

# RESIDUES OF ORGANOHALOGEN CONTAMINANTS IN SURFACE WATER FROM JINSHAN SECOND INDUSTRIAL PARK IN YANGTZE RIVER DELTA

Yihui Zhou\*, Yanling Qiu, Jianfu Zhao, Zhiliang Zhu

State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

## Introduction

Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), described as persistent organic pollutants (POPs), have been of worldwide concern owing to their toxicity, long range transport, persistence and bioaccumulation. They can enter the aquatic environment through atmosphere precipitation, runoff from land as well as industrial discharges and pose adverse effects to human and wildlife. Jinshan Second Industrial Park is located in southwest of Shanghai, the heart zone of the Hangzhou Bay Coast and the Yangtze River Delta (YRD) city cluster, mainly producing and concentration on fine chemical industry, e.g. catalysts, cosolvent, food additives, chemicals for electronics, paper making, and biochemical, in which showing potential POPs pollution sources. However, most studies on POPs pollution have been carried out in agricultural production, and less knowledge was on environmental impacts of industrial activities. A sampling program was conducted to collect surface water samples at the river system of the industrial park from September to October 2011 to assess the environmental impacts of industrial activities in transporting organohalogen contaminants from upstream areas to downstream areas.

## Materials and methods

### Sample collection

A total of 36 surface water samples were collected at 11 sites along the river system around the Jinshan second industrial park from September to October 2011. For comparison, 12 water samples from 3 sites and 24 water samples from 6 sites were collected in the upstream section of the industrial park (agricultural area, A1-A3) and industrial park (I1-I6), respectively.

Water samples (4L for each) collected at sampling sites were placed directly into amber glass bottles, which were washed successively with detergent, tap water, distilled water and the sample water. The glass bottles were filled to the top with the sample water to eliminate air bubbles and capped with Teflon-lined caps. All samples were stored in darkness at 4 °C in the laboratory for subsequent analysis.

### Sample Extraction

The water samples were passed through a 0.45 µm glass micro-fiber membrane on the SPE-Filtration device (CNW 3-Station SPE Disk Manifold) to separate particulate matters from water phase. The filtered water samples (water phase) were spiked with 20 ml methanol and a recovery standard containing CB-53 and CB-200, and then extracted using a SPE-Filtration device, according to modified EPA 508.1 method. The C18 Empore membrane (47mm) was first conditioned with 10 ml 1:1 (v/v) DCM: EtOAc, followed by 2\*5ml methanol and 2\*5 ml superpure water. Water samples were passed through the membrane at a flow rate of 6 ml min<sup>-1</sup> under vacuum. After all of the water samples passed through the membrane, the membrane was eluted with 10 ml EtOAc, 10 ml DCM and 6 ml 1:1 (v/v) DCM: EtOAc successively. Then the collected elution was cleaned with anhydrous Na<sub>2</sub>SO<sub>4</sub> to remove water.

The suspended particle samples were freeze-dried, spiked with PCB 53 and PCB 200 as recovery surrogates, and Soxhlet extracted for 48 hours at 70 °C with 100 ml 1:1 acetone: cyclo-hexane.

The extracts both from water samples and suspended particle samples were concentrated to 1 ml by rotary-evaporation and under a gentle stream of nitrogen. The concentrated extracts were cleaned with silica gel column

to remove impurities and isolate, and the analytes in the column were eluted with 1:1 (v/v) DCM:cyclo-hexane. The elutes were further concentrated to approximately 1 ml by gentle stream of nitrogen at room temperature and then further purified on a 1 g florisil column (Supelco--LC-18, 57100-U). A 5 ml acetone/ cyclo-hexane (1:9 v: v) was used to elute OCPs and PCBs, then the elutes from the florisil column were reduced in volume and exchanged into hexane and concentrated to 100  $\mu$ l. Finally, CB30 and CB189 were added as the internal standard before GC-ECD analysis.

### Instrumental Analysis

The instrumental analysis of organochlorine pesticides and PCBs was carried out on a Gas Chromatography (GC Agilent 7890), equipped with a  $^{63}\text{Ni}$  electron capture detector (ECD). The gas chromatography column was a HP-5 column (30 m  $\times$  320  $\mu$ m) coated with [5%-phenyl] methyl polysiloxane at a film thickness of 0.22  $\mu$ m. Nitrogen was the carrier gas at a constant flow rate of 1.5 ml min $^{-1}$  and was also used as a make-up gas at a constant flow rate of 28.5 ml min $^{-1}$ . The oven temperature was programmed from 80  $^{\circ}\text{C}$  (held for 2 min) to 150  $^{\circ}\text{C}$  at a rate of 20  $^{\circ}\text{C}$  /min, then increased to 190  $^{\circ}\text{C}$  at a rate of 4  $^{\circ}\text{C}$  /min, to 230  $^{\circ}\text{C}$  at a rate of 1  $^{\circ}\text{C}$  /min, and continually increased to 300  $^{\circ}\text{C}$  at a rate of 20  $^{\circ}\text{C}$  /min (held for 5 min). The temperatures of the injector and detector were set at 260  $^{\circ}\text{C}$  and 300  $^{\circ}\text{C}$ , respectively. The GC peaks were identified by accurate assignment of retention time for each standard within  $\pm 0.5\%$ . The residue levels of OCPs and PCBs were quantitatively determined by internal standard method using peak area. The correlation coefficient of calibration curves of OCPs and PCBs were all greater than 0.999.

### QA/QC

Blank samples consisting of all laboratory reagents were analyzed with every five samples. Results for OCPs/PCB congeners in all samples were blank subtracted using values from each batch. Recoveries for CB53 ranged from 68% to 117%, with average 90%; for CB200, recoveries ranged from 74% to 126%, with average 88%.

## Results and discussion

### OCPs residues

The concentrations of  $\Sigma 22\text{OCPs}$  (sum of 22 OCP components) in all sampling sites in water were 10.0-269.2 ng/L (average 95.8 ng/L), higher than those in Pearl River Estuary, South China Sea and Dianshan Lake (Table 1). The average concentration in water of industrial park was 125.1 ng/L, higher than that in upstream samples (average 37.3 ng/L). Similar results were also found in particulate matters (average 93.1 ng/L in industrial park, 69.3 ng/L in upstream samples), indicating industrial pollution caused the increasing of OCPs concentrations in water in some extent.

**Table 1 Total concentration of OCPs in water from various sites in China (ng/L)**

Location	Concentration Range	Average Concentration	Reference
Jiulongjiang Estuary, China	115.4-414.7	191.5	Zhang et al., 2002
Pearal River Estuary, China	4.44-634.6	88.31	Zhang, 2001
South China Sea, China	1.27-121.8	16.49	Zhang, 2001
Dianshan Lake, China	0.95-7.95	/	Qiu et al., 2011
Rivers in Jinshan, Shanghai, China	10.0-269.2	95.8	This study

Heptachlor was the dominant pollutant in industrial park, contributing 53.5% in water and 66.9% in particulate matters, the percent of which were especially higher than that in upstream samples (3.4% in water and 0.4 % in particulate matters). Heptachlor had never been used in large amounts in East China and the compounds detected in water samples from the Yangtze River were probably originated from long range air transport from neighboring regions around Jiangsu Province through atmospheric deposition entering water environment (Zhou

et al. 2008). Thus, the detected heptachlor in upstream water could be from atmospheric deposition, while high percent of heptachlor in industrial park were mainly releasing from industrial activities.

HCHs were another dominant compound detected in industrial park, about 25.8% and 9.1% in water and suspend particulate, respectively. However, the percent of HCHs in upstream area is close or higher (23.4% in water and 19.1 % in particulate matters). The compositional data for HCHs showed that the relative abundances of  $\alpha$ -HCH and  $\gamma$ -HCH were 18.5% and 10.4%, respectively, and  $\alpha$ -HCH/ $\gamma$ -HCH was smaller than 3 (1.78), implying that technical HCHs was not the source of HCHs existed in this region (Yu et al., 2008). Besides, high percentage of  $\beta$ -HCH in water (57.4%) suggested that the contamination by HCHs was not from a new input source because  $\beta$ -HCH is more persistent and less volatile than other HCH isomers and it tends to accumulate more readily in the environment (Middeldorp et al., 1996; Quintero et al., 2005). It is therefore that high concentration of HCHs in industrial park was not related to industrial pollution.

The percent of DDTs in industrial park was also high in water (6.6%) and suspend particulate (13.7%), much lower than that in upstream area (46.1% and 41.4% in water and suspend particulate), indicating that the source of DDTs in industrial park was from the agricultural pollution upstream. As one of the common pesticides, p,p'-DDT was broadly applied in the past in China. Technical DDT generally contains 75% p,p'-DDT, 15% o,p'-DDT, 5% p,p'-DDE and <5% p,p'-DDD. The average composition of DDT isomers measured in water samples of industrial park was o,p'-DDT(32.7%) > p,p'-DDD (20.0%) > p,p'-DDT(11.6%) > p,p'-DDE(18.5%), while it was p,p'-DDT(30.2%) > o,p'-DDT(11.0%) > p,p'-DDD (7.3%) > p,p'-DDE(4.6%) in upstream agricultural area. DDT can be biodegraded to DDD under anaerobic conditions, so it can be inferred from the high percentage of p,p'-DDD in industrial park that the DDTs input was historical. According to previous studies, a ratio of (DDE + DDD)/DDTs > 0.5 can be thought of as being due to longterm weathering (Hites and Day, 1992). Here ratios of (DDE + DDD)/DDTs were 1.43 and 1.26 in industrial park and upstream area, respectively, which infers that DDTs input at these sites was historical, and significant degradation has occurred.

### PCBs residues

The concentrations of  $\Sigma$ 15PCBs (sum of 15 PCB congeners) in all sampling sites in water were 39.3-261.0 ng/L (average 101.6 ng/L), higher than those in Yangtze River, Dianshan Lake, and Haihe River and Dagu Drainage River, lower than Taihu Lake, Jiulongjiang Estuary and Daya Bay (Table 2). The average concentration in water of industrial park was 114.4 ng/L, higher than that in upstream samples (average 76.0 ng/L), as well as that in particulate matters (average 21.8 ng/L in industrial park, 16.3 ng/L in upstream samples), indicating that increasing of PCBs concentrations in water was also related to industrial pollution.

**Table 2 Total concentrations of PCBs in water from various sites in China (ng/L)**

Location	Concentration Range	Average Concentration	Reference
Jiulongjiang Estuary, China	0.1-1501	177.9	Zhou et al., 2000
Daya Bay, China	91.1-1355.3	313.6	Zhou et al., 2001
Taihu Lake, China	/	631	Wang et al., 2003
Haihe River and Dagu Drainage River, China	0.775-154		Liu et al., 2007
Yangtze River, China	N.D.-25.7	11.1	Hu et al., 2011
Dianshan Lake, China	N.D.-6.84	/	Qiu et al., 2011
Rivers in Jinshan, Shanghai, China	39.3-261	101.6	This study

The proportions of the various PCB congeners in water phase differed significantly, with congeners containing 3-6 chlorine atoms accounting for more than 90% of the total PCBs. The homolog distribution of PCBs in the study area followed the order: tetra-PCBs > hexa-PCBs > penta-PCBs  $\approx$  tri-PCBs > hepta-PCBs > deca-PCBs  $\approx$  octa-PCBs, which indirectly reflected the production and use of PCBs in China. It has been reported that approximately 10,000 tons of PCBs were produced in China from 1965 to 1974, mostly as PCB<sub>3</sub> and PCB<sub>5</sub> (Zhao et al., 2010). Congeners containing 3-5 chlorine atoms were the main congeners in PCB<sub>3</sub>, which was utilized in capacitor production (Zhao et al., 2010). Therefore, these congeners accounted for a high proportion

of the water samples. The dominant PCB congeners in industrial park were CB44 and CB52. The percent of CB44 was higher in industrial park (46.91%) than in upstream area (19.29%), while CB52 was on the contrary. This indicates that the CB44 in water from industrial park probably originated from sources related to industrial activities, and CB52 was not.

## Conclusion

The average concentrations of  $\sum 22$ OCPs (sum of 22 OCP components) in water and suspend particulate of industrial park were 29.8 and 93.1 ng/L, respectively, all of which were higher than that in upstream samples (18.7 and 69.3 ng/L). Heptachlor, HCHs and DDTs were the dominant compounds detected in industrial park, but only heptachlor was the pollutant releasing from industrial activities, which contributing 53.5% and 66.9% in water and suspend particulate, respectively. The average concentration in water of industrial park was also higher than that in upstream area, showing that increasing of PCBs concentrations in water was also related to industrial pollution. The homolog distribution of PCBs in the study area followed the order: tetra-PCBs > hexa-PCBs > penta-PCBs  $\approx$  tri-PCBs > hepta-PCBs > deca-PCBs  $\approx$  octa-PCBs and 3-6 chlorine atoms accounting for more than 90% of the total PCBs. The dominant PCB congeners in industrial park were CB44 and CB52. However, only CB44 was probably originated from industrial activities.

## Acknowledgements

This work was supported by the Major National Water Special Project (2009ZX07104-002-05) and State Key Laboratory of Pollution Control and Resource Reuse Foundation (No.PCRRY11015).

## References

1. He H, Hu GJ, Sun C, Chen SL, Yang MN, Li J, Zhao Y, Wang H. (2011) *Environ Sci Pollut Res* 18:638-648.
2. Hites RK, Day HR. (1992) *Bull. Environ. Contam. Toxicol.* 48:259-264.
3. Liu HX, Zhang QH, Wang YW, Cai ZW, Jiang GB. (2007) *Chemosphere* 68:1772-1778.
4. Middeldorp PJM, Jaspers M, Zehnder AJB, Schraa G. (1996) *Environmental Science and Technology* 30:2345-2349.
5. Quintero JC, Moreira MT, Feijoo G, Lema JM. (2005) *Chemosphere* 61:528-536.
6. Qiu YL, Cao Y, Zhou YH, Wang Y, Zhu ZL, Zhao JF, Yin DQ. (2011) *Processes in the Yangtze River System—Experiences and Perspectives* (ISBN 978-3-89336-744-3) 123:49.
7. Wang H, Wang CX, Wu WZ, Mo Z, Wang ZJ. (2003) *Chemosphere* 50:557-562.
8. Yu M, Luo XJ, Chen SJ, Mai BX, Zeng EY. (2008) *Environmental Toxicology and Chemistry* 27:10-17.
9. Zhao L, Hou H, Zhou YY, Xue ND, Li HY, Li FS. (2010) *Chemosphere* 78:1285-1293.
10. Zhou JL, Hong H, Zhang Z, Maskaoui K, Chen W. (2000) *Water Res* 34:2132-2150.
11. Zhou JL, Maskaoui K, Qiu YW, Hong HS, Wang ZD. (2001) *Environ Pollut* 113:373-384.
12. Zhang ZL. (2001) Environmental Behavior and Primary Assessment of Organic Pesticides in the Estuarine Agricultural Watershed, Ph.D Thesis, Xiamen University, China.
13. Zhang ZL, Hong HS, Wang XH, Lin JQ, Chen WQ, Xu L. (2002) *Marine Pollution Bulletin* 45 (1-12):397-402.
14. Zhou RB, Zhu LZ, Chen YY. (2008) *Environ Monit Assess* 136:277-287.