Occurrence and fate of perfluoroalkyl substances in marine sediments from the Chinese Bohai Sea, Yellow Sea, and East China Sea

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ABSTRACT

In this study, 166 surface sediments and 3 sediment cores from the Bohai Sea (BS), Yellow Sea (YS) and East China Sea (ECS) in China were collected to investigate the spatial and temporal distributions and the transport of PFASs. PFASs concentrations in the surface sediments ranged from below detection limit (<LOD) to 2.78 ng g⁻¹ with an average value of 0.55 ng g⁻¹ on a dry weight basis (dw). A general decreasing trend of PFASs from the coast areas to the open sea was found. Multivariate regression analysis indicated pH and longitude were the major factors influencing surficial distributions of PFASs in the sampling areas ($R^2 = 0.29$, $p < 0.01$). Total PFASs concentrations in the sediment cores ranged from <LOD to 1.65 ng g⁻¹ dw, with an increasing trend from the lower to the upper layers, corresponding well to the increasing production and usage in China in recent years.

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1. Introduction

Per- and polyfluoroalkyl Substances (PFASs), such as perfluorocarboxylates (PFCAs) and perfluorosulfonates (PFASs), have been widely used in the past six decades as additives in surface coatings of carpets, leather, papers, and textiles, as well as in fire-fighting foams, pesticides, paints, etc. Their excellent thermal and chemical stability renders PFASs highly persistent in the environment, evidenced by their ubiquitous global detection (Cai et al., 2012b) and accumulations in human and wildlife (Kelly et al., 2009; Li et al., 2013). In 2009, perfluorooctanesulfonate (PFOS) and its salts were listed in the Stockholm Convention as Persistent Organic Pollutants (POPs) (Loi et al., 2011).

Production and usage of PFASs in China has increased rapidly in recent years. A large proportion of the total production output in China was from coastal provinces/cities, including Zhejiang, Fujian, Guangdong, Jiangsu, Liaoning and Shanghai (Chen et al., 2009), adjacent to the Bohai Sea (BS), Yellow Sea (YS), East China Sea (ECS), and South China Sea (SCS). Recently, PFASs have been detected in the coastal marine environment of China. Chen et al. investigated

PFASs in the water and sediment from coastal northern BS and found sediment was an important sink for perfluoroundecanoic acid (Chen et al., 2011). Pan et al. found low PFASs concentrations in mollusks from the coastal waters in the BS (Pan et al., 2010). The investigation on the PFASs in coastal waters of Hong Kong, South China indicated that PFASs in the sampling areas were strongly influenced by discharge from the Pearl River (So et al., 2004). Cai et al. considered the Yangtze River as an important source of PFASs found in the coastal waters of southern China (Cai et al., 2012a).

In spite of the ubiquitous existence of PFASs in the global environment, the mechanisms of long range transport of the PFASs and their precursors across continents and on global scales remain unclear. Relatively volatile perfluoroalkyl precursors such as fluorotelomer alcohols (FTOHs), perfluoroalkyl sulfonamides (FASAs) and perfluoroalkylsulfonamidoethanols (FASEs) were transported via the atmosphere and subject to photolytic degradation in the air (Ellis et al., 2004, 2003), whereas the ionisable PFASs such as PFCAs and PFASs are predominantly transported via the ocean current (Prevedouros et al., 2006).

This work is a systematic survey of PFASs in the sediments of the BS, YS and ECS of China. The primary objective of this work was to depict the spatial and temporal distribution patterns of PFASs in the three sea regions of China. The large number of samples allowed us to examine the factors influencing the accumulation of PFASs in

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marine sediments. The large geographical coverage enabled us to gain insights into the anthropogenic impacts, the transport pathways, and the environmental fate of PFASs in the sampling areas.

2. Materials and methods

2.1. Sample collection

The entire study area encloses the BS, YS and ECS, extending 2000 km from south to north and totaling about 1,230,000 km² water surface (Fig. 1). The major mud areas and the dominant ocean currents are shown in Fig. S1. The BS is a semi-enclosed shallow (mean depth 26 m) marginal sea receiving waters from more than 40 rivers in northern China. The YS is located between Chinese mainland to the west and Korean Peninsula to the east, with an average depth of 44 m. ECS is mostly on a

continental shelf with water depth <200 m, and its water flow is strongly influenced by the freshwater input from the Yangtze River and the saline Kuroshio Current (Yanao and Matsuno, 2013). The YS and ECS constitute the western margin of the North Pacific Ocean.

Sediment sampling was carried out onboard of *R/V Dong Fang Hong 2* in 2011 and 2012. The sampling locations are shown in Fig. 1, and additional information is summarized in Table S1. In all, 166 surface sediments were collected using a stainless steel box sampler and transferred to polyethylene bags. Three sediment cores were collected. Core-1 and Core-2 were collected in the ECS in 2011, and Core-3 was in the YS in 2012, all from the mud areas of the shelf. The sediment cores were sectioned onboard into 1 cm intervals using a stainless steel cutter. A total of 111 core slices were obtained. All samples were kept in a shipboard refrigerator immediately after sampling, and subsequently freeze-dried and ground after being transported to the laboratory. All the samples were stored frozen at −20 °C until analysis.

Fig. 1. Study area and sampling sites of surface sediments (small red dots) and sediment cores (large orange dots). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Chemicals and reagents

A mixture (PFAC-MXB) of 6 PFCAs (C_7 – C_{12}) and 3 PFASs (C_4 , C_6 , C_8) was purchased from Wellington Laboratories (Canada). Carbon-13 labeled $^{13}C_4$ PFOS and $^{13}C_4$ PFOA were also purchased from Wellington. Methanol (HPLC grade) was purchased from J.T.Baker (USA). Ammonium acetate was purchased from Alfa Aesar (Ward Hill, MA, USA). Water was prepared by a Milli-Q Advantage A10 system (Millipore Corp., USA). Oasis-HLB cartridge (6 cc, 150 mg), made in Ireland, was purchased from Waters Corp. (Milford, MA, USA).

2.3. Sample preparation and instrumental analysis

5 g of sediment samples was weighed into a 50-mL polypropylene tube and spiked with internal standards ($^{13}C_4$ PFOS and $^{13}C_4$ PFOA, 5 ng each). 20 mL of methanol was added as extracting agent. The mixture was sonicated for 20 min and centrifuged at 3500 rpm for 10 min. The supernatant was transferred into a new tube. The remnant solution was extracted twice by shaking with 10 mL of methanol. The extracts were concentrated to 1 mL under a stream of N_2 .

Solid phase extraction (SPE) was used for sample cleanup. The Oasis-HLB SPE cartridge was preconditioned with 7 mL of methanol and 7 mL of Milli-Q water. The concentrated extract was diluted with 40 mL deionized water and loaded on the preconditioned cartridge by gravity, after which 5 mL of methanol/water (1:4) was loaded. Target analytes were eluted by 10 mL methanol. The elution was concentrated to 1 mL by gentle stream of N_2 and transferred to an injection vial.

Analysis of PFASs was performed using a HPLC-ESI-/MS/MS system consisted of a Waters 2695 Alliance high performance liquid chromatography and a Waters Quattro Premier XE triple-quadrupole mass spectrometry (Waters Corp., Milford, MA). For each run, 10 μ L of the sample was separated on a Dionex Acclaim 120 C18 column (5 μ m, 4.6 mm i.d. $\times$ 150 mm length; Dionex, Sunnyvale, CA, USA). Methanol (A) and 10 mM ammoniumacetate aqueous solution (B) were used as mobile phases. The flow rate was 1.0 mL min⁻¹. The dualistic gradient started at 28% B, changed to 5% B in 4 min linearly, returned to 28% B in 3 min linearly, and then balanced for 3 min. The precursor and product ions were listed in Table S1.

2.4. Quality assurance/quality control

The method limit of quantification (MLQ) was determined as ten times of the signal-to-noise ratio. The MLQs were 0.04 ng g⁻¹ dry weight (dw) for PFBS, 0.01 ng g⁻¹ dw for PFHxS, PFOS, PFHpA, PFOA, and PFNA, and 0.005 ng g⁻¹ dw for PFDA, PFUnDA and PFDoDA. Detailed information of the matrix spike recoveries and the Standard Reference Materials (SRMs) results was shown in Table S2 and Table S3. One procedural blank was performed for every batch of 7 samples. All of the 9 target compounds in the blanks were below their respective LODs. More detailed information about the quality assurance and quality control is listed in the Supplementary materials.

2.5. Total organic carbon (TOC) and pH measurements

TOC was analyzed by an O.I. analytical solids TOC analyzer (O.I. Analytical, USA). Briefly, about 90 mg of samples were placed into the pre-combusted quartz sample cup. Before the analysis, phosphoric acid (1.0 mol L⁻¹) was added to remove the inorganic carbon.

To determine the pH of sediment, 4 g of dry sediment was weighed into a 50 mL polypropylene tube. Then, 10 mL of 1.0 M KCl solution was added to the tube, which was then well shaken. After standing for 30 min, the supernatant was taken and its pH was measured by a Thermo Orion 3 Star pH Benchtop meter (Li et al., 2005).

2.6. Statistical analysis

Statistical analysis was performed with the software SPSS 17.0. Spearman's rank correlation test was used for correlation analysis and a value of $p < 0.05$ was considered to be significant. The multivariate linear regression was performed using the stepwise method.

3. Results and discussion

Nine PFASs were detected, including perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), perfluorooctanesulfonate (PFOS), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA) and perfluorododecanoate (PFDoDA). Their detection rates and concentrations were summarized in Table 1 for surface sediments, with complete data compiled in Table S4. Table S5 presents all concentrations for core samples based on dry weight.

3.1. Concentration and spatial distribution of PFASs in surface sediments

In 165 of the 166 individual surface sediment samples, at least one PFAS was detected. The total concentrations of PFASs (Σ_9 PFASs) averaged 0.55 ng g⁻¹ dw with a median of 0.43 ng g⁻¹ dw and a maximum of 2.98 ng g⁻¹ dw. The spatial distribution of Σ_9 PFASs in the surface sediments was shown in Fig. 2. The Σ_9 PFASs in the sediments in the different sampling areas were in the ranking of BS > ECS > YS based on both the mean and median (Table 1). Generally, Σ_9 PFASs were higher near the coast than in remote areas.

In the BS, the highest Σ_9 PFASs were 2.98 ng g⁻¹ dw at site B28, which is close to the shore. No obvious spatial trends of PFASs were found along the sampling transects. As BS is semi-enclosed, the exchanges of the seawater are restricted. This reduces the dissipation of the pollutants. Relatively high concentrations of Σ_9 PFASs were found near the Yellow River estuary and Liaohe River estuary, reflecting the influence of sources on land. In the YS, the concentrations of Σ_9 PFASs ranged from <LOD at site Y34 to 2.76 ng g⁻¹ dw at Y66, which is located in the mud areas. Similar to the BS, the spatial gradient is not obvious in the YS. In the ECS, the highest Σ_9 PFASs of 1.77 ng g⁻¹ dw was found at site E52. A decreasing gradient was found from the nearshore locations to the open waters (Fig. 2a). The ECS has a dynamic coastal region (Liu et al., 2007), which is influenced by the input from the Yangtze River.

The Yellow Sea warm current (YSWC) and Yellow Sea coastal current (YSCC) facilitate the movement of fine sediment particles (Fig. S1), resulting in the formation of the mud areas in the central YS and BS. Similarly, the Zhejiang-Fujian coastal current (ZFCC), the Tsushima warm current (TaWC) and the Kuroshio warm current (KWC) contribute to the exchange of the seawater and result in the mud areas along the coast of the ECS (Fig. S1). The mud areas with finer sediment particles have accumulated higher concentrations of PFASs than the non-depositional zones (Fig. 2). Post depositional lateral movement of the sediment, or “focusing”, carries the fine sediment to the mud areas (Cheng et al., 2004; Liu et al., 2006). For

Table 1
Concentrations (ng g⁻¹ dw) and detection frequencies (df) of PFASs in surface sediments.

	Chinese Bohai Sea (BS), N = 29				Yellow Sea (YS), N = 66				East China Sea (ECS), N = 71			
	Range	Median	Mean	df (%)	Range	Median	Mean	df (%)	Range	Median	Mean	df (%)
PFBS	<LOD–0.11	<LOD	<MQL	38	<LOD–0.10	<LOD	0.01	18	<LOD–0.19	<LOD	0.01	15
PFHxS	<LOD–0.02	<LOD	<LOD	3	<LOD–0.09	<LOD	<MQL	12	<LOD–0.33	<LOD	0.01	15
PFOS	<LOD–0.15	0.06	0.06	79	<LOD–0.40	0.07	0.09	92	<LOD–0.89	0.04	0.10	77
PFHpA	<LOD–0.04	0.02	0.02	52	<LOD–0.07	<LOD	<MQL	17	<LOD–0.06	<LOD	<MQL	13
PFOA	0.06–2.70	0.28	0.54	100	<LOD–1.52	0.13	0.19	95	<LOD–0.87	0.12	0.18	99
PFNA	<LOD–0.31	0.05	0.05	79	<LOD–0.39	0.06	0.08	83	<LOD–0.31	0.04	0.06	70
PFDA	<LOD–0.04	0.12	0.01	62	<LOD–0.12	0.14	0.02	64	<LOD–0.12	0.03	0.03	72
PFUnDA	<LOD–0.12	0.06	0.05	76	<LOD–0.23	0.07	0.08	92	<LOD–0.17	0.06	0.06	80
PFDoDA	<LOD–0.05	<LOD	<MQL	14	<LOD–0.1	<LOD	0.01	35	<LOD–0.57	0.02	0.06	59
Σ_9 PFASs	0.06–2.98	0.58	0.77	100	<LOD–2.76	0.36	0.49	98	0.03–1.77	0.41	0.52	100

Fig. 2. Spatial distributions of (a) total PFASs (ng g⁻¹ dw), (b) sediment pH, (c) sediment TOC, and (d) PFOS/PFOA ratio.

hydrophobic chemicals, adsorption to particles tends to be higher in the finer fractions due to their larger surface area to mass ratio (Zhao et al., 2012). Similar observations have been reported for dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs) and short chain chlorinated paraffins (SCCPs) in the same general study area (Hu et al., 2011; Zeng et al., 2013).

Available data in PFASs concentrations in surface sediments worldwide are compared in Fig. 3. The comparison suggests that the PFASs pollution of the study area is moderate on a global perspective. For PFOA, the concentrations found in this work were higher than those from previous studies from coastal regions of the northern Bohai Sea in China (Chen et al., 2011), comparable to those from the German Bight of the North Sea (Theobald et al., 2012), the west coast of Korea (Naile et al., 2013), and Cantabrian Sea in northern Spain (Gómez et al., 2011), but lower than those reported from Indonesian coastal waters (Harino et al., 2012). The PFOS concentrations in these three sea areas were higher than those in Daliao River of northeast China (Bao et al., 2009; Yang et al., 2011), Taihu Lake (Yang et al., 2011), and rivers in Shanghai (Bao et al., 2010), comparable to those in Baiyangdian Lake of northern China (Shi et al., 2012), and the Baltic Sea (Theobald et al., 2012), but lower than those in Guangzhou, China (Bao et al., 2010), west coast of Korea (Naile et al., 2013), San Francisco Bay (Higgins et al., 2005), and the German Bight of the North Sea (Theobald et al., 2012).

3.2. PFASs composition analysis

Composition and correlation analysis among the different PFASs can be applied as a tracer of the possible sources of PFASs by atmospheric depositions or marine current in the marine ecosystem (Ahrens et al., 2009a; Simcik and Dorweiler, 2005). The dominance of PFOS and PFOA in total PFASs has been previously reported in various environmental matrices (Myers et al., 2012; Zhang et al., 2010). In this study, composition analysis indicated that PFOA was the most dominant compound with the highest concentrations and detection frequencies, followed by PFOS and PFUnDA (Fig. S2). Spearman's correlation analysis indicated that, on a 95% confidence level, PFOA was positively correlated with PFOS, PFHpA, PFNA, PFDA, and PFUnDA. PFOS was positively correlated with PFHpA, PFNA, PFDA, and PFUnDA (Table S6). The

significant positive correlations among these compounds suggest that their contamination levels might be all mainly influenced by human activities.

The PFOS/PFOA ratio was examined in some studies with the intention of identifying source regions (Simcik and Dorweiler, 2005; So et al., 2004). In this work, the PFOS/PFOA ratios in the surface sediments ($N = 166$) are mostly <1 across the study area (Table S7), but with the >1 values at several spots (Fig. 2d). In the BS, the ratios are all <1 , and the highest was 0.93 at site B17, which is closest to the mouth of Liaohe River. PFOA was found more abundant than PFOS in the sediments from Dagu and Chentaizi drainage river in Tianjin (Pan et al., 2011), in agreement with the observation of this work for the sites nearest to Tianjin. However, the opposite was found in Daliao River (Bao et al., 2009; Yang et al., 2011) and the coastal regions of the north and east parts of BS (Chen et al., 2011). In the YS, average PFOS/PFOA ratio is statistically higher than that in BS ($p < 0.05$) but still below 1. Higher ratios were found in the northern and eastern YS, near Liaoning Province and the west coast of Korean Peninsula, where PFOS was previously reported dominant over PFOA (Naile et al., 2013). In the northern region, the ratio tends to increase from south to north and in the southern region the increasing trend was from west to east. In the ECS, the ratio PFOS/PFOA is generally higher than in the other two seas, with a decreasing trend from the coastal mud areas to the open sea. The concentration of PFOS was higher than PFOA in river sediments from Shanghai (Bao et al., 2010), which is consistent with the finding of this work for nearshore sampling sites such as E54, E59, etc. These results demonstrate a general spatial distribution pattern featuring higher PFOS/PFOA ratio closer to sources. Comparing the two chemicals, PFOA is more prone to migration with ocean current whereas PFOS has higher affinity to particles and sediments (Higgins and Luthy, 2006).

Young et al. indicated that PFDA and PFUnDA found in the environment came from oxidation of PFASs precursors, because their productions are very limited (Young et al., 2007). The high detection frequencies of PFDA and PFUnDA in the sediments of this study (Table 1) implied that the indirect sources such as the atmospheric oxidation of PFASs precursors or other processes might be sources of the PFASs in the sediments of the study area.

Fig. 3. Comparison of PFASs concentrations in sediments worldwide (Ahrens et al., 2009b; Ahrens et al., 2011; Bao et al., 2010; Gómez et al., 2011; Higgins et al., 2005; Li et al., 2011; Naile et al., 2013; Naile et al., 2010; Nakata et al., 2006; Sakurai et al., 2010; Thompson et al., 2011; Wang et al., 2011; Yang et al., 2011).

3.3. Influencing factors for PFASs distribution

The TOC and pH of the sediment samples, and the longitude and latitude of the sampling locations were examined individually and in combination for their correlation with the PFASs concentrations. Table S8 showed the results of single-variable regressions. The sediment pH ranged from 7.70 to 8.70. The dependence of concentrations on sediment pH is highly significant for all individual PFASs and $\sum_9$ PFASs (Table S8). It was suggested that the pH can change the organic matter surface charge thus influence the PFASs distributions and the accumulations in the sediments (Ahrens et al., 2009b; Higgins and Luthy, 2006). For example, Higgins et al. have found increasing sorption of PFASs with decreasing pH of approximately 0.37 log units per unit pH in the pH range of 5.7–7.5 (Higgins and Luthy, 2006), and Ahrens et al. pointed out that concentrations of PFOS, PFNA, and PFDoDA in sediment cores increased with the decreasing pH value (Ahrens et al., 2009b). Sediment TOC ranged from 0.08 to 2.82. TOC normalized concentrations in surface sediments had similar spatial distributions as those based dry weight (Fig. S3). Linear and positive regressions of PFASs on TOC were moderate in general, and appeared to be compound and location dependent (Table S8). The weaker dependence of PFASs on TOC compared with pH suggests that the hydrophobicity is less influential than ionization in affecting PFASs sorption. Dependence on the latitude and longitude of the locations has also been identified between Germany and South Africa in the marine atmosphere (Jahnke et al., 2007), and in the seawater from Atlantic Ocean and the Canadian Arctic Ocean (Benskin et al., 2012). In this work, the dry weight based PFOA concentration was found to decrease with the latitude ($p < 0.01$) and longitude ($p = 0.04$) in the

BS, while in the entire coverage of study area, PFOA decreased with longitude but increased with latitude.

Multivariate regression analyses were carried out to examine the combined impact of the four independent variables including longitude, latitude, pH and TOC. Table S9 summarizes those that are statistically significant ($p < 0.05$). Take $\sum_9$ PFASs in the whole region as an example. The model suggests that pH and longitude were the key factor that influenced the spatial distribution of PFASs in the marine environmental in China, which accounted for 29% of the variation in the concentrations of $\sum_9$ PFASs in the sediments (Table S9). The predicted concentrations using the multi-variable models were compared with the measured concentrations (Fig. 4). On the whole, the most important factor influencing the spatial distributions of PFASs in the sediments is pH, followed by the longitude. In the BS, $\sum_9$ PFASs were influenced by TOC. PFOA was influenced by latitude and pH, whereas PFOS was mainly controlled by pH. In YS, $\sum_9$ PFASs, PFOS and PFOA were mainly controlled by pH of the sediments. In ECS, $\sum_9$ PFASs and PFOA were jointly controlled by pH and TOC and PFOS was mainly affected by pH (Fig. 4, Table S9).

The characteristics of PFASs such as chain length and their functional groups can also be the important factors for their distribution. For example, CF_2 moiety could increase the sorption to sediment materials for both the PFCAs and the PFASs. (Higgins and Luthy, 2006).

3.4. Temporal trends of PFASs from sediment cores

Sediment cores can preserve the historical records and provide the valuable temporal trends of pollutants in the marine

Fig. 4. Comparison of the predicted concentrations using the multi-variable models with the measured concentrations.

environment (Zushi et al., 2010). In this study, 3 sediment cores were collected from the mud areas (Fig. 1, Fig. S1). The concentrations of Σ_9 PFASs in cores 1, 2, 3 were in the range of <LOD–1.21, <LOD–1.65 and <LOD–1.59 ng g⁻¹ dw, respectively. These were higher than those from Tokyo Bay, Japan (Ahrens et al., 2009b). Generally, PFASs in the 3 sediment cores had similar increasing trends with relatively higher levels in the upper slices than that in the bottom samples (Fig. 5), consistent with the enhanced usage and production in China in recent years. In core-1, the highest concentration of PFASs was found in the top layer (1–2 cm). A decreasing trend with the sampling depth was found from top layer to the middle sediment segments (0–17 cm). However, at the deeper sediment segments (17–37 cm), except the slice with the sampling depth of 17 cm, the core showed a slightly increasing trend. The concentrations of PFASs in the upper layers in core-2 and core-3 had the higher concentrations than that in core-1, and the temporal trends of PFASs in cores-2 and 3 had slightly different trends from core-1. In core-2, concentration of PFASs decreased generally from top to the bottom, and the highest concentration was found in the 6–7 cm. In core-3, concentrations were also found to decrease from top to the bottom layers, and the highest concentration was found in the 9–10 cm. The increasing concentrations of PFASs in the sediment cores hinted the inputs of PFASs to the sampling areas are increasing.

Composition analysis indicated PFOS and PFOA were the predominant pollutants among the targeted compounds in the core samples. Different from the concentrations in surface sediments, PFBS were detected in more than 60% of the core samples. In core-1, PFOS, PFOA, PFNA and PFUnDA concentrations were significantly negatively related to depth, with increasing trends from the bottom to top layer; whereas no such trends were evident for PFBS, PFHxS, PFHpA, PFDA and PFDoDA. In core-2, PFHxS, PFOA, PFNA, PFDA and PFUnDA showed significantly negatively relationship with depth ($p < 0.05$) whereas in core-3, only PFOA and PFNA concentrations were significantly negatively related to depth.

The temporal trends of PFASs in sediment cores have been reported in the worldwide. Bao et al. found overall decreasing trend along depth in sediment cores from Daliao River system, Zhujiang River and the Huangpu River (Bao et al., 2009, 2010). Zushi et al. found that a gradual decrease for PFOS after the early 1990s in the sediment core of Tokyo Bay, Japan (Zushi et al., 2010), which was different from the results in our work. Ahrens et al. revealed that Σ PFASs concentrations in the sediment core samples from Tokyo Bay generally increased from bottom to the top but got lower close to the surface (Ahrens et al., 2009b). Myers et al. indicated that the

concentrations of PFOS in Niagara River suspended solids decreased during the period of 2001–2006 while that of PFOA showed an increasing trend, but PFOS deposition increased in Lake Ontario cores (Myers et al., 2012). Yeung et al. found that temporal fluxes of PFOS generally increased from 1950s to 2005 in Lake Ontario (Yeung et al., 2013). Related to different production and usage histories in different regions of the world might be responsible for the temporal variation.

Environmental releases of C8-chained PFASs are expected to decrease dramatically and concomitantly (Paul et al., 2008). Human exposure to these compounds has decreased, which has resulted in the decrease in the human blood or serum with half-lives 4.2–8.2 years (Glynn et al., 2012; Olsen et al., 2012). While in the environment especially in the remote area such as the Arctic, inflection point for the temporal trend of PFASs may be postponed due to the slow reductions in the current “reservoir” (such as in the ocean water, marine sediment, etc) and continuous long range transport of PFASs and their precursors to the remote areas and oceans (Nash et al., 2010). A survey on the source identification and emission estimation of PFOS in China indicated that the production in China increased rapidly from 2001 to 2006 and kept constant from 2007 to 2011 for some acceptable purpose even after PFOS and its related salt were listed into Stockholm Convention in 2009 (Xie et al., 2013). PFOS emission density in eastern areas is significantly higher than that in the western areas, especially along the coasts (Xie et al., 2013). Some evaluations on the PBT (Persistence, bio-accumulation, and toxicity) of PFOS alternative have been sponsored by the government to reduce the production of PFOS and its related product. However, a detailed inventory for the product, usage of PFOS and PFOS-based product in the Chinese market is still needed to better understand the overall emissions inventory scenario to the environment.

4. Conclusion

This study traced the spatial and temporal distribution patterns of PFASs in sediments from BS, YS and ECS. PFASs concentrations in the study region were moderate on a global perspective. Spatial distribution showed a general decreasing trend of PFASs from the coast areas to the open sea. Ocean current might be the dominant source of PFASs to the sediment and the most important factor influencing the spatial distributions of PFASs in the sediments was pH, followed by the longitude. The results help us gain insights into the long range transport of PFASs. The increasing trend of PFASs concentrations from the lower to the upper layers corresponds well

Fig. 5. Temporal trends of PFOS, PFOA and Σ_9 PFASs in the three sediment cores.

to the increasing production and usage in China in recent years, necessitating future studies on the impacts on the ecosystem and on human health.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2014.07.018>.

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