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# Pentachlorophenol Residues in Suspended Particulate Matter and Sediments from the Yangtze River Catchment of Wuhan, China

**Z. W. Tang · Z. F. Yang · Z. Y. Shen · J. F. Niu**

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Pentachlorophenol (PCP) and its salts, most notably sodium pentachlorophenate (Na-PCP), are widely used as biocides in the protection of timber and textiles throughout the world (Giggord et al. 1995; Muir and Eduljee 1999). Because of their toxicity, endocrine disturbing effect, mutagenicity, carcinogenicity, and bioaccumulation, PCP and its salts have raised great concern worldwide (Muir and Eduljee 1999). Moreover, findings show that some more toxic polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are impurities in commercial Na-PCP products.

Ding et al. (1990) reported that approximately 50 ng/g of 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin (2, 3, 7, 8-TCDD) remained in commercial Na-PCP in China. Because of numerous applications, PCP has been found to present extensively in organisms and the environment, particularly in the aquatic environment (Giggord et al., 1995; Muir and Eduljee 1999; Zheng et al. 2000). In China, because of the the low cost and high efficiency associated with PCP or Na-PCP, large amounts of were used in a plague area to control schistosomiasis, a parasitic disease of epidemic proportions (Schecter et al. 1996). Moreover, PCP or Na-PCP also was widely used in aquiculture as a clean pond reagent in China (Hong et al. 2005). Although the production and usage of PCP and its salts have been officially banned in China, their adverse biologic effects may last for a long time because of their persistence and previous long-term usage.

Z. W. Tang · Z. F. Yang · Z. Y. Shen (✉) ·
J. F. Niu
State Key Laboratory of Water Environment Simulation,
School of Environment, Beijing Normal University,
Beijing 100875, People's Republic of China
e-mail: z.y.shen@163.com

Several studies investigating the distribution of PCP in the aquatic environment near Guangzhou, Nanjing, Yueyang, and Chengdou were conducted (Hong et al. 2005; Xu et al. 2000; Zheng et al. 1997; Zheng et al. 2000). The results demonstrated a wide occurrence of PCP in the aquasystem of China. However, there still was very limited information on PCP residues in other regions, especially in the historic schistosomiasis plague area in the Yangtze River catchment. With approximately 8 million residents, Wuhan is the largest city located in middle reaches of the Yangtze River.

The Yangtze River catchment of Wuhan is a typical catchment with some tributaries and many lakes, which are resources for fishery products. These rivers also are the direct drinking water supply for residents in the region and downstream of the Yangtze River. Historically, PCP and Na-PCP have been used frequently and intensively to control the severe schistosomiasis plague or as a clean pond reagent in the catchment. To date, however, little is known about PCP residues in the environment of the surrounding area.

This study aimed to determine PCP levels in suspended particular matter (SPM) and surface sediments, and thus to locate the possible sources of PCP in the Yangtze River catchment of Wuhan.

## Materials and Methods

A total of 36 surface sediments were collected from the Yangtze River catchment of Wuhan in July and December 2005. Of these samples, 23 were collected in December 2005. Details of the sampling locations are shown in Figure 1. The surface sediment samples were collected by

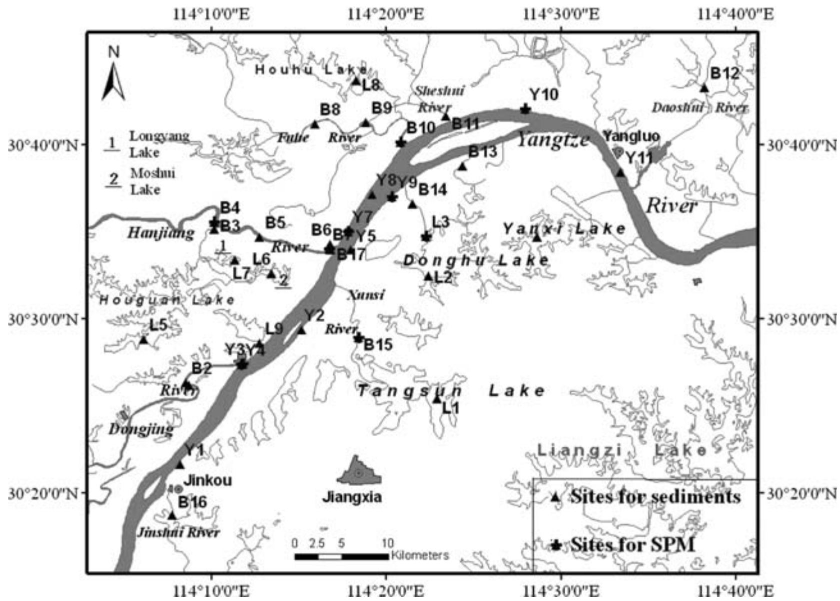


**Fig. 1** Map showing sampling sites of the Yangtze River catchment of Wuhan

a Van Veen grab. Approximately the top 2 cm of the sediments was taken and placed in a precleaned aluminum box using a stainless steel spoon. The SPM samples were collected at a selected location. Three samples were collected from the Yangtze River in July 2005, and eight were collected selectively in December 2005 (Figure 1). The SPM samples were collected after bulk filtration using a stainless filter equipped with a self-priming pump and an 0.8-μm glass filter membrane. Followed filtrations, filter membranes with SPM were taken into solvent-rinsed aluminum containers. All samples were stored at –20°C before analysis.

The stock standard solution of PCP was purchased from National Research Center for Certified Reference Materials of China. All the solvents used were of analytical grade and redistilled to remove impurities before use. The stainless filter was obtained from the Yellow River Water Conservancy Committee of China. The 0.8-μm glass filter membrane was purchased from the Beijing Shenghe Faith Membrane Company of China, Beijing, China.

The procedure for extraction of PCP from air-dried sediments or SPM was a modification of the method described by Polese and Ribeiro (1998) and Sun et al. (2003). Briefly, 5 g of sediment or SPM sample was placed in a conical flask, and about 1 mL of sulfuric acid ($H_2SO_4$) 9 mol/L was added to adjust the pH value to less than 1.0. The sample then was extracted with 30 mL of hexane/acetone mixture (1:1, v/v) in an ultrasonic bath for 1 h twice. The extract was concentrated to about 2 mL and removed to a separating funnel. Then 5 mL of concentrated sulfate was added to remove the impurities two or three times until the extracts turned clear. The organic phase was washed with 10 mL of Milli-Q water twice.

After 100 mL of potassium carbonate ($K_2CO_3$) 0.2 mol/L solution had been used to remove the organic phase, the water phase including PCP was placed in the separating funnel again and acetylated by adding 0.5 mL of acetic anhydride. The pentachlorophenyl acetate derivative then was extracted with 10 mL of n-hexane. The extract was dehydrated and evaporated down to 1 mL for gas chromatography (GC) analysis using a gentle stream of high-pure nitrogen.

The identification and quantification of PCP derivatives were accomplished by an Varian CP 3800 gas chromatograph equipped with a $^{63}$Ni electron capture detector and a 30 m × 0.25-mm × 0.25-μm DB-5 capillary column (J&W Scientific, Folsom, California, America). The initial oven temperature was set to 100°C, which was maintained for 1 min, then increased to 250°C at a rate of 10°C/min, and finally maintained at 250°C for 10 min. The temperature of the injector and the detector was maintained at 250°C and 280°C, respectively. Nitrogen was used as the carrier gas with a flow of 1 mL/min.

Pentachlorophenyl acetate was identified by the average retention time of derivatives of 1 mg/L PCP standard and confirmed by gas chromatography (GC) / mass spectrometer (MS). The levels of the PCP derivatives were quantitatively determined by the external standard method using peak area. The response of the GC was calibrated for every working day. For every set of eight samples, a procedural blank and a spiked sample with standards were used to check for the interference and cross-contamination. With the detection limit in the samples set at five times the noise of the baseline, the instrument detection limit was 4.19 pg. The method detection limit was 0.53 ng/g. The spiked recoveries of PCP ranged from 80.5% to 99.8%, and the relative standard deviation was 8.6%.

To determine pH value, 10 g of air-dried sediments was mixed with 10 mL of deionized water and allowed to stand for 30 min. For total organic carbon (TOC) analysis, the ground-sieved samples were treated with 1.6% (v/v) hydrochloric acid to remove inorganic carbon, then oven dried again at 60°C. Organic carbon was measured on a Liqui TOC analyzer (Elementar, Hanau, Germany) at a combustion temperature of 950°C. The grain size of the sediment was measured with a SALD-3001 laser diffraction particle analyzer (Shimadzu, Kyoto, Japan).

## Results and Discussion

Pentachlorophenol was detected in 8 of 28 river sediments. The PCP concentrations ranged from less than 0.53 to 3.47 ng/g on the basis of dry weight (dw). The highest PCP level was found at site B13 located at Tsingshan Port, a tributary of the Yangtze River (Table 1). As compared with the river sediments, higher PCP levels, varying from 0.65 to 12.78 ng/g dw, were identified in six samples of eight lake sediments (Figure 2a). In the mainstream of the Yangtze River, there was no obvious difference in PCP levels between the flood season and the dry season.

Pentachlorophenol residues also were measured in 11 SPM samples. The PCP concentrations varied from less than 0.53 to 88.80 ng/g dw, with a mean value of 10.66 ng/g dw. The detection rate for PCP in SPM reached 72.7%, and the levels shown in Figure 2b indicate a wide occurrence of this compound. Shown as broken columns in Figure 2b, an extremely high level of PCP was observed in SPM collected in the middle reach of the Xunsi River, which flows across a more industrialized area. Similar to the distribution in the Yangtze River, no obvious difference can be seen in the PCP levels of SPM samples in the two sampling seasons.

The PCP levels in sediments from the tributaries of the Yangtze River were similar, varying from 0.59 to 3.47 ng/g dw. The maximum was observed at Tsingshan Port, a mixed zone with both industrial and shipping activities. This sampling site had a relatively steady deposition. Besides a hydrodynamic effect, the fresh inputs are attributable to the high level of PCP in its sediments. Moreover, high detection rates were found in the Fuhe River and the Sheshui River, which flow across more industrialized and epidemic areas, indicating that historical usage together with industrial discharge contribute commonly to the PCP residues.

As the largest tributary of the Yangtze River, the Hanjiang River flows across the severe schistosomiasis plague area, and high PCP levels were expected in its sediments. However, PCP was detected only at site B7 in its entry to Yangtze River. The lack of PCP in the sediments of the Hanjiang River may be attributable to its large flows and rapid current velocity.

In the mainstream of the Yangtze River, PCP was detected only in 2 of 11 sediment samples. The low detection rate could be attributable mainly to less PCP input from its upper reaches. Moreover, the hydrodynamic influence on PCP distribution should be emphasized. The Yangtze River is characterized by large flows of water and suspended sediment. Dilution by the vast amounts of water and sediments from its upper reaches may be important for the distribution of hydrophobic organic contaminants. Meanwhile, the rapid current velocity also prevents the deposition of fine suspended particles.

In this study, the levels of PCP generally were higher in lake sediments than in river sediments. A lake is a rela-

**Table 1** Pentachlorophenol (PCP) levels and physicochemical property of surface sediment samples in the Yangtze River catchment of Wuhan

| Sample location | n | PCP levels (ng/g dw) | pH Values | Clay contents (%) |
|---|---|---|---|---|
| Yangtze River | 11 | <0.64–1.68 | 7.65–8.10 | 4.92–33.79 |
| | | 0.38 ± 0.58 | 7.89 ± 0.13 | 21.60 ± 10.52 |
| Hanjiang River | 4 | <0.64–0.87 | 7.83–8.21 | 2.79–16.07 |
| | | 0.34 ± 0.42 | 8.00 ± 0.17 | 7.36 ± 5.33 |
| Fuhe River | 3 | <0.64–0.77 | 7.08–7.46 | 33.34–42.75 |
| | | 0.46 ± 0.40 | 7.21 ± 0.21 | 38.75 ± 4.86 |
| Sheshui River | 1 | 0.59 | 7.08 | 51.62 |
| Dongjing River | 2 | <0.64–0.628 | 7.42–7.62 | 31.17–42.01 |
| Tsingshan Port | 1 | 3.47 | 7.7 | 34.96 |
| Others | 6 | <0.64 | 6.94–7.51 | 30.31–43.30 |
| | | | 7.11 ± 0.36 | 36.77 ± 5.36 |
| Lakes | 8 | <0.64–12.78 | 6.25–7.23 | 25.77–49.10 |
| | | 3.47 ± 4.61 | 6.82 ± 0.36 | 37.28 ± 8.34 |

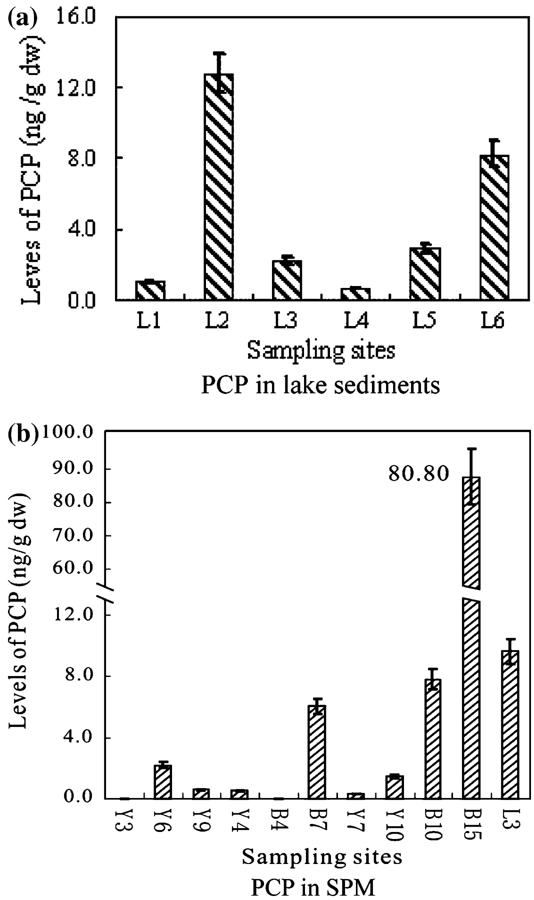


**Fig. 2** Concentrations of pentachlorophenol (PCP) in lake sediments and in suspended particle matter (SPM) from the Yangtze River catchments of Wuhan

tively steady independent system, whereas a river is a quite mobile system. In a river, the contaminants can be easily diffused and diluted by the flow of the river. Relatively higher levels of PCP were observed at the sites of Donghu Lake and Moshui Lake, located in a more industrialized and urbanized region. Presumably, the industrial discharge plays a vital role in the polluted sediments. This result is different from that of studies conducted in Pear River Delta in China, which found more pollution occurring in this rural region (Hong et al. 2005). Meanwhile, PCP also was detected in Houguan Lake, Tangsun Lake, and Yanxi Lake, all located in rural regions. This may be reason why PCP or PCP-Na was directly used historically as a schistosome control in the region.

On the other hand, the lakes were devoted to the culture of single-species or multiobject species of fish. Usually, PCP was used historically to kill the other species in the lakes (Hong et al. 2005). Therefore, these PCP residues in lakes can be attributed mainly to PCP used both as schistosome control and as a common clean pond reagents.

The relationship between the physicochemical properties of sediments and PCP distribution also was studied in this region. The characteristics of sediment samples from the different locations are shown in Table 1. Further analysis showed no correlation between the PCP levels and either clay content (n = 14; $R = 0.07$; $p > 0.05$) or pH values (n = 14; $R = 0.14$; $p > 0.05$). On the contrary, correlation analysis showed a significant positive correlation between TOC and PCP concentrations (Figure 3). It is well documented that hydrophobic organic substances are mainly adsorbed by particles through partition, which correlates with the content of organic carbon (Golding et al. 2005). Paaso et al. (2002) found that humic matter plays a key role in the release of sediment-adsorbed PCP. These results also indicate that TOC is an important factor in the distribution of PCP in sediments.

A different pattern of PCP distribution was found in SPM, as detailed in Figure 2b. In the Xunsi River, the PCP level was extremely high in SPM samples, whereas it was below the detection limit in the sediment of this study. The high PCP residue in its SPM could be explained by major instantaneous discharges from city industry. Moreover, higher PCP levels also were found in the Fuhe River, which flows across industrialized and urbanized areas and receives much more industrial sewage.

In this study, relatively higher levels of PCP were observed in the SPM of Donghu Lake (Figure 2b), a lake with more eutrophication. In this lake, a large amount of green alga and phytoplankton was observed, and the SPM was made up mainly of phytoplankton. The PCP residue in this SPM sample was likely attributable mainly to phytoplankton adsorbing or containing much of the PCP. Simultaneously, a high PCP level was measured in its sediments. Resuspension by bioturbation also may result in the PCP release of contaminated surface sediments (Warren et al. 2003). In the mainstream of the Yangtze River, the maximum PCP was found at site Y10 located at its

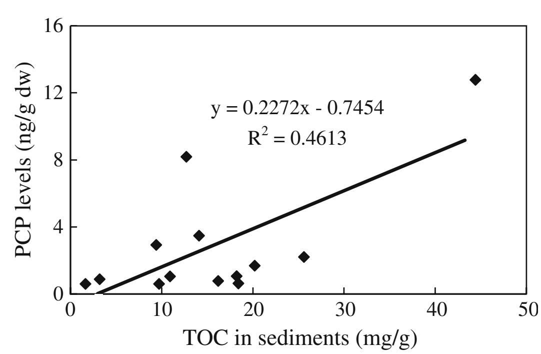


**Fig. 3** Correlation analysis between pentachlorophenol (PCP) and total organic carbon (TOC) of sediments. The relationship was determined from samples with PCP levels above the detection limit. Sites L4 and B9 were excluded because their TOCs were exceptional

lower reaches (Figure 2b). Perhaps, the residue of SPM from the mainstream was influenced by inputs from the tributaries of the Yangtze River.

China has no environmental standards for PCP in freshwater sediments or SPM. Therefore, the levels were assessed using a criteria presented by Muir and Eduljee (1999) for risk appraisal purposes. These authors established the predicted no-effect concentration (PNEC) of PCP in freshwater sediment (25 ng/g) and freshwater SPM (15 ng/g) based on the water quality objective of 1 μg/L (Muir and Eduljee 1999). The PCP levels in the studied sediments all were below the PNEC. The PCP levels in SPM samples also were below the PNEC, except for the sample from the Xunsi River.

In addition, the PCP levels of these sediments also were less than the standard set by the Netherlands, which regulated a level below 20 ng/g dw (Honnen et al. 2001). Pentachlorophenol is a weak acid with a pKa value of 4.74. However, its ionic form dominates in aqueous solution (Muir and Eduljee 1999). With increasing pH, PCP adsorption by sediments or particles decreases, and it tends to be released into water. On the other hand, although PCP concentrations in the aquatic environment are relatively lower, their potential hazard is important because of PCP bioaccumulation in the tissues of animals and humans via the food chain.

Furthermore, PCDD/Fs are commonly found in PCP products in China (Ding et al. 1990). Moreover, PCP and Na-PCP via the food chain is considered to be one of the most significant intake routes of PCDD/Fs for consumers (Muir and Eduljee 1999). Especially in the studied region, great quantities of fishery products have been obtained from the freshwater environment every year. Consequently, PCP residues in the sediments and SPM from both the rivers and the lakes should be of concern.

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