Bull. Environ. Contam. Toxicol. (2004) 73:339–346
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DOI: 10.1007/s00128-004-0433-x

Bulletin of Environmental Contamination and Toxicology

Semivolatile Organic Pollutants in Water, Suspended Solids, and Surface Sediments of the Huaihe River, Jiangsu Section, People's Republic of China

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Received: 8 November 2003/Accepted: 13 May 2004

The Huaihe river basin, located between the Yellow River and the Yangtze River in the eastern part of P. R. China, is the most populated areas, which extends about 500 km from north to south, and 800 km from east to west. The Huaihe River is probably the most polluted one of China's three largest rivers. In 1994 and 1995 a succession of catastrophic pollution accidents in the Huaihe River valley set off alarm bells ringing at the highest levels of the central government. Recently, the Chinese government has increased efforts to protect the environment from further deterioration, especially in Huainan and Bangbu, two towns in Anhui province. There is, however, only limited information available with regard to the organic pollution, especially in the section of Jiangsu Province. Jiangsu is one of the fastest developing provinces in economy and construction in China today. The organic contaminants are resulting from the expanding of the scales of production and life. Many of the industrial and agricultural pollutants may cause death, disease, behavioral abnormalities, genetic mutations, physiological malfunctions in organisms (people or animals) or their offspring. These pollutants enter the environment as a result of indiscriminate spraying of pesticides for insect control, oil spillage, fossil fuel consumption, automobiles exhausting waste discharge. Migration of chemicals from soil to water and vice versa cause an accumulation of multiple residues in water and agricultural produce designed for animal or human consumption (Singh, et al. 1998; Tyler et al. 1998; Wang et al. 2003).

Solid-phase extraction (SPE) has been extensively used to recover nonpolar organic chemicals from water (Hinkley a Bidleman, 1989; Wang et al., 2003). SPE technique provides high extraction efficiencies while reducing solvent usage and extraction time necessary for classical extraction methods such as liquid-solvent extractions. In this study, SPE technique was applied to collect organic pollutants in water samples. Suspend solids and sediment samples were extracted using a soxhlet apparatus, then cleaned using silicagel adsorption chromatography. Pollution monitoring is important for the protection of waters and forms the basis for the development of action plans (Sturm et al., 1998). It is reported that Triolein-Semi-permeable membrane device has been used to sample and monitor the concentrations of toxic organic pollutants in the sections of Xinyang and Huainan in the Huaihe River in previous studies (Wang, et al.1999). However, the investigation of semivolatile organic pollutants in Jiangsu section of

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the Huaihe River has not been reported. Our study was undertaken as a part of more extensive research program (ICA4-CT-2001-10039) on cataloging water pollutants (chemicals) and their effects on human health, aiming to accurately determine the trace baseline of organic chemicals in the Huaihe River.

MATERIALS AND METHODS

The reagents used were all HPLC grade and were purchased from Merck KgaA, 64271 Darmstadt, Germany. There are four kinds of mixture standard used in our study, namely EPA 625 Base-Neutral 2, EPA 625 Base-Neutral 3, EPA 625 Base-Neutral 4 (200.0 $\mu g \cdot ml^{-1}$ per compound); and EPA 625 Phenol Mix (500.0-2500.0 $\mu g \cdot ml^{-1}$ per compound), which were purchased from Superco Park. Bellefonte, PA, USA. Internal standard chemical Hexamethylbenzene, purity $\geq 99\%$ (GC), was purchased from Sigma-Aldrin. SPE-Filtration devices with a vacuum pump and eight connectors, SPE units, 1g Octadecyl (C_{18}) Bakerbo catridges and 0.45 μm glass-fibre filters were supplied by Technical University of Graz (TU Graz), Austria.

That sampling took place during the summer of 2002 when river flows were high. The studied area spread between 118° and 119° in east longitude, between 33° and 34° in north latitude, just in Jiangsu Province of the Huaihe River. Total 12 water samples and 6 sediment samples (Due to high flow velocity and large amount of water of the Huaihe River, some of sediments could not be taken.) were collected from the three fixed stations, namely Xiao Zui (XZ), typical ecological agricultural district, the Huaihe River Bridge (HRB), located in county city, and Hongguang Chemical Plant (HCP), representing industrial section. The water samples (4 L), collected at about 1m below the water surface, were collected in pre-cleaned (with hexane and acetone) and pre-rinsed (with river water from sampling station) glass bottles. Duplicated samples were taken in each section. Sediment samples were collected using a stainless steel dredge; approximately 1kg of the middle of each sample was put in clean glassware, duplicated samples were taken each section. Care was taken to avoid any contamination by passing ships or exhaust fumes during their transport to the laboratory.

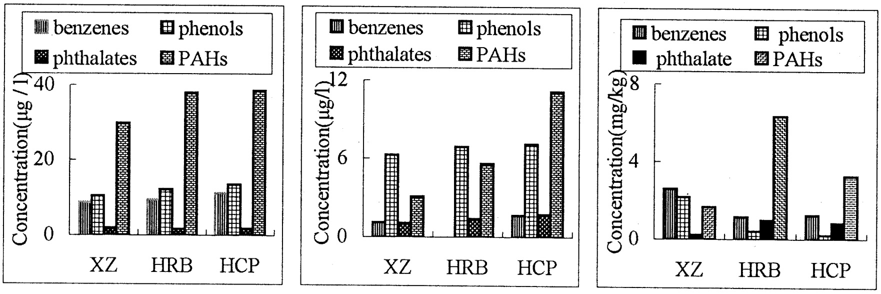
The water samples were passed through 0.45 μm glass micro-fibre filters on the SPE-Filtration device to separate the particulate fraction from the liquid phase. Octadecyl (C_{18}) Bakerbo SPE cartridges were preconditioned by eluting 5 ml of n-hexane-acetone (1:1, v/v), followed by 5 ml methanol and distilled water. Utilizing a vacuum pump control flow rate of water at 1.0 $ml \cdot min^{-1}$. After the entire sample was extracted, the vacuum was left on allowing the air to pass through the SPE for 1 min as a drying step. The loaded SPE cartridges were then eluted with 3×10 ml dichloromethane (DCM) and 3×10 ml n-hexane. The eluate was dried over anhydrous sodium sulfate and concentrated to about 2 ml by a rotary evaporator under a vacuum and further concentrated to 1 ml in high pure nitrogen for GC analysis.

A 20g freeze-dried and homogenized surface sediments or a filter with suspended solids, adding 1g copper power (to remove the interference of sulphur), were extracted by 160 ml n-hexane:acetone (1:1, v/v) in a water bath (70 °C) for 24 h using a soxhlet apparatus. The extracts were concentrated to about 2 ml by a rotary evaporator under a vacuum and further concentrated to 1 ml in high pure nitrogen. All suspended solids and sediment samples concentrated extracts were passed through a silicagel column (6 ml) with a layer of 0.5 g Na_2SO_4 on the top. The elution was repeated by 10 ml dichloromethane and 10 ml n-hexane, and the collected solution was concentrated by means of a rotary evaporator to nearly 2ml under a vacuum and further concentrated to 1ml in high pure nitrogen. All prepared sample was transferred into a glass micro-vial for GC injection after addition of 10 μl internal standard (5 $\mu g \cdot ml^{-1}$ Hexamethylbenzene).

The identification was based on mass chromatograms obtained from major mass fragment ions of different classes of compounds. MS operation condition: scan range of 45-550 *m/z*, scan rate of 0.1 $scan \cdot s^{-1}$, electron energy of 70 eV. The individual components in the mix of standard compounds were identified using computer matches to standard reference mass spectra of the National Institute of Standards and Technology (NIST) library and the identification was confirmed by comparison to reference compounds available. The concentrations of organic chemicals were determined using HP 6890 GC equipped with flame ionization detector (FID). Chromatography conditions were as follows: column, HP-5 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness), carrier gas, nitrogen at a flow rate of 1.8 $ml \cdot min^{-1}$, the injector temperature 250°C, the detector temperature 320 °C, injector volume 1.0 μl with the splitless mode for 1 min and the oven temperature gradient. The oven temperature was initially set at 40 °C and held for 4 min, ramped by 8 $°C \cdot min^{-1}$ to 180 °C, 3 $°C \cdot min^{-1}$ to 250 °C, at last 8$°C \cdot min^{-1}$ to 320 °C and held for 6 min. The series of ramps was selected primarily to optimize the separation of chemicals. The chromatograms were recorded and analyzed by the software of HP Chem-station. The recognition of chemicals in the extracts was based on retention times of standard samples by operating GC/MS. The quantitative determination of organic pollutants was achieved using the method of internal standards and the calibration curves. Analysis of two blanks (4L double-distilled water) was subjected to assess the interference from the regents and glassware and as water samples control; analysis of blanked filters was suspended solids or sediment samples control. Analyte recoveries from water, suspended solids or sediments samples were conducted by standard addition. The detection limits for the investigated semivolatile organic compounds based on the above method are 0.025-0.130 $\mu g \cdot ml^{-1}$.

RESULTS AND DISCUSSION

The recoveries of standard compounds distribute from 56% to 113%, with the relative standard derivation less than 20%. The analytes of recoveries from suspended solids or sediments were between 67% and 96%, with the relative standard derivatives less than 15%. The recoveries of compounds from water depended on a number of factors such as sample volume, the ionic strength, pH of



(a) (b) (c)

Figure 1. Mean concentration of substituted benzenes, phenols, phthalates and PAHs in water (a), suspended solids (b) and sediments (c) from the Huaihe River.

the water samples, different sorbent and sorbent treatment (Font et al., 1993, Sun et al., 2002), but the method produced the results in a good reproducibility and repeatability. The recoveries and analysis of external standards were merely used to monitor method performance and to establish calibration curve. After correcting for concentrations, the analytical results showed a good agreement with known samples. There were no impurities revealed by the blank runs, which indicating that there was no interference affected the analytical quality.

Table 1, 2 and 3 listed the organic pollutants detected in water, suspended solids and sediments from the Huaihe River. The sample of site HRB$_1$ is missing because of it broken during transport to the laboratory. 22 kinds of organic pollutants have been detected in water samples, 21 in suspended solids and 30 in sediments, respectively, most of which belong to priority pollutants. The compounds include polynuclear aromatic hydrocarbons (PAHs), phthalates, substituted phenols and benzenes. Samples collected near town or industrial area were not only with much higher number of chemicals but also higher concentrations compared to ecological agriculture area. Table 1 and 2 present the contamination levels of organic pollutants in the dissolved phase and particulate phase of water samples. Comparison of them, it was observed that very similar spatial pattern of organic pollutants existed in waters and suspended solids at each station studied. In the first sampling station (XZ), 18 chemicals were detected in water samples, the concentrations of these compounds varied from 0.10 μg·L^{-1} to 23.84 μg·L^{-1}, and 14 chemicals in suspended solids samples, concentrations from 0.08 μg·L^{-1} to 8.08 μg·L^{-1}. The Huaihe River Bridge station (HRB), 22 chemicals were detected in water samples and the concentrations of these compounds varied from 0.05 μg·L^{-1} to 17.56 μg·L^{-1}, and 14 chemicals in suspended solids samples, concentrations from 0.03 μg·L^{-1} to 4.05 μg·L^{-1}. The Hongguang Chemical Plant station (HCP), 22 chemicals were detected in water samples, the concentrations of these compounds varied from 0.09 μg·L^{-1} to 30.11 μg·L^{-1}; and 21 chemicals in suspended solids samples, concentrations from 0.09 μg·L^{-1} to 6.41 μg·L^{-1}.From Figure.1 (a) and (b), the concentrations of chemicals in water samples are slightly higher than in the corresponding suspended solids. However, it should be noted that the mean mass concentration of suspended solids was about 0.13 g·L^{-1}, the relative concentration of pollutants per unit mass suspended solids is 10-1000 times higher than in water samples. The results also indicated that PAHs were prevalent contaminants in water samples or suspended solids, especially in water samples, which likely due to industrial and human activity. The total amount of PAHs in three stations ranged from 29.90 $\mu g\cdot L^{-1}$ to 38.62 $\mu g\cdot L^{-1}$, occupying 58.5-61.9% of all pollutants. The higher PAHs concentration in sites XZ and HCP may result from shipping activities, including ship discharges. PAHs in the HRB may primarily be from combustion in Xuyi town. The mean concentration of four classifications detected in waters or the corresponded suspended solids did not vary greatly at different sections. This result is attributed to the complete dilution and mixture of pollutants from agricultural runoff and industrial wastewater discharge due to high flow velocity and water amount in raining season.

Table 1. Semivolatile organic pollutants in water samples in the Huaihe River.

Pollutants	Concentrations ($\mu g\cdot L^{-1}$) in water samples										
	XZ_1	XZ_2	$XZ_{2'}$	XZ_3	HRB_2	$HRB_{2'}$	HRB_3	HCP_1	HCP_2	$HCP_{2'}$	HCP_3
1,2-dichlorobenzene							0.28				0.47
hexachloroethane						0.62		0.35	0.36	0.41	0.25
bis(2-chloroethoxy)methane	2.04	1.87	1.97	1.65	1.29	0.83	1.07	2.32	1.55	2.22	2.01
4-chlorophenylphenyl ether		0.16	0.36	0.97	1.01	0.05	3.64	1.35	2.48	0.31	1.61
hexachlorobenzene		1.20			1.39	1.34	1.19	1.15	1.37	1.19	1.30
2,4-dinitrotoluene	5.92	5.87	5.65	7.05	6.68	5.67	4.52	6.62	6.30	5.89	5.62
Total substituted benzenes	**7.96**	**9.10**	**7.98**	**9.67**	**10.38**	**8.53**	**10.69**	**11.78**	**12.06**	**10.02**	**11.26**
2-methyl-4,6-dinitrophenol		0.95	0.80	1.32	1.55	1.59	1.01	1.51	1.15	1.11	1.42
pentachlorophenol	1.04	2.69	1.23	0.90	0.13	2.45	2.46	3.85	4.11	2.98	4.35
2-nitrophenol	3.14	3.59	3.80	2.80	2.78	1.90	2.02	4.13	2.85	4.36	3.51
2,4-dinitrophenol	0.10	0.25	0.17	0.40	0.16	0.13	0.23	0.13	0.17	0.20	0.17
4-nitrophenol	4.29	5.46	4.90	4.16	5.95	10.47	6.57	4.42	5.20	5.46	4.80
Total substituted phenols	**8.58**	**12.93**	**10.89**	**9.58**	**10.56**	**16.54**	**12.28**	**14.04**	**13.47**	**14.10**	**14.24**
butyl benzyl phthalate	0.70	1.24	1.03	0.69	1.08	0.68	0.61	0.83	1.59	0.83	0.86
di-n-octyl phthalate	1.01	1.18	1.21	0.99	0.98	0.55	0.56	0.96	1.11	0.86	0.88
Total phthalates	**1.71**	**2.42**	**2.23**	**1.69**	**2.06**	**1.23**	**1.17**	**1.79**	**2.70**	**1.69**	**1.74**
fluorene	0.22	0.15		0.36	0.44	0.52	0.41	0.09	0.36	0.17	0.21
acenaphthene					2.98	3.63	3.14	3.08	3.22	3.05	3.06
anthracene				4.47		0.11			0.17	0.18	
benzo(a) anthracene	3.01	4.47	4.33	3.04	7.78	3.63	4.36	7.14	9.13	5.75	7.55
chrysene	3.81	5.89	5.80	4.06	5.57	2.68	3.06	5.12	4.08	4.92	3.28
benzo(a) pyrene	1.07	1.44	1.56	1.04	1.30	0.55	0.72	1.29	1.22	1.21	0.88
indeno(1,2,3-cd) pyrene			5.61	5.52	3.75	6.84	7.63	6.66	7.75	4.70	5.53
dibenzo(a,h)anthracene					0.05	0.06	0.06	0.33	0.28	0.17	0.20
benzo(g,h,i) perylene		18.68	21.24	23.84	14.32	17.56	11.09	16.76	18.62	18.59	30.11
Total PAHs	**8.11**	**30.30**	**38.53**	**42.33**	**36.20**	**35.59**	**30.46**	**40.47**	**44.81**	**38.72**	**50.83**

Table 2. Semivolatile organic pollutants in suspended Solids in the Huaihe River.

Pollutants	Concentrations ($\mu g \cdot L^{-1}$) in suspended solids										
	XZ_1	XZ_2	$XZ_{2'}$	XZ_3	HRB_2	$HRB_{2'}$	HRB_3	HCP_1	HCP_2	$HCP_{2'}$	HCP_3
1,2-dichlorobenzene	0.24							0.22	0.46	0.57	0.61
1,2,4-trichlorobenzene	0.19							0.58	0.63	0.57	0.39
hexachlorobenzene	1.35	0.72	0.65	1.42				0.60	0.65	0.66	0.70
Total substituted benzenes	**1.77**	**0.72**	**0.65**	**1.42**				**1.41**	**1.74**	**1.79**	**1.70**
2-nitrophenol								0.17	0.38	0.37	0.32
2,4-dinitrophenol	0.21	0.12	0.16	0.33	0.06	0.03	0.15	0.22	0.29	0.09	0.17
4-nitrophenol	8.08	5.63	5.08	5.54	6.38	6.26	4.50	6.41	4.20	4.24	5.72
pentachlorophenol					1.21	1.17	1.03	1.35	2.17	1.57	0.90
Total substituted phenols	**8.28**	**5.76**	**5.23**	**5.87**	**7.66**	**7.45**	**5.67**	**8.16**	**7.03**	**6.27**	**7.10**
diethyl phthalate					0.14	0.21		0.12	0.16	0.13	0.89
butyl benzyl phthalate	0.53	0.43	0.32	0.73	0.60	0.61	0.37	1.19	0.40	0.43	0.33
di-n-octyl phthalate	0.63	0.41	0.82	0.53	0.48	0.46	1.39	0.51	1.11	1.22	0.49
Total phthalates	**1.16**	**0.84**	**1.14**	**1.25**	**1.22**	**1.28**	**1.76**	**1.82**	**1.68**	**1.77**	**1.71**
acenaphthene								3.04	3.07	3.00	3.16
fluorene	0.79	0.38	0.69	0.80	1.69	1.53	0.90	1.93	1.42	1.36	0.72
anthracene	0.18			0.44	0.24	0.12	0.15	0.47	0.35	0.28	0.42
phenanthrene				0.29	0.15	0.11	0.13	0.37	0.21	0.33	0.34
pyrene				1.08	0.98	1.03	0.74	1.18	1.53	1.28	1.37
chrysene	1.33	0.08	0.29	0.23							
benzo(k)fluoranthene	1.80	0.46	0.60	0.450	0.66	0.36	0.54	0.36	0.51	0.39	0.69
benzo(a)pyrene	0.46	0.78	0.84	0.51	0.47	0.30	0.99	0.16	0.80	0.87	1.03
indeno(1,2,3-cd)pyrene					0.41	0.60	1.33	2.00	0.49	0.53	0.67
dibenzo(a,h)anthracene					0.59	0.79	0.51	1.05	2.18	2.08	1.97
benzo(ghi) perylene					0.61	0.50	0.44	0.84	0.90	0.67	0.66
Total PAHs	**4.56**	**1.70**	**2.41**	**3.79**	**5.80**	**5.33**	**5.71**	**11.41**	**11.45**	**10.78**	**11.01**

Table 3. Semivolatile organic pollutants in Sediments of Huaihe River

Pollutant	Concentration (mg kg^{-1}) in sediment					
	XZ_1	XZ3	HRB1	HRB3	HCP1	HCP3
1,2-dichlorobenzene	0.10	0.09	0.06	0.06	0.01	
hexachloroethane	0.12	0.14				
hexachlorobenzene	0.08	0.07	0.28	0.32	0.40	0.33
4-chlorophenylphenyl ether	0.05	0.06			0.02	0.04
N-nitrosodi-n-propylamine	0.37	0.37				
N-nitrosodimethyl amine	0.69	0.70	0.01	0.03	0.12	0.10
azobenzene	0.31	0.29	0.17	0.19	0.13	0.14

Table 3. Continued

Pollutants	Concentration ($mg\ kg^{-1}$) in sediment					
	XZ_1	XZ3	HRB1	HRB3	HCP1	HCP3
2,4-dinitrotoluene	0.83	0.91	0.66	0.52	0.62	0.58
Total substituted benzenes	**2.55**	**2.63**	**1.18**	**1.12**	**1.31**	**1.19**
phenol			0.09	0.10		
2,4-dimethylphenol	0.10	0.09				
2-nitrophenol	0.07	0.05	0.05	0.05	0.04	0.05
2,4-dichlorophenol	0.09	0.11				
2,4-dinitrophenol	0.09	0.06			0.06	0.05
4-nitrophenol	1.88	1.85	0.08	0.10	0.01	0.03
pentachlorophenol			0.19	0.17	0.09	0.11
Total substituted phenols	**2.16**	**2.16**	**0.42**	**0.41**	**0.20**	**0.23**
diethyl phthalate			0.64	0.65	0.55	0.57
di-n-octyl phthalate	0.19	0.19	0.19	0.20	0.15	0.17
butyl benzyl phthalate	0.08	0.06	0.16	0.14	0.12	0.12
Total phthalates	**0.26**	**0.25**	**1.00**	**0.99**	**0.83**	**0.85**
acenaphthene	0.68	0.73	1.81	1.93	2.86	2.53
fluorene	0.09	0.06	2.58	3.01	2.26	2.33
anthracene			0.14	0.12		
phenanthrene			0.07	0.07		
fluoranthene			0.20	0.20	0.02	0.04
pyrene			0.09	0.08		
chrysene	0.02	0.04	0.09	0.12	0.01	0.02
benzo(k) fluoranthene	0.20	0.31	0.34	0.33	0.21	0.20
benzo(a) pyrene	0.14	0.16	0.15	0.16	0.17	0.15
indeno(1,2,3-cd) pyrene	0.05	0.03	0.18	0.19	0.02	0.04
dibenzo (a,h)anthracene	0.44	0.28	0.19	0.18	0.19	0.19
benzo(g,h,i) perylene	0.04	0.03	0.23	0.26	0.05	0.06
Total PAHs	**1.66**	**1.64**	**6.05**	**6.63**	**5.77**	**0.69**

In above tables, XZ, HRB, HCP represents sampling station site; 1,2,3 indicates left, middle and right of the sampling section of the Huaihe River; 2' is replication of 2; HRB_1 of water and suspended solids samples, missing.

From Table 3, the number of pollutants in sediments (30) was higher than in water or suspended solids samples. Mean concentration of contaminants is higher 2-3 magnitude than in water or suspended solids. According to Figure.1(c), for XZ site, substituted benzenes and phenols were widely distributed, accounting for 71.3% of total amount of pollutants. These chemicals seem to be the frequently used as plastic materials and surface-active agent, etc. in recently years. Although the site was ecological agriculture area, not more heavily polluted by domestic or industrial water discharge, while the part may suffered from effluent of Anhui province in the past decades. Concentration distribution of substituted benzenes, phenols and phthalates is similar in sites of HRB and HCP, PAHs in site HRB is higher than in site HCP.

Acknowledgments. The authors acknowledge the financial support provided by National Basic Research Program of China (No. 2003CB415002), European Commission International Scientific Cooperative Project (contract ICA4–CT-2001-10039), the National Natural Science Foundation (20177008) and 863 Project (2001AA640601-4) of China throughout the conduct of the research. Special thanks are extended to the anonymous reviewer's comments on this paper.

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