Distribution of dichlorodiphenyltrichloroethane and hexachlorocyclohexane in urban soils and risk assessment

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Abstract

This study deals with the distribution of dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs) in urban soils, their possible sources and probabilistic human and environmental health risk. The average concentrations of total HCHs and total DDTs in the soils were in the range of 0.56-8.52 μg kg^{-1} and 0.54-37.42 μg kg^{-1}, respectively, which were lower than guideline limits. The compositional analysis of HCH isomers reflects contaminations from recent usage. However, isomeric ratios between DDT, DDE and DDD, indicate anaerobic degradation of DDT and contaminations from aged DDT. Human and environmental health risk assessment was carried out by the estimation of lifetime average daily dose (LADD), incremental life time cancer risk (ILCR) and non carcinogenic health hazard quotient (HQ). LADD of total pesticides (HCH and DDT) for human adults and children was ranged between 3.3×10^{-9}-6.6×10^{-8} mg $kg^{-1}d^{-1}$and 1.7×10^{-8}-3.4×10^{-7}mg kg^{-1} d^{-1}, respectively. The cumulative ILCR for adults and children was ranged from 5.1×10^{-9} to 4.6×10^{-8} and 2.6×10^{-8} to 2.4×10^{-7}, respectively. The HQ was ranged between 1.8×10^{-6}-1.4×10^{-4} and 9.5×10^{-6}-7.2×10^{-4}, respectively for adults and children. These estimated ILCR and HQ were within the safe acceptable limits, indicating negligible risk to the residents of the study area.

Introduction

Dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH), which are highly toxic organic pollutants, also known for their long range atmospheric transport affecting regions far from their release sources.[1] In May 2001, DDT was listed as one of the 12 persistent organic pollutants by the Stockholm convention. Recently in 2009, HCH isomers (α-HCH, β-HCH and γ-HCH) were also included in the same category.[2] In several European countries, DDT and HCH had been already prohibited or strictly restricted but these are still being produced, exported and also used in many countries around the globe due to their low cost and various uses in industries and public health programmes. DDTs and HCHs are a major concern because of their persistence, bioaccumulation, toxicity, and long-range environmental transport ability. They have been recognized for their potential to adversely affect wide variety of plant and animal species, including humans.[3–6] These are also known as endocrine-disrupting pesticides to human beings, as their exposure through occupational and environmental means was found closely associated with cancer of the breast, ovary, prostate, testis, and thyroid in humans.[7]

The characteristic properties of DDT and HCH make them accumulative in soil, sediments, biota and human tissues for longer period.[8–9] Due to the quantity of soil, strong sorption of these pollutants by the organic matter present in the soil and resistance to degradation, soils are generally known as the sink and source for these pollutants.[10] DDT and HCH migrate from contaminated soils to other environmental compartments (sediment, water, atmosphere, and biota) through volatilization, erosion of soil particles, ground water or surface water transport, and bio-concentration in biota.

Human health risk assessment due to exposure to toxic contaminants had been undertaken worldwide for more than 30 years in various environmental media and foodstuff.[11] Humans may get exposed to toxic contaminants, mainly through the consumption of contaminated food and occupational environments, but a significant exposure can also takes place through soil intake via ingestion, inhalation or dermal contact, because of close proximity of soil to humans.[12–14] In urban areas, soils are contaminated with organic contaminants such as organochlorines (OCs), consequently adults and children may get exposed to health risk through ingestion of soil from their local areas.[15–16] For this reason, it is important that soil ingestion could be considered in any risk assessments involving their potential as harmful persistent organic pollutants.[17–19]

Previous studies in India, have reported DDT and HCH concentrations in agricultural soils from different provinces of India such as Haryana,[20–21] National Capital Region[22–23]and UP,[22,24–25] but work has never been conducted on urban residential soils in India. Documented research exists worldwide, to predict the risk to the residents' health, based on pesticide residue distribution in residential soils of urban and suburban areas.[26–28] Therefore, this study was conducted; i) to estimate HCH and DDT levels in urban soils, ii) to identify the sources of the HCH and DDT, and iii) to estimate the potential of human and environmental health risks.

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Material and Methods

Study area and sampling

Kurukshetra city is a developing town in Thanesar sub-district of the Haryana state of India, located at 160 km north of New Delhi the capital of India. This city with the population of 641 thousands covering a stretch of approximately 120 km^2 area is extended between geographical coordinates of 29.97°N and 76.85°E. The climatic conditions are very hot in summer (>47°C) and during winters it is cold (<1°C) with average annual rainfall of 582 mm.

Sampling was carried out during June 2012 from thirteen locations covering hospital, residential, tourist places, educational and busy traffic intersections areas. Approximately, 500 grams of soil was collected from three points of each sampling location (Figure 1). After collection, materials such as pebbles, plant leaves and wood sticks were removed manually. Collected soils from each location were mixed thoroughly to ensure the true representative samples of each location. Then a sufficient quantity of soil was transferred into cleaned wide mouth amber glass Teflon lined bottles.

Labeled containers with soil samples were transported with ice to the laboratory and kept at 4°C until further extraction.

Chemicals and solvents

Chemicals (anhydrous sodium sulphate, silver nitrate, potassium hydroxide, and sulphuric acid) and solvents (acetone, methanol, dichloromethane, and hexane) were purchased from Merck, India. Silica gel 60 (0.063-0.100 mm) was purchased from Supelco (Sigma-Aldrich, St. Louis, MO, USA). Silica gel, potassium hydroxide and sodium sulphate were cleaned separately with methanol, dichloromethane and acetone in Soxhlet extractor for 8 h each, and stored in air tight containers at 130°C. Individual pesticide reference standard solutions of HCHs (α-HCH, β-HCH, γ-HCH, and δ-HCH) and DDTs (*p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT) were procured from Supelco (Sigma-Aldrich).

Sample extraction

Soil samples were extracted using pressurized liquid extraction procedure as per USEPA's Methods.[29] Briefly, 15-20 g sample was homogenized and dried by mixing with diatomaceous earth (ASE prep DE, Dionex, USA) to get free-flowing powder. The extraction was carried out with accelerated solvent extractor (ASE-350, Dionex)[30] using acetone: hexane (v/v, 1:1) in two cycles with 5 min. static time. The ASE was operated at 1500 psi and the oven was heated to 100°C. The extracts were concentrated to 2.0 mL using Rotatory Vacuum evaporator (Eyela, Tokyo, Japan).

Chromatographic column cleanup

The multilayered silica gel column chromatography was performed for fractionation and to remove interfering organic and polar species. Briefly multilayered silica gel column (300×30 mm) was packed from bottom to upward with 2.5 g silica gel, 4.0 g silver nitrate coated silica gel, 2.5 silica gel, 4.0 basic silica gel, 2.5 g silica gel, 12.0 g acid silica and 5.0 g anhydrous sodium sulphate. The column was pre-rinsed with 100 mL n-hexane before sample was loaded. The elution of analytes was subsequently carried out using 170 mL hexane and concentrated to 2.0 mL. The eluted extract was concentrated using Rotatory Vacuum evaporator and under gentle stream of pure nitrogen in Turbo Vap (Caliper, Princeton, NJ, USA) to 1.0 mL. The extract was transferred into autosampler vial and 1 μL was injected onto a gas chromatograph equipped with an electron capture detector (GC-ECD) for quantification.

Instrumental analysis

Analysis of HCH (α-HCH, β-HCH, γ-HCH, and δ–HCH) and DDT (*p,p'*-DDE, p,p'-DDD, *o,p'*-DDT and *p,p'*-DDT)isomers was carried out using gas chromatograph (Perkin Elmer, Clarus 500) attached with autosampler and equipped with an electron capture detector (ECD, ^{63}Ni). Compound separations were done on Elite-1, fused silica capillary column 25 m×0.20 mm with 0.33 μm particle film (5% diphenylpolysiloxane, 95% dimethylpolysiloxane). The column oven temperature of the gas chromatograph was initially maintained at 170°C and increased to 220°C (7°C min^{-1}); temperature was further ramped to 250°C at 5°C min^{-1} and held for 6.86 min. The temperatures of injector and detector were maintained at 250°C and 350°C, respectively. Nitrogen gas (purified laboratory grade) was used as carrier at the flow rate of 1.0 mL min^{-1}.

Analytical quality control

Certified reference standard solutions were used for instrument calibration and other quality control studies. Concentrations of target compounds were determined with an external standard method comparing peak area in samples with the standards. Peak identification was conducted with the accurate retention time of each standard using five levels of calibration curves of standards (r^2 value, 0.999). Appropriate quality assurance quality control analyses were performed. Procedural blanks were analyzed to check cross contamination and interferences (analyzed concentrations were below the method detection limit; MDL). Random duplicate samples analysis (standard deviation <5), calibration verification (standard deviation <5) and matrix-spiked studies were carried out for quality control. Samples were spiked with known working standard solutions of analytes, extracted and analyzed in the same way as the real samples. Recoveries were in the range of 86-107% (±3-11%) for each compound. Each sample was analyzed in duplicate and the average of representative data used in calculations. Concentrations below reporting limit (0.01 μg kg^{-1}) were considered as zero in calculations. Moisture content of the samples was separately determined to report results on dry weight basis in μg·kg^{-1}.

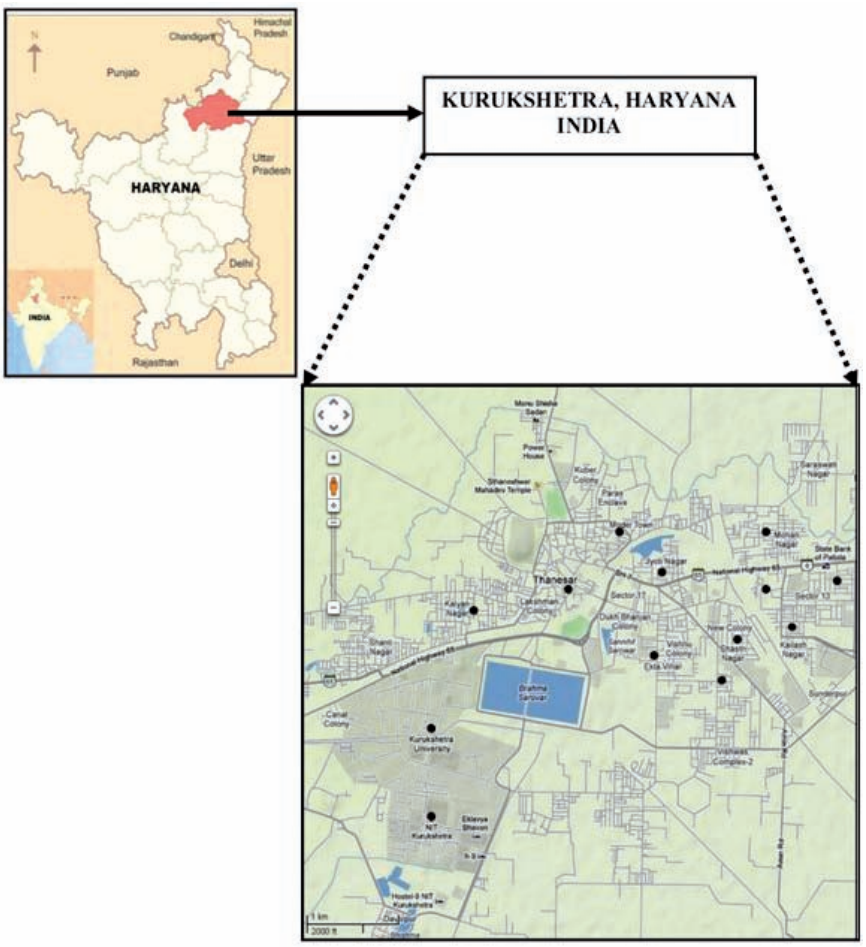


Figure 1. Map showing study area and sampling locations.

Assessment of human health risk

Ingestion, inhalation and dermal contact are considered as the main pathways for intake of contaminants in humans. In this study, incremental lifetime cancer risk (ILCR) to humans was assessed by calculating the lifetime average daily dose (LADD) of HCHs and DDTs through ingestion of soils.[6,31] The following equations were used for estimating the LADD and ILCR.

$$\text{LADD (mg kg}^{-1}\text{ day}^{-1}) = (Cs \times IR \times F \times EF \times ED)/(BW \times AT)$$

$$\text{Incremental Life time Cancer Risk (ILCR)} = \text{LADD} \times \text{CSF}$$

$$\text{Hazard Quotient (HQ)} = \text{LADD/RfD}$$

Where, Cs is the pollutant concentration in soil (mg kg^{-1}), IR is the soil ingestion rate (100 mg d^{-1} for adult and 200 mg d^{-1} for children), F is the unit conversion factor, EF is exposure frequency (365 days/year), ED is the life time exposure duration (adults, 70 years; children, 12 years), BW is the body weight (adults, 70 kg; children, 27 kg), and AT is the averaging time for carcinogens (EF×ED). CSF and RfD is cancer oral cancer slope factor and reference dose for a particular compound intake (mg kg^{-1}d^{-1}), respectively.[32]

Results

The observed concentrations of individual HCH and DDT isomers and their total in soils from this study were presented in Table 1. Total HCHs and DDTs concentrations were ranged between 0.56-8.52 μg kg^{-1} and 0.54-37.42 μg kg^{-1} with averaged values of 3.00±0.54 μg kg^{-1} and 7.88±3.07 μg kg^{-1}, respectively. The individual HCH isomers; α-HCH (1.07 μg kg^{-1}), β-HCH (1.40 μg kg^{-1}), γ-HCH (1.2 3μg kg^{-1}), and δ-HCH (0.76 μg kg^{-1}) accounted for 9.1%, 7.9%, 9.5% and 1.1%, respectively to total pesticides. However, DDT isomers contributed more to the total pesticides. The average concentration of *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT was 2.32 μg kg^{-1}, 4.18 μg kg^{-1}, 4.47 μg kg^{-1} and 1.71 μg kg^{-1}, respectively, and accounted for 21.4%, 23.6%, 19.0% and 8.4%, respectively to total pesticides. DDTs were higher than HCHs and contributed for 59% to total OCs (Figure 2). The spatial distribution of total pesticides is presented in Table 2.

Table 1. Concentration range and mean of dichlorodiphenyltrichloroethane and hexachlorocyclohexane isomers in soils (μg kg^{-1}).

Compounds	Range		Mean	SD	SE
	Min	Max			
HCH isomers					
α-HCH	0.56	2.09	1.07	0.46	0.13
β-HCH	0.54	3.24	1.40	0.90	0.25
γ-HCH	0.75	2.24	1.23	0.41	0.11
δ-HCH	0.57	0.95	0.76	0.27	0.07
∑HCH	0.56	8.52	3.00	1.93	0.54
DDT isomers					
p,p'-DDE	0.54	8.49	2.32	2.38	0.66
p,p'-DDD	0.66	18.03	4.18	5.81	1.61
o,p'-DDT	0.59	10.90	4.47	4.98	1.38
p,p'-DDT	0.55	7.06	1.71	2.38	0.66
∑DDT	0.54	37.42	7.88	11.07	3.07
Total	2.29	45.94	10.88	12.85	2.74

DDT, dichlorodiphenyltrichloroethanes; HCH, hexachlorocyclohexane; SD, standard deviation; SE, standard error=SD/√n.

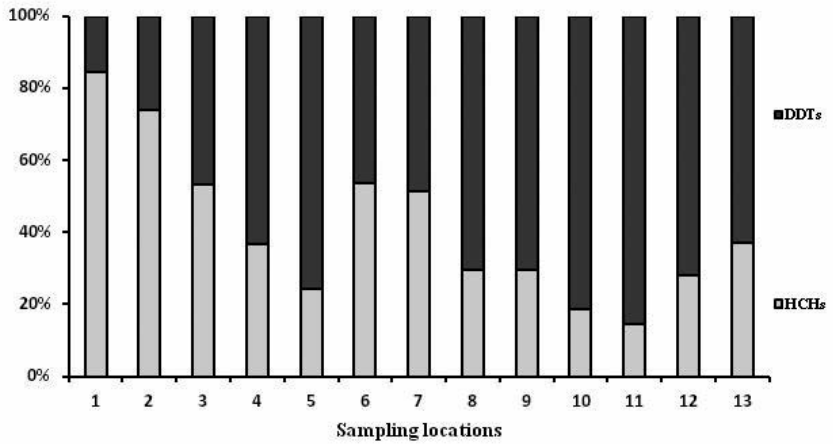


Figure 2. Percentage of dichlorodiphenyltrichloroethanes and hexachlorocyclohexanes in soils at different locations.

Table 2. Concentration of total pesticides in soils at different locations (μg kg-1).

Location	Range		Mean	SD	SE
	Min	Max			
1	0.54	1.17	0.87	0.28	0.08
2	0.88	1.32	1.12	0.22	0.06
3	0.59	0.84	0.69	0.11	0.03
4	0.56	1.61	1.04	0.40	0.11
5	0.56	1.05	0.76	0.26	0.07
6	0.54	1.07	0.78	0.24	0.07
7	0.95	2.09	1.43	0.59	0.16
8	0.77	4.34	2.14	1.59	0.44
9	0.93	5.38	2.03	1.69	0.47
10	0.95	18.03	6.56	6.26	1.73
11	0.75	10.86	4.24	3.66	1.01
12	0.57	1.85	1.31	0.53	0.15
13	0.66	1.30	0.96	0.29	0.08

SD, standard deviation; SE, standard error.

Discussion

Possible source identification of dichlorodiphenyltrichloroethanes and hexachlorocyclohexanes

Compositional analysis of HCH and DDT isomers in the environment is used to identify the contamination sources. Generally, HCH is available as technical HCH and lindane formulations. Technical HCH has been produced and used in India as a broad-spectrum pesticide for agricultural purposes until it was banned. γ-HCH formulation is registered for use in public health practices to control vector borne diseases. The technical HCH contains the mixture of five isomers with the percentage of 55-80% (α-HCH), 5-14% (β-HCH), 8-15% (γ-HCH), 2-16% (δ-HCH) and 3-5% (ε-HCH), and lindane formulations contains >90% of γ-HCH.[33] In this study, α-HCH, β-HCH, and γ-HCH occupied 33%, 35%, 29% and 4%, respectively of total HCH concentration. These changes may be due to metabolic degradation of original components of HCH, which indicate that much of HCH is metabolized to the other isomers. These changes may be comparatively fast in tropical regions with high ambient temperature and humid soils, as well as higher intensity of solar radiations.[34,35] Predominance of β-HCH isomer in the HCH compositions in the studied soils with 35% percent was much higher than that of technical HCH (5-14%, β-HCH), indicating a past (historical) technical HCH contamination, rather than current input. High β-HCH concentrations can be explained by lower vapor pressure and much slow degradation compared to other HCHs, additionally, α-HCH and γ-HCH can be transformed to β-HCH.[35] Walker *et al*. studied and reported the potential of γ-HCH transformation into other isomers of HCH. γ-HCH may be transformed by sunlight and through biological degradation in soil into α-HCH.[36,37] The ratio of α-HCH to γ-HCH has been widely used to identify the possible sources of HCH. Ratio between 3 and 7 (α/γ-HCH) indicates fresh input of technical HCH,[38] while reduced ratio of ≤1, suggests lindane source.[34] The estimated ratio of α/γ-HCH in this study varied between 0.54-1.65 with the mean value of 1.03 and reflects usage of lindane.

The hypothesis of DDT sources to the environment was elucidated by evaluating the pattern of individual major compounds of DDTs (DDT, DDD and DDE). Therefore, the ratio between the DDT, DDE and DDD is widely used to identify the possible sources for aged or recent inputs of DDT.[39] Ratio of DDT/(DDD+DDE) greater than 1 indicates DDT input in last five years, and lower ratios indicates aged DDT (microbial degradation).[19,40] The observed ratio of DDT/(DDD+DDE) for this study was ranged between 0.09 to 2.39 with an average value of 0.75, indicating that DDT inputs to this area is both past and present input but dominated by bio-transformation of DDT used in past. The vapour pressure of *o,p'*-DDT is 7.5 times higher than *p,p'*-DDT leading to greater volatilization of *o,p'*-DDT to the atmosphere,[41,42] and *p,p'*-DDT metabolizes much faster in a tropical environment. In the present study, occurrence order of DDT isomers was; *o,p'*-DDT >*p,p'*-DDD >*p,p'*-DDE >*p,p'*-DDT. Generally, technical grade DDT constitute 77.1% *p,p'*-DDT, 14.9% *o,p'*-DDT, 4.0% *p,p'*-DDE, 0.1% *o,p'*-DDE, 0.3% *p,p'*-DDD, 0.1% *o,p'*-DDD, and a number of unidentified compounds (3.5%). However, in this study we observed that *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD occupied 12%, 26%, 30%, and 33%, respectively of total DDT. With contrast to DDT technical components, there are great changes because of its metabolic transformation. In soil, DDT can be transformed to stable and toxic metabolites as DDE and DDD under aerobic and anaerobic conditions, respectively.[43,44] In this study, the concentration of DDD was higher than DDE (Table 1), indicating the anaerobic degradation pathway as the most probable degradation pathway of DDT. Because this area is dominated by paddy fields, where anaerobic degradation in soils may takes place. The *o,p'*-DDT/*p,p'*-DDT ratio was reported to be 0.2~0.26 in technical DDT and ~7.5 in dicofol products.[45] The ratio of *o,p'*-DDT/*p,p'*-DDT in the studied soils of Kurukshetra, India was ranged from 1.48 to 2.73 with the mean of 1.92. This ratio of *o,p* -DDT/*p,p* -DDT was lower than that of dicofol but higher than that of technical DDT. These observations suggest contamination from aged DDT but not from dicofol.

Table 3. Life time average daily dose (mg kg^{-1} d^{-1}) of dichlorodiphenyltrichloroethanes and hexachlorocyclohexanes for adults and children through ingestion of soils.

Compounds	Adults			Children		
	Min	Max	Mean	Min	Max	Mean
HCH isomers						
α-HCH	8.0×10^{-10}	3.0×10^{-9}	1.5×10^{-9}	4.2×10^{-9}	1.6×10^{-8}	7.9×10^{-9}
β-HCH	7.7×10^{-10}	4.6×10^{-9}	2.0×10^{-9}	4.0×10^{-9}	2.4×10^{-8}	1.0×10^{-8}
γ-HCH	1.1×10^{-9}	3.2×10^{-9}	1.8×10^{-9}	5.6×10^{-9}	1.7×10^{-8}	9.1×10^{-9}
δ-HCH	8.1×10^{-10}	1.4×10^{-9}	1.1×10^{-9}	4.2×10^{-9}	7.0×10^{-8}	5.6×10^{-9}
∑HCH	8.0×10^{-10}	1.2×10^{-8}	4.3×10^{-9}	4.1×10^{-9}	6.3×10^{-8}	2.2×10^{-8}
DDT isomers						
p,p×-DDE	7.7×10^{-10}	1.2×10^{-8}	3.3×10^{-9}	4.0×10^{-9}	6.3×10^{-8}	1.7×10^{-8}
p,p×-DDD	9.4×10^{-10}	2.6×10^{-8}	6.0×10^{-9}	4.9×10^{-9}	1.3×10^{-8}	3.1×10^{-8}
o,p×-DDT	8.4×10^{-10}	1.6×10^{-8}	6.4×10^{-9}	4.4×10^{-9}	8.1×10^{-8}	3.3×10^{-8}
p,p×-DDT	7.8×10^{-10}	1.0×10^{-8}	2.4×10^{-9}	4.1×10^{-9}	5.2×10^{-8}	1.3×10^{-8}
∑DDT	7.7×10^{-10}	5.3×10^{-8}	1.1×10^{-8}	4.0×10^{-9}	2.8×10^{-7}	5.8×10^{-8}
Total	3.3×10^{-9}	6.6×10^{-8}	1.6×10^{-8}	1.7×10^{-8}	3.4×10^{-7}	8.1×10^{-8}

DDT, dichlorodiphenyltrichloroethane; HCH, hexachlorocyclohexane.

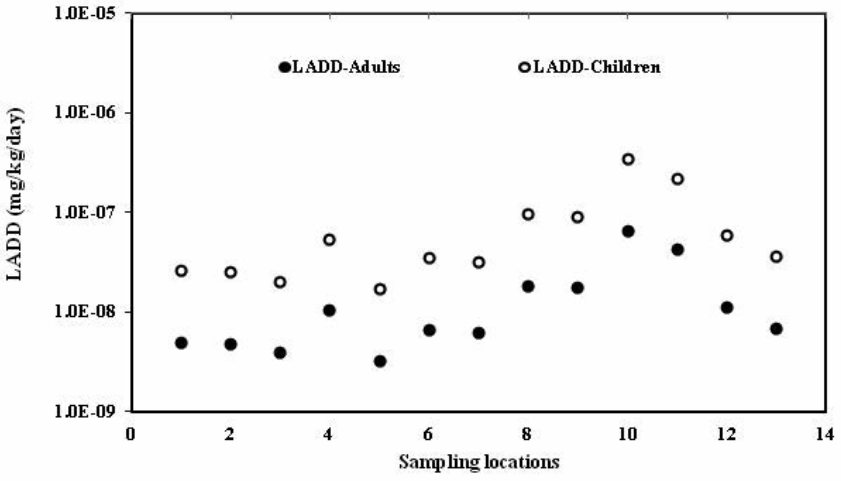


Figure 3. Life time average daily dose (LADD) organochlorines for human adults and children at different locations.

Human health risk assessment of dichlorodiphenyltrichloroethanes and hexachlorocyclohexanes

Human health risk assessment was based on assumption that adults and children may be exposed to toxic contaminants in soil. Uptake of OCs via ingestion of soil or dust or via dermal contact may cause harmful effects on humans. Adult human and children exposure to HCHs and DDTs through soil ingestion was assessed in this study, considering the fact that adults and children remain exposed for all the days in a year during the life span of 70 years and 12 years. Human health risk was assessed by estimating the incremental LADD followed by ILCR. The lifetime average daily dose is the amount of chemical intake per kg of body weight per day, which may cause adverse health effects when absorbed into the body over a long period of time.

Estimated LADD of individual HCH and DDT isomers and their total (HCHs and DDTs) for human was presented in Table 3 and Figure 3. Total estimated LADD was ranged between 3.3×10^{-10}-6.6×10^{-8} mg kg^{-1} d^{-1}and 1.7×10^{-8}-3.4×10^{-7} mg kg^{-1} d^{-1}, with the mean value of 1.6×10^{-8} mg kg^{-1} d^{-1}and 8.1×10^{-8} mg kg^{-1} d^{-1}, respectively for adults and children. The average LADD of HCHs for adults and children was 4.3×10^{-9} mg kg^{-1} d^{-1} (range, 8.0×10^{-10}-1.2×10^{-8} mg kg^{-1} d^{-1}) and 2.2×10^{-8} mg kg^{-1} d^{-1} (range, 4.1×10^{-9}-6.3×10^{-8} mg kg^{-1} d^{-1}), respectively. However, average LADD of DDTs was 1.1×10^{-8} mg kg^{-1} d^{-1} (range, 7.7×10^{-10}-5.3×10^{-8} mg kg^{-1} d^{-1}) and 5.8×10^{-8} mg kg^{-1} d^{-1} (range, 4.0×10^{-9}-2.8×10^{-7} mg kg^{-1} d^{-1}), respectively for adults and children.

The cumulative ILCR from HCHs and DDTs for human was estimated and ranged from 5.1×10^{-9} to 4.6×10^{-8} (mean, 1.6×10^{-8}) and 2.6×10^{-8} to 2.4×10^{-7} (mean, 8.4×10^{-8}), respectively (Table 4, Figure 4).The contribution of ILCR from HCHs to adults and children was 1.3×10^{-8} (ranges, 2.6×10^{-9} to 3.1×10^{-8}) and 6.6×10^{-8} (ranges, 1.3×10^{-8} to 1.6×10^{-7}), respectively. However, ILCR from DDTs was ranged between 2.6×10^{-10}-1.6×10^{-8} (mean, 3.5×10^{-9}) and 1.4×10^{-9}-8.1×10^{-8} (mean, 1.8×10^{-8}) respectively, for adults and children. This estimated ILCR was much lower than acceptable risk distribution range (10^{-6}-10^{-4}).[32]

Health hazard quotient (HQ) is the exact measure of the magnitude of exposure potential or a quantifiable potential for developing non-carcinogenic health effects after averaged exposure period. The quantified health HQs for total pesticides (HCHs and DDTs) through soil ingestion pathway for adults and children were ranged between 1.8×10^{-6} to 1.4×10^{-4} and 9.5×10^{-6} to 7.2×10^{-4}

Table 4. Incremental life time cancer risk due to dichlorodiphenyltrichloroethanes and hexachlorocyclohexanes exposure to adults and children through ingestion of soils.

Compounds	Adults			Children		
	Min	Max	Mean	Min	Max	Mean
HCH isomers						
α-HCH	5.0×10^{-9}	1.9×10^{-8}	9.6×10^{-9}	2.6×10^{-8}	9.8×10^{-8}	5.0×10^{-8}
β-HCH	1.4×10^{-9}	8.3×10^{-9}	3.6×10^{-9}	7.2×10^{-9}	4.3×10^{-8}	1.9×10^{-8}
γ-HCH	1.2×10^{-9}	3.5×10^{-9}	1.9×10^{-9}	6.1×10^{-9}	1.8×10^{-8}	10.0×10^{-9}
δ-HCH -*	-	-	-	-	-	
∑HCH	2.6×10^{-9}	3.1×10^{-8}	1.3×10^{-8}	1.3×10^{-8}	1.6×10^{-7}	6.6×10^{-8}
DDT isomers						
p,p×-DDE	2.6×10^{-10}	4.1×10^{-9}	1.1×10^{-9}	1.4×10^{-9}	2.1×10^{-8}	5.9×10^{-9}
p,p×-DDD	2.3×10^{-10}	6.2×10^{-9}	1.4×10^{-9}	1.2×10^{-9}	3.2×10^{-8}	7.4×10^{-9}
o,p×-DDT	2.9×10^{-10}	5.3×10^{-9}	2.1×10^{-9}	1.5×10^{-9}	2.8×10^{-8}	1.1×10^{-9}
p,p×-DDT	2.7×10^{-10}	3.4×10^{-9}	8.3×10^{-10}	1.4×10^{-9}	1.8×10^{-8}	4.3×10^{-9}
∑DDT	2.6×10^{-10}	1.6×10^{-8}	3.5×10^{-9}	1.4×10^{-9}	8.1×10^{-8}	1.8×10^{-8}
Total	5.1×10^{-9}	4.6×10^{-8}	1.6×10^{-8}	2.6×10^{-8}	2.4×10^{-7}	8.4×10^{-8}

*Not calculated due to cancer slope oral factor (CSF) not assigned. DDT, dichlorodiphenyltrichloroethane; HCH, hexachlorocyclohexane.

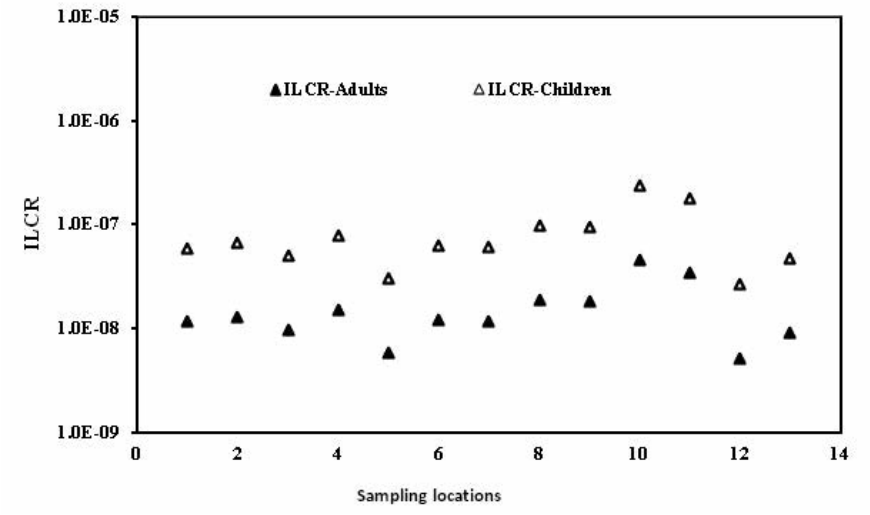


Figure 4. Incremental life time cancer risk (ILCR) to human adults and children from organochlorines at different locations.

Table 5. Non-carcinogenic health hazard due to dichlorodiphenyltrichloroethanes and hexachlorocyclohexanes exposure to adults and children through ingestion of soils.

Compounds	Adults			Children		
	Min	Max	Mean	Min	Max	Mean
HCH isomers						
α-HCH	1.0×10^{-7}	3.7×10^{-7}	1.9×10^{-7}	5.2×10^{-7}	1.9×10^{-6}	9.9×10^{-7}
β-HCH	-*	-	-	-	-	-
γ-HCH	3.6×10^{-6}	1.1×10^{-5}	5.8×10^{-6}	1.9×10^{-6}	5.5×10^{-5}	3.0×10^{-5}
δ-HCH	-	-	-	-	-	-
∑HCH	1.0×10^{-7}	1.1×10^{-5}	5.1×10^{-6}	5.2×10^{-7}	5.7×10^{-5}	2.7×10^{-5}
DDT isomers						
p,p×-DDE	-	-	-	-	-	-
p,p×-DDD	-	-	-	-	-	-
o,p×-DDT	1.7×10^{-6}	3.1×10^{-5}	1.3×10^{-5}	8.7×10^{-6}	1.6×10^{-4}	6.6×10^{-5}
p,p×-DDT	8.1×10^{-6}	1.0×10^{-4}	2.5×10^{-5}	4.2×10^{-5}	5.4×10^{-4}	1.3×10^{-4}
∑DDT	1.7×10^{-6}	1.4×10^{-4}	2.5×10^{-5}	9.5×10^{-6}	7.2×10^{-4}	1.3×10^{-4}
Total	1.8×10^{-6}	1.4×10^{-4}	2.5×10^{-5}	9.5×10^{-6}	7.2×10^{-4}	1.3×10^{-4}

*Not calculated due to reference dose (RfD) not assigned. DDT, dichlorodiphenyltrichloroethane; HCH, hexachlorocyclohexane.

for adults and children, respectively (Table 5, Figure 5).The average HQ of HCHs, DDTs and total OCs for adults and children was 5.1×10^{-6} and 2.7×10^{-5}, 2.5×10^{-5} and 1.3×10^{-4}, and 2.5×10^{-5} and 1.3×10^{-4}, respectively. These estimated HQ values were much below the acceptable safe risk level (HQ≤1), indicating negligible risk to the residents of Kurukshetra, India.

Comparison of levels of dichlorodiphenyltrichloroethanes and hexachlorocyclohexanes in soils with other regions

HCH and DDT isomers have been reported as worldwide contaminants. Results of this study were compared with earlier studies on soils in India and from European and other tropical countries (Table 6). Concentrations of total HCH and total DDT were comparatively lower than other studies on soils from India and other countries. Reported concentrations of HCH and DDT in agriculture soil from India are available in literature but work on urban soil is not available. Therefore, this study was compared with data on agriculture soils in India. During 1990s, concentration of ∑HCH and ∑DDT in soils from India was observed as high as 430 μg kg^{-1} and 940 μg kg^{-1}, respectively,[20,24] however, during 2010s the concentrations of ∑HCH and ∑DDT were observed up to 255 μg kg^{-1} and 74 μg kg^{-1}, respectively.[21–23] This decreasing trend during 1990s to 2010s may be due to restricted use of these compounds in India.

Concentrations obtained from this study were lower than studies reported for urban and agriculture soils from other countries. Sayed and Malik[46] reported ∑DDT ranging between below detection limit (BDL)-1538 μg kg^{-1}and ∑HCH ranging between BDL-119 μg kg^{-1} in urban soils from Pakistan. Surface soils from Vietnam had ∑DDT and ∑HCH levels in the ranges of BDL-171.83 μg kg^{-1} and BDL-20.57 μg kg^{-1}, respectively.[47] Levels of ∑DDT and ∑HCH in urban soils from different location in China were in the ranges of 0.7-972.2μg kg^{-1} and BDL-1095 μg kg^{-1}, respectively.[16–26,48–52] However, in agriculture soils from China, the ∑DDT and ∑HCH levels were in the ranges of 7.6-662.9 μg kg^{-1} and 0.2-103.9 μg kg^{-1}, respectively.[39–52]

Rebeca *et al.*[53] and Diaz-Barriga *et al.*[14] reported ∑DDT in rural soils from Chiapas (BDL-26,980 μg kg^{-1}) and Chihuahua (1-788 μg kg^{-1}) of Mexico. Ferre-Huguet *et al.*[27] reported 126-316 μg kg^{-1} of total DDT in village surface soils from Catalonia, Spain. The reported concentrations of ∑DDT and ∑HCH in surface soils from Romania were 3.5-1542 μg kg^{-1} and 0.7-90 μg kg^{-1}, respectively.

Ecological risk assessment of dichlorodiphenyltrichloroethanes and hexachlorocyclohexanes

Ecological risk assessment is expressed as a function of environmental exposure and ecotoxicological effects. This is usually expressed as the comparison of the estimated environmental concentration with guideline concentrations. Environmental soil quality guidelines (SQG_E)

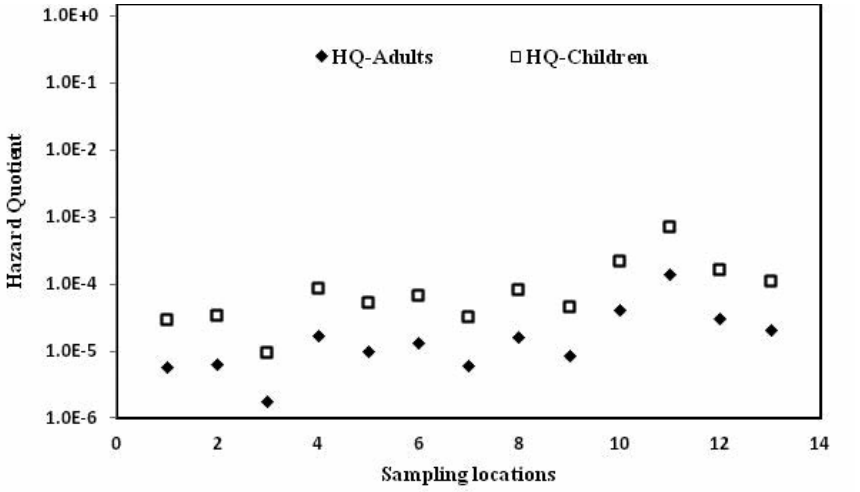


Figure 5. Health hazard quotient (HQ) for adults and children at different locations.

Table 6. Levels of dichlorodiphenyltrichloroethane and hexachlorocyclohexane in soils (mg kg-1): comparison with this study (in italics).

Country	Land use	∑DDT	∑HCH	Ref.
Kurukshetra, India	*Urban*	*7.88±3.07*	*3.00±0.54*	*Present*
Haryana, India	Paddy field	39±12	134±59	20
Haryana, India	Agriculture	1-66	2-51	21
NCR, India	Agriculture	-	0.20-212.20	22
North UP, India	Agriculture	-	5.61-255.12	22
NCR, India	Agriculture	1.61±0.33	34.96±5.87	23
Farukkhabad, India	Agriculture	BDL-940	BDL-430	24
Unnao, India	Surface	BDL-74.06	0.08-7.25	25
KS Kaku, Pakistan	Urban	0-1538	0-119	46
Hanoi, Vietnam	Surface	BDL-171.83	BDL-20.57	47
Tianjin, China	Industrial	73.9	654	15
Beijing, China	School yard	93.68	2.25	16
Beijing, China	Urban park	162.0	10.54	26
Guangzhou, China	Agriculture	7.6-662.9	0.2-103.9	39
Tianjin, China	Urban	ND-616.98	ND-92.74	48
Tianjin, China	Suburban	0.7-972.2	1.3-1095	49
Shanghai, China	Urban	0.77-247.45	ND-10.38	50
Taiyuan, China	Urban	1.8-100	1.4-45	51
Zhangjiagang, China	Urban/rural	88.9	99	56
Guanting and Miyun, China	Watershed	ND-116.74	ND-5.56	57
Chihuahua, Mexico	Rural	1-788	-	14
Catalonia, Spain	Village	126-316	-	27
Romania	Surface	3.5-1542	0.7-90	49
Chiapas, Mexico	Village	ND-26,980	-	53

DDT, dichlorodiphenyltrichloroethane; HCH, hexachlorocyclohexane; BDL, below detection limit; ND, not detected.

are usually based on data from toxicity studies of plants and invertebrates from soils contact for different land uses. The concept of land uses does not provide adequate protection for ecological receptors. Therefore, soil quality guidelines for residential/parkland and agricultural land uses are based on models designed to protect primary, secondary, and tertiary consumers from ingestion of contaminated soil and food.[54] The soil and food ingestion guidelines are the lowest of three values designed to protect primary, secondary, and tertiary consumers from ingestion of contaminated soil and food. First value is modeled for the protection of primary consumers (soil → plant → herbivore pathway), second value is modeled for the protection of secondary consumers (soil → plant → herbivore → predator pathway) and the third value is modeled for the protection of tertiary consumers (soil → invertebrate → secondary consumer → predator pathway).

For all land uses, the preliminary soil contact values are also called threshold effects concentration (TEC). TECs are those, above which adverse effects are not expected or rarely occur on the majority of organisms and soils are considered to be clean to marginally low polluted. Environmental guidelines for HCHs and DDTs in soil and sediments have not yet been established in India. Therefore, recommended soil quality guidelines from National Oceanography and Atmospheric Administration USA and Canadian government were applied in this study for evaluation of ecotoxicological effects of HCHs and DDTs. The Canadian government established guideline concentration of total DDT as 700 μg kg^{-1} (agricultural and residential/parkland use) and 12,000 μg kg^{-1} (commercial and industrial land use).[55] However, NOAA recommended HCH target values of 20 μg kg^{-1} for agricultural land use and 2000 μg kg^{-1} for urban park and residential land use.[56] The observed concentrations of total DDT and total HCH in soils from the studied area of Kurukshetra, India were 7.88±3.07 μg kg^{-1} and 3.00±0.54 μg kg^{-1}, respectively, which were much lower than stipulated guideline values for the protection of environmental and human health.

The quality of soil may be classified on the basis of the concentration of both HCHs and DDTs.[16] Low polluted (below 50 μg kg^{-1}), light polluted (50-500 μg kg^{-1}), moderate polluted (500-1000 μg kg^{-1}), and heavily polluted (>1000 μg kg^{-1}). Thus, the soils of Kurukshetra, Haryana, India may be classified as low polluted soil with HCHs and DDTs.

Conclusions

DDTs and HCHs in soils collected from near residential, roadside, school, hospital and parkland areas of Kurukshetra Haryana, India were determined in this study. The results provided useful information on DDT and HCH residues in soil of a tropical developing city in India, their probable sources and probabilistic human and environmental health risk. The concentrations of DDT sand total HCHs were below the guideline limits set by the USA and Canadian government, therefore soils may be classified as low polluted. The predominance of β-HCH and α/γ-HCH ratio in HCHs suggested that they were from historical contamination of HCHs. The estimated isomeric ratio between DDT, DDE and DDD isomers indicates anaerobic degradation of DDT and contaminations from aged DDT but not from dicofol products.

LADD, ILCR and non-carcinogenic health HQ estimates shows low or negligible health risk for humans and environment in this area of study.

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