

OCPS IN SURFICIAL WATER AND SEDIMENT IN THE SONGHUA RIVER, CHINA

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1. Introduction

Organochlorine pesticides (OCPs), such as hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethane (DDTs), were widely used in agriculture in history worldwide, because of their low price and high effectiveness. OCPs have been attracted global concern due to their persistence, low biodegradability, wide range distribution in the environment and chronic adverse effects on wildlife and humans. Although their production, usage and disposal have been regulated or prohibited in most of the developed countries, OCPs are still used at present in many developing countries. As a large producer and consumer of OCPs, China produced 4 and 0.27 million tons of technical HCHs and DDTs over years before the “opening and reform” in China, which accounted for 33% and 20% of total productions of the world¹. So far, wide and intensive applications of OCPs have resulted in definite environmental pollution and human risk in various regions in China. The Songhua River, the third largest river in China, locates in the northeast of China and passes through the Jilin, Heilongjiang and Inner Mongolia Provinces. The main stream of the Songhua River is 939 km long, and covers the total surface area of 545,000 km². The Songhua River is one of the important rivers for water supply and irrigation in Northeastern China. Compared with other rivers in South China, the Songhua River was the only one river covered by ice for more than 5 months a year. Furthermore, the Songhua River is one of the most contaminated rivers in China, due to the industrial and agricultural activities along the river. The major aim of this study was to study the residual level, spatial distribution and seasonal variation of OCPs in the Songhua River.

2. Materials and methods

2.1 Sample collection

Water and sediment samples were collected in April (ice melting period), August (water abundance period) 2007 and January (ice covering period) 2008, respectively. The samples were collected in 14 various sites along the Songhua River from Jilin Province to the boundary between China and Russia (see Fig. 1), among which, two were downstream of industrial sites (1# and 5#), nine were downstream of business/residential sites (2#, 6#, 7#, 8#, 9#, 10#, 12#, 13#, and 14#), two were upstream of industrial/business sites (4# and 11#), and one was downstream of rural sites (3#). Water samples were collected by using brown glass bottles with Teflon-lined cap. After sampling, water samples were added 100 mL dichloromethane to prevent bacterial degradation. For sediment, five subsamples were pooled together to make one representative sample for each site, which was stored in an aluminum container at -20 °C until extraction².



Fig. 1. Sampling sites of water and sediment along the Songhua River, China

2.2. Analytical procedure

Water samples were extracted using the liquid–liquid extraction method, developed at the National Laboratory for Environmental Testing at Environment Canada, which can be found in our previous study³. Sediment samples were extracted by Soxhlet extraction method according to our previous study⁴. The clean-up procedure was modified from our previous study⁵. OCPs were analyzed by an Agilent 6890N gas chromatograph coupled with an Agilent 5973 mass spectrometer detector in selected ion monitoring mode. Separation was achieved on a HP-5MS capillary column (30 m×0.25 mm×0.25 μm, Agilent Co., USA). The column temperature programs were as follows: held at 80°C for 1 min, then raised from 80 to 160°C by 10°C min⁻¹ and held for 1 min, then from 160 to 250°C by 2°C min⁻¹, at last from 250 to 300°C by 30°C min⁻¹ and held for 5 min.

2.3. QA/QC

Matrix-spiked samples were analyzed to monitor method recovery. The average recoveries of all 19 OCPs are ranged from 79% to 133% and from 86% to 131% for water and sediment, respectively. Blank samples were included at a rate of one for every ten samples, and all results were blank corrected. The method detection limits (MDLs) of the 19 OCPs ranged from 5 to 16 ng/kg dw for sediments, and 0.03–0.37 ng/L for waters.

3. Results and discussion

3.1. Concentrations of OCPs in water and sediments

Only 16 OCPs were identified in the water samples, included hexachlorobenzene (HCB), HCH (α -HCH, β -HCH, γ -HCH), heptachlor epoxide, DDT (p,p' -DDT, o,p' -DDT, p,p' -DDD, p,p' -DDE), cis-chlordane(CC), trans-chlordane (TC), trans-nonachlor (TN), methoxychlor (METH), aldrin, endrin, dieldrin. The concentrations of methoxychlor (METH), aldrin, endrin, dieldrin, were lower than their detection limits. For CC, TC and TN, only some samples had higher concentration than their detection limits. HCHs and DDTs in all water samples were higher than their detection limits. The total OCP concentration in water samples ranged from 2.65 to 9.07 ng/L, with a mean concentration of 5.98 ng/L. The concentrations of Σ HCHs and Σ DDTs were ranged from 2.53 to 7.66 ng/L (mean value of 5.98 ng/L) and from ND to 0.93 ng/L (mean value of 0.08 ng/L), respectively. The highest Σ HCHs concentration was found at 6# (Bayan), and the lowest Σ HCHs concentration was found at 8# (Tonghe). The highest Σ DDTs concentration was found at 13# (Fujin), which was the downstream of the major business/residential site along the Songhua River (See Fig. 2).

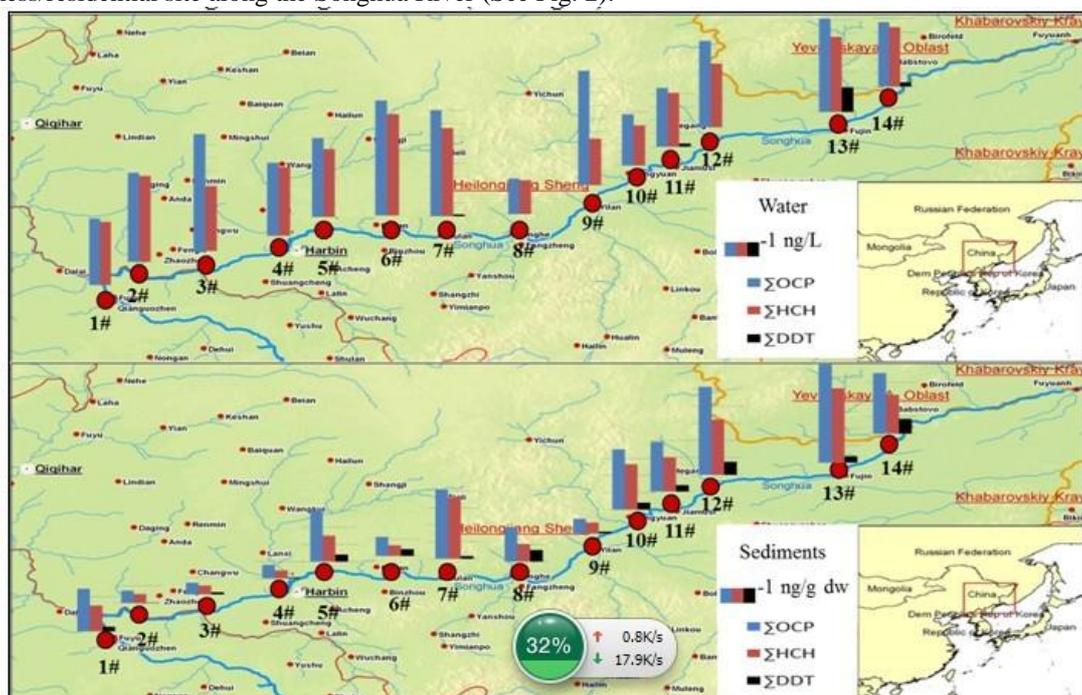


Fig. 2. Spatial distribution of the mean concentration of OCPs in water (ng/L) and sediment (ng/g dw) in the Songhua River, China

All of the 19 OCPs were identified in the sediment samples of the Songhua River. The concentrations of METH, HCB, Aldrin, endrin, dieldrin, and CC were lower than their detection limits. p,p'-DDE and p,p'-DDD were detected in most of sediment samples, but p,p'-DDT and o,p'-DDT could be detected in small portion of sediment samples. Same as water samples, HCHs and DDTs were detected in all samples. The Σ OCPs concentrations in sediment ranged from 0.70 to 6.01 ng/g dw, with a mean concentration of 2.87 ng/g dw. The concentrations of Σ HCHs and Σ DDTs were 0.45-4.24 ng/g dw (the mean concentration of 1.88 ng/g dw) and 0.04-1.58 ng/g dw (the mean concentration of 0.48 ng/g dw), respectively. As shown in Fig. 2, the highest concentrations of Σ HCHs and Σ DDTs were found at 5# (downstream of Harbin), 7# (Mulan), and downstream of the Songhua River (12#, 13#, 14#). The lowest Σ HCHs concentration was found at 4# (upstream of Harbin). It is interesting to note that the concentrations of OCPs in sediment in downstream of the Songhua River were higher than those of upstream of river, which indicated the sources along the river.

3.2. Composition of HCHs

Usually, technical HCHs contain 60–70% of α -HCH, 5–12% of β -HCH, 10–12% of γ -HCH and 6–10% of δ -HCH, respectively, with the ratio of α/γ -HCH between 3 and 7. Among the isomers of HCHs, β -HCH was the most stable and relatively resistant to microbial degradation. Therefore, predominance of β -HCH could be used for exploring source of historical usage of HCHs. Regarding the compositions of HCH isomers measured in water samples in the Songhua River, the highest percentage of β -HCH was found in all samples (75%-84%), followed by γ -HCH (11%-18%) (See Fig. 3). For sediment samples, the same compositional profile of HCHs was found, except for the 7# sample. So it can be concluded that the abundance of β -HCH indicated that the HCHs may be came from the historical used HCHs in the river region.

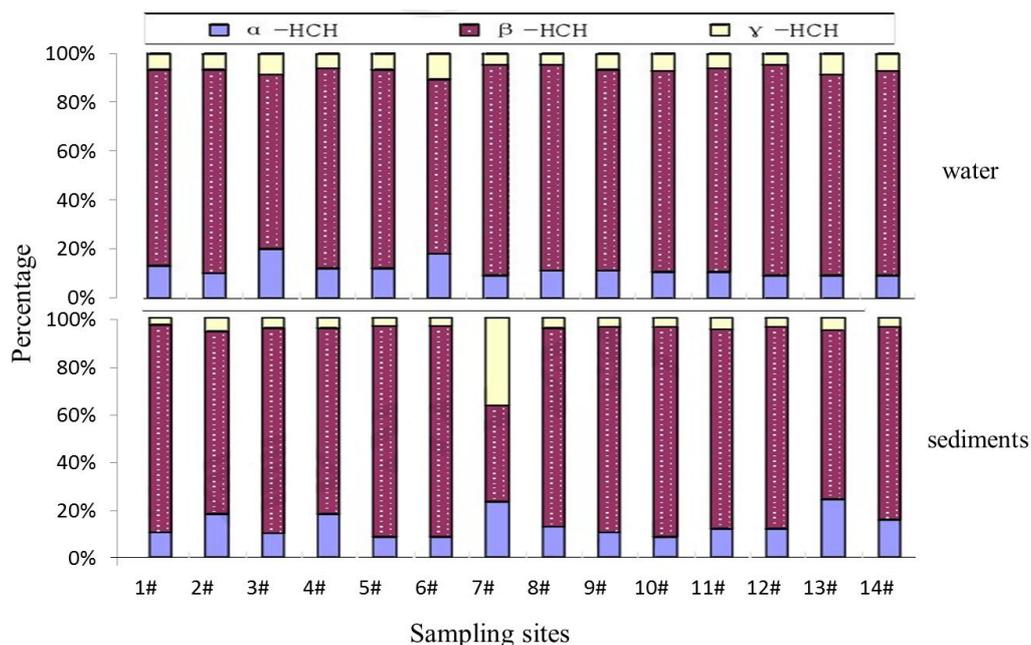


Fig. 3. Composition of HCHs in surface water and sediment samples in the Songhua River, China

3.3. Compositions of DDT

The relative proportions of the parent DDT and its metabolites can be used as indicators for assessing the contamination source. If there was no new technical DDT input, the compositional percentage of DDT would decrease and that of the metabolites (DDE and DDD) would increase, since DDT can be biodegraded under aerobic conditions to DDE and under anaerobic condition to DDD. Therefore, the ratio of DDT to (DDE+DDD) could be used as an indicator to identify the recent input of technical DDT. The ratio of DDT/(DDE+DDD) was higher than 1 at sampling sites 6# and 8# during ice melting period, and at sampling site 8# during water abundance period. For other sites, all the ratios were lower than 1, which indicated that the source of DDT in the river sediment may be from the historical used DDT. Furthermore, except for the site 8# during ice melting

period, the ratios of DDD/DDE were all lower than 1. This observation indicated that the technical DDTs can be more easily biodegraded to DDE under aerobic conditions, other than DDD under anaerobic condition.

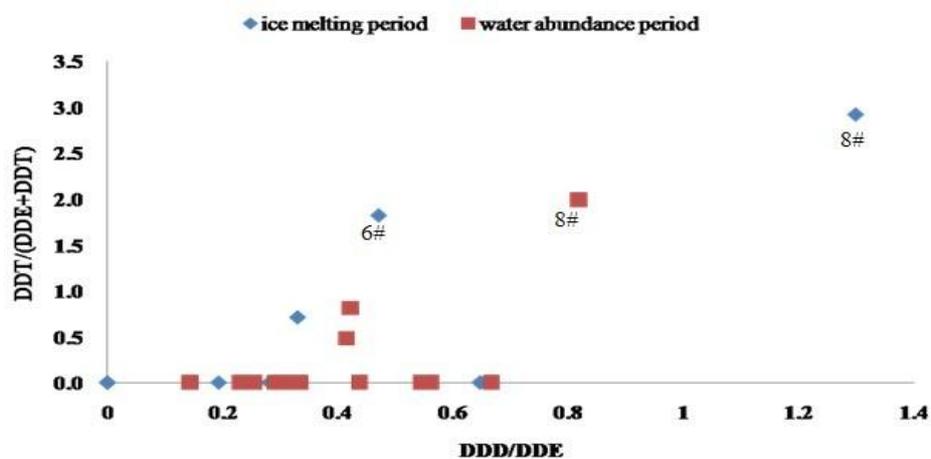


Fig. 4. Compositions of DDTs in sediment in two periods in the Songhua River, China

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