

Selected Organochlorine Pesticides in Surface Soil in Heilongjiang River Basin, China

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Abstract

Surface soil samples (0-20cm) were collected from 8 sites (one background site and 7 rural sites) across Heilongjiang River Basin (HRB) in China in 2005, to assess concentration level of HCH (1,2,3,4,5,6-hexachlorocyclohexane) and DDT (Dichlorodiphenyltrichloroethane) in soil. Average concentration of HCHs (α -HCH, β -HCH, and γ -HCH) for all 8 samples was 1.9 ng/g dry weight (dw) and ranged from 0.004 ng/g dw at the background site to 9.8 ng/g at one of the rural sites. The mean concentrations of Σ DDT (o,p'-DDT, p,p'-DDT, p,p'-DDE, and p,p'-DDD) in soil was 1.2 ng/g dw for all 8 samples, and ranged from below detection limit at the background site to 6.1 ng/g dw. It was found that both HCH and DDT in soil of HRB had weathered pattern, and the effects due to the use of lindane and dicofol in this region were minor. The concentration of Σ HCH and Σ DDT in HRB are in general lower than other regions in China.

Introduction

Organochlorine pesticides (OCPs) is a common name of a group of pesticides consisting of benzene and chlorine. Some of OCPs belong to Persistent Organic Pollutants (POPs) that are semi-volatile, bioaccumulative, persistent and toxic^{1,2}. OCPs are ubiquitous pollutants due to their long-range transport potential. These chemicals have even been found in remote areas like the Arctic³. Considering their harmful effects on man and wildlife, many international agreements are now coming into effect to reduce future environmental burdens.

In China, technical HCH (1,2,3,4,5,6-hexachlorocyclohexane) and DDT (Dichlorodiphenyltrichloroethane) were widely used in agriculture, which was the main pesticides accounting for about 78% of total pesticide production and usage before they were banned in 1983^{4,5}. The Heilongjiang River Basin (HRB) in China includes almost whole territory of Heilongjiang Province and parts of Jilin Province and Nei Menggu (Inner-Mongolia) autonomous region. Both agriculture and industry are relatively well developed within the basin. Between 1952 and 1983 the total usage in the HRB was 100 kt for technical HCH, and 5 kt for DDT, respectively, and the usage of lindane in the HRB was 0.1 kt from 1991 to 2000⁶.

In this study, the results of HCHs and DDTs concentrations in surface soil from 8 sites across Heilongjiang River Basin (HRB) in China are presented.

Material and methods

Sampling. Surface soil samples (0-20cm) were collected from 8 sites across HRB in China in 2005, among which, 1 are background site (B01), 7 are rural sites (R01-07) (Figure 1). All rural samples were from croplands. Samples were collected using a clean stainless steel spade. Five sections of soil, taken over an area of several square meters, were bulked together and mixed evenly to form one sample. Overlying vegetation was removed prior to collection of the sample. Samples were put in a solvent-rinsed glass bottle with Teflon-lined cap, sent to the laboratories in Harbin Institute of Technology where they were stored frozen (-20°C) until required for extraction.

Analytical methods. Details of sample process and analysis are presented elsewhere⁷. Briefly, samples were treated, extracted, and analyzed according to the methods established at the National Laboratory for Environmental Testing (NLET), Environment Canada. Five grams of soil were isolated for percent moisture determination and total organic carbon measurement, and 20g of each soil sample were accurately measured into a pre-cleaned extraction thimble and spiked with a recovery standard containing CB65 and 155. The samples were then Soxhlet extracted for 24h using acetone and hexane (1:1v/v). Extracts were cleaned and fractionated using silica chromatography which consisted of 2.5cm of anhydrous sodium sulfate, overlaid with 8cm of 3%

deactivated silica gel, and topped with another 2.5cm of anhydrous sodium sulfate. Once the column was pre-rinsed with 25ml of hexane, the sample was added and eluted with 40ml of hexane and then with 60ml mixture of hexane and dichloromethane(DCM, 1:1v/v). Fractions were blown down to about 1 ml under a gentle stream of UHP nitrogen and solvent-exchanged into isoctane. The internal standards CB30 and 204 were added to correct for volume difference.

Extracts of HCH and DDT were determined by GC-ECNI-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°C and 300°C. A 30-m DB-5MS column with 0.25mm i.d. and 0.25µm film thickness was operated with a helium carrier gas. The GC oven temperature program was as follows: initially held at 80 °C for 1 min, 10°C·min⁻¹ to 160°C, 20°C·min⁻¹ to 250 °C, 30°C·min⁻¹ to 300 °C, held for 5 min. The instrument was operated in selected ion mode (SIM). All OCPs calibration and internal standards were purchased from AccuStandard Inc. The method detection limits (MDLs) lower limit for quantitative analysis were 50 pg/mL for α-HCH, 550 pg/mL for β-HCH, 30 pg/mL for γ-HCH, 300 pg/mL for p,p'-DDE, 800 pg/mL for p,p'-DDD, 450 pg/mL for o,p'-DDT, 3500 pg/mL for p,p'-DDT. All samples were spiked with a labeled recovery standard (CB 65 and 155) prior to extraction. Sample recoveries averaged for CB 65 112±11% and for CB 155 111±12% in all samples. Blank samples were included for 8 soil extracted, and all results were blank corrected.

Results and discussion

HCHs. Concentrations of ΣHCH (α-HCH, β-HCH, and γ-HCH) in soil for each site, shown in Figure 1, had an average of 1.9 ng/g dry weight (dw) for all 8 samples and ranged from 0.004 ng/g dw at the background site B01 to 9.8 ng/g dw at site R02.

Two types of HCH products are manufactured throughout the world: technical HCH (containing about 55-80% α-HCH, 5-14% β-HCH, 8-15% γ-HCH) and lindane (γ-HCH>99%)⁵. Among the HCH isomers, β-HCH is the most persistent and less volatile isomer and tends to accumulate in soils in the source region, while α- and γ-HCH are more volatile and have a tendency to move to other places through atmospheric local and long-range transport. This is clearly shown from Figure 2. Concentration of β-HCH of the sample from the background site B01 was under detection limit while those for α- and γ-HCH are detectable, indicating that the residue of HCHs in this site is from other regions through atmospheric local or even long-range transport. On the other hand, β-HCH predominated the HCH compositions in the rural soil samples with percentages in ΣHCH from 37% to 89%. This was much higher than that of technical HCH, indicating a historical local technical HCH contamination rather than a fresh source.



Figure 1 Concentration of ΣHCH in surface soil samples from 8 sites in HRB, China.

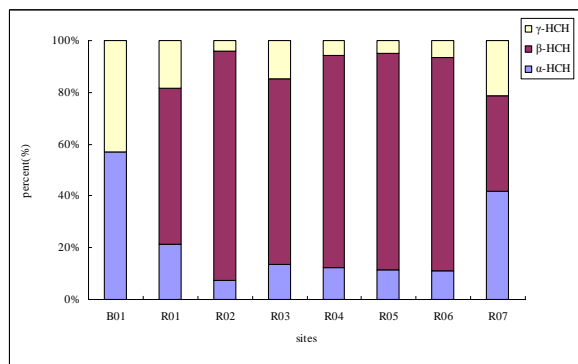


Figure 2 Percentage of HCH isomers in 8 surface soil samples

Based on the composition of two main HCH pesticide formulations, a high α/γ -ratio of HCHs in soils indicates the input of technical HCH and a low ratio for the use of lindane. Table 1 presents α/γ -HCH ratios for all 8 samples, which were from 0.92 to 2.3 with a mean value of 1.7. These were much lower than that of technical HCH (~5-6), indicating that the HCHs in studied soils were weathered residues of HCHs, technical HCHs in particular, used many years ago, and the influence of lindane use to the composition of HCHs in soil was minor.

Table 1 α/γ -HCH ratios in surface soil samples

Sites	B01	R01	R02	R03	R04	R05	R06	R07	mean
α/γ -ratio	1.333	1.158	1.820	0.915	2.159	2.294	1.702	1.942	1.666

DDTs. Concentrations of \sum DDT (o,p'-DDT, p,p'-DDT, p,p'-DDE, p,p'-DDD) in surface soil samples for each site, shown in Figure 3, had an average of 1.2 ng/g dw for all 8 samples and ranged from below detection limit (BDL) at Site B01 to 6.1 ng/g dw at site R06.



Figure 3. Concentration of \sum DDT in surface soil samples from 8 sites in HRB, China

Technical DDT typically contains 85% p,p'-DDT and 15% o,p'-DDT. In soil, DDT is microbially transformed to the stable and toxic metabolites DDE and DDD. The rate of transformation depends on several factors, including soil type, temperature, moisture and organic carbon content. In general, a small value (usually between 0.5 to 2) of the ratio of DDT/ (DDD+DDE) indicates weathered DD^{8,9}. As shown in Table 2, ratios less than 2.2 for the p,p'-DDT/(DDE+DDD) suggest a weathered pattern of DDT in the surface soils in the HRB.

High ratio of o,p'-DDT/p,p'-DDT has been used as an indicator for the source of dicofol, a pesticides used in China and contains a large portion of o,p'-DDT impurity¹⁰. Very low ratios of o,p'-DDT/p,p'-DDT were found in this study (Table 2), indicating very little source of dicofol in this region, which is expected, since the use of dicofol has not been common in this region. Dicofol has been widely used on cotton fields in China.

Table 2 pp'-DDT/(DDE+DDD) ratio and op'-DDT/pp'-DDT ratio in surface soil samples

Sites	B01	R01	R02	R03	R04	R05	R06	R07
p,p'-DDT/(DDE+DDD) ratio	-	0	2.187	0	1.452	1.229	0.999	0.875
o,p'-DDT/p,p'-DDT ratio	-	-	0.082	-	0.159	0	0.083	0.107

Comparison with published data. As shown in Table 3, the concentration of Σ HCH and Σ DDT in Heilongjiang River Basin lower than other places in China and Dehradun of India.

Table 3 Concentration of Σ HCH and Σ DDT in different region (ng/g dw)

Region	Σ HCH	Σ DDT	Year	Source
HRB ^a	0.0037-9.8205	0-6.1096	2005	This study
Pearl River Delta ⁷	0.05-24	0.52-414	2006	8
Guangzhou ⁷	0.19-42.3	3.58-831	2005	8
Tianjing ⁷	386.5-4689.1	628.1-2840.5	2002	8
Dehradun of India ⁷	122-638	13-238	2003	8

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