POLYCHLORINATED BIPHENYLS（PCBS）LEVELS IN SEDIMENT OF THE SECOND SONGHUA RIVER

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Abstract

Polychlorinated Biphenyls (PCBs) were measured by GC and GC/MS in several different sediment samples from the Second Songhua River, and we researched PCBs levels and distribution. Total PCBs concentration in sediment varied from 0.8 to 85.9 ng/g, the distribution character : the concentration of PCBs reduced from Jilin , and the main compounds were di-PCB, tri-CBs, tetra-PCB, penta-PCB and little hexa-PCB. The result suggested that mainly PCBs source was point pollution, namely industrial sewage and city life sewage.

Introduction

Polychlorinated biphenyls (PCBs), as persistent organic pollutants (POPs), have been extensively concerned during the last 30 years in view of their extensive production and usage, their atmospheric long-range transport (ALRT), persistence ,bioaccumulation tendency, potential toxicity and impact on both ecosystems and human health. Prior to 1975, PCBs generally used as dielectric fluid, impregnant, organic thinner and paint additive.

While domestic and abroad concerned to virulent matter harm, our country also developed study on PCBs in pollution, distribution and emission sources. Up to now, the research in sediment focused on the eastern part of the country, especially some major rivers such as Yangtze River, Zhujiang River, and Yellow River, and estuarial areas in rivers, such as Minjiang, Zhujiang, and Jiulongjiang. Those areas were mostly important in economy, so the research was very important significance to environment and society.

Songhua River is the most important river in northeast China, so from 1980s many people have been researched on the pollution in the second Songhua River. This study aims to assess the character of the PCBs situation and study on PCBs in sediment on pollution, distribution and emission sources.

Materials and Methods

Sediment samples Sites. The sediment samplings used in this study have been got in November 2005 in the Second Songhua River. All sites were shown in **Figure 1**. The samples were collected using a stainless steel grab bottle which was cleaned before using. The sampling depth was 0~10cm after removal of the litter layer. Five cores were mixed together to form one sample and we used pre-cleaned glass bottles with Teflon covered to minimize the possibility for contamination. The samplings were freeze dried and stored under -20℃ in a freezer until extraction(1-3).

Extraction and cleanup. Samples were treated, extracted, and analyzed according to the methods established at the National Laboratory for Environmental Testing (NLET), Environment Canada. The wet sediment was thawed and then mix thoroughly with a metal spatula to obtain homogeneity(4-6). Weigh out 25 g of wet sediment sample into a pre-cleaned extraction thimble and spiked a recovery standard containing CB65 and 155, mix thoroughly。The samples were then Soxhlet extracted for 18 h using acetone and hexane (1:1 v/v). Secured the beaker in an water bath （temperature is about 80℃） and control the recycle about 8 times per an hour。

Before the cleanup procedure we used sodium sulphate to get out water, and then Concentrate the extract to approximately 2mL. The sampler extracts were cleaned on 10g silica gel column and Concentrated approximately 2mL. Finally added 15 mL isooctane and Concentrated it to approximately 1 mL. Adjust the final volume to 1 mL with iso-octane .then added internal standard PCB30 and PCB204, and mix thoroughly.

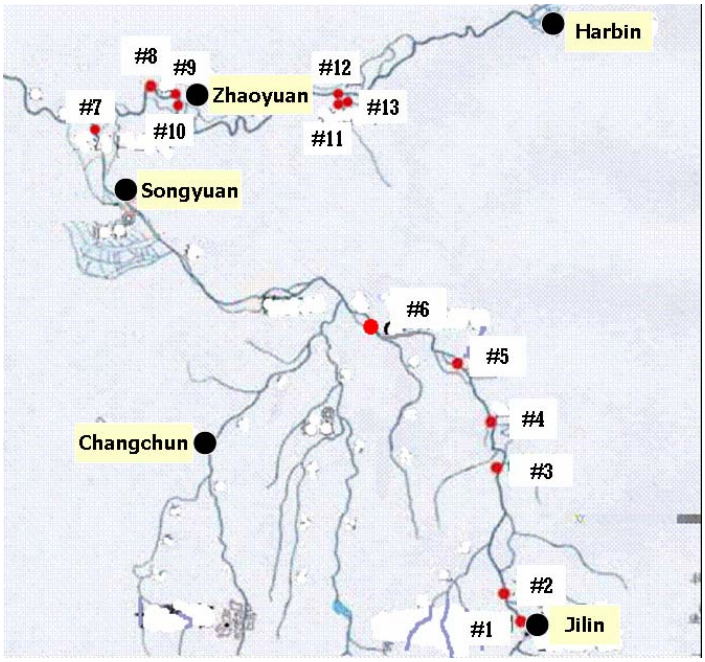

Figure 1. Locations of sampling sites on the Second Songhua River.

PCB congeners were determined by gas chromatography-negative ionization mass spectrometry (GC/MS) using an Agilent 6890 GC-5973N mass selective detector (MSD) equipped with a split/splitless injector. Injector and detector temperatures were kept at 250 and 300℃, respectively. A 60m×0.25mm×0.25μm DB-5MS column film thickness was operated with a helium carrier gas with a flow of 1mLmin^{-1}. The temperature program was as follows: initially held at 70℃ for1 min,10℃min^{-1} to 160℃,then 2℃ min^{-1} to 280℃, held for 10min. Transfer line, ion source, and quadrupole temperatures were kept at 250℃,150℃,and 106℃,respectively. The internal standards were purchased from Accu Standard Inc.The following compounds were routinely detected in all samplings: CB-4/10, 5/8, 6, 7, 9, 12, 13, 15, 26, 28/31, 32, 33, 42, 45, 47/48, 49, 52, 53, 64, 70, 74, 77, 81, 83, 84, 85, 87, 89, 91, 92, 94, 95, 97, 99, 100, 101, 118, 123, 110, 131, 135/144, 153/132, 149.

QA/QC. All analytical procedures were monitored using strict quality assurance and control measures. method spike and method blanks consisting of preextracted page bags were extracted and analyzed in the same way as the samples. There were not any objects in the laboratory blanks, indicating contamination was negligible during transport, storage, and analysis. The method detection limit (MDL) was calculated as three times the standard deviation (SD) of the mean blank. In case the concentration of a compound was below MDL, the value of 1/2 MDL was inserted. Concentrations for most congeners were above the detection limit. Recoveries were between 86.7%~109.0% for all the compounds studied. Instrument performance was monitored using quality control standards after every six samples analyzed on the instrument.

Results and discussion

PCB congeners were found in all sediment samples, and concentration of individual and total PCBs detected in sediment samples in the Second Songhua River are summarized in **Figure2**. From the detected result we can knew, the main compounds were di-PCB, tri-PCB, tetra-PCB, penta-PCB, and less hexa-PCB. Sample site #1 is near Jilin which was a middle city in Jilin province. And the total PCBs in sediment were the highest and the concentration was low gradually with apart from the Jilin city. So the source of PCBs was from city sewage. Before Sample site #7 had another city, the City of Songyuan, so the total PCBs in sediment increases. So cities were the main pollution sources.

Usually di-PCB was used as pesticide, so the concentration of di-PCB was high in city wastewater. tri-PCB mainly was used for capacitor, coloring matter and intermediate production of pesticide, so the concentration of tri-PCB was high in industrial wastewater. And penta-PCB which was used as additive in paint was high in industrial wastewater. From the **Figure1,** sampling sites #1 and #7 had higher di-PCB ,tri-PCB and penta-PCB, so point sources affected more than surface source.

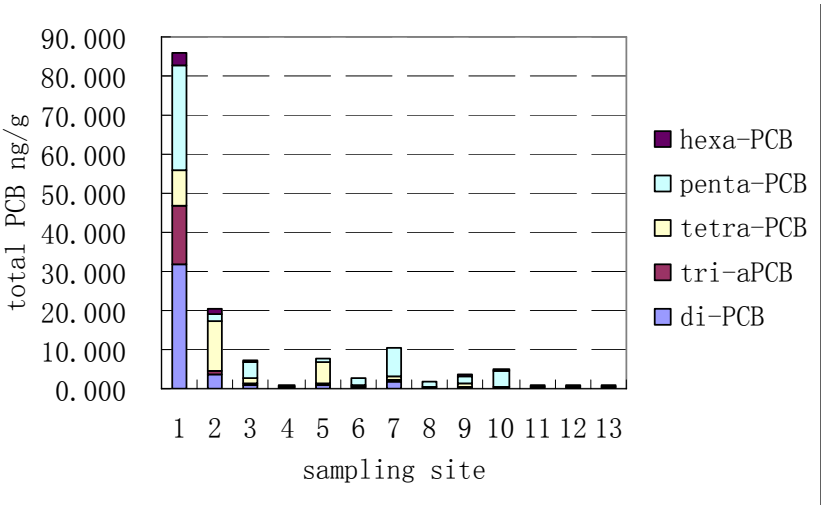

Figure 2 Total PCBs and PCB homologues in samplings

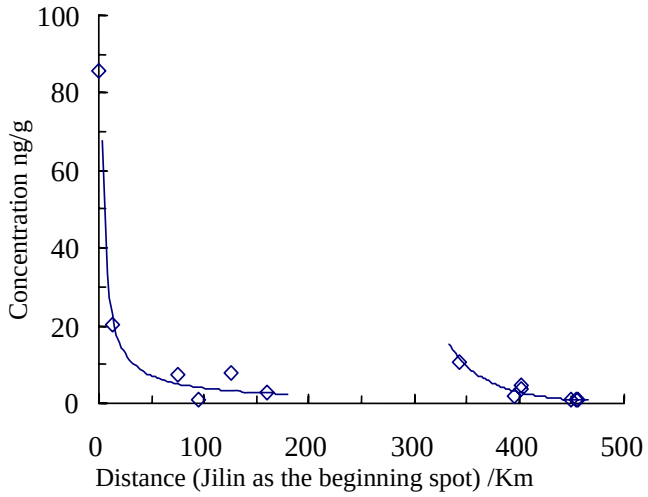

Figure 3. Total PCBs and PCB homologues in samplings

Figure 3 showed total PCBs concentration decreased from upstream to downstream. Sample site #1 was the highest point, so the decline had been observed in environmental compartments and was often related to distance from source areas. Liu (7) had detected some drain areas near water supply plant, life wastewater, chemical factory and paper mill wastewater treatment plant in Jilin city in 1998, the highest concentration was 337 ng/g, much higher than the concentration in sample in Site #1. And with the distance PCBs was declined , because there were fewer industries at the downstream

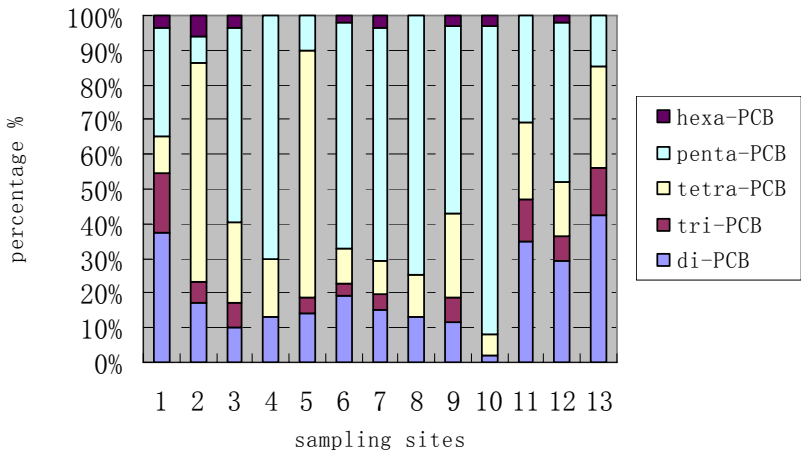

Figure 4. PCB composition (%) in sampling sites

Fihure 4 depicts the PCB composition in every sampling site for di-PCB, tri-PCB, tetra-PCB, penta-PCB and hexa-PCB. The average proportion were 19.2%，9.1%，20.2%，47.4% and 5.4%. Especially tri-PCB and hexa-PCB were not detected in some places.

Acknowledgements

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References

1. Fatin Samara; Christina W. Tsai; Diana S.Aga. Determination of potential sources of PCBs and PBDEs in sediment of the Niagara River. *Environmental Pollution*. 2006,139,489-497.
2. Ying Xing, Yonglong Lu, Richard W. Dawson, Yajuan Shi. A spatial temporal assessment of pollution from PCBs in China. *Chemosphere*,2005,60,731-739.
3. Characterization of trace organic contaminants in marine sediment from Yeongil Bay:2. Dioxin-like and estrogenic activities. *Environment Pollution*, 2006,142,48-57.
4. S. N. Meijer, W. A. Ocwenden, E. Steinnes, B.P. Corrigan. Spatial and Temporal Trends of POPs in Norwegian and UK Background Air: Implications for Global Cycling. Environ. Sci. Technol. 2003,37,454-461.
5. Bainer Lohmann, Foday M., Jaward, Louise Durham, Jonathan Barber. Potential Contamination of Shipboard Air Samples by Diffusive Emissions of PCBs and Other Organic Pollutants: Implications and Solutions. *Environ. Sci. Technol.* 2004,38,3965-3970.
6. Jonathan B. Butcher, And Edward A. Garvey. PCB Loading from Sediment in the Hudson River: Congener Signature Analysis of Pathways. *Environ. Sci. Technol*. 2004, 38,3232-3238.
7. Liu Jiang, Wang Wenhua,Wang Zijian. Sorts and contents of persistent pollutants in the sediment samples of the Second Songhua River. *China Environ. Sci*. 1998,18,518-520.