

Residues of Hexachlorocyclohexane Isomers and Their Distribution Characteristics in Soils in the Tianjin Area, China

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Abstract. Hexachlorocyclohexane (HCH) has a history of use in China. This paper presents the results of an investigation of HCH residue isomers and their distribution characteristics in soils near Tianjin, China. One hundred eighty-eight soil samples were collected from the Tianjin area. Four HCH isomers— α -HCH, β -HCH, γ -HCH, and δ -HCH—were detected using gas chromatography for all samples. Concentrations of the Σ HCH ranged from 1.3 to 1095 ng g⁻¹, among which β -HCH accounted for 52.5%. In addition, residues of HCH within Tianjin's urban areas were found to be higher. No significant differences were found between the residues of HCH in soils from waste irrigation areas and those in other areas. Total organic carbon content was determined to impact the residue levels of HCH in soils, while pH value and clay content were not related to concentrations of HCH. In general, all HCH isomers in soil samples had abnormally high residue levels, possibly the result of continuous use of HCH in this area.

Hexachlorocyclohexane (HCH) was first synthesized in 1825 by Michael Faraday, but the pesticidal properties were not identified until 1942 (Smith 1991). HCH has several isomers including α -, β -, γ -, and δ -HCH. The γ -isomer, also known as lindane, is the isomer with the highest pesticidal activity. Technical mixtures of all isomers, however, have been used as commercial pesticides (Li 1999a, b). These commercial mixtures typically contain about 60–70% α -HCH, 5–12% β -HCH, 10–12% γ -HCH, and 6–10% δ -HCH (Willett *et al.* 1998). HCH was widely used as an insecticide on fruits and vegetables, rice paddies, trees, and animals and as a seed treatment in the middle of the last century (Haugen *et al.* 1998). It also has been applied topically to people for the treatment of parasites. That HCH isomers are highly persistent in the environment and accumulation at higher trophic levels has been known for some

time (Moore and Walker 1964; Moore and Tatton 1965; Tatton and Ruzicka 1967). As with other organochlorine pesticides, HCH isomers are toxic to humans, especially to the central nervous system (CNS) (Willett *et al.* 1998). Many countries have stopped the use of HCH (Walker *et al.* 1999). China banned the use of organochlorine pesticides in the early 1980s (Cheng 1990). But in some areas of China, the residue levels of HCHs detected were comparatively high recently (Li *et al.* 1998).

Tianjin (116°42'05"–118°03'31"E longitude and 38°33'57"–40°14'57"N latitude) is one of the largest cities in northern China. Agriculture remains the major land use in its suburban areas. From the 1960s to the 1980s, large amounts of pesticides were used in the agricultural areas of Tianjin. Furthermore, wastewater has often been used to irrigate the soil, given the shortage of water in the region for the past 40 years (Tianjin EPA 1996). Accordingly, the history of pollution in the area is long and the sources of various contaminants complex. The main objective of the present study was to investigate the residue levels of HCH in the soils and identify possible differences in exposure levels.

Materials and Methods

Sample Collection

One hundred eighty-eight soil samples were collected from the Tianjin area in May 2001. The sampling locations covered 12,000 km², with a relatively uniform distribution (see Fig. 1). At each sample location, five samples were collected from a 100 × 100-m² plot and then thoroughly mixed to form a composite sample. All of the surface soils (10 cm) were collected using acid-cleaned stainless-steel scoops, then transferred to precleaned amber glass containers. All samples were maintained at 4°C prior to chemical analysis.

Sample Analysis

Reagents and Standards. All solvents used were distilled-in-glass (PR grade) and checked for interference prior to use. Granular anhy-

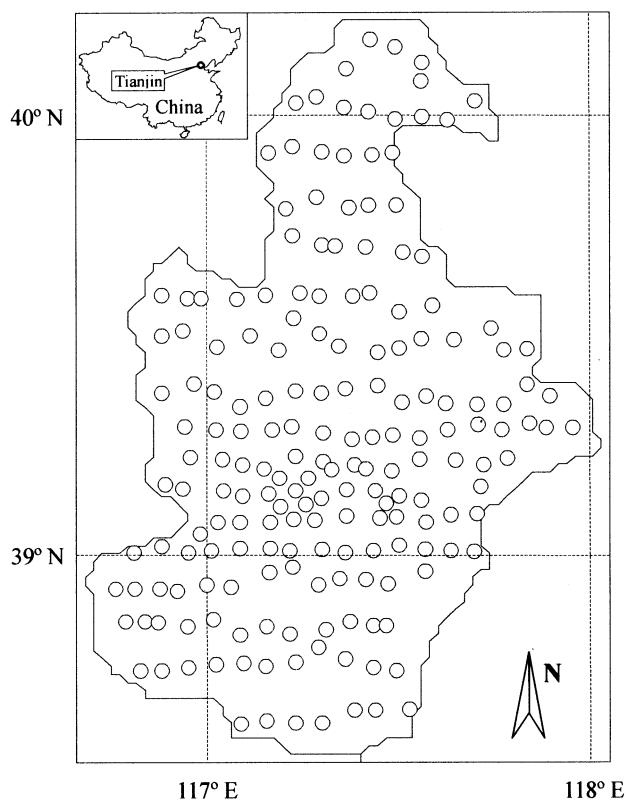


Fig. 1. Map of sample locations in the Tianjin area

drous sodium sulfate (AR grade) was heated to 650°C for 2 h prior to use. Florisil (60–100 mesh; PR grade) was activated at 130°C for 24 h and then kept in a closed container until used. The standards for α -HCH, β -HCH, γ -HCH, and δ -HCH were purchased from Chem-Service Corporation, Canada.

Extraction. The extraction of soil samples was carried out using an accelerated solvent extractor (DIONEX ASE 300) because of its previous evaluation as a possible rapid, low-solvent replacement for Soxhlet (Fisher *et al.* 1997). A 20-g soil sample (preground to pass through a size 70 mesh) was mixed with anhydrous sodium sulfate and packed into the 34-ml cell. The sample was then extracted for 5 min with 1:1 *n*-hexane/acetone at 100°C and 1500-psi pressure. The solvent extracts were collected in a precleaned collection vial.

Cleanup. The extracts were washed with a 100-ml solution of 4% sodium sulfate in a separating funnel, cleaned with approximately 15 ml of fuming sulfuric acid after removing the solution mixed with acetone, and cleaned twice with a 100-ml solution of 4% sodium sulfate. Elemental sulfur was removed by adsorption onto activated copper powder. The extracts were then concentrated to about 3 ml in a rotary evaporator at a temperature below 38°C. A chromatography column (10-mm ID \times 15 cm) with a stopcock at the bottom was filled with *n*-hexane, then 5 g of florisil was added and the column covered with a layer of sand mixed with anhydrous sodium sulfate to a depth of 20 mm. The *n*-hexane was drained until the solvent level reached the top of the sand. Then the remaining extracts were transferred to the florisil column, followed by elution with a mixture of 100 ml of 90% *n*-hexane and 10% acetone elution solvent at a rate of 1–2 ml/min. The eluate from the florisil column was collected and concentrated in the rotary evaporator. The residue was picked up with 3 ml of *n*-hexane,

transferred to a graduated test tube, and reduced to 1 ml with a stream of nitrogen.

Chromatographic Analysis. Samples were analyzed using an Agilent Gas Chromatograph 6890 equipped with a ^{63}Ni electron capture detector (μECD) and a HP-5 column (30 m \times 0.32-mm ID, 0.25- μm film thickness). Samples were injected by autosampling at 50°C in the splitless mode with a venting time of 0.75 min. The oven temperature was programmed to increase from 50 to 150°C at a rate of 10°C/min, then at 3°C/min to 240°C, where the temperature was maintained for 15 min. Nitrogen was used as the carrier gas (1 ml/min) and makeup gas (60 ml/min). Injector and detector temperatures were 220 and 280°C, respectively. Peak areas were quantified using mirex as the internal standard and calculated with Chemstation software (from Agilent). Recoveries of α -HCH, β -HCH, γ -HCH, and δ -HCH for fortified samples were 72.8, 93.2, 79.1, and 73.2%, respectively. The detection limits for the soil samples were 0.01 ng g $^{-1}$ for β -HCH and 0.05 ng g $^{-1}$ for α -HCH, γ -HCH, and δ -HCH. A procedural blank was run with every set of 20. The mean blanks were 0.12, 0.18, 0.15, and 0.19 ng g $^{-1}$ for α -HCH, β -HCH, γ -HCH, and δ -HCH, respectively. Two duplicates were measured for every sample.

Data Process

ANOVA and *t*-test were carried out using SPSS 10.0 statistical software, while the contour maps were protracted using Surfer 7.0.

Results

A log-normal distribution was identified for the measured data by Kolmogorov–Smirnov test and log transformation was, therefore, performed. The concentrations of the four HCH isomers are presented in Table 1. Differences in the residues of some HCH isomers between the urban area and other areas are listed in Table 2. The temporal changes in the contaminants at different times are indicated in Figure 2.

The data in Table 1 show that organochlorine pesticides were detected in almost all of the soil samples from Tianjin. Concentrations of the ΣHCH ranged from 1.3 to 1095 ng g $^{-1}$. The residue of β -HCH was the highest among the four HCH isomers (from 0.3 to 1043 ng g $^{-1}$). The other three isomers, α -HCH, γ -HCH, and δ -HCH, had the same concentration levels in the soil (mean concentrations of 7.0, 5.5, and 9.3 ng g $^{-1}$, respectively). β -HCH was the main contaminant, accounting for 52.5% of the total isomers. γ -HCH, on the other hand, was the minimum, accounting for only 12.1%.

From Table 2 it can be seen that the concentrations of α -HCH, β -HCH, and ΣHCH in the urban area were significantly higher than those identified for other areas. Although HCH has been used as an insecticide on crops for a long time, it also has been applied topically to humans for treatment of lice and scabies (Willett *et al.* 1998).

The results presented in Figure 2 indicate some differences between the residues of the ΣHCH in soils from 12 regions of Tianjin 20 years ago (Tianjin EPA 1986) and the results obtained in the present study (Fig. 2). The mean of ΣHCH residues in the whole Tianjin area decreased from 186.8 to 29.1 ng g $^{-1}$ after 20 years. Ninety-eight percent of the ΣHCH in soils from Bodi was degraded, and the residual

Table 1. Concentrations (ng g^{-1} , dry weight) of α -HCH, β -HCH, γ -HCH, δ -HCH, and Σ HCH^a in soil samples from Tianjin, China^b

	α -HCH	β -HCH	γ -HCH	δ -HCH	Σ HCH
Mean	7.0	24.0	5.5	9.3	45.8
SD	23.8	91.8	20.6	43.2	141
Maximum	296	1043	269	551	1095
Minimum	0.3	0.3	0.05	0.4	1.3
Geometric mean	2.5	5.0	2.0	2.5	14.5
Median	2.0	3.7	1.8	1.9	9.8
Proportion (%)	15.2	52.5	12.1	20.3	100

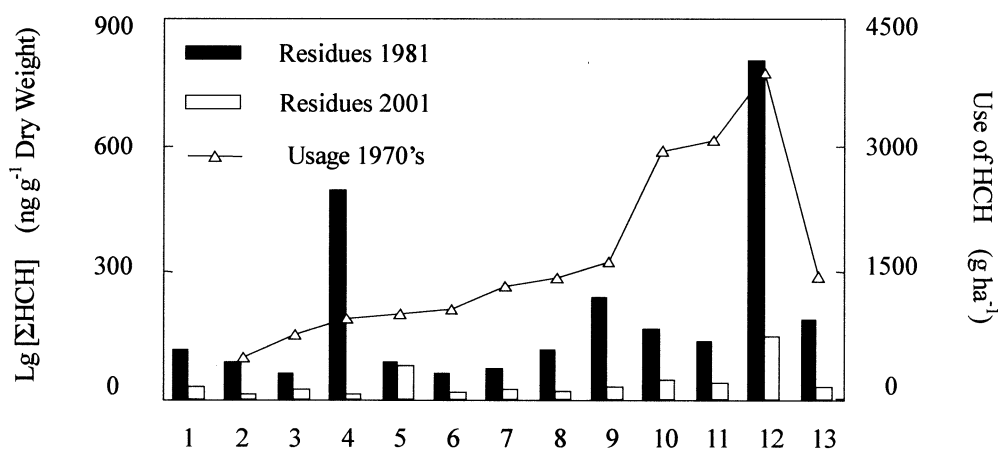
^a Σ HCH represents the sum of the α -HCH, β -HCH, γ -HCH, and δ -HCH concentrations.

^b Mean, standard deviation, maximum, minimum, geometric mean, and median were calculated assuming that the measurements below the detection limit were equal to the detection limit; detection limits for individual soil samples ranged from 0.01 to 0.05 ng g^{-1} .

Table 2. Geometric mean and *t*-test of HCH isomers using log-transformed concentrations between the urban area and other areas (ng g^{-1} , dry weight)

	α -HCH	β -HCH	γ -HCH	δ -HCH	Σ HCH
Geometric mean					
Urban area (<i>n</i> = 18)	4.5	10.6	2.7	5.1	19.8
Other areas (<i>n</i> = 170)	2.4	4.6	2.0	2.4	10.0
<i>t</i> -test					
<i>t</i>	2.293	2.318	0.92	1.641	2.178
<i>p</i> value	0.023*	0.022*	0.359	0.118	0.031*

Note. * Significant at the 0.05 level.

**Fig. 2.** The temporal changes of Σ HCH in soils from different regions

ratios for Σ HCH in soils from other regions (Dagang, Dongli, Ji, Jinnan, Jinghai, Ninghe, Wuqing, and Xiqing) ranged from 15 to 30%. Beicheng, Hangu, and Tanggu were exceptions to the abnormally high residue levels of Σ HCH (1094.6, 1050.4, and 1078.9 ng g^{-1} , respectively) in soil samples collected purposely from the circumambience of three pesticide-production plants. Residue levels of Σ HCH remain high in those regions where residual levels of Σ HCH were high in 1981 (Jinnan), and they are low in regions where they were low 20 years ago (Jinghai, Ninghe). The residual ratios of Σ HCH, however, remain high in soils from most regions. In general, it could be seen that the residues of Σ HCH in soils were influenced by their residual levels 20 years ago.

Discussion

Concentrations of HCH Isomers

All HCH isomers had higher residue levels than those identified in other reports (Harner *et al.* 1999; Kim and Smith 2001) (see Table 1). β -HCH, whose maximum concentration was above 1043 ng g^{-1} , accounted for more than 50% of the total HCH isomers. Similar results were found in another study (Cavanagh *et al.* 1999). The degradation rates of HCH isomers depend, to a large extent, on different environmental conditions. In many cases the removal rates of HCH isomers from a HCH technical mixture-treated agriculture plot were α - > γ - >

δ - > β -HCH (Chessells *et al.* 1988; Willett *et al.* 1998). β -HCH is the most persistent isomer with respect to both chemical and microbial degradation (Willett *et al.* 1998; Manz *et al.* 2001). This possibly follows from the fact that all of its chlorines are in equatorial positions (Buser and Müller 1995).

China has banned the use of technical HCH since 1983 and lindane since 1993 (Cheng 1990; Zhang 1996). As such, residues of HCH isomers from Tianjin soils should be lower based on degrading reaction kinetic algebra (Mackay 1991). Residual levels of HCH isomers, however, were found to be much higher than theoretically expected. This seems to support the idea that use of HCH in this area has not stopped completely, given the abnormally high concentrations of HCH isomers still found in the soils there.

Concentrations in Wastewater Irrigation Areas

Wastewater has been used to irrigate the agricultural soils in the Tianjin area since 1958, primarily due to the shortage of water (Tianjin EPA 1996). Three big sewer canals containing city sewage and industrial wastewater flow through Tianjin. The samples collected from the wastewater irrigation areas (WIA; $n = 126$) were compared with those from non-wastewater irrigation areas (NWIA; $n = 62$). Three types of soils from WIA were classified based on their usage history: pure wastewater irrigation ($n = 41$), interval wastewater irrigation ($n = 11$), and clean-wastewater mixture irrigation ($n = 10$). For most HCH isomers (β -HCH, γ -HCH, δ -HCH) and Σ HCH, there were no significant differences among the different irrigation areas except for α -HCH ($p = 0.03$). Although pollution from heavy metals such as Cd, Hg, As, Cu, Pb, and Cr in these wastewater irrigation areas was severe, contamination stemming from the use of organic pesticides has not been clearly established (Hu 1999). Based on the results associated with this study, it appears that the type of irrigation is not the main factor affecting the concentrations of HCH isomers.

Effect of Soil Properties

Soil particles form a fine mesh that filters solid material out of seeping water; simultaneously the soil pores function as a storage site for materials. Humus provides for a firmer fixation, with numerous contaminants attached to them. Soil characters such as pH, clay content, and total organic content (TOC) are thought to have some role in determining the concentrations of pollutants (Fellenberg 2000). As an important feature of soil, pH could influence some characters of the soil. Likewise, some compounds in the soil, such as organochlorine pesticides, could also be affected. The pH values for the areas considered in the present study ranged from 5.22 to 9.03, with most of them in the range 7.0–9.0. A correlation analysis carried out between pH (after Box–Cox power transformation) and Σ HCH (in logarithm) detected no significant correlation ($r = -0.032$, $p = 0.661 > 0.05$). Stevenson (1982) found that nonionic pesticides were not affected by pH changes, a result similar to the results here.

For the soils examined in this research, the clay content ranged from 17.1 to 50.7%, while the TOC ranged from 7.5 to

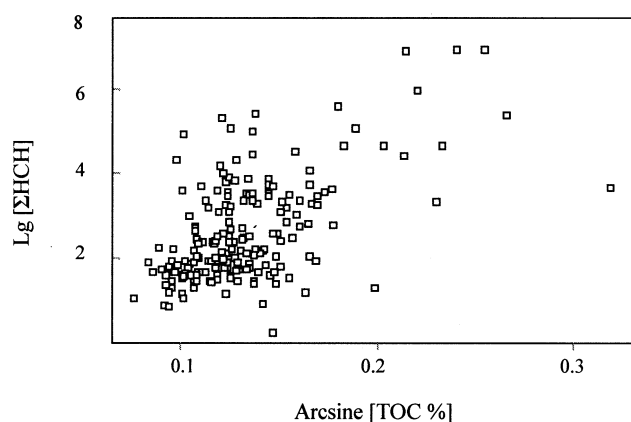


Fig. 3. Scatterplot of $\log[\Sigma\text{HCH}]$ and $\arcsine[\text{TOC} \ %]$ in soils from Tianjin

31.4%. Based on the results of normality test, both clay content and TOC were trigonometrically transformed for normality. Arcsine-clay and arcsine-TOC were used to analyze the relationships with residues of Σ HCH (transformed to logarithm). As with pH, the correlation between the clay content and Σ HCH was not significant ($r = 0.133$, $p = 0.069 > 0.05$). Some of the characteristics of HCH, such as high vapor pressure, high volatility, and high solubility in water, may be responsible for the nonsignificant outcome. Sanger (1999) reported that the distribution of organic contaminants was not concordant with the clay content of the sediment and the amount of TOC (Sanger *et al.* 1999). But in this study, there was a strong positive correlation between the TOC and the residue of Σ HCH ($r = 0.594$, $p < 0.0001$) (Fig. 3). Contour maps of TOC and Σ DDT in the soil samples are shown in Figure 4. High concentrations of Σ HCH can be seen in the middle, southern, and eastern parts of Tianjin, indicating a strong association with TOC. In other studies (Boehm and Farrington 1984; Barrick and Prah 1987) similar positive correlations between TOC and organic contaminants were also reported. Humic acid constitutes the main portion of soil organic constituents. In most cases, humic acid and various organic contaminants are subject to strong interactions (Alawi *et al.* 1995; Park *et al.* 2000). It is possible that such interactions may lead to the correlation between them.

Effect of HCH Usage

The quantity of organochlorine pesticides used between 1970 and 1980 was considered to be a factor influencing HCH concentrations in agriculture soils. About 200 villages are variously distributed in the suburbs of Tianjin. Information about the quantities of HCH usage in these villages was surveyed (Tianjin EPA, not published). Since the locations of DDT application data do not match the surface sampling locations, the data were geometrically interpolated, taking the reciprocal of squared distance as the weighting factor.

The interpolated application rate at the soil sampling locations ranged from 1.95×10^{-1} to $85.5 \times 10^{-1} \text{ kg ha}^{-1}$. Based on these ranges, two groups were classified according to cal-

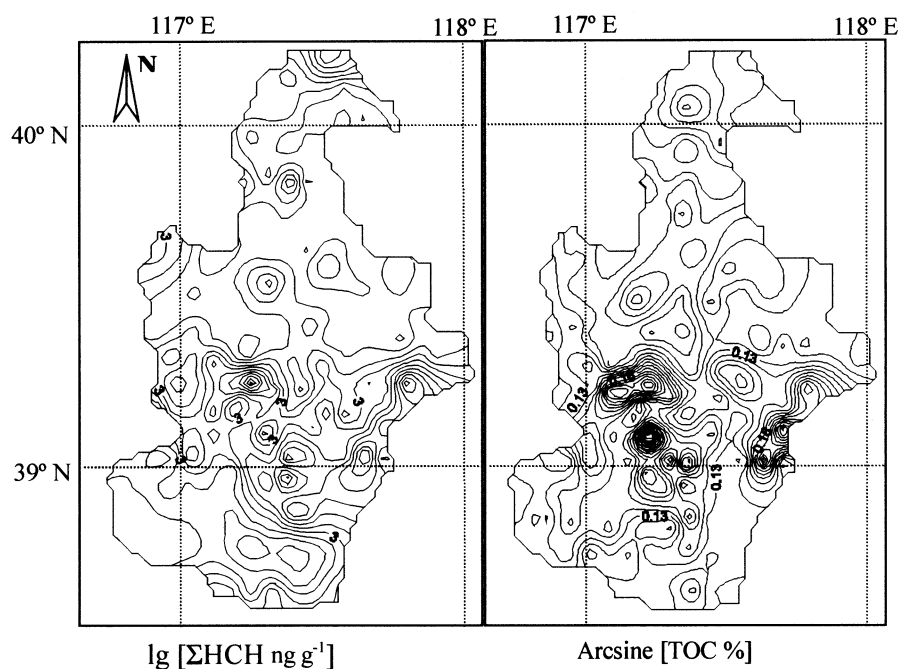


Fig. 4. Contour maps of $\log[\Sigma\text{HCH}]$ and $\arcsine[\text{TOC}]$ in soil samples from Tianjin

culated application rates: Group 1, with application rates of less than $15.00 \times 10^{-1} \text{ kg ha}^{-1}$ ($n = 96$), and Group 2, where the application rates exceeded $15.00 \times 10^{-1} \text{ kg ha}^{-1}$ ($n = 92$). The t -test results for each of the HCH compounds were found to be significant (t , -2.916 to -5.052 ; p , 0.000 – 0.004). The concentrations of HCHs in Group 2 were all higher than those identified in Group 1. A Pearson correlation analysis was also carried out between the residue of ΣHCH (in log form) and prior usage of HCH ($r = 0.311$, $p = 0.0001$). The results indicate that the greater the previous use of HCH, the higher the residues of HCH at present. It seems evident that the amount of previous HCH usage is responsible for the present residue levels of HCH in soils.

Conclusions

High concentrations of HCH isomers were detected in soils in and around Tianjin, China. Among the isomers detected, β -HCH accounted for slightly more than half of the total HCH residues. Since use of HCH has been banned for approximately 20 years, the abnormally high concentrations of HCH isomers in soils seems to suggest that HCH is still being used in the area. No significant differences were found in the HCH residues in soils associated with different irrigation techniques, despite the fact that wastewater has been used as an irrigation technique in Tianjin since 1958. In addition, significant concentrations of HCH were also found within the urban district. With the exception of TOC, other soil features such as pH value and clay content were not found to have influenced the concentrations of HCH residues found in the soil. The residues of ΣHCH associated with the historic usage of HCHs in the region, in addition to some potential current use of HCH, might explain the levels of contaminants found today.

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