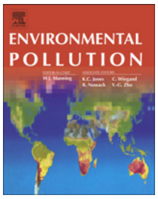
Environmental Pollution 161 (2012) 162–169

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol



Spatial distribution of per- and polyfluoroalkyl compounds in coastal waters from the East to South China Sea

Minghong Cai [a,b,*], Zhen Zhao [c,d,e], Haizhen Yang [a], Zhigao Yin [a], Qingquan Hong [f], Renate Sturm [c], Ralf Ebinghaus [c], Lutz Ahrens [c,1], Minggang Cai [f], Jianfeng He [b], Zhiyong Xie [c,**]

[a] *College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China*
[b] *SOA Key Laboratory for Polar Science, Polar Research Institute of China, Shanghai 200136, China*
[c] *Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research GmbH, Institute of Coastal Research, Max-Planck Straße 1, D-21502 Geesthacht, Germany*
[d] *Yantai Institute of Coastal Zone Research, CAS, Yantai 264003, China*
[e] *Graduate School of the Chinese Academy of Sciences, Beijing 100039, China*
[f] *College of Oceanography and Environmental Science, Xiamen University, Xiamen 361005, China*

A R T I C L E I N F O

Article history:
Received 2 May 2011
Received in revised form
19 September 2011
Accepted 24 September 2011

Keywords:
Perfluoroalkyl compounds
Polyfluoroalkyl compounds
PFCs
Coastal waters
East China Sea
South China Sea

A B S T R A C T

The spatial distribution of per- and polyfluoroalkyl compounds (PFCs) were investigated in coastal waters collected onboard research vessel *Snow Dragon* from the East to South China Sea in 2010. All samples were prepared by solid-phase extraction and analyzed using high performance liquid chromatography/negative electrospray ionization-tandem mass spectrometry (HPLC/(−)ESI-MS/MS). Concentrations of 9 PFCs, including C_4 and C_8 (PFBS, PFOS) perfluoroalkyl sulfonate (PFSAs), C_5–C_9 and C_{13} (PFPA, PFHxA, PFHpA, PFOA, PFNA, PFTriDA) perfluoroalkyl carboxylates (PFCAs), and *N*-ethyl perfluorooctane sulfonamide (EtFOSA) were quantified. The ΣPFC concentrations ranged from 133 pg/L to 3320 pg/L, with PFOA (37.5–1541 pg/L), PFBS (23.0–941 pg/L) and PFHpA (0–422 pg/L) as dominant compounds. Concentrations of PFCs were greater in coastal waters along Shanghai, Ningbo, Taizhou, Xiamen and along coastal cities of the Guangdong province compared to less populated areas along the east Chinese coast. Additionally, the comparison with other seawater PFC measurements showed lower levels in this study.

1. Introduction

Per- and polyfluoroalkyl compounds (PFCs) are persistent against the typical environmental degradation processes and have been found ubiquitously in water (Saito et al., 2003; Schultz et al., 2004; So et al., 2004; Yamashita et al., 2005; Ahrens et al., 2010a,b; Busch et al., 2010), air (Martin et al., 2002; Stock et al., 2004, 2007; Jahnke et al., 2007), sediment (Bao et al., 2009, 2010; Gómez et al., 2011; Yang et al., 2011), sludge (Higgins et al., 2005), precipitation (Liu et al., 2009), wildlife (Giesy and Kannan, 2001; Li et al., 2008a,b) and humans (Yeung et al., 2006, 2008; Jin et al., 2007) around the globe. Because of their chemical characteristics, including extraordinary stability, hydrophobicity, oleophobicity and surfactant characteristics, many PFCs have been broadly applied to industrial and domestic production in the past half-century (OECD, 2002; Prevedouros et al., 2006). PFCs are used in numerous products, such as textile protectors, coatings, plastics, fire fighting foams, photolithography, electronic chemicals, shampoos, stain repellents for furniture, carpets and pesticides, or as fluoropolymer additives (Kissa, 2001; Guo et al., 2008; Yu et al., 2009). During the production and usage of these products, PFCs can be released into the environment, where they can bioaccumulate (Martin et al., 2004; Houde et al., 2006) and have potentially adverse effects on humans and wildlife (Austin et al., 2003; Martin et al., 2003; Shi et al., 2008).

In general, neutral precursors of PFCs can undergo long-range transport via the atmosphere, whereas ionic PFCs can be transported by ocean currents (Yamashita et al., 2005; Jahnke et al., 2007). The ionic PFCs have a high water solubility, low pK_a values and are therefore almost completely dissociated at environmentally relevant pH values (Kissa, 2001). They can be found mostly in water or can be bind to particles, sediments and soils (Higgins and Luthy, 2006). Neutral PFCs such as perfluoroalkyl sulfonamides (FASAs), perfluoroalkyl sulfonamidoethanols (FASEs) and fluorotelomer alcohols (FTOHs) are less water-soluble and more volatile than ionic PFCs.

---

* Corresponding author.
** Corresponding author.
E-mail addresses: caiminghong@pric.gov.cn (M. Cai), zhiyong.xie@hzg.de (Z. Xie).
[1] Current address: Air Quality Research Division, Science and Technology Branch, Environment Canada, 4905 Dufferin Street, Downsview, Ontario M3H 5T4, Canada.

0269-7491/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envpol.2011.09.045

They can degrade in the atmosphere (Ellis et al., 2004; Martin et al., 2006) as well as under aerobic conditions in activated sludge (Rhoads et al., 2008) to perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs), which are the final degradation products and very persistent in the environment. The main sources of PFCs in the aqueous environment are industrial or municipal wastewater treatment plant (WWTP) effluents (Schultz et al., 2006; Bossi et al., 2008; Clara et al., 2008), runoff from contaminated soil by precipitation (Skutlarek et al., 2006), accidental spills or by the release of non-treated discharges (Paul et al., 2009), landfills (Kallenborn et al., 2004), precipitation (Scott et al., 2006) or after the usage of aqueous film forming foams (AFFFs) (Moody and Field, 2000). The PFCs can be further moved directly or via rivers into the coastal environments, which have become vulnerable areas because of their intermediate position between open seas and human activities. The increase in population and industrial pressure along rivers and coastal areas pose an important threat on those coastal ecosystems since contaminants such as PFCs can be accumulated in the marine food chain and also humans can be exposed via fish and seafood consumption (Sánchez-Avila et al., 2010).

Since manufacture of PFCs began, it is estimated that 96,000 t of the feedstock for electrofluorination, namely perfluorooctanesulfonyl fluoride (POSF) was produced between 1970 and 2002 (Paul et al., 2009), which were manufactured primarily by two major producers of PFCs, 3M and Dupont, and in 2000, 3M produced 78% of the annual total volume (Paul et al., 2009). In 2000, the major manufacturer of PFCs, the 3M Company, agreed to phase-out the production of POSF, which is a major precursor of several PFCs such as perfluorooctane sulfonate (PFOS) (Prevedouros et al., 2006). In addition, the European Union (EU) formed a directive in December 2006 which prohibits the general use of PFOS after June 2008 (European Parliament and Council, 2006). But there is still a growing demand for substances with the unique properties of PFCs, and thus other PFCs are replacing PFOS (Ahrens et al., 2009c). In the last 10 years, the production of POSF has shifted from North America and Europe primarily to China. The production has increased by a factor of four from 2004 to 2006, by which time the production exceeded 200 t per year (Bao et al., 2009). Moreover, approximately 100 t of the POSF production in China was exported to South America and a small amount to Europe (Bao et al., 2009). Therefore, the investigations and research on the environmental fate of PFCs in China is highly essential in order to draw a complete picture of this type of pollution for upcoming notational assessments.

In China, studies on the occurrence of PFCs in coastal waters have focused on the industrialized areas, such as Hong Kong, the Pearl River Delta (So et al., 2004) and Dalian (Ju et al., 2008). In order to get a better understanding of the sources and transport pathway of PFCs in the aqueous phase in China, more water samples in other coastal regions are needed. The coastal areas from the East to South China Sea receives the pollution impact of the four main industrialized provinces in China including Shanghai, Zhejiang, Fujian and Guangdong, which are highly urbanized and industrialized with electricity and electronics, printing, petrochemicals, chemical fabrics, textiles, as well as pulp and paper industries. In addition, discharge waters of various rivers, especially Pearl River and Yangtze River, contribute to the pollution of coastal ecosystems. The Pearl River Delta and Yangtze River Delta totally contributed to around 30% of annual China gross domestic products (GDP) (National Bureau of Statistics of China, 2010). The Pearl River receives its industrial and domestic contaminants mainly from Guangzhou, the capital city of Guangdong province, which is a highly urbanized and industrialized area (Mai et al., 2002), while the Yangtze River is one of the biggest by discharge volume in the world and flows from the Tibetan Plateau across southwest, central and eastern China (Shen et al., 2006).

The aim of this study was to investigate the occurrence and spatial distribution of PFCs in coastal waters close to urbanized/industrial areas in China. Surface water samples were collected in coastal waters from the East (Shanghai) to South China Sea (Shenzhen) ($n = 21$). We examined the composition profiles and correlation between individual PFCs to identify sources in the sampling area. Finally, we compared our data with other studies from China and other parts of the world to evaluate the spatial distribution of PFCs.

2. Materials and methods

2.1. Chemicals and reagents

The standards used in this study are described elsewhere (Ahrens et al., 2009a) (for details see Table S1, Supplementary material). Methanol (pesticide residues grade) was purchased from LGC Standards GmbH, Germany, and ammonium hydroxide (25% for analysis) from Merck (Darmstadt, Germany). Oasis WAX cartridge (6 cm^3, 150 mg) was purchased from Waters, Milford, MA, USA.

2.2. Sample collection and sample pretreatment

Surface water samples were taken onboard the research vessel *Snow Dragon* at 21 stations from East (Shanghai) to South China Sea (Shenzhen) in November 2010 (Fig. 1). Sampling sites were chosen in coastal areas to show the influence of the potential pollution sources (i.e. cities, industrial areas, rivers). One liter of surface water (0–0.2 m) was collected from each sampling station (distance to the coast: >20 km) by using a stainless steel bucket. Water samples were stored in 1 L polypropylene (PP) bottles. All the equipment including the stainless steel bucket and PP bottles were precleaned by rinsing with methanol, distilled water, and then seawater from the specific locations before sampling. In addition, duplicate samples were collected at sampling stations 9, 12, 17 and 18 for quality control. The seawater samples were stored at 4 °C in darkness before extraction.

The samples were filtered using glass fiber filters (GFF, Whatman, 47 mm, >1.2 μm, Banbury Oxon, UK). Five field blanks (FB) were stored and transported to test for possible external contamination. For the FB, 1 L Millipore water (GmbH, Schwalbach, Germany) passed through a WAX cartridge, stored in a PP bottle, and then extracted in the same manner as "real samples".

2.3. Sample extraction

The filtrated sample (1 L) was extracted by solid-phase extraction (SPE) with Waters Oasis WAX cartridges in a clean lab, similar as described elsewhere (Taniyasu et al., 2005; Ahrens et al., 2009a). Prior to extraction, the samples were spiked with 400 pg absolute of an internal standard (IS) mix (see Table S1, Supplementary material). Briefly, after preconditioning with 10 mL methanol and 10 mL distilled Millipore water, the cartridge was loaded with approximately 1–2 drops per second. The cartridge was then dried for 30 min under vacuum by which time another WAX cartridge was connected on the top of the sample cartridge to clean the air passed through elution performed using 10 mL methanol with 0.1% ammonium hydroxide. The extracts were concentrated to 150 μL under a nitrogen stream(N_2, purity $> 99.999\%$, Linde Gas, Pullach, Germany) and spiked with 20 ng absolute of the injection standard (InjS) d_5-EtFOSAA (InjS, 50 μL of a 0.4 ng mL^{-1} solution (Ahrens et al., 2009a)).

2.4. Instrumental analysis

An HP 1100 HPLC-system (Agilent Technologies, Vintage park, CA, USA) was used with a Synergi Hydro RP 80A column (150 × 2 mm, 4 μm, Phenomenex, Aschaffenburg, Germany combined with a suitable guard column; Synergi Hydro RP, 20 × 2 mm, 2 μm). Modifications of the HPLC system were made as described elsewhere (Yamashita et al., 2004) to eliminate instrumental blank contamination. The triple-quadrupole mass spectrometer, supplied by Applied Biosystems/MDS SCIEX (Agilent Technologies, Vintage park, CA, USA), used an electrospray ionization (ESI) interface in negative ionization mode (Ahrens et al., 2009a).

2.5. Data analysis

Quantification was performed by the internal standard method. An 8-point calibration curve (0, 0.5, 1, 2.5, 5, 7.5, 10, 15 pg/μL) was used for calculation. For peak integration only the base peak of a compound was used. The isomers were not included in the peak integration, because of the lack of standards.

2.6. Statistical analysis

A Pearson rank correlation analysis was used to assess the correlations among PFCs in water samples collected from the East to South China Sea.

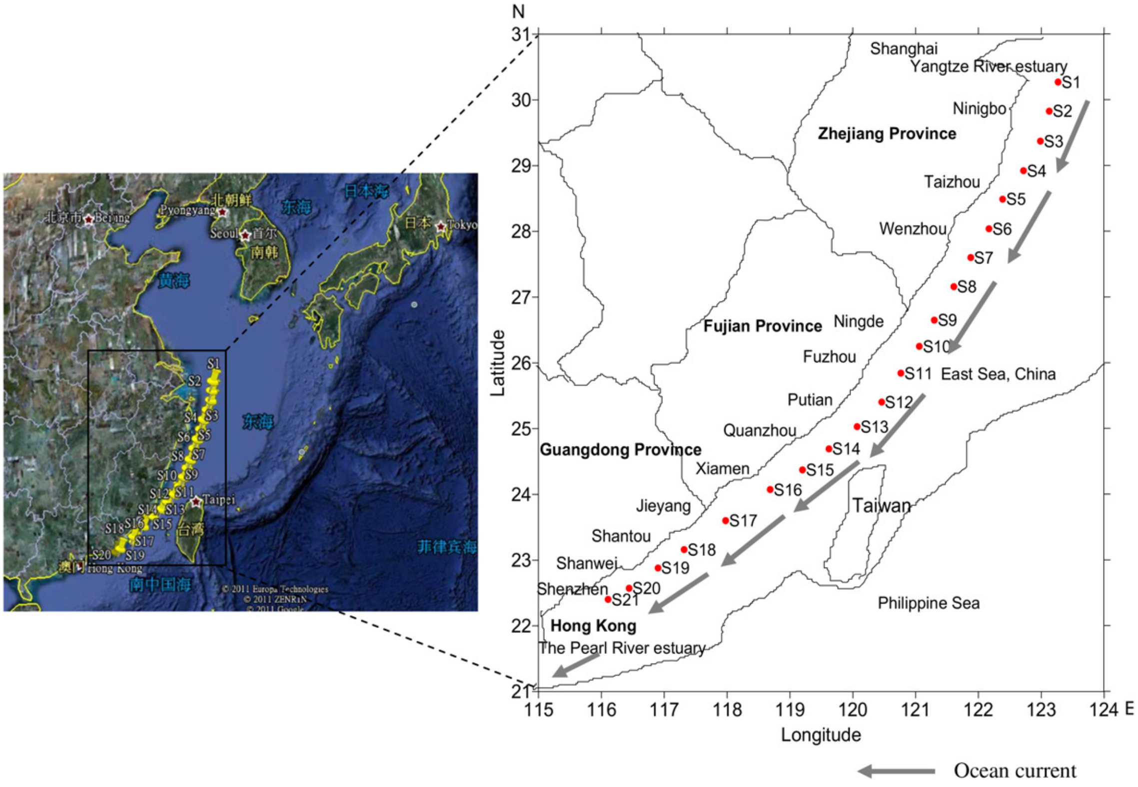


Fig. 1. Map showing the sampling locations and ocean current from the East to South China Sea.

2.7. Quality control

For quality assurance and quality control, recovery of each spiked sample, instrument detection limit (IDL), method quantification limit (MQL), field blank, matrix spike recoveries and duplicate samples were measured (for details see Tables S2 and S3, Supplementary material). The IDL and MQL were calculated at a signal to noise ratio (S/N) of 3 and 10, respectively. The MQL ranged from 6.27 pg/L for perfluorodecane sulfonate (PFDS) to 128.2 pg/L for perfluorobutanoate (PFBA). In field blank samples, perfluorobutane sulfonate (PFBS), perfluoroheptane sulfonate (PFHpS) and perfluorooctanoate (PFOA) were found above the MQL (67.9 pg/L for PFBS, 23.1 pg/L for PFHpS and 42.6 pg/L for PFOA, respectively), and therefore the concentrations were blank corrected afterward. As both methanol and Millipore water have been detected for certain PFCs (e.g. PFOA, PFBA, PFBS, PFNA, PFHpS, PFHpA) the methanol was distilled and the Millipore water was cleaned with Oasis WAX cartridge to eliminate the contamination. The matrix spike recoveries were determined at 400 pg/L and they ranged between 38 ± 44% for d_9-EtFOSE and 100 ± 84% for [$^{18}O_2$]-PFHxS. Breakthrough of PFCs was tested by using tandem Oasis WAX cartridges to extract 1 L seawater spiked with 400 pg internal standards. PFCs in the upper cartridge accounted for more than 80% of the sum determined from both cartridges. However, there were no internal standards detectable in the lower cartridge, indicting little breakthrough for PFCs with Oasis WAX cartridge. The recoveries of the internal standards were estimated by comparing the intensity of each internal standard in real sample and the average intensity in 8 calibration solutions (Table S3). It is noted that the matrix of the samples can significantly alter the response, that it is very important to use suitable isotope internal standards for individual target compounds.

3. Results and discussion

3.1. Concentrations of PFCs in coastal waters from the East to South China Sea

In this study, overall 9 of the 24 selected PFCs were found in the surface water samples at 21 sampling stations (for details see Table S4, Supplementary material). The quantified PFCs included C_5–C_9 and C_{13} PFCAs (i.e. perfluoropentanoate (PFPA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), PFOA, perfluorononanoate (PFNA), perfluorotridecanoate (PFTriDA)), C_4 and C_8 PFSAs (PFBS, PFOS) and *N*-ethyl perfluorooctane sulfonamide (EtFOSA). The spatial distribution of individual PFC concentrations in coastal waters from the East to South China Sea is shown in Fig. 2. The ΣPFC concentrations range from 133 pg/L (sampling station S14) to 3320 pg/L (sampling station S17). All of the water samples contained detectable concentrations of PFOA and PFBS. Concentrations of PFOA and PFBS ranged from 37.5 to 1542 pg/L and from 23.0 to 941 pg/L, respectively. PFHpA and PFOS were frequently detected in 95% and 62% of the samples, respectively, but the concentrations of these PFCs were less than those of PFOA and PFBS, ranging from $<$11.3 to 422 pg/L for PFHpA and from $<$20.7 to 70.3 pg/L for PFOS, respectively. PFHxA, PFPA, PFNA, EtFOSA and PFTriDA were detected less frequently (i.e. 33%, 19%, 14%, 14% and 5%, respectively) with a concentration range of $<$27.2–304 pg/L, $<$20.3–439 pg/L, $<$22.5–37.9 pg/L, $<$23.6–279 and $<$4.8–27.5 pg/L, respectively.

In all the compositions, PFOA was the predominant PFC with a composition of ∼42%, followed by PFHpA (∼26%) and PFBS (∼24%). The greatest concentrations of PFOA, PFHpA and PFBS were detected at location S5 (1542 pg/L), S10 (422 pg/L) and S17 (941 pg/L), while concentrations of PFOA, PFHpA and PFBS were generally low at sampling stations S10 (37.5 pg/L), S14 ($<$11.3) and S7 (23.0 pg/L), respectively.

Concentration of PFCs were about 4 times higher in the coastal waters at sampling station S1–S5 (average of 1854 pg/L) and S16–S20 (average of 1969 pg/L) in comparison to sampling station S6–S15 (average of 492 pg/L). During the sampling periods (November, dry season), the ocean currents, driven by the prevailing northeasterly winds, move along the shore from northeast the southwest (So et al., 2004). Thus, the runoff from the Yangtze River and Pearl River estuary moved westward toward the southwest shoreline (Fig. 1). The concentration of PFCs in the water

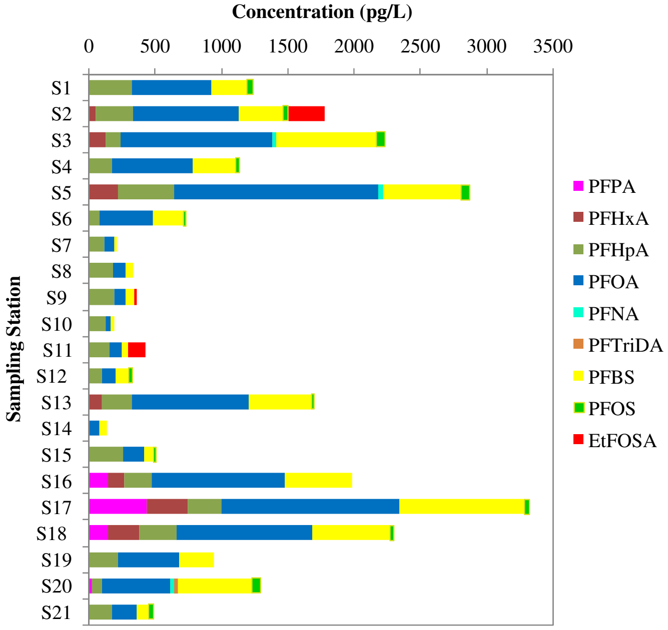


Fig. 2. Spatial distribution of individual PFC concentrations in the coastal waters from the East to South China Sea.

samples of Yangtze River estuary in Shanghai ranged from 29 to 289 ng/L (average of 120 ng/L) (So et al., 2007). Therefore, the Yangtze River should be considered as a potential source of the coastal areas from sampling station S1–S5. Elevated PFC concentrations were also observed along the shoreline of the Guangdong province (i.e. sampling station S16–S20), which indicates that the industrialized regions in this area are potential sources of PFCs and the economic development seems to be associated with the PFC emission amount. Interestingly, the seawater concentration of PFCs at sampling station S21 was about 4 times lower than that from S16 to S20. This could probably be the results of dilution effects with greater volume of seawater from off-shore of South China Sea. Additionally, the coastal water concentration of ΣPFCs was about 3.5 times higher at sampling station S13 (1700 pg/L, coastal waters from the Putian, Fujian Province) in comparison to sampling station S6–S15 (average of 492 pg/L), indicating the existence of a point source in this area of Putian. Two big harbors (Meizhou harbor and Fuqing harbor) were probably responsible for higher concentrations of PFCs close to the coastal area of sampling station S13. It was previously reported that the use of paints and grease repellence for ship and dock protection could contribute to the relatively high presence of PFCs in port seawaters, and shipping and boat maintenance in the ports can also be responsible for the release of PFCs to surrounding waters (Paul et al., 2009; Sánchez-Avila et al., 2010). Additionally, accidental spills or the release of non-treated discharges of wastewater should be considered. However, the identification of the source need further research for the coastal area at sampling station S13.

3.2. Identification of sources of individual PFCs

PFOA, PFHpA and PFBS were the predominated PFCs in this study, and similar results were reported in German coast and Baltic Sea of German (Ahrens et al., 2010a). However, this is not consistent with the results in other studies, which reported that PFOS and PFOA were the dominating compounds in surface water in coastal areas, such as coastal waters of NW Mediterranean (Sánchez-Avila et al., 2010), Korea (So et al., 2004; Naile et al., 2010), Tokyo Bay (Japan) (Yamashita et al., 2005), and Cantabrian Sea (Gómez et al., 2011). The different composition pattern indicates that the regions were influenced by different sources. However, the ocean currents, adsorption to particles and atmospheric deposition can also influence the composition pattern. The dominance of PFOA and PFOS in coastal waters might indicate that the contamination originated from WWTP effluents where they were found to be the predominant PFCs, such as in Denmark (Bossi et al., 2008), Georgia and Kentucky (USA) (Loganathan et al., 2007), Germany (Ahrens et al., 2009c), Canada (Furdui et al., 2008), Austria (Clara et al., 2008) and Catalonia (Sánchez-Avila et al., 2010). In our study, the concentration of PFBS (average of 302 pg/L) was about one order of magnitude higher than that of PFOS (average of 24 pg/L), This can be partly attributed to the increasing production of *N*-methyl perfluorobutane sulfonamidoethanol (MeFBSE) and related products with four perfluorinated carbons, which was introduced after the voluntary phase-out of POSF by the 3M Company in 2000 (D'Eon et al., 2006). Our results indicate that the emissions of PFOS into the aqueous environment decreased whereas the C_4-based compounds PFBS became the predominant PFSA. Besides PFOA and PFBS, PFHpA was one of the predominant PFCs in this study. High PFHpA concentrations have been also found previously in tributaries of the Pearl River in Guangzhou (average of 1139 pg/L) (So et al., 2007), Nanjing and Shanghai along the Yangtze River (average of 310 and 3550 pg/L, respectively) (So et al., 2007), and Taihu lake in Jiangsu Province (average of 1700 pg/L) (Yang et al., 2011). This indicates that there are potential sources for PFHpA in the southeast regions of China, which lead to the contamination of the China Sea with PFHpA.

The concentration of PFOA was generally one order of magnitude higher (~22 times) than that of PFOS in water samples. In contrast, PFOS is the predominant compound in wildlife (Kannan et al., 2001a,b), which can be explained by its higher bioaccumulation potential, whereas PFOA has a higher water solubility (Brooke et al., 2004) and lower sorption potential to sediment (Higgins and Luthy, 2006). On the other hand, the PFOA concentrations are usually higher in open-ocean waters compared to PFOS, which can be explained by different amount of discharge into the aqueous environment, different sources (Prevedouros et al., 2006; Paul et al., 2009), different degradation process of the precursors (Ellis et al., 2004; D'Eon et al., 2006) and different physico-chemical characteristics.

Individual PFC concentrations at different sampling were correlated with each other (see Table S5). The concentrations of PFOA and

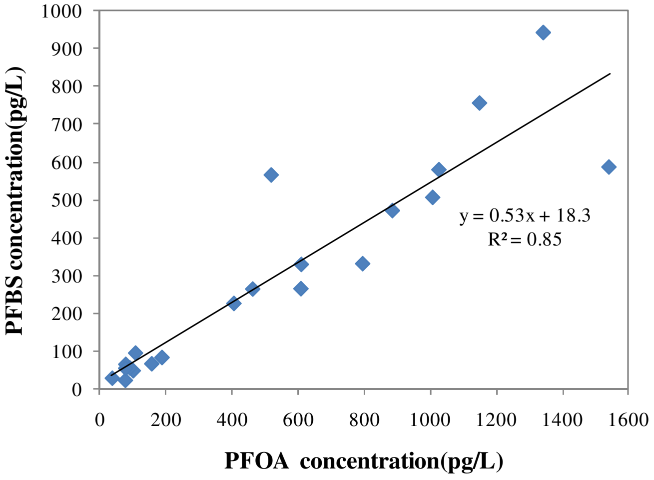


Fig. 3. Correlations between PFBS and PFOA concentrations in surface waters from the East to South China Sea.

PFBS were positively correlated (Spearman Correlations: $r_s = 0.96$, $P < 0.01$ Table S5 in the Supplementary material; $R^2 = 0.85$, Fig. 3), and the concentration of PFOA was positively correlated with those of PFHxA ($r_s = 0.83$, $P < 0.01$), PFOS ($r_s = 0.67$, $P < 0.01$), PFHpA ($r_s = 0.53$, $P < 0.05$), which indicates that the source of these compounds are related. Young et al. (2007) found a positive correlation between PFNA and PFOA with slope of ~1 in snow samples from remote ice caps that were contaminated atmospherically by precursors, in this case of 8:2 FTOH. PFNA and PFOA were correlated with a slope of ~0.4 in the Atlantic Ocean and ~0.2 in Northern Europe, which can be partly explained by atmospheric deposition (Ahrens et al., 2009a, 2010b). However, in the present study, PFNA was detected only in 14% of the samples, and the correlation between PFNA and PFOA resulted in a slope of ~0.0084, which

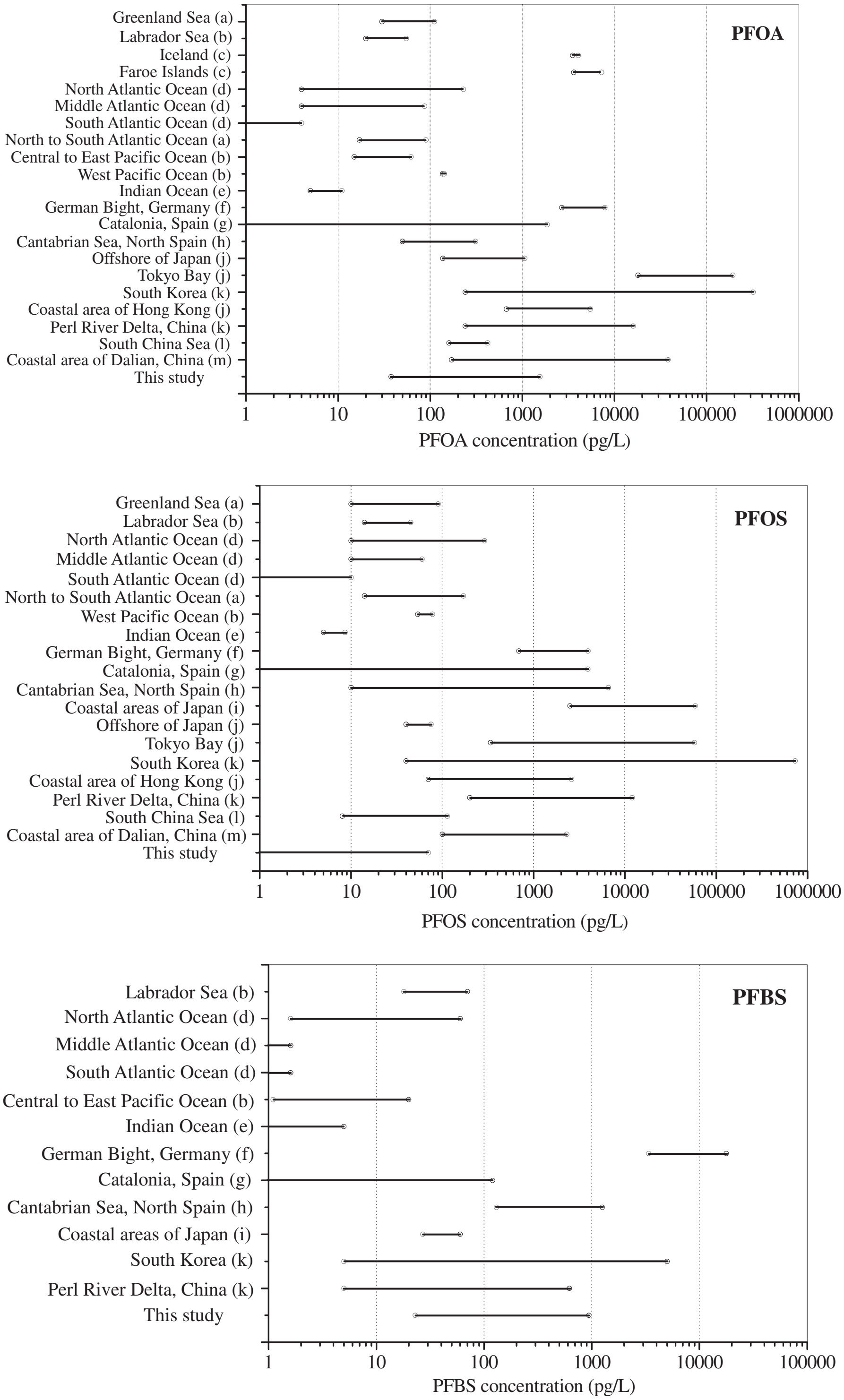


Fig. 4. Concentrations (minimum, maximum) of PFOA, PFOS and PFBS in seawater in the open-ocean and the coastal areas in pg/L ((a) Theobald et al., 2007, (b) Yamashita et al., 2008, (c) Kallenborn et al., 2004, (d) Ahrens et al., 2009a, (e) Wei et al., 2007, (f) Ahrens et al., 2009b, (g) Sánchez-Avila et al., 2010, (h) Gómez et al., 2011, (i) Taniyasu et al., 2003, (j) Yamashita et al., 2005, (k) So et al., 2004, (l) Yamashita et al., 2004, (m) Ju et al., 2008).

indicated that PFOA and PFNA originated from direct emissions or further transported by the ocean current rather than atmosphere transport of precursor compounds. Simcik and Dorweiler (2005) found that the ratio of PFHpA to PFOA increased with increasing distance from non-atmospheric source and suggested that a high ratio would be a good tracer of atmospheric deposition. In this study, only a few sampling stations (i.e. S7, S8, S9, S10, S11, and S15) had PFHpA/PFOA ratios greater than 1, which suggests that the PFCs in the China Sea originated from direct sources. However, atmospheric deposition should be also considered as a source at sampling station S7–S11. The concentration of PFBS was positively correlated with that of PFOS ($r_s = 0.71$, $P < 0.01$), which indicate that these two PFCs originated from similar sources. It could be also explained by using of PFBS-based products as substitute chemicals for PFOS-based products due to its low bioaccumulation in mammals in recent years (Chengelis et al., 2009). In addition, a positive correlation was also found between the concentrations of PFBS and PFHxA ($r_s = 0.79$, $P < 0.01$), PFHpA and PFHxA ($r_s = 0.50$, $P < 0.05$), which suggest a common pollution source of these compounds into the marine environment.

3.3. Comparison of PFC concentrations in this study with those in other surface seawater studies

A global comparison of PFCs in surface seawater is shown in Fig. 4 using the minimum and maximum PFOA, PFOS and PFBS concentrations. In previous studies for coastal areas, higher concentration of PFOA was found in Tokyo Bay and South Korea (Taniyasu et al., 2005; Yamashita et al., 2005), while lower concentration was observed in coastal areas of Catalonia and Cantabrian Sea in Spain (Sánchez-Avila et al., 2010; Gómez et al., 2011), and China, such as South China Sea (Yamashita et al., 2004) and in the East to South China Sea (this study). In particular, PFOA concentrations in Tokyo Bay and South Korea were about 1–2 order of magnitude higher than other coastal waters (So et al., 2004; Yamashita et al., 2005). However, the concentrations of PFOA in coastal waters were generally 1–2 orders of magnitude higher than in open-ocean waters, which suggest industrial areas are considered as potential sources for PFCs. Interestingly, the concentration of PFOA was relatively high in seawaters of Iceland and Faroe Islands in the Arctic environment (Kallenborn et al., 2004). This can be explained by neutral, volatile precursor compounds, which can undergo long-range atmospheric transport and be degraded in remote regions (Ellis et al., 2004; Martin et al., 2006; Schenker et al., 2008) or by the direct transport of ionic PFCs by oceanic currents or by means of sea-spray (Armitage et al., 2006; McMurdo et al., 2008).

The higher concentration of PFOS was found in coastal areas of Tokyo Bay (Japan) and South Korea (Taniyasu et al., 2003; So et al., 2004; Yamashita et al., 2005), where one of the lowest concentrations were observed in the China Sea from this study. Generally, the concentrations of PFOS in coastal waters were 1–2 orders of magnitude higher than in open-ocean waters. However, the relatively low concentration of PFOS detected in coastal areas of China in this study was comparable to that in open-ocean waters and in the Arctic waters. In contrast, about 2 orders of magnitude higher concentrations of PFOS were found in the estuaries of the Yangtze River (average of 5137 pg/L) and the Pearl River (average of 7325 pg/L) compared to this study (So et al., 2004, 2007). This suggests that PFOS can be removed easily from the water phase by bioaccumulation in the marine food chain or sorption to particles (Higgins et al., 2005). On the other hand, the PFBS concentration exceed the PFOS concentration by about one order of magnitude in this study which can be explained by different emissions rates but also by its less bioaccumulation potential and less sorption potential to particles. The concentration of PFBS in this study was comparable to that in other coastal regions, such as Catalonia and Cantabrian Sea in Spain, coastal areas of Japan, South Korea and Pearl River of China (Taniyasu et al., 2003; So et al., 2004; Sánchez-Avila et al., 2010; Gómez et al., 2011). Higher concentrations of PFBS were found in coastal areas of the German Bight and South Korea (So et al., 2004; Ahrens et al., 2009b), and lower concentrations were observed in coastal areas of Japan, Catalonia in Spain (Taniyasu et al., 2003; Sánchez-Avila et al., 2010). Generally, the concentrations of PFBS in coastal waters were generally 1–2 orders of magnitude higher than that in open-ocean waters, which is similar to that of PFOA and PFOS.

4. Conclusions

Only a few studies exist about the spatial distribution of PFCs in coastal waters. It is important to identify the sources for individual PFCs and their distribution mechanism. The spatial distribution and sources of individual PFCs from the East to South China Sea were investigated. PFOA, PFBS, PFHpA, and PFOS were found ubiquitously in coastal waters in this study, which suggests that these compounds are entering the marine environment from rivers or harbors in this area and can potentially undergo long-range transportation via the ocean currents (Yamashita et al., 2005). Dilution process, bioaccumulation in the marine food web or adsorption to suspended particle matter could be responsible for the decreasing concentrations from the river estuaries of the Yangtze River and Pearl River to the coastal area of the China Sea (Higgins and Luthy, 2006; Theobald et al., 2007). Nevertheless, the Yangtze River is probably one of the main sources of the PFCs in the studied area, and the emission of PFCs in Guangdong province is much higher than that in Fujian province, attributing to higher levels of economic development.

Overall, the spatial distribution data obtained in this study is useful for global transport models (Armitage et al., 2006), in which industrial areas are considered as source of PFCs, and ocean water is important as a sink and for transport of these compounds. The ubiquitous presence of PFCs along the coast is an indicator of their widespread distribution and gives evidence on the risk that may pose to the overall area. However, the understanding of the global geochemical cycle of PFCs in water is an important challenge for the future. Additionally, the occurrence of high concentrations of PFCs in coastal waters could possibly be problematic, because they are bioavailable and can accumulate in the marine food chain. Chemical "fingerprints" may help to identify specific sources of PFC contamination into the aqueous environment. This research is very important for the understanding of the transportation and the fate of PFCs in the marine environment.

Acknowledgments

We wish to express our sincere gratitude to all the members of the 27th Chinese National Antarctic Research Expedition (CHINARE-27). This research was supported by the National Natural Science Foundation of China (No. 40776003) and Ocean Public Welfare Scientific Research Project, State Oceanic Administration People's Republic of China (No. 200805095).

Appendix. Supplementary material

Supplementary material related to this article can be found online at doi:10.1016/j.envpol.2011.09.045.

References

Ahrens, L., Barber, J.L., Xie, Z., Ebinghaus, R., 2009a. Longitudinal and latitudinal distribution of perfluoroalkyl compounds in the surface water of the Atlantic Ocean. Environmental Science & Technology 43, 3122–3127.

Ahrens, L., Felizeter, S., Ebinghaus, R., 2009b. Spatial distribution of polyfluoroalkyl compounds in seawater of the German Bight. Chemosphere 76, 179–184.

Ahrens, L., Felizeter, S., Sturm, R., Xie, Z., Ebinghaus, R., 2009c. Polyfluorinated compounds in waste water treatment plant effluents and surface waters along the river Elbe, Germany. Marine Pollution Bulletin 58, 1326–1333.

Ahrens, L., Gerwinski, W., Theobald, N., Ebinghaus, R., 2010a. Sources of polyfluoroalkyl compounds in the North Sea, Baltic Sea and Norwegian Sea: evidence from their spatial distribution in surface water. Marine Pollution Bulletin 60, 255–260.

Ahrens, L., Xie, Z., Ebinghaus, R., 2010b. Distribution of perfluoroalkyl compounds in seawater from Northern Europe, Atlantic Ocean, and Southern Ocean. Chemosphere 78, 1011–1016.

Armitage, J., Cousins, I.T., Prevedouros, K., Russell, M.H., Macleod, M., Korzeniowski, S.H., 2006. Modeling global-scale fate and transport of perfluorooctanoate emitted from direct sources. Environmental Science & Technology 40, 6969–6975.

Austin, M.E., Kasturi, B.S., Barber, M., Kannan, K., MohanKumar, P.S., MohanKumar, S.M.J., 2003. Neuroendocrine effects of perfluorooctane sulfonate in rats. Environmental Health Perspective 111, 1485–1489.

Bao, J., Jin, Y., Liu, W., Ran, X., Zhang, Z., 2009. Perfluorinated compounds in sediments from the Daliao River system of northeast China. Chemosphere 77, 652–657.

Bao, J., Liu, W., Jin, Y., Ran, X., Zhang, Z., 2010. Perfluorinated compounds in urban river sediments from Guangzhao and Shanghai of China. Chemosphere 80, 123–130.

Bossi, R., Strand, J., Sortkjær, O., Larsen, M.M., 2008. Perfluoroalkyl compounds in Danish wastewater treatment plants and aquatic environments. Environment International 34, 443–450.

Brooke, D., Footitt, A., Nwaogu, T.A., 2004. Environmental Risk Evaluation Report: Perfluorooctanesulfonate (PFOS). Environmental Agency, UK. Rotherdam.

Busch, J., Ahrens, L., Xie, Z., Sturm, R., Ebinghaus, R., 2010. Polyfluoroalkyl compounds in the East Greenland Arctic Ocean. Journal of Environmental Monitoring 12, 1242–1246.

Chengelis, C.P., Kirkpatrick, J.B., Myers, N.R., Shinohara, M., Stetson, P.L., Sved, D.W., 2009. Comparison of the toxicokinetic behavior of perfluorohexanoic acid (PFHxA) and nonafluorobutane-1-sulfonic acid (PFBS) in cynomolgus monkeys and rats. Reproductive Toxicology 27, 400–406.

Clara, M., Scheffknecht, C., Scharf, S., Weiss, S., Gans, O., 2008. Emissions of perfluorinated alkylated substances (PFAS) from point source-identification of relevant branches. Water Science and Technology 58, 59–66.

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. Environmental Science & Technology 40, 1862–1868.

Ellis, D.A., Martin, J.W., De Silva, A.O., Mabury, S.A., Hurley, M.D., Sulbaek Andersen, M.P., Wallington, T.J., 2004. Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. Environmental Science & Technology 38, 3316–3321.

European Parliament and Council, 2006. Directive 2006/122/ECOF.

Furdui, V.I., Crozier, P.W., Reiner, E.J., Mabury, S.A., 2008. Trace level determination of perfluorinated compounds in water by direct injection. Chemosphere 73, S24–S30.

Giesy, J.P., Kannan, K., 2001. Global distribution of perfluorooctane sulfonate in wildlife. Environmental Science & Technology 35, 1339–1342.

Gómez, C., Vicente, J., Echavarri-Erasun, B., Porte, C., Lacorte, S., 2011. Occurrence of perfluorinated compounds in water, sediment and mussels from the Cantabrian Sea (North Spain). Marine Pollution Bulletin 62, 948–955.

Guo, R., Zhou, Q., Cai, Y., Jiang, G., 2008. Determination of perfluorooctanesulfonate and perfluorooctanoic acid in sewage sludge samples using liquid chromatography/quadrupole time-of-flight mass spectrometry. Talanta 75, 1394–1399.

Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. Environmental Science & Technology 39, 3946–3956.

Higgins, C.P., Luthy, R.G., 2006. Sorption of perfluorinated surfactants on sediments. Environmental Science & Technology 40, 7251–7256.

Houde, M., Bujas, T.A.D., Small, J., Wells, R.S., Fair, P.A., Bossart, G.D., Solomon, K.R., Muir, D.C.G., 2006. Biomagnification of perfluoroalkyl compounds in the bottlenose dolphin (*Tursiops truncatus*) food web. Environmental Science & Technology 40, 4138–4144.

Jahnke, A., Berger, U., Ebinghaus, R., Temme, C., 2007. Latitudinal gradient of airborne polyfluorinated alkyl substances in the marine atmosphere between Germany and South Africa (53 °N–33 °S). Environmental Science & Technology 41, 3055–3061.

Jin, Y., Saito, N., Harada, K.H., Inoue, K., Koizumi, A., 2007. Historical trends in human serum levels of perfluorooctanoate and perfluorooctane sulfonate in Shenyang, China. The Tohoku Journal of Experimental Medicine 212, 63–70.

Ju, X., Jin, Y., Sasaki, K., Saito, N., 2008. Perfluorinated surfactants in surface, subsurface water and microlayer from Dalian coastal waters in China. Environmental Science & Technology 42, 3538–3542.

Kallenborn, R., Berger, U., Järnberg, U., 2004. Perfluorinated alkylated substances (PFAS) in the Nordic environment. Tema Nord, 1–107.

Kannan, K., Franson, J.C., Bowerman, W.W., Hansen, K.J., Jones, P.D., Giesy, J.P., 2001a. Perfluorooctane sulfonate in fish-eating water birds including bald eagles and albatrosses. Environmental Science & Technology 35, 3065–3070.

Kannan, K., Koistinen, J., Beckmen, K., Evans, T., Gorzelany, J.F., Hansen, K.J., Jones, P.D., Helle, E., Nyman, M., Giesy, J.P., 2001b. Accumulation of perfluorooctane sulfonate in marine mammals. Environmental Science & Technology 35, 1593–1598.

Kissa, E., 2001. Fluorinated Surfactants and Repellents, vol. 97. Marcel Dekker.

Li, X., Yeung, L.W.Y., Taniyasu, S., Li, M., Zhang, H., Liu, D., Lam, P.K.S., Yamashita, N., Dai, J., 2008a. Perfluorooctanesulfonate and related fluorochemicals in the Amur Tiger (Panthera tigris altaica) from China. Environmental Science & Technology 42, 7078–7083.

Li, X., Yeung, L.W.Y., Xu, M., Taniyasu, S., Lam, P.K.S., Yamashita, N., Dai, J., 2008b. Perfluorooctane sulfonate (PFOS) and other fluorochemicals in fish blood collected near the outfall of wastewater treatment plant (WWTP) in Beijing. Environmental Pollution 156, 1298–1303.

Liu, W., Dong, G., Jin, Y., Sasaki, K., Saito, N., Sato, I., Tsuda, S., Nakayama, S.F., 2009. Occurrence of perfluoroalkyl acids in precipitation from Shenyang, China. Chinese Science Bulletin 54, 2440–2445.

Loganathan, B.G., Sajwan, K.S., Sinclair, E., Kumar, K.S., Kannan, K., 2007. Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. Water Research 41, 4611–4620.

Mai, B., Fu, J., Sheng, G., Kang, Y., Lin, Z., Zhang, G., Min, Y., Zeng, E.Y., 2002. Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. Environmental Pollution 117, 457–474.

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 organic and analysis by gas chromatography/chemical ionization mass spectrometry. Analytical Chemistry 74, 584–590.

Martin, J.W., Mabury, S.A., Solomon, K.R., Muir, D.C.G., 2003. Bioconcentration and tissue distribution of perfluorinated acids in rainbow trout (*Oncorhynchus mykiss*). Environmental Toxicology and Chemistry 22, 196–204.

Martin, J.W., Whittle, D.M., Muir, D.C.G., Mabury, S.A., 2004. Perfluoroalkyl contaminants in a food web from Lake Ontario. Environmental Science & Technology 38, 5379–5385.

Martin, J.W., Ellis, D.A., Mabury, S.A., 2006. Atmospheric chemistry of perfluoroalkanesulfonamides: kinetic and product studies of the OH radical and Cl atom initiated oxidation of N-Ethyl perfluorobutanesulfonamide. Environmental Science & Technology 40, 864–872.

McMurdo, C.J., Ellis, D.A., Webster, E., Butler, J., Christensen, R.D., Reid, L.K., 2008. Aerosol enrichment of the surfactant PFO and mediation of the water–air transport of gaseous PFOA. Environmental Science & Technology 42, 3969–3974.

Moody, C.A., Field, J.A., 2000. Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams. Environmental Science & Technology 34, 3864–3870.

Naile, J.E., Khim, J.S., Wang, T., Chen, C., Luo, W., Kwon, B., Park, J., Koh, C., Jones, P.D., Lu, Y., Giesy, J.P., 2010. Perfluorinated compounds in water, sediment, soil and biota from estuarine and coastal areas of Korea. Environmental Pollution 158, 1237–1244.

National Bureau of Statistics of China, 2010. China Statistical Yearbook.

OECD, September 17, 2002. Draft Assessment of Perfluorooctane Sulfonate (PFOS) and Its Salts: Complete Assessment. ENV/JM/RD.

Paul, A.G., Jones, K.C., Sweetman, A.J., 2009. A first global production, emission, and environmental inventory for perfluorooctane sulfonate. Environmental Science & Technology 43, 386–392.

Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. Environmental Science & Technology 40, 32–44.

Rhoads, K.R., Janssen, E.M.L., Luthy, R.G., Criddle, C.S., 2008. Aerobic biotransformation and fate of N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE) in activated sludge. Environmental Science & Technology 42, 2873–2878.

Saito, N., Sasaki, K., Nakatome, K., Harada, K., Yoshinaga, T., Koizumi, A., 2003. Perfluorooctane sulfonate concentrations in surface water in Japan. Archives of Environmental Contamination and Toxicology 45, 149–158.

Sánchez-Avila, J., Meyer, J., Lacorte, S., 2010. Spatial distribution and sources of perfluorochemicals in the NW Mediterranean coastal waters (Catalonia, Spain). Environmental Pollution 158, 2833–2840.

Schenker, U., Scheringer, M., Macleod, M., Martin, J.W., Cousins, I.T., Hungerbühler, K., 2008. Contribution of volatile precursor substances to the flux of perfluorooctanoate to the Arctic. Environmental Science & Technology 42, 3710–3716.

Schultz, M.M., Barofsky, D.F., Field, J.A., 2004. Quantitative determination of fluorotelomer sulfonates in groundwater by LC MS/MS. Environmental Science & Technology 38, 1828–1835.

Schultz, M.M., Higgins, C.P., Huset, C.A., Luthy, R.G., Barofsky, D.F., Field, J.A., 2006. Fluorochemical mass flows in a municipal wastewater treatment facility. Environmental Science & Technology 40, 7350–7357.

Scott, B.F., Spencer, C., Mabury, S.A., Muir, D.C.G., 2006. Poly and perfluorinated carboxylates in North American precipitation. Environmental Science & Technology 40, 7167–7174.

Shen, M., Yu, Y., Zheng, G.J., Yu, H., Lam, P.K.S., Feng, J., Wei, Z., 2006. Polychlorinated biphenyls and polybrominated diphenyl ethers in surface sediments from the Yangtze River Delta. Marine Pollution Bulletin 52, 1299–1309.

Shi, X., Du, Y., Lam, P.K.S., Wu, R.S.S., Zhou, B., 2008. Developmental toxicity and alteration of gene expression in zebrafish embryos exposed to PFOS. Toxicology and Applied Pharmacology 230, 23–32.

Simcik, M.F., Dorweiler, K.J., 2005. Ratio of perfluorochemical concentrations as a tracer of atmospheric deposition to surface waters. Environmental Science & Technology 39, 8678–8683.

Skutlarek, D., Exner, M., Färber, H., 2006. Perfluorinated surfactants in surface and drinking waters. Environmental Science and Pollution Research 13, 299–307.

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. Environmental Science & Technology 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. Environmental Science & Technology 38, 991–996.

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.

Stock, N.L., Furdui, V.I., Muir, D.C.G., Mabury, S.A., 2007. Perfluoroalkyl contaminants in the Canadian Arctic: evidence of atmospheric transport and local contamination. Environmental Science & Technology 41, 3529–3536.

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. Environmental Science & Technology 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. Journal of Chromatography A 1093, 89–97.

Theobald, N., Gerwinski, W., Caliebe, C., Haarich, M., 2007. Development and Validation of a Method for the Determination of Polyfluorinated Organic Substances in Sea Water, Sediments and Biota – Occurrence of These Compounds in the North and Baltic Seas. http://www.umweltbundesamt.de/.

Wei, S., Chen, L.Q., Taniyasu, S., So, M.K., Murphy, M.B., Yamashita, N., Yeung, L.W.Y., Lam, P.K.S., 2007. Distribution of perfluorinated compounds in surface seawaters between Asia and Antarctica. Marine Pollution Bulletin 54, 1813–1838.

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. Environmental Science & Technology 38, 5522–5528.

Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Petrick, G., Gamo, T., 2005. A global survey of perfluorinated acids in oceans. Marine Pollution Bulletin 51, 658–668.

Yamashita, N., Taniyasu, S., Petrick, G., Wei, S., Gamo, T., Lam, P.K.S., Kannan, K., 2008. Perfluorinated acids as novel chemical tracers of global circulation of ocean waters. Chemosphere 70, 1247–1255.

Yang, L., Zhu, L., Liu, Z., 2011. Occurrence and partition of perfluorinated compounds in water and sediment from Liao River and Taihu Lake, China. Chemosphere 83, 806–814.

Yeung, L.W.Y., So, M.K., Jiang, G., Taniyasu, S., Yamashita, N., Song, M., Wu, Y., Li, J., Giesy, J.P., Guruge, K.S., Lam, P.K.S., 2006. Perfluorooctanesulfonate and related fluorochemicals in human blood samples from China. Environmental Science & Technology 40, 715–720.

Yeung, L.W.Y., Miyake, Y., Taniyasu, S., Wang, Y., Yu, H., So, M.K., Jiang, G., Wu, Y., Li, J., Giesy, J.P., Yamashita, N., Lam, P.K.S., 2008. Perfluorinated compounds and total and extractable organic fluorine in human blood samples from China. Environmental Science & Technology 42, 8140–8145.

Young, C.J., Furdui, V.I., Franklin, J., Koerner, R.M., Muir, D.C.G., Mabury, S.A., 2007. Perfluorinated acids in Arctic snow: new evidence for atmospheric formation. Environmental Science & Technology 41, 3455–3461.

Yu, J., Hu, J., Tanaka, S., Fujii, S., 2009. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in sewage treatment plants. Water Research 43, 2399–2408.