.3)
		2	49 ± 4.8	46–52	PFBS(19)
	Upstream	3	16 ± 1.6	15–18	PFOA(3.7)
3		15 ± 1.3	13–16	PFBS(4.2)	
Main stream (MS)	Urban Guangzhou	4	23 ± 3.0	19–26	PFOA(6.7)
	Downstream	3	15 ± 1.3	13–16	PFBS(4.2)
Sha Wan stream (SW)		3	4.0 ± 0.83	3.0–4.5	PFOS(1.0)

Table 4Comparison of PFAA concentrations (ng L^{-1} ; mean value in parentheses) in surface water samples from rivers all over the world.

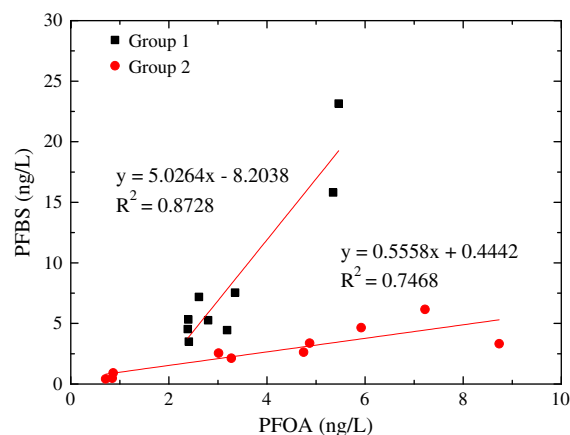
Location	Sampling year	Number of PFAAs	PFAAs	PFOS	PFBS	PFOA	Reference
Pearl River, China	2012	13	3.0–52 (19)	0.52–11 (3.3)	0.42–23 (5.4)	0.71–8.7 (3.7)	This study
Pearl River, China	2004	9	2.24–99.34 (20)	0.90–99 (23)	<0.03–3.4 (0.57)	0.85–13 (4.3)	(So et al., 2007)
Yangtze River, China	2004	10	30–290 (41)	0.62–14 (1.7)	0.96–2.1 (0.77)	22–260 (35)	(So et al., 2007)
Haihe River, China	2010	9	12–74	2.0–7.6 (3.7)	–	4.4–42 (15)	(Li et al., 2011)
Rhine River (upstream), Germany	2008	8	4.1–39 (21)	1.4–6.4 (3.7)	0.59–6.6 (3.2)	0.61–3.4 (2.1)	(Möller et al., 2010)
Rhine River (downstream), Germany	2008	8	120–270 (181)	3.0–7.3 (4.1)	15–120 (45)	2.3–4.1 (3.1)	(Möller et al., 2010)
River Ruhr, Germany	2008	8	65–97 (76)	0.89–10 (4.2)	2.9–11 (7.1)	8.9–18 (14.3)	(Möller et al., 2010)
Spanish Rivers	2009	5	2.2–22 (12)	<0.03–0.64 (5.1)	<0.07–0.88 (0.50)	0.79–9.6 (5.1)	(Sanchez-Avila et al., 2010)

**Fig. 3.** Composition profiles of PFAAs in the surface water samples of the Pearl River.

soil/street surface runoff are suggested as non-point sources (Ahrens, 2011).

A Spearman rank correlation analysis was conducted between the PFAAs analyzed in this study. Significant positive correlations were observed between the C4–C10 PFCAs. With the exception of PFHpS, the other PFSAs also exhibited significant correlations with each other. PFHpS was also positively correlated with PFHxA, PFHpA, PFNA, PFBS, and PFHxS, which suggests that PFHpS may have other potential sources. Of the three most abundant PFAAs (i.e., PFOA, PFBS, and PFOS), PFOA has weak correlation with PFBS ($r = 0.376$) and PFOS ($r = 0.410$), and PFBS has strong correlation with PFOS ($r = 0.722$), which suggests that PFBS and PFOS may have common sources.

The relationship between the concentrations of PFBS and PFOA was further analyzed. Linear correlations were found when the data were separated into two groups (see Fig. 4). Group 1 includes the DJ and the downstream MS samples which indicates the influence of the DJ tributary. Group 2 includes the rest of the samples, i.e., the upstream MS, urban MS, and SW samples. The strong correlations found in our data showed that PFOA and PFBS might originate from common sources. However, the different slope of PFBS/PFOA suggests a different source profile of PFAAs in the tributaries of the Pearl River. The higher slope of PFBS/PFOA observed in Group 1 may be attributed to industry-related sources, as discussed above. The manufacture and usage of PFOA and its related chemicals have

**Fig. 4.** Linear correlation between PFOA and PFBS in the surface water samples of the Pearl River.

been effectively limited after the voluntary stewardship program launched by the US Environmental Protection Agency in 2006 (US Environmental Protection Agency, 2006). The use of short-chain PFSAs (e.g., PFBS) as substitutes after the phase-out of PFOS might explain the increase in the PFBS concentration. Similar results have been observed in other rivers, such as the Rhine River in Germany (Möller et al., 2010). Some previous studies have focused on the profiles of PFAAs in point sources, such as WWTPs and specific industries (Lin et al., 2009; Ahrens et al., 2009a; Chen et al., 2012). However, this type of work is still scarce and needs to be conducted in the PRD region. Thus, further research should be conducted to understand the difference in the slope of PFBS/PFOA in the different tributaries of the Pearl River and to investigate the source profiles of PFAAs from specific point sources.

3.3. Comparison with other studies

The comparison of the concentrations of Σ PFAAs, PFOS, PFBS, and PFOA in the rivers is shown in Table 4. The mean concentrations of Σ PFAAs were lower than those found in a previous study conducted in the Pearl River in November 2004 (34 ng L^{-1}), whereas the range of the PFOA concentration was comparable. The PFOS concentration exhibited a large decrease in the industrial area in 2012, whereas the PFOS level in the less-developed region

(i.e., SW) was similar. The concentration of PFBS, especially that found in the DJ samples, was higher than that obtained in previous study. Higher PFBS concentrations have been found in sediment samples from the Pearl River compared with the Yangtze River (Bao et al., 2010). This finding indicates the change in the source profiles of PFAAs after the phase-out of PFOS-related products and the production of their substitutes.

Compared with the results in the Rhine River, the concentrations of PFAAs in this study were lower than those obtained in the downstream samples (120–270 ng L⁻¹) but comparable to those obtained in the upstream samples (4.1–39 ng L⁻¹). PFBS was reported to be the predominant PFSA in the River Rhine, and industries were suggested to be the main sources (Möller et al., 2010). Higher concentrations of ΣPFAAs were found in the River Ruhr, where the most abundant PFAA was PFOA, whereas the levels of PFBS and PFOS were similar (Möller et al., 2010). Markedly higher concentrations of PFBS and PFOA were observed in this study compared to those detected in Spanish rivers, although the range of the PFOA concentration was comparable (Sanchez-Avila et al., 2010).

4. Conclusions

PFAAs, including PFCAs and PFASs, were investigated in the tributaries of the Pearl River in southern China. The concentration of ΣPFAAs was in the range of 3.0–52 ng L⁻¹, which is comparable to that obtained in a previous study in the Pearl River that was conducted in November 2004. A decrease in the PFOS concentration and an increase in the PFBS concentration were observed. These differences were due to the global phase-out of PFOS and the rise in the manufacturing and consumption of PFOS substitutes, such as PFBS. The highest concentration range of PFAAs was observed in DJ, which is one of the tributaries of the Pearl River. The industries in the city of Dongguan are likely the major sources of the relatively high levels of PFAAs and the predominance of PFBS. In the MS samples, the contributions of urban point sources (WWTPs) and non-point sources (precipitation) were suggested. The surface water in the SW stream was found to be less contaminated by PFAAs. Linear correlations between PFBS and PFOA were found in the tributaries of the Pearl River, but these exhibited different PFBS/PFOA slopes, which indicate the different source profiles of PFAAs in the tributaries of the Pearl River.

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References

- Ahrens, L., 2011. Polyfluoroalkyl compounds in the aquatic environment: a review of their occurrence and fate. *J. Environ. Monit.* 13, 20–31.
- Ahrens, L., Felizeter, S., Sturm, R., Xie, Z.Y., Ebinghaus, R., 2009a. Polyfluorinated compounds in waste water treatment plant effluents and surface waters along the River Elbe, Germany. *Mar. Pollut. Bull.* 58, 1326–1333.
- Ahrens, L., Plassmann, M., Xie, Z.Y., Ebinghaus, R., 2009b. Determination of polyfluoroalkyl compounds in water and suspended particulate matter in the river Elbe and North Sea, Germany. *Front. Environ. Sci. Eng. China* 3, 152–170.
- Ahrens, L., Gerwinski, W., Theobald, N., Ebinghaus, R., 2010. Sources of polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: evidence from their spatial distribution in surface water. *Mar. Pollut. Bull.* 60, 255–260.
- Bao, J., Liu, W., Liu, L., Jin, Y., Ran, X., Zhang, Z., 2010. Perfluorinated compounds in urban river sediments from Guangzhou and Shanghai of China. *Chemosphere* 80, 123–130.
- Bao, J., Liu, W., Liu, L., Jin, Y.H., Dai, J.Y., Ran, X.R., Zhang, Z.X., Tsuda, S., 2011. Perfluorinated compounds in the environment and the blood of residents living near fluorochemical plants in Fuxin, China. *Environ. Sci. Technol.* 45, 8075–8080.
- Bao, L.J., Maruya, K.A., Snyder, S.A., Zeng, E.Y., 2012. China's water pollution by persistent organic pollutants. *Environ. Pollut.* 163, 100–108.
- Busch, J., Ahrens, L., Xie, Z.Y., Sturm, R., Ebinghaus, R., 2010a. Polyfluoroalkyl compounds in the East Greenland Arctic Ocean. *J. Environ. Monit.* 12, 1242–1246.
- Busch, J., Ahrens, L., Sturm, R., Ebinghaus, R., 2010b. Polyfluoroalkyl compounds in landfill leachates. *Environ. Pollut.* 158, 1467–1471.
- Cai, M.H., Yang, H.Z., Xie, Z.Y., Zhao, Z., Wang, F., Lu, Z.B., Sturm, R., Ebinghaus, R., 2012. Per- and polyfluoroalkyl substances in snow, lake, surface runoff water and coastal seawater in Fildes Peninsula, King George Island, Antarctica. *J. Hazard. Mater.* 209, 335–342.
- Chen, H., Zhang, C., Han, J.B., Yu, Y.X., Zhang, P., 2012. PFOS and PFOA in influents, effluents, and biosolids of Chinese wastewater treatment plants and effluent-receiving marine environments. *Environ. Pollut.* 170, 26–31.
- Delinsky, A.D., Strynar, M.J., McCann, P.J., Varns, J.L., McMillan, L., Nakayama, S.F., Lindstrom, A.B., 2010. Geographical distribution of perfluorinated compounds in fish from Minnesota Lakes and Rivers. *Environ. Sci. Technol.* 44, 2549–2554.
- D'Eon, J.C., Hurley, M.D., Wallington, T.J., Mabury, S.A., 2006. Atmospheric chemistry of N-methyl perfluorobutane sulfonamidoethanol, C₄F₉SO₂N(CH₃)CH₂CH₂OH: kinetics and mechanism of reaction with OH. *Environ. Sci. Technol.* 40, 1862–1868.
- Goosey, E., Harrad, S., 2012. Perfluoroalkyl substances in UK indoor and outdoor air: spatial and seasonal variation, and implications for human exposure. *Environ. Int.* 45, 86–90.
- Houde, M., Wells, R.S., Fair, P.A., Bossart, G.D., Hohn, A.A., Rowles, T.K., Sweeney, J.C., Solomon, K.R., Muir, D.C.G., 2005. Polyfluoroalkyl compounds in free-ranging bottlenose dolphins (*Tursiops truncatus*) from the Gulf of Mexico and the Atlantic Ocean. *Environ. Sci. Technol.* 39, 6591–6598.
- 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.
- Jin, Y.H., Liu, W., Sato, I., Nakayama, S.F., Sasaki, K., Saito, N., Tsuda, S., 2009. PFOS and PFOA in environmental and tap water in China. *Chemosphere* 77, 605–611.
- Li, F., Sun, H., Hao, Z., He, N., Zhao, L., Zhang, T., Sun, T., 2011. Perfluorinated compounds in Haihe River and Dagu Drainage Canal in Tianjin, China. *Chemosphere* 84, 265–271.
- Lin, A.Y.C., Panchangam, S.C., Lo, C.C., 2009. The impact of semiconductor, electronics and optoelectronic industries on downstream perfluorinated chemical contamination in Taiwanese rivers. *Environ. Pollut.* 157, 1365–1372.
- Liu, W., Jin, Y., Quan, X., Sasaki, K., Saito, N., Nakayama, S.F., Sato, I., Tsuda, S., 2009. Perfluorosulfonates and perfluorocarboxylates in snow and rain in Dalian, China. *Environ. Int.* 35, 737–742.
- Llorca, M., Farre, M., Pico, Y., Muller, J., Knepper, T.P., Barcelo, D., 2012. Analysis of perfluoroalkyl substances in waters from Germany and Spain. *Sci. Total Environ.* 431, 139–150.
- Ministry of Environmental Protection of China, 2008. Preliminary Information on Risk Management Evaluation of PFOS's in China. <http://chm.pops.int/Portals/0/Repository/comments_draftRME2008/UNEP-POPS-POPRC-DRME-08-CHI-SCCP.English.PDF>).
- Möller, A., Ahrens, L., Sturm, R., Westerveld, J., van der Wielen, F., Ebinghaus, R., de Voogt, P., 2010. Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. *Environ. Pollut.* 158, 3243–3250.
- Müller, C.E., Gerecke, A.C., Bogdal, C., Wang, Z.Y., Scheringer, M., Hungerbühler, K., 2012. Atmospheric fate of poly- and perfluorinated alkyl substances (PFASs): I. Day–night patterns of air concentrations in summer in Zurich, Switzerland. *Environ. Pollut.* 169, 196–203.
- OECD, O.F.E.C.-o.a.D., 2002. Hazard assessment of perfluorooctane sulfonate (PFOS) and its salts.
- Pan, G., You, C., 2010. Sediment–water distribution of perfluorooctane sulfonate (PFOS) in Yangtze River Estuary. *Environ. Pollut.* 158, 1363–1367.
- Paul, A.G., Jones, K.C., Sweetman, A.J., 2009. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. *Environ. Sci. Technol.* 43, 386–392.
- Sanchez-Avila, J., Meyer, J., Lacorte, S., 2010. Spatial distribution and sources of perfluorochemicals in the NW Mediterranean coastal waters (Catalonia, Spain). *Environ. Pollut.* 158, 2833–2840.
- So, M.K., Miyake, Y., Yeung, W.Y., Ho, Y.M., Taniyasu, S., Rostkowski, P., Yamashita, N., Zhou, B.S., Shi, X.J., Wang, J.X., Giesy, J.P., Yu, H., Lam, P.K.S., 2007. Perfluorinated compounds in the Pearl River and Yangtze River of China. *Chemosphere* 68, 2085–2095.
- Sun, H.W., Zhang, X.Z., Wang, L., Zhang, T., Li, F.S., He, N., Alder, A., 2012. Perfluoroalkyl compounds in municipal WWTPs in Tianjin, China – concentrations, distribution and mass flow. *Environ. Sci. Pollut. Res.* 19, 1405–1415.
- US Environmental Protection Agency, 2006. PFOA Stewardship Program. Docket EPA-HQ-OPPT-2006-0621.
- Wang, T.Y., Khim, J.S., Chen, C.L., Naile, J.E., Lu, Y.L., Kannan, K., Park, J., Luo, W., Jiao, W.T., Hu, W.Y., Giesy, J.P., 2012. Perfluorinated compounds in surface waters from Northern China: comparison to level of industrialization. *Environ. Int.* 42, 37–46.
- 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.
- Zhang, K., Zhang, B.Z., Li, S.M., Zeng, E.Y., 2011. Regional dynamics of persistent organic pollutants (POPs) in the Pearl River Delta, China: implications and perspectives. *Environ. Pollut.* 159, 2301–2309.

Zhao, Z., Xie, Z.Y., Moller, A., Sturm, R., Tang, J.H., Zhang, G., Ebinghaus, R., 2012. Distribution and long-range transport of polyfluoroalkyl substances in the Arctic, Atlantic Ocean and Antarctic coast. *Environ. Pollut.* 170, 71–77.

Zhou, Z., Shi, Y.L., Li, W.H., Xu, L., Cai, Y.Q., 2012. Perfluorinated compounds in surface water and organisms from Baiyangdian Lake in North China: source profiles, bioaccumulation and potential risk. *Bull. Environ. Contam. Toxicol.* 89, 519–524.