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Perfluoroalkyl substances and organochlorine pesticides in sediments from Huaihe watershed in China

Jing Meng^{1,2}, Tieyu Wang^{1,*}, Pei Wang^{1,2}, John P. Giesy³, Yonglong Lu¹

1. State Key Laboratory of Urban and Regional Ecology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. Email: sea-mengjing@163.com

2. University of Chinese Academy of Sciences, Beijing 100049, China

3. Department of Veterinary Biomedical Sciences and Toxicology Centre, University of Saskatchewan, Saskatoon, Saskatchewan, Canada

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ABSTRACT

Twelve perfluoroalkyl substances (PFASs) and nine organochlorine pesticides (OCPs) were quantified in surface sediments from the Huaihe River, China, along which there are intensive industrial and agricultural activities. Concentrations of PFASs ranged from 0.06 to 0.46 ng/g dry weight (dw), and concentrations of OCPs ranged from 1.48 to 32.65 ng/g dw. Compared with other areas in China, concentrations of PFASs were lesser than the national mean value, while concentrations of OCPs were moderate. Concentrations of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) ranged from n.d. (not detected) to 0.03 and n.d. to 0.10 ng/g dw, respectively. Among the three groups of OCPs, mean concentrations of hexachlorocyclohexane and its isomers (HCHs), dichlorodiphenyltrichloroethane and its metabolites (DDTs) and hexachlorobenzene (HCB) were 5.62 ± 4.35 , 2.43 ± 3.12 and 1.55 ± 4.17 ng/g dw, respectively. Concentrations of HCHs and DDTs decreased from upstream to downstream along the mainstream of the Huaihe River. When compared to sediment quality guidelines (SQGs), concentrations of HCHs, DDTs and HCB would pose adverse biological effects. In general, contamination by PFASs in the upstream of the Huaihe River was more severe than that in the downstream, which was mainly caused by interception from dams, locks and industrial emissions. And OCPs from tributaries, especially the Yinghe River and Wohe River, were higher than those from Huaihe mainstream, and primarily came from historical inputs.

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Introduction

Persistent organic pollutants (POPs) remain a major environmental issue due to their potential to bioaccumulation, persistence in the environment, and toxicity to wildlife and humans (Jaspers et al., 2013; Yang et al., 2013). Perfluoroalkyl substances (PFASs) and organochlorine pesticides (OCPs) are two classes of POPs with different applications and emission sources. PFASs are regarded as emerging contaminants and

mostly associated with industrial and urban areas (Boulanger et al., 2005). PFASs have been used in a wide range of applications: in industry as polymers, surfactants, lubricants, and pesticides, and in consumer products as textile coatings, nonstick coatings, stain repellent, food packaging, firefighting foams, and more (OECD, 2002). Accumulation of PFASs in the environment mainly comes from two sources, including releases from manufacture, applications and usage of related products, and formed as chemical impurities or by breakdown

* Corresponding author. E-mail: wangty@rcees.ac.cn (Tieyu Wang).

of precursors (Paul et al., 2009). Currently, due to the lack of appropriate alternative products, perfluorooctane sulfonate (PFOS) and related substances are still manufactured and used in China (Zhang et al., 2012).

OCPs received global attention soon after the publication of Silent Spring in 1962 (Abbott et al., 1965). From 1950s to 1970s, OCPs, such as HCHs and DDTs, accounted for approximately 80% of the total pesticides produced. It was estimated that the total historical usage of HCHs and DDTs in China were 4460 kt and 270 kt, respectively (Wei et al., 2007). Being an important agricultural region, Anhui Province has applied a large amount of OCPs even without any local manufacture of DDTs and HCHs (Ministry of Environment Protection of China, 2007).

The Huaihe River, located in central China, has a watershed area of 270,000 km² and serves 165 million residents. Textile, household appliances, steel, cement and fertilizer are the major industries distributed along the Huaihe River (Anhui Bureau of Statistics, 2010). Due to the lack of effective urban planning, rapid urbanization and industrialization have led to adverse consequences. Deliberate and accidental releases of domestic sewage and industrial effluents enter into the Huaihe River and cause serious pollution that has drawn attention from scientists and regulators (Wang et al., 2009a, 2009b; Feng et al., 2011, 2012; Fu et al., 2011). We presented the first investigation on spatial distribution and sources analysis of PFASs in soils around the Huaihe River (Meng et al., 2013). Sediments are usually regarded as an important sink for POPs, and also act as a secondary source to overlying water due to desorption (Bettinetti et al., 2003). Emerging POPs, such as PFASs in sediments are under intensive investigation, however, there were no studies on PFASs in sediments from the Huaihe River till now, and only one study has reported concentrations of PFASs in surface water from the Jiangsu reach of the Huaihe River (Yu et al., 2013). Although OCPs in sediments from the upstream and downstream of the Huaihe River have been reported (Huang et al., 2006; Sun et al., 2010), little information was available for OCPs from the Anhui reach. The objectives of this study were to determine the concentrations, distribution, and transportation of PFASs and OCPs in sediments along the Anhui reach of the Huaihe River, a heavily polluted section, to identify sources and potential risks, and thus to provide information and

scientific support for future management and protection of such heavily polluted watershed in China.

1. Materials and methods

1.1. Sample collection

A survey of the mainstream of the Huaihe River and its five main tributaries was conducted in the Anhui reach of the Huaihe River, which has a catchment of 66,900 km². Geographically from west to east, tributaries flowing into the Huaihe River are the Yinghe, Pihe, Xifeihe, Dongfeihe and Wohe Rivers. Eighteen sediment samples were collected from these rivers in October 2008 (Fig. 1). Surface sediments (top 1–10 cm) were collected using a grab sampler. Wet sediments were transported to the laboratory in polypropylene bottles, freeze-dried, sieved through a 2 mm mesh, and then stored in pre-cleaned glass jars at 4°C until further analysis.

1.2. Standards and reagents

Twelve PFASs (purity for each PFC > 98%), including perfluorobutanoic acid (C4, PFBA), perfluoropentanoic acid (C5, PFPeA), perfluorohexanoic acid (C6, PFHxA), perfluoroheptanoic acid (C7, PFHpA), perfluorooctanoic acid (C8, PFOA), perfluorononanoic acid (C9, PFNA), perfluorodecanoic acid (C10, PFDA), perfluoroundecanoic acid (C11, PFUDA), perfluorobutane sulfonate (C4, PFBS), perfluorohexane sulfonate (C6, PFHxS), perfluorooctane sulfonate (C8, PFOS), and perfluorodecane sulfonate (C10, PFDS) were obtained from Wellington Laboratories (Guelph, Canada). Standard solution, containing α , β , γ , δ -HCH, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDE, *p,p'*-DDD and HCB was purchased from National Research Center for Certified Reference Materials of China. HPLC grade methanol, tetrabutylammonium hydrogensulfate (TBAHS), methyl tert-butyl ether (MTBE), ammonium acetate, n-hexane and dichloromethane were obtained from J.T. Baker (Phillipsburg, USA). Analytical grade anhydrous sodium sulfate was obtained from Beijing Chemical Factory, China. 2,4,5,6-Tetrachloro-mxylene (TCMX) and solid phase extraction (SPE) cartridge for OCPs were purchased from Supelco (Bellefonte,

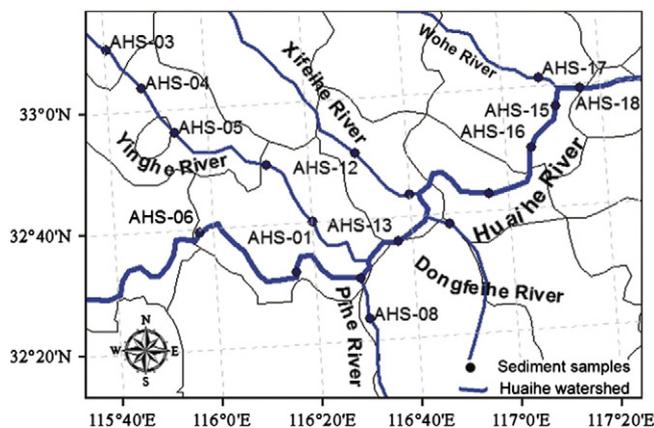


Fig. 1 – Sediment sampling area and sites in the Huaihe watershed, China.

Table 1 – Limit of detection (LOD) and matrix spike recovery (MSR) (mean ± SD) of perfluoroalkyl substances (PFASs) and organochlorine pesticides (OCPs).

	LOD (ng/g dw)	MSR (%)	Detection rate (%)
Perfluorobutanoic acid (C4, PFBA)	0.10	100 ± 5	7 ^a (38.9) ^b
Perfluoropentanoic acid (C5, PFPeA)	0.03	104 ± 3	0 (0)
Perfluorohexanoic acid (C6, PFHxA)	0.01	110 ± 3	7 (38.9)
Perfluoroheptanoic acid (C7, PFHpA)	0.02	96 ± 6	0 (0)
Perfluorooctanoic acid (C8, PFOA)	0.01	100 ± 11	14 (77.8)
Perfluorononanoic acid (C9, PFNA)	0.01	109 ± 2	11 (61.1)
Perfluorodecanoic acid (C10, PFDA)	0.01	103 ± 7	8 (44.4)
Perfluoroundecanoic acid (C11, PFUdA)	0.02	90 ± 4	10 (55.6)
Perfluorobutane sulfonate (C4, PFBS)	0.01	119 ± 4	18 (100)
Perfluorohexane sulfonate (C6, PFHxS)	0.01	114 ± 8	5 (27.8)
Perfluorooctane sulfonate (C8, PFOS)	0.01	117 ± 2	17 (94.4)
Perfluorodecane sulfonate (C10, PFDS)	0.02	86 ± 6	2 (11.1)
α-HCH	0.15	82 ± 7	5 (27.8)
β-HCH	0.20	81 ± 9	16 (88.9)
γ-HCH	0.05	84 ± 5	0 (0)
δ-HCH	0.05	90 ± 6	0 (0)
<i>p,p'</i> -DDE	0.10	93 ± 5	11 (61.1)
<i>p,p'</i> -DDD	0.20	87 ± 9	4 (22.2)
<i>o,p'</i> -DDT	0.10	90 ± 1	0 (0)
<i>p,p'</i> -DDT	0.10	92 ± 3	7 (38.9)
HCB	0.24	78 ± 6	5 (27.8)

^a Number of samples detected.
^b Occurrence.

USA). SPE cartridge for PFASs was purchased from Waters (Milford, USA).

1.3. Quantification of PFASs

PFASs were extracted based on a previously described method with slight modification (Naile et al., 2010). Generally, 2.5 g sediment was wetted with 2 mL Milli-Q water, and mixed with 1 mL 0.5 TBAHS and 2 mL of 25 mmol/L sodium acetate by vortexing. Subsequently, 5 mL MTBE was added, followed by shaking and centrifuging, and then the supernatant was collected. This process was repeated three times, and a final combined volume of 15 mL MTBE wash was obtained. The eluent was brought to dryness under a gentle stream of high purity nitrogen, and reconstituted in 1 mL methanol. The 1 mL eluent was transferred into a 50 mL PP tube and Milli-Q water was added to 50 mL, before passing through a SPE cartridge. The cartridge was preconditioned with 4 mL of 0.1% ammonia in methanol, 4 mL methanol and 4 mL Milli-Q water. 50 mL eluent was loaded into the cartridge, and then washed with 20 mL Milli-Q water and 4 mL 25 mmol/L sodium acetate. The eluent was discarded and the cartridge was allowed to run dry. Target analytes were eluted with 4 mL methanol, followed by 4 mL 0.1% ammonia in methanol. The eluent was reduced to 1 mL under a gentle stream of high purity nitrogen, then filtered through a 0.2 μm nylon filter, and transferred into a 1.5 mL PP auto-sampler vial fitted with PP cap.

All target analytes were analyzed by an Agilent 1290 high performance liquid chromatography system coupled with an Agilent 6460 triple tandem quadrupole mass spectrometer (HPLC-MS/MS) (Agilent Technologies, Palo Alto, USA) operated under negative electrospray ionization (ESI) mode. Analytes were separated on a C18 analytical column, with 2 mmol/L ammonium acetate as an ionization aid and 100% acetonitrile

as the mobile phase. Chromatograms were recorded by the use of multiple-reaction monitoring mode (MRM), and if possible at least two transition ions per-analyte were monitored. The optimal settings for collision energies and declustering potential were determined for the transitions of each analyte.

1.4. Quantification of OCPs

Extraction of OCPs was accomplished using a previously described method (Wang et al., 2009c). Briefly, 5.0 g sample was mixed with 1 g anhydrous sodium sulfate, and 1 mL 0.08 mg/L TCMX. By ultrasonic treatment and centrifugal separation, the mixture was extracted twice with 35 mL of hexane/dichloromethane (1:1, V/V). The combined supernatant was transferred to a K-D flask and was evaporated to approximately 2 mL, and further purified by passing through a SPE cartridge. The cartridge was loaded with 1 g silica gel and 1 g anhydrous sodium sulfate, and was activated with 10 mL hexane. Analytes were eluted with 20 mL of hexane/dichloromethane (7:3, V/V). Then eluent was concentrated to 1 mL under a gentle stream of great-purity nitrogen for GC analysis.

OCPs were separated, identified and quantified using an Agilent 6890 gas chromatography (GC), which was equipped with a ⁶³Ni electron capture detector (μECD) (Agilent Technologies, Palo Alto, USA). Separation of target analytes was accomplished by a silica capillary column, operated in splitless injection mode and using ultra-pure nitrogen as the carrier gas and make-up gas. The injector and detector temperatures were 220°C and 300°C, respectively. The oven temperature was initially set at 100°C with a 2 min hold, ramped at 10°C/min to 160°C with a 2 min hold, 4°C/min to 230°C with a 5 min hold, 10°C/min to 270°C with a 2 min hold. The OCPs were identified by matching retention time to the standards and were quantified using peak area.

1.5. Quality control and quality assurance

Procedural blanks were prepared for every six samples to check potential contamination. All blanks were less than the limit of detection (LOD), where the LOD was defined as three times of signal-to-noise ratio (S/N). Duplicate samples and matrix spiked with standard solution were analyzed for every three sediment samples. Relative standard deviation of duplicate samples was less than 20%, which were acceptable. Matrix spike recoveries (MSR) of PFASs ranged from 86% ± 6% to 119% ± 4%, and recoveries of OCPs ranged between 78% ± 6% and 93% ± 5%, which were acceptable. The LODs of PFASs and OCPs were 0.01–0.10 ng/g dry weight (dw) and 0.05–0.24 ng/g dw, respectively (Table 1).

2. Results and discussion

2.1. Occurrence of PFASs and OCPs in sediments

Among the twelve individual PFASs investigated, ten PFASs were detected. PFASs were detected in all sediment samples. Total concentrations of PFASs ranged from 0.06 to 0.46 ng/g dw with a mean of 0.19 ± 0.12 ng/g dw (Table 2). Concentrations of perfluorocarboxylates (PFCAs) ranged from 0.01 to 0.40 ng/g dw and concentrations of perfluorosulfonates (PFSAs) were between 0.02 and 0.18 ng/g dw. Among the PFCAs, PFBA was predominant in sediments, with concentration ranging from n.d. to 0.31 ng/g dw (a mean of 0.07 ± 0.10 ng/g dw), while concentration of PFOA was between n.d. and 0.03 ng/g dw. Among the PFSAs, concentration of PFOS was the highest and ranged from n.d. to 0.10 ng/g dw, with a mean of 0.04 ± 0.02 ng/g dw. Concentration of PFOS was higher than that of PFOA, which was consistent with results of previous studies, because PFOS tends

to absorb more to sediment than PFOA (Senthilkumar et al., 2007; Becker et al., 2008; Wang et al., 2011).

Among the four isomers of HCH, only α-HCH and β-HCH were detected, while among the four DDT congeners, *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT were detected (Table 1). Concentrations of OCPs ranged from 1.48 to 32.65 ng/g dw with a mean of 9.60 ± 9.06 ng/g dw. Mean concentrations of HCHs, DDTs and HCB were 5.62 ± 4.35 ng/g dw, 2.43 ± 3.12 ng/g dw and 1.55 ± 4.17 ng/g dw, respectively (Table 2). When compared with other six major rivers in China, concentrations of OCPs in sediments of the Huaihe River were generally moderate and lower than those in sediments from the Daliao (Wang et al., 2007), Haihe (Yang et al., 2005), Yangtze (Liu et al., 2008) and Pearl Rivers (Fung et al., 2005), but higher than concentrations in sediments from the Songhua (He et al., 2008) and Yellow Rivers (Wang et al., 2010). Considering that agriculture is the primary source of OCPs, variation in concentrations in sediments among these rivers is mainly a result of regional differences in crops (Li et al., 2001). Concentrations of PFASs were almost two orders of magnitude lower than those of OCPs. This showed that although OCPs had been banned for about three decades in China, their residues in sediments were still higher than emerging pollutants, and might induce secondary contamination to rivers through the desorption action.

2.2. Spatial distribution of PFASs and OCPs in sediments

Concentrations of PFASs in sediment from the Huaihe River didn't show significant differences (Fig. 2a). The highest concentration of PFASs occurred at site AHS-17 (0.46 ng/g dw) in the Wohe River and PFBA accounted for 67.7% with a concentration of 0.31 ng/g dw. There is one industrial park with businesses that manufacture and/or process packaging, textile, rubber and fluorine materials. These industries possibly had direct relationship with the higher emissions of PFASs in the tributary. Concentration of PFASs at site AHS-06 in the mainstream of the Huaihe River ranked second with a concentration of 0.38 ng/g dw followed by the concentration of PFASs at site AHS-07 (0.34 ng/g dw) and AHS-01 (0.32 ng/g dw). There is a drainage outlet in the upstream of site AHS-06, which directly caused the high concentration of PFASs. The Linhuaigang Dam is located near AHS-07, which intercepts the Huaihe River. PFASs from the upstream were adsorbed by sediment and led to great residues at site AHS-07. Two chemical plants nearby the AHS-01 also contributed significantly to the great concentration of PFASs.

Mean concentrations of OCPs in sediments from the mainstream of the Huaihe River and its five tributaries were ranked as follows: Dongfeihe (32.65 ng/g dw), Yinghe (14.35 ± 9.56 ng/g dw), Wohe (13.19 ng/g dw), Huaihe (5.33 ± 4.45 ng/g dw), Pihe (4.30 ng/g dw) and Xifeihe Rivers (4.09 ± 0.76 ng/g dw) (Fig. 2b). AHS-02, AHS-03, and AHS-04 from the Yinghe River, AHS-10 from the Dongfeihe River, AHS-14 from the mainstream of the Huaihe River and AHS-17 from the Wohe River had higher concentrations of OCPs than those from other 12 sampling sites. Sites where sediments contained higher concentrations of OCPs had similar characteristics. Generally, β-HCH contributed the highest proportion for OCPs at site AHS-02, AHS-04, AHS-10 and AHS-17 (54.35%–82.45%). OCPs at AHS-14 were mostly comprised of *p,p'*-DDT, which contributed

Table 2 – Concentrations of perfluoroalkyl substances (PFASs) and organochlorine pesticides (OCPs) (unit: ng/g dw).

	Minimum	Maximum	Median	Mean	SD
PFBA	n.d.	0.31	n.d.	0.07	0.10
PFHxA	n.d.	0.02	n.d.	0.00	0.01
PFOA	n.d.	0.03	0.01	0.01	0.01
PFNA	n.d.	0.02	0.01	0.01	0.01
PFDA	n.d.	0.04	n.d.	0.01	0.01
PFUdA	n.d.	0.04	0.02	0.01	0.01
PFCAs	0.01	0.40	0.08	0.12	0.10
PFBS	0.01	0.05	0.01	0.02	0.01
PFHxS	n.d.	0.03	n.d.	0.00	0.01
PFOS	n.d.	0.10	0.04	0.04	0.02
PFDS	n.d.	0.12	n.d.	0.01	0.03
PFSAs	0.02	0.18	0.06	0.07	0.04
PFASs	0.06	0.46	0.15	0.19	0.12
α-HCH	n.d.	7.09	n.d.	0.68	1.72
β-HCH	n.d.	20.42	3.72	4.94	5.16
HCHs	1.19	22.73	3.90	5.62	4.35
<i>p,p'</i> -DDE	n.d.	2.08	0.64	0.64	0.63
<i>p,p'</i> -DDD	n.d.	3.70	n.d.	0.42	0.96
<i>p,p'</i> -DDT	n.d.	10.37	n.d.	1.37	2.57
DDTs	n.d.	10.37	1.09	2.43	3.12
HCB	n.d.	16.85	n.d.	1.55	4.17
OCPs	1.48	32.65	5.11	9.60	9.06

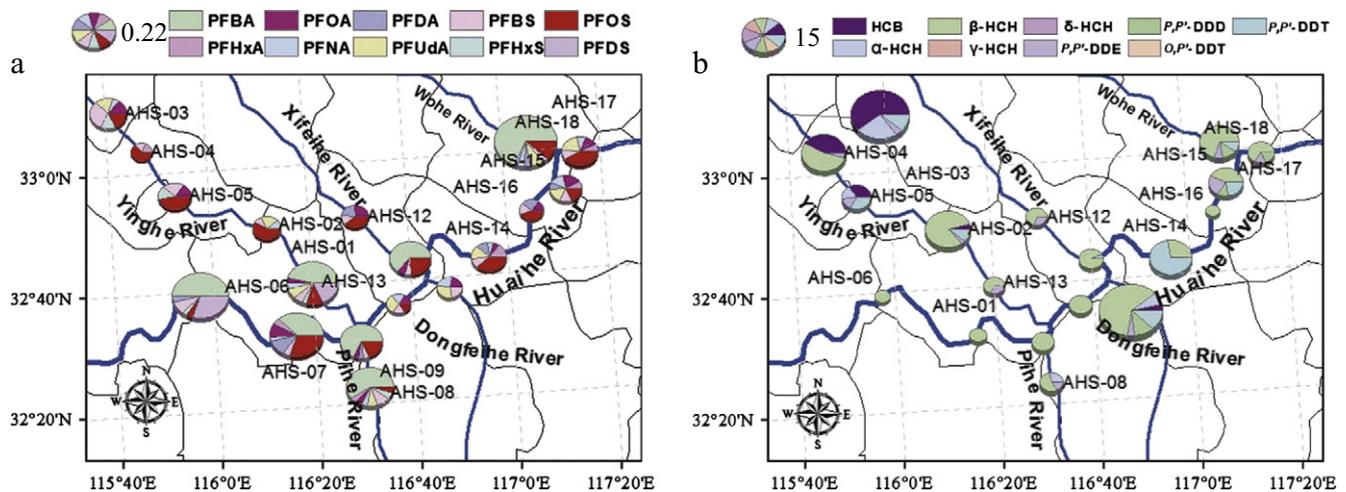


Fig. 2 – Spatial distribution and contribution of individual perfluoroalkyl substances (PFASs) (a) and organochlorine pesticides (OCPs) (b) in sediments. The number of 0.22 or 15 means the concentration of PFASs or OCPs according to the pie size.

72.11% to total OCPs. Sediment at site AHS-03 had a higher concentration of HCB (16.85 ng/g dw), and HCB comprised 60.00% of total OCPs, followed by α -HCH, which accounted for 25.24% of total OCPs. Historically, there was a pesticide factory at site AHS-03, which possibly discharged a large volume of wastes into the Huaihe River. The higher concentrations of OCPs in the environment were associated with the greater incidences of cancers in local residents, which mainly involved cancers of the esophagus and stomach (Liu, 2010). It is known that OCPs are associated with carcinogenic, teratogenic and mutagenic effects, and could induce different kinds of diseases (Safe, 1995; Willett et al., 1998).

2.3. Composition and potential source of PFASs and OCPs

Relative percentage of individual PFASs in sediments from the mainstream of the Huaihe River were different from those in sediments from the five tributaries (Fig. 2a). PFBS and PFOS were the predominant PFASs and accounted for 63.04% at sites AHS-02, AHS-03, AHS-04 and AHS-05 from the Yinghe River. PFBA was dominant at sites AHS-06, AHS-07, AHS-08 and AHS-09 from the upstream reach of the Huaihe and Pihe Rivers. PFOS was predominant at sites AHS-13, AHS-14, AHS-15, AHS-16 and AHS-18 from the downstream reach of the Huaihe River. PFASs in aquatic systems can arise from point sources, such as sewage outfalls, and non-point sources, such as dry and wet deposition or runoff inputs (Furl et al., 2011). Among the PFCAs analyzed, PFBA was predominant, with concentration ranging from n.d. to 0.31 ng/g dw. The predominance of PFBA was similar to the situation in Tokyo Bay, Japan, where PFBA contributed 52% to total PFASs (Ahrens et al., 2010). The higher concentration of PFBA indicated the shift of production and usage from C8 PFASs to shorter-carbon chain PFASs. The fact also revealed the impact of point sources (Thompson et al., 2011). As for the shorter chain PFCAs (C4–C7, apart from PFBA), detection rates and concentrations of PFPeA, PFHxA and PFHpA were less than those of C8 PFC. Among the longer chain PFCAs (C8–C11), detection rates of PFOA, PFNA, PFDA and PFUdA were relatively higher. This general trend is

consistent with the result of a previous study (Myers et al., 2012). Among the PFASs analyzed, PFOS was predominant with a mean concentration of 0.04 ± 0.02 ng/g dw. According to recent reports on PFOS sources in Anhui Province, metal plating and fire-fighting were the main industries to release PFOS (Zhang et al., 2012; Xie et al., 2013). No related factories were found located near the sampling areas in this study. Non-point sources, rather than discharges from individual factories, probably contributed to the relatively even distribution of PFOS. Although the detected concentration of PFBS were lesser, ranging from 0.01 to 0.05 ng/g dw, but detection rate of PFBS reached up to 100%. The prevalent detection of PFBS was also related to production and usage of alternatives to PFOS (Carter and Farrell, 2010).

Differences in relative concentrations of HCH isomers or DDT congeners can be used to determine possible sources. Typically, the technical mixture of HCH consists of 60%–70% α -HCH, 5%–12% β -HCH, 10%–15% γ -HCH and 6%–10% δ -HCH, respectively (Buser and Muller, 1995). In this study, γ -HCH and δ -HCH were not detected and the detection rate of α -HCH was only 27.8%. The highest detection rate (88.9%) and mean concentration (4.94 ± 5.16 ng/g dw) of β -HCH was observed, and β -HCH contributed 87.90% to total HCHs, with a mean concentration of 5.62 ± 4.35 ng/g dw (Table 2). Because of lower water solubility and vapor pressure comparing with α -HCH and γ -HCH, β -HCH is the most stable and resistant to microbial degradation. And α -HCH and γ -HCH could be converted to β -HCH. Generally, the predominance of β -HCH indicates no recent emissions of technical HCH. In contrast, the dominance of more volatile α -HCH and γ -HCH indicates long-range transport (Willett et al., 1998). Therefore, HCHs in sediments from the Huaihe River mainly resulted from emissions and conversion of local technical HCHs.

Technical DDT generally contains 5% p,p' -DDE, <5% p,p' -DDD, 15% o,p' -DDT and 75% p,p' -DDT (Pandit et al., 2006). In this study, apart from o,p' -DDT, which was not detected, p,p' -DDE, p,p' -DDD and p,p' -DDT accounted for 26.34%, 17.28% and 56.38% of total DDTs, respectively (Table 2). DDT can be biodegraded to DDE under aerobic conditions and to DDD under anaerobic conditions

(Bossi et al., 1992). This information can be used to determine relative contribution of technical DDT. Based on the results of previous studies, a ratio of DDT/(DDE + DDD) < 1 indicates long-term weathering (Hitch and Day, 1992). In this study, a ratio of DDT/(DDE + DDD) > 1 was found at sites AHS-02, AHS-03, AHS-05 and AHS-14. The predominant DDT at these sites was *p,p'*-DDT, indicating that there were recent inputs of technical DDT. Conversely, DDTs at other sites were the result of historical emissions and long-term degradation.

The detection rate of HCB was only 27.8% and HCB accounted for 16.15% of total OCPs (Table 2). Except for site AHS-10, the other four sites are located in the Yinghe River. Concentration of HCB showed a decreasing trend from the upstream to downstream, which indicated the dilution of HCB by discharge of the Yinghe River. HCB is primarily generated by incomplete combustion, old dumpsites or chemical processes, such as the manufacture of chlorinated solvents, chlorinated aromatics and pesticides (Barber et al., 2005). There was a pesticide plant close to site AHS-03, where the concentration of HCB was the highest. Although the plant was closed several years ago, past-emitted HCB was the likely source at this site. In addition, there is heavy ship traffic along the Huaihe River, including transportation vessels, sand carriers and fishing boats. These ships stir and change the flow of river water, which consequently affect adsorption of contaminants by sediment. Therefore, OCPs in sediments partly came from other areas carried by ships and this activity disturbed the normal flow from upstream to downstream.

2.4. Adverse effects of PFASs and OCPs in the Huaihe Watershed

Predicted no-effect concentration (PNEC) was used as a threshold value for protecting wildlife and as a parameter for the ecological risk assessment of pollutants (Beach et al., 2006; Giesy et al., 2010). In this study, PNECs of PFOA and PFOS in sediments were suggested based on the equilibrium partitioning method, using the PNECs in freshwater and distribution coefficient (K_d) (Zushi

et al., 2012). The PNEC of PFOS in fresh water is 25 µg/L (UK Environment Agency, 2004), and PNEC of PFOA is 1250 µg/L (Colombo et al., 2008).

$$K_d = \frac{C_s}{C_w} \tag{1}$$

where, C_s (ng/g dw) and C_w (ng/L) are the concentrations of PFASs in sediment and water samples, respectively.

Due to the lack of concentrations of PFASs in water from the Anhui reach of the Huaihe River, the C_w from the Jiangsu reach were used as estimated value to calculate the K_d . The mean C_w for PFOS and PFOA were 4.7 and 18 ng/L, respectively (Yu et al., 2013). Therefore, the mean K_d values of PFOS and PFOA were 8.51×10^{-3} and 5.56×10^{-4} L/g, and the calculated PNECs of PFOS and PFOA for sediment were 0.21 and 0.70 µg/g dw, respectively. Concentrations of PFOS in the Huaihe River ranged from n.d. to 0.10 ng/g dw, so PFOS didn't pose potential risks to benthic invertebrates. Concentrations of PFOA were between n.d. and 0.03 ng/g dw and also didn't exceed the PNEC based on equilibrium partitioning. Although the concentration of PFBA was the highest in the Huaihe River, studies on toxicity of PFBA were scarce and no PNEC value was available. Considerable uncertainty was associated with the PNEC values derived via the partitioning method (Zhao et al., 2013).

Environmental standards for OCPs in freshwater sediment have not been set in China. Therefore, potential environmental risk of OCPs was evaluated by comparing measured values with published sediment quality guidelines (SQGs). The threshold effect level (TEL) corresponds to the concentration below which adverse ecological effects are expected to occur only rarely, and the probable effect level (PEL) defines the concentration above which adverse effects are expected to occur frequently (MacDonald et al., 2000). Based on the SQGs established by Canada (CCME, 2002), the TEL and PEL of *p,p'*-DDE, *p,p'*-DDD, and *o,p'*-DDT + *p,p'*-DDT were applied. No *o,p'*-DDT were detected in sediments. Concentrations of *p,p'*-DDE in sediment from AHS-14 and *p,p'*-DDD in sediment from AHS-10 exceeded the TEL, while concentrations of *p,p'*-DDT from the other five sites (AHS-02, AHS-03, AHS-05, AHS-10 and AHS-15) exceeded the TEL and one (AHS-14) exceeded the PEL (Fig. 3). These results revealed that the risk of *p,p'*-DDT was more serious than that of other two DDT congeners. By comparison with the SQGs published by MacDonald et al. (1996), it was noted that the concentrations of DDTs at five sites (AHS-03, AHS-10, AHS-14, AHS-15, AHS-17) all exceeded the TEL. Based on threshold effect concentrations (TEC) and the probable effect concentrations (PEC) (Gomez-Gutierrez et al., 2007), the evaluated risk of DDT congeners was similar to the result derived by comparison with the TEL and PEL. The five detected concentrations of HCB were between the TEC and the PEC, which indicated some hazard and need more detailed research. The least effect level (LEL) was cited to evaluate risk of HCHs. The LEL indicates the concentration of sediment contamination that can be tolerated by the majority of benthic organisms. The LELs for α-HCH and β-HCH are 6 and 5 ng/g dw, respectively (Ontario Ministry of Environment and Energy, 1993). Therefore, α-HCH from AHS-03 and β-HCH from AHS-02, 04, 10, 17 exceeding corresponding LELs would pose certain risk to benthic organisms.

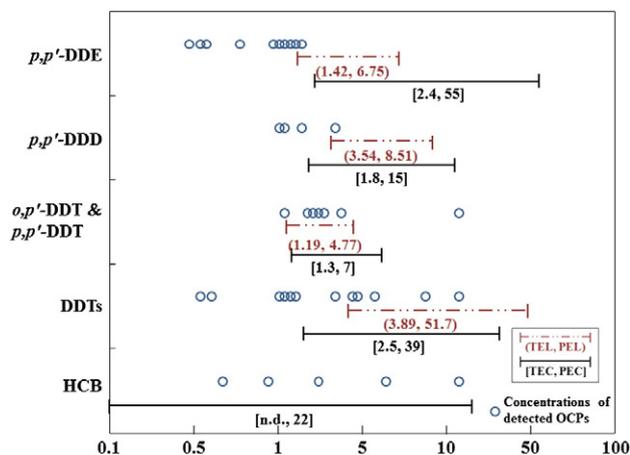


Fig. 3 – Comparison of organochlorine pesticides (OCPs) in sediments from the Huaihe River to various sediment quality guidelines. TEL (threshold effect level) and PEL (probable effect level); TEC (threshold effect concentration) and PEC (probable effect concentration).

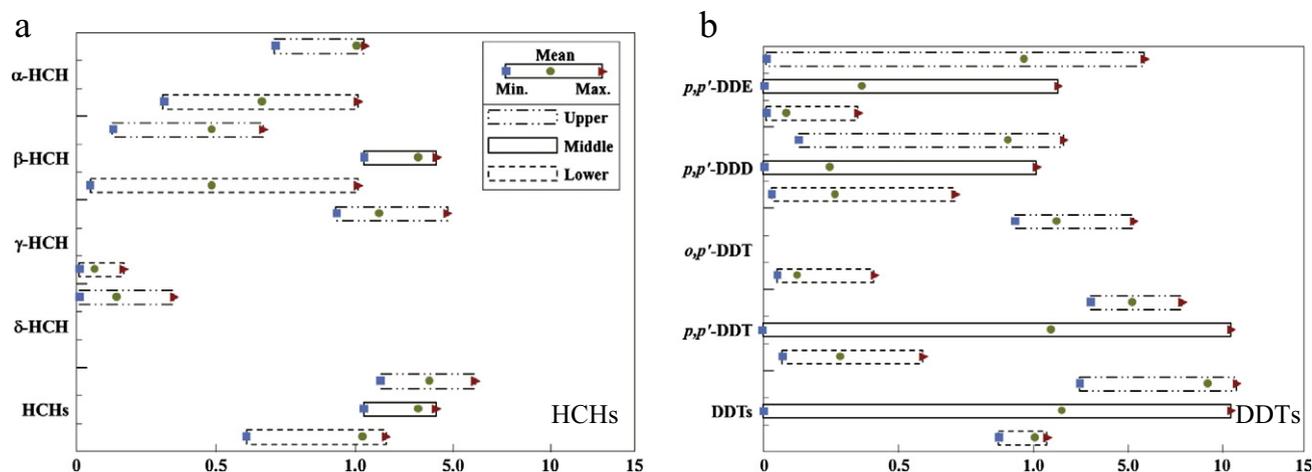


Fig. 4 – Concentrations of perfluoroalkyl substances (PFASs) (a) and organochlorine pesticides (OCPs) (b) (ng/g dw) in sediments from the mainstream of the Huaihe River.

2.5. Comparison with previous studies of Huaihe Watershed

There were no reported PFASs in sediments from the Huaihe River. Concentrations of PFOA and PFOS in sediments from Anhui reach of the Huaihe River were the least, when comparing with other studied watersheds in China, including the rivers of Pearl (PFOA, 0.09–0.29 ng/g dw; PFOS, n.d. –3.1 ng/g dw), Huangpu (PFOA, 0.2–0.64 ng/g dw; PFOS, n.d. –0.46 ng/g dw), Liao (PFOA, n.d. –27.9 ng/g dw; PFOS, n.d. –6.6 ng/g dw), and Haihe (PFOA, 0.9–3.7 ng/g dw; PFOS, 1.8–7.3 ng/g dw), and the Yangtze Estuary (PFOS, 72.9–536.7 ng/g dw), north Bohai Sea (PFOA, n.d. –0.54 ng/g dw; PFOS, n.d. –1.97 ng/g dw) (Bao et al., 2010; Pan and You, 2010; Li et al., 2011; Wang et al., 2011; Yang et al., 2011). Concentrations of PFOA and PFOS were also lesser than those from other countries, including several rivers in Japan (PFOA, n.d. –3.9 ng/g dw; PFOS, n.d. –11 ng/g dw), west coast of Korea (PFOA and PFOS, <2.0 ng/g dw), San Francisco Bay, USA (PFOA, n.d. –0.63 ng/g dw; PFOS, n.d. –3.07 ng/g dw) (Higgins et al., 2005; Senthilkumar et al., 2007; Naile et al., 2010). Median concentrations of PFOA and PFOS that can be extracted from limited literature were 0.30 and 0.54 ng/g dw, respectively (Zareitalabad et al., 2013). Although local leading industries could be the source of PFASs, the industrial proportion and scales were relatively small. Therefore, contamination by PFOA and PFOS from the Anhui reach of the Huaihe River was less severe than that in most studied watersheds.

When compared with concentrations of OCPs in sediments from the Henan reach and Jiangsu reach of Huaihe mainstream, concentrations in the Henan reach were the highest, with 4.53 ng/g dw for HCHs and 11.07 ng/g dw for DDTs (Sun et al., 2010), followed by those from the Anhui reach, while those from the Jiangsu reach were the least, with concentrations of 1.31 ng/g dw for HCHs and 0.99 ng/g dw for DDTs (Huang et al., 2006). Concentrations of HCHs and DDTs in sediments generally showed a decreasing trend from upstream to downstream (Fig. 4).

Among HCH isomers, although only β -HCH was detected in sediments from the Anhui reach, concentration of β -HCH was the highest (Fig. 4a). Except for β -HCH, contamination by α -HCH and γ -HCH from the Henan and Jiangsu reach was also

serious, especially γ -HCH from the Henan reach. These results indicated massive historical use of technical HCH, slow degradation or possible new inputs. In fact, the usage of technical HCH in Jiangsu Province reached up to 500 kt, which ranked first among all the provinces of China; and the usage in Henan was about 350 kt, which ranked third (Li et al., 2001). The actual residues from these three sections were not consistent with their historical usage, which was caused mainly by different rates of degradation in the environment. In addition, concentrations of DDTs were higher than those of HCHs in each section of the Huaihe River. Among four DDT congeners, p,p' -DDT was predominant, followed by p,p' -DDE (Fig. 4b). The HCHs and DDTs from the agricultural region in the upstream could transport along the Huaihe River and deposit in sediments from the downstream. Therefore, apart from local emission, residues from upstream were also an important source and possibly posed adverse effects on sediments from the downstream. In general, sediments from the Henan, Anhui and Jiangsu reaches exhibited similar contamination by HCHs and DDTs in terms of both concentration and composition.

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REFERENCES

- Abbott, D.C., Harrison, R.B., Tatton, J.O., Thomson, J., 1965. Organochlorine pesticides in the atmosphere environment. *Nature* 208, 1317–1318.
- Ahrens, L., Taniyasu, S., Yeung, L.W.Y., Yamashita, N., Lam, P.K.S., Ebinghaus, R., 2010. Distribution of polyfluoroalkyl compounds in water, suspended particulate matter and sediment from Tokyo Bay, Japan. *Chemosphere* 79 (3), 266–272.

- Anhui Bureau of Statistics, 2010. *Anhui Statistical Yearbook*, (Anhui, China).
- Bao, J., Liu, W., Liu, L., Jin, Y.H., Ran, X.R., Zhang, Z.X., 2010. Perfluorinated compounds in urban river sediments from Guangzhou and Shanghai of China. *Chemosphere* 80 (2), 123–130.
- Barber, J.L., Sweetman, A.J., van Wijk, D., Jones, K.C., 2005. Hexachlorobenzene in the global environment: emissions, levels, distribution, trends and processes. *Sci. Total Environ.* 349 (1–3), 1–44.
- Beach, S.A., Newsted, J.L., Coody, K., Giesy, J.P., 2006. Ecotoxicological evaluation of perfluorooctanesulfonate (PFOS). *Rev. Environ. Contam. Toxicol.* 186, 133–174.
- Becker, A.M., Gerstmann, S., Frank, H., 2008. Perfluorooctanoic acid and perfluorooctane sulfonate in the sediment of the Roter Main River, Bayreuth, Germany. *Environ. Pollut.* 156 (3), 818–820.
- Bettinetti, R., Giarei, C., Provini, A., 2003. Chemical analysis and sediment toxicity bioassays to assess the contamination of the River Lambro (Northern Italy). *Arch. Environ. Contam. Toxicol.* 45 (1), 72–78.
- Bossi, R., Larsen, B., Premazzi, G., 1992. Polychlorinated biphenyl congeners and other chlorinated hydrocarbons in bottom sediment cores of Lake Garda (Italy). *Sci. Total Environ.* 121, 77–93.
- Boulanger, B., Vargo, J.D., Schnoor, J.L., Hornbuckle, K.C., 2005. Evaluation of perfluorooctane surfactants in a wastewater treatment system and in a commercial surface protection product. *Environ. Sci. Technol.* 39 (15), 5524–5530.
- Buser, H.R., Muller, M.D., 1995. Isomer and enantioselective degradation of hexachlorocyclohexane isomers in sewage-sludge under anaerobic conditions. *Environ. Sci. Technol.* 29 (3), 664–672.
- Carter, K.E., Farrell, J., 2010. Removal of perfluorooctane and perfluorobutane sulfonate from water via carbon adsorption and ion exchange. *Sep. Sci. Technol.* 45 (6), 762–767.
- CCME (Canadian Council of Ministers of the Environment), 2002. Canadian sediment quality guidelines for the protection of aquatic life. <http://st-ts.ccme.ca/?chems=all&chapters=3&pdf=1>.
- Colombo, I., de Wolf, W., Thompson, R.S., Farrar, D.G., Hoke, R.A., L'Haridon, J., 2008. Acute and chronic aquatic toxicity of ammonium perfluorooctanoate (APFO) to freshwater organisms. *Ecotoxicol. Environ. Saf.* 71 (3), 749–756.
- Feng, J.L., Zhai, M.X., Liu, Q., Sun, J.H., Guo, J.J., 2011. Residues of organochlorine pesticides (OCPs) in upper reach of the Huaihe River, East China. *Ecotoxicol. Environ. Saf.* 74 (8), 2252–2259.
- Feng, J.L., Zhai, M.X., Sun, J.H., Liu, Q., 2012. Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in sediment from the upper reach of Huaihe River, East China. *Environ. Sci. Pollut. Res.* 19 (4), 1097–1106.
- Fu, J., Ding, Y.H., Li, L., Sheng, S., Wen, T., Yu, L.J., et al., 2011. Polycyclic aromatic hydrocarbons and ecotoxicological characterization of sediments from the Huaihe River, China. *J. Environ. Monit.* 13 (3), 597–604.
- Fung, C.N., Zheng, G.J., Connell, D.W., Zhang, X., Wong, H.L., Giesy, J.P., et al., 2005. Risks posed by trace organic contaminants in coastal sediments in the Pearl River Delta, China. *Mar. Pollut. Bull.* 50 (10), 1036–1049.
- Furl, C.V., Meredith, C.A., Strynar, M.J., Nakayama, S.F., 2011. Relative importance of wastewater treatment plants and non-point sources of perfluorinated compounds to Washington State rivers. *Sci. Total Environ.* 409 (15), 2902–2907.
- Giesy, J.P., Naile, J., Yi, W., Khim, J.S., Jones, P.D., Newsted, J.L., 2010. Aquatic toxicology of perfluorinated chemicals. *Rev. Environ. Contam. Toxicol.* 202, 1–52.
- Gomez-Gutierrez, A., Garnacho, E., Bayona, J.M., Albaiges, J., 2007. Screening ecological risk assessment of persistent organic pollutants in Mediterranean Sea sediments. *Environ. Int.* 33 (7), 867–876.
- He, M., Wang, H., Lin, C., Quan, X., Guo, W., Yang, Z., 2008. Distribution of persistent organochlorine residues in sediments from the Songhuajiang River, northeast China. *Environ. Technol.* 29 (3), 303–314.
- Higgins, C.P., Field, J.A., Criddle, C.S., Luthy, R.G., 2005. Quantitative determination of perfluorochemicals in sediments and domestic sludge. *Environ. Sci. Technol.* 39 (11), 3946–3956.
- Hitch, R.K., Day, H.R., 1992. Unusual persistence of DDT in some western USA soils. *Bull. Environ. Contam. Toxicol.* 48 (2), 259–264.
- Huang, H., Ou, W.H., Wang, L.S., 2006. Semivolatile organic compounds, organochlorine pesticides and heavy metals in sediments and risk assessment in Huaihe River of China. *J. Environ. Sci.* 18 (2), 236–241.
- Jaspers, V.L.B., Sonne, C., Soler-Rodriguez, F., Boertmann, D., Dietz, R., Eens, M., et al., 2013. Persistent organic pollutants and methoxylated polybrominated diphenyl ethers in different tissues of white-tailed eagles (*Haliaeetus albicilla*) from West Greenland. *Environ. Pollut.* 175, 137–146.
- Li, Y.F., Cai, D.J., Shan, Z.J., Zhu, Z.L., 2001. Gridded usage inventories of technical hexachlorocyclohexane and lindane for china with 1/6° latitude by 1/4° longitude resolution. *Arch. Environ. Contam. Toxicol.* 41 (3), 261–266.
- Li, F.S., Sun, H.W., Hao, Z.N., He, N., Zhao, L.J., Zhang, T., et al., 2011. Perfluorinated compounds in Haihe River and Dagou Drainage Canal in Tianjin, China. *Chemosphere* 84 (2), 265–271.
- Liu, L., 2010. Made in China: cancer villages. *Environment* 52 (2), 8–21.
- Liu, M., Cheng, S.B., Ou, D.N., Yang, Y., Liu, H.L., Hou, L.J., et al., 2008. Organochlorine pesticides in surface sediments and suspended particulate matters from the Yangtze estuary, China. *Environ. Pollut.* 156 (1), 168–173.
- MacDonald, D.D., Carr, R.S., Calder, F.D., Long, E.R., Ingersoll, C.G., 1996. Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology* 5 (4), 253–278.
- MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch. Environ. Contam. Toxicol.* 39 (1), 20–31.
- Meng, J., Wang, T.Y., Wang, P., Giesy, J.P., Lu, Y.L., 2013. Perfluorinated compounds and organochlorine pesticides in soils around Huaihe River: a heavily contaminated watershed in Central China. *Environ. Sci. Pollut. Res.* 20 (6), 3965–3974.
- Ministry of Environment Protection of China, 2007. National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants. http://www.pops.int/documents/implementation/nips/submissions/China_NIP_En.pdf.
- Myers, A.L., Crozier, P.W., Helm, P.A., Brimacombe, C., Furdui, V.I., Reiner, E.J., et al., 2012. Fate, distribution, and contrasting temporal trends of perfluoroalkyl substances (PFASs) in Lake Ontario, Canada. *Environ. Int.* 44, 92–99.
- Naile, J.E., Khim, J.S., Wang, T.Y., Chen, C.L., Luo, W., Kwon, B.O., et al., 2010. Perfluorinated compounds in water, sediment, soil and biota from estuarine and coastal areas of Korea. *Environ. Pollut.* 158 (5), 1237–1244.
- OECD, 2002. Hazard Assessment of Perfluorooctane Sulfonate (PFOS) and its Salts. ENV/JM/RD(2002) 17/FINAL .
- Ontario Ministry of Environment and Energy, 1993. Guidelines for the protection and management of aquatic sediment quality in Ontario. http://www.itrcweb.org/contseds-bioavailability/References/guide_aquatic_sed93.pdf.
- Pan, G., You, C., 2010. Sediment-water distribution of perfluorooctane sulfonate (PFOS) in Yangtze River Estuary. *Environ. Pollut.* 158 (5), 1363–1367.
- Pandit, G.G., Sahu, S.K., Sharma, S., Puranik, V., 2006. Distribution and fate of persistent organochlorine pesticides in coastal marine environment of Mumbai. *Environ. Int.* 32 (2), 240–243.

- 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 (2), 386–392.
- Safe, S.H., 1995. Environmental and dietary estrogens and human health—is there a problem? *Environ. Health Perspect.* 103 (4), 346–351.
- Senthilkumar, K., Ohi, E., Sajwan, K., Takasuga, T., Kannan, K., 2007. Perfluorinated compounds in river water, river sediment, market fish, and wildlife samples from Japan. *Bull. Environ. Contam. Toxicol.* 79 (4), 427–431.
- Sun, J.H., Feng, J.L., Liu, Q., Li, Q.L., 2010. Distribution and sources of organochlorine pesticides (OCPs) in sediments from upper reach of Huaihe River, East China. *J. Hazard. Mater.* 184 (1–3), 141–146.
- Thompson, J., Roach, A., Eaglesham, G., Bartkow, M.E., Edge, K., Mueller, J.F., 2011. Perfluorinated alkyl acids in water, sediment and wildlife from Sydney Harbour and surroundings. *Mar. Pollut. Bull.* 62 (12), 2869–2875.
- UK Environment Agency, 2004. Environmental risk evaluation report: perfluorooctanesulphonate. http://www.pops.int/documents/meetings/poprc/submissions/Comments_2006/sia/pfos.uk.risk.eval.report.2004.pdf.
- Wang, H.Z., He, M.C., Lin, C., Quan, X.C., Guo, W., Yang, Z.F., 2007. Monitoring and assessment of persistent organochlorine residues in sediments from the Daliaohe river watershed, Northeast of China. *Environ. Monit. Assess.* 133 (1–3), 231–242.
- Wang, B., Yu, G., Huang, J., Yu, Y.J., Hu, H.Y., Wang, L.S., 2009a. Tiered aquatic ecological risk assessment of organochlorine pesticides and their mixture in Jiangsu reach of Huaihe River, China. *Environ. Monit. Assess.* 157 (1–4), 29–42.
- Wang, B., Yu, G., Yu, Y.J., Huang, J., Hu, H.Y., Wang, L.S., 2009b. Health risk assessment of organic pollutants in Jiangsu Reach of the Huaihe River, China. *Water Sci. Technol.* 59 (5), 907–916.
- Wang, G., Lu, Y.L., Li, J., Wang, T.Y., Han, J.Y., Luo, W., et al., 2009c. Regional differences and sources of organochlorine pesticides in soils surrounding chemical industrial parks. *Environ. Monit. Assess.* 152 (1–4), 259–269.
- Wang, G.L., Ma, L.M., Sun, J.H., Zhang, G., 2010. Occurrence and distribution of organochlorine pesticides (DDT and HCH) in sediments from the middle and downstream reaches of the Yellow River, China. *Environ. Monit. Assess.* 168 (1–4), 511–521.
- Wang, T.Y., Lu, Y.L., Chen, C.L., Naile, J.E., Khim, J.S., Park, J., et al., 2011. Perfluorinated compounds in estuarine and coastal areas of north Bohai Sea, China. *Mar. Pollut. Bull.* 62 (8), 1905–1914.
- Wei, D.B., Kameya, T., Urano, K., 2007. Environmental management of pesticidal POPs in China: past, present and future. *Environ. Int.* 33 (7), 894–902.
- Willett, K.L., Ulrich, E.M., Hites, R.A., 1998. Differential toxicity and environmental fates of hexachlorocyclohexane isomers. *Environ. Sci. Technol.* 32 (15), 2197–2207.
- Xie, S.W., Wang, T.Y., Liu, S.J., Jones, K.C., Sweetman, A.J., Lu, Y.L., 2013. Industrial source identification and emission estimation of perfluorooctane sulfonate in China. *Environ. Int.* 52, 1–8.
- Yang, R.Q., Lü, A.H., Shi, J.B., Jiang, G.B., 2005. The levels and distribution of organochlorine pesticides (OCPs) in sediments from the Haihe River, China. *Chemosphere* 61 (3), 347–354.
- Yang, L.P., Zhu, L.Y., Liu, Z.T., 2011. Occurrence and partition of perfluorinated compounds in water and sediment from Liao River and Taihu Lake, China. *Chemosphere* 83 (6), 806–814.
- Yang, Q.Y., Qiu, X.H., Li, R., Liu, S.S., Li, K.Q., Wang, F.F., et al., 2013. Exposure to typical persistent organic pollutants from an electronic waste recycling site in Northern China. *Chemosphere* 91 (2), 205–211.
- Yu, N.Y., Shi, W., Zhang, B.B., Su, G.Y., Feng, J.F., Zhang, X.W., et al., 2013. Occurrence of perfluoroalkyl acids including perfluorooctane sulfonate isomers in Huai River Basin and Taihu Lake in Jiangsu Province, China. *Environ. Sci. Technol.* 47 (2), 710–717.
- Zareitalabad, P., Siemens, J., Hamer, M., Amelung, W., 2013. Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) in surface waters, sediments, soils and wastewater — a review on concentrations and distribution coefficients. *Chemosphere* 91 (6), 725–732.
- Zhang, L., Liu, J.G., Hu, J.X., Liu, C., Guo, W.G., Wang, Q., et al., 2012. The inventory of sources, environmental releases and risk assessment for perfluorooctane sulfonate in China. *Environ. Pollut.* 165, 193–198.
- Zhao, Z., Tang, J.H., Xie, Z.Y., Chen, Y.J., Pan, X.H., Zhong, G.C., et al., 2013. Perfluoroalkyl acids (PFAAs) in riverine and coastal sediments of Laizhou Bay, North China. *Sci. Total Environ.* 447, 415–423.
- Zushi, Y., Hogarh, J.N., Masunaga, S., 2012. Progress and perspective of perfluorinated compound risk assessment and management in various countries and institutes. *Clean Technol. Environ.* 14 (1), 9–20.