POLYCYCLIC AROMATIC HYDROCARBONS AND CHLORINATED PESTICIDES IN URBAN SOILS: DISTRIBUTION AND HEALTH RISK POTENTIAL TO HUMAN POPULATION

Kumar B[1], Sajwan K[2*], Senthilkumar K[2], Verma VK[1], Gaur R[1], Mishra M[1], Kumar S[1], Sharma CS[1]

[1] Central Pollution Control Board, East Arjun Nagar, Delhi, India-110032; [2] Department of Natural Sciences, Savannah State University, Savannah, GA 31404, USA

Introduction

The characteristic properties of PAHs and chlorinated pesticides (HCH & DDT) make them accumulate in soil, sediments, biota and humans for longer period. Humans with various exposure pathways to these pollutants have been recognized for their potential to cause health effects in different organs[1-3]. Cumulative effects of long range atmospheric transport and local sources are the important sources of these pollutants in urban areas.

Humans are exposed to toxic contaminants, mainly through the consumption of contaminated food and occupational environments. Through soil intake via unintentional ingestion, inhalation or dermal contact seems to another significant exposures[4]. Consequently, in this study we emphasized on quantification of 16 PAHs and selected persistent chlorinated pesticides (HCH & DDT) in urban soils from a developing city of Haryana state in India for the assessment of environmental and human health risk by PAHs and legacy pesticides.

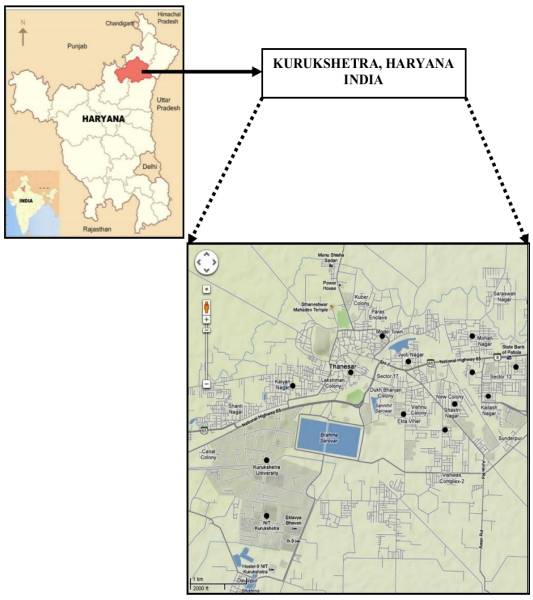

Figure : Map with study area and sampling locations

Material and methods

Study area, the Kurukshetra city is located between geographical coordinates of 29.97°N and 76.85°E in the north Indian province of Haryana (Figure 1). The climatic conditions in this area are very hot in summer (>47 °C) and cold during winters (<1°C) with average annual rainfall of ~600 mm. Soil sampling was carried out during June 2012 from thirteen urban locations near human activity areas. From each location, approximately 1/2 kg of soil was collected in the duplicates and mixed thoroughly. Sufficient quantity of the sample was transferred to clean wide mouth amber glass containers and preserved with ice, transported to the laboratory where they were kept at 4^0C until extraction.

Homogenized sample was mixed with diatomaceous earth (ASE prep DE, Dionex, USA) and extraction was carried out with accelerated solvent extractor (ASE-350, Dionex, USA) 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 100^0C. The extracts were concentrated to 2.0 ml using Rotatory Vacuum evaporator (Eyela, Japan) and subjected to activated silica gel (100–200 mesh) column chromatography (25 cm × 10 mm id). Briefly, the concentrated extract was transferred on to the top of the column and was first eluted with hexane containing aliphatic hydrocarbons and that was discarded. Final elution was made with dichloromethane, which was retained for analysis and concentrated. An additional hexane was added to the concentrated extracts and evaporated to remove traces of dichloromethane. Final extract was 2 mL in hexane, and out of this one mL was solvent exchanged to acetonitrile for PAH analysis by HPLC and remaining part used for pesticide analysis by GC-ECD.

Sixteen priority PAHs was analyzed by HPLC system (Agilent 1100 Series) equipped with Diode Array Detector (DAD, λ=254 nm), quaternary pump and degasser was described elsewhere[5]. Analysis of HCH (α-HCH, β-HCH and γ-HCH) and DDT (*o,p'*-DDT and *p,p'*-DDT) isomers was carried out using gas chromatograph (Perkin Elmer, Clarus 500) equipped with an electron capture detector (ECD, ^{63}Ni) on Elite-1 fused silica capillary column (25 m x 0.20 mm with 0.33 µm particle). Reference standards were purchased from Supelco (Sigma-Aldrich, USA) and used in quality control analysis. Procedural blanks, random duplicate samples, five level calibration curves (r^2, 0.99), calibration verification (<10%) and matrix spiked recovery was carried out. Method detection limits were obtained by processing the eight aliquots of a sample spiked to produce a valid response (s/n >3) and multiplying the standard deviation by $t_{students}$ value for eight replicates at 99% confidence level. Statistically calculated value (MDL) of 1.0 µg kg^{-1} and 0.01 µg kg^{-1} for PAHs and pesticides, respectively was used during data interpretation. Recovery of matrix spiked compounds was in the range of 85-112% (±5-15%).

Incremental lifetime cancer risk (ILCR) to humans was assessed by calculating the lifetime average daily dose (LADD) of PAHs, HCHs and DDTs[6]. The equations used for estimating LADD and ILCR were described in our recent study[5].

Results and discussions

Concentrations of total PAHs in soils were ranged between 16-2538 µg kg^{-1}, with the mean concentration of 632±45 µg kg^{-1} (Table 1). Greater concentrations in soils near busy traffic intersection were noticed. Benzo(g,h,i)perylene and dibenzo(a,h)anthracene were the prominent PAHs at all the locations. The average concentration of probable human carcinogenic PAHs (ΣC-PAHs) was 569±38.8 µg kg^{-1}, and accounted for more than 90% of total PAHsIn general soils contained high molecular weight PAHs (97%) and consequently low ratio of LMW_{PAHs} to HMW_{PAHs} (<1.0), indicating pyrolytic origin of PAHs. In this study, the calculated isomer ratio of Flt/(Flt+Pyr), BaA/(BaA+Chr), BaP/Bpe, Ipy/(Ipy+Bpe) and BaP/(BaP+Chr) was 0.56, 0.56, 0.80, 0.25 and 0.56, respectively. These observed ratios indicate pyrogenic sources of PAHs from combustion of coal, woods, grass, and petroleum particularly through vehicle engines.

Table 1: PAH concentrations and health hazard (LADD and ILCR) estimate for human adults and children

Parameters	Unit	Range		Mean
		Min	Max	
Concentrations				
∑PAHs	µg kg^{-1}	16	2538	632
∑C-PAHs	µg kg^{-1}	6.8	2538	569
LADD				
Adults	mg kg^{-1} d^{-1}	2.3x10^{-8}	3.6x10^{-6}	9.0x10^{-7}
Children	mg kg^{-1} d^{-1}	1.2x10^{-7}	1.9x10^{-5}	4.7x10^{-6}
ILCR				
Adults	-	3.2x10^{-9}	5.0x10^{-5}	1.8x10^{-5}
Children	-	1.6x10^{-8}	2.6x10^{-4}	9.3x10^{-5}

∑PAHs=Sum of 16 PAHs, ∑C-PAHs = Sum of probable carcinogenic PAHs

Table 2: HCH and DDT in soils (µg kg^{-1}), LADD (mg kg^{-1} day^{-1}) and ILCR for human adults and children

Compounds	Concentrations		LADD		ILCR	
	Range	Mean	Adults	Children	Adults	Children
α-HCH	0.56-2.1	1.1	1.5x10^{-9}	7.9x10^{-9}	9.6x10^{-9}	5.0x10^{-8}
β-HCH	0.54-3.2	1.4	2.0x10^{-9}	1.0x10^{-8}	3.6x10^{-9}	1.9x10^{-8}
γ-HCH	0.75-2.2	1.2	1.8x10^{-9}	9.1x10^{-9}	1.9x10^{-9}	1.0x10^{-8}
o,p'-DDT	0.59-11	4.5	6.4x10^{-9}	3.3x10^{-8}	2.2x10^{-9}	1.1x10^{-8}
p,p'-DDT	0.55-7.1	1.7	2.4x10^{-9}	1.3x10^{-8}	8.3x10^{-10}	4.3x10^{-9}
Total	1.2-22	5.9	8.4x10^{-9}	4.3x10^{-8}	1.4x10^{-8}	7.4x10^{-8}

The concentrations of total pesticides were ranged between 1.2-22 μg kg^{-1}, with an average value of 5.9±1.4 μg kg^{-1}. The isomers concentration of α-HCH, β-HCH, γ-HCH, *o,p'*-DDT and *p,p'*-DDT, was ranged between 0.56-2.1 μg kg^{-1}, 0.54-3.2 μg kg^{-1},0.75-2.2 μg kg^{-1}, 0.59-11 μg kg^{-1} and 0.55-7.1 μg kg^{-1}, respectively with their mean values of 1.1 μg kg^{-1}, 1.4 μg kg^{-1}, 1.2 μg kg^{-1}, 4.5 μg kg^{-1} and 1.7 μg kg^{-1}, respectively (Table 2). Compositional analysis of HCH and DDT isomers were used to identify the contamination sources. The ratio of α-HCH to γ-HCH between 3 and 7 indicates fresh input of technical HCH, while a reduced ratio of ≤1, suggests linden sources[7-8]. The estimated ratio of α/γ-HCH in this study varied between 0.54-1.7 with the mean value of 1.0 reflects of lindane contaminations. 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[9-10]. The ratio of *o,p'*-DDT/*p,p'*-DDT in the studied soils was ranged from 1.48-2.73 with the mean of 1.92. This ratio of *o,p'*-DDT/*p,p'*-DDT were lower than that of dicofol but higher than that of technical DDT. These observations suggest contamination from aged DDT but not from dicofol.

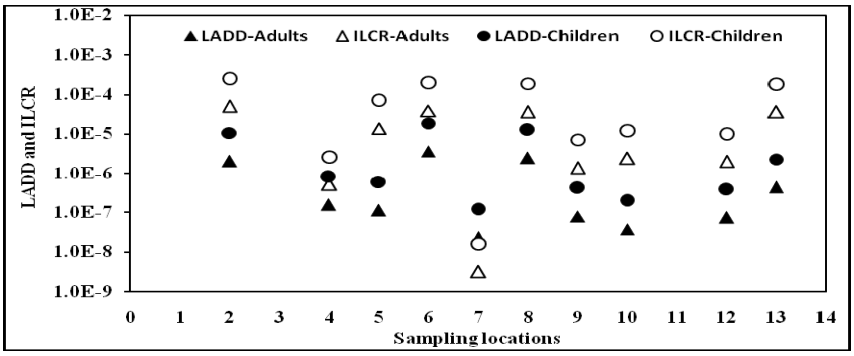

Figure 2: LADD and ILCR to humans due to PAHs exposure through soil ingestion.

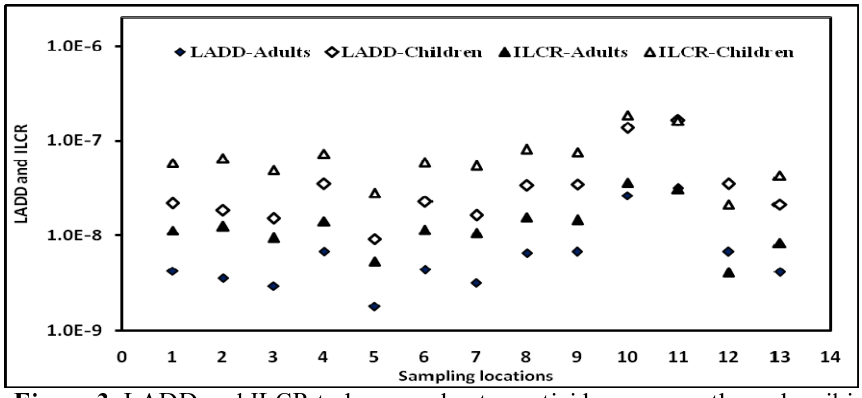

Figure 3: LADD and ILCR to humans due to pesticide exposure through soil ingestion

The human health risk assessment was based on the assumption that human adults and children may be exposed to toxic contaminants through soil. Adult human and children's exposure to PAHs, HCHs and DDTs through soil ingestion was assessed in this study, considering that adults and children exposed for all the days in a year during the life span. Human health risk was assessed by estimating the incremental lifetime average daily dose (LADD) followed by incremental lifetime cancer risk (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. The average LADD of priority PAHs through soil ingestion by an adult and children in urban areas of Kurukshetra was $9.0x10^{-7}$ mg kg^{-1} d^{-1} and $4.7x10^{-6}$ mg kg^{-1} d^{-1}, respectively. However, LADD varied significantly between $2.3x10^{-8}$-$3.6x10^{-6}$ mg kg^{-1} d^{-1} and $1.2x10^{-7}$-$1.9x10^{-5}$ mg kg^{-1} d^{-1}, respectively for adults and children (Table 1, Figure 2). On the basis of LADD, incremental lifetime

cancer risk from exposure to PAHs through soil ingestion, ranged from $3.2x10^{-9}$ to$5.0x10^{-5}$ and $1.6x10^{-8}$ to $2.6x10^{-4}$ for adults and children, respectively. Estimated LADD of total pesticides (HCHs and DDTs) was ranged between $1.8x10^{-9}$ – $3.2x10^{-8}$ mg kg^{-1} d^{-1} and $9.2x10^{-9}$ – $1.6x10^{-7}$ mg kg^{-1} d^{-1}, with the mean value of $8.4x10^{-9}$ mg kg^{-1} d^{-1} and $4.3x10^{-8}$ mg kg^{-1} d^{-1}, respectively for adults and children (Table 2, Figure 3). This estimated ILCR was lower than acceptable risk distribution ranges of 10^{-6} to 10^{-4} [11].

Environmental guidelines for PAHs and pesticides in soil have not yet been established in India. Therefore, established soil quality guidelines from NOAA, USA[12] and Canadian government[13-14] were applied for the assessment of the ecotoxicological health effect of these pollutants. The observed concentrations of PAHs, DDT and HCH in soils from the studied area of Kurukshetra, India were lower than stipulated guideline values for the protection of environmental and human health. Furthermore, contamination of Kurukshetra soils with PAHs and pesticides (HCH and DDT) was categorized by the classification given by Maliszewska-Kordibach[15] and Wang *et al* [16], respectively. The observed concentration of total PAHs and pesticides in our study, classified the area as a low contaminated category.

Acknowledgements
The authors are grateful to Chairman and Member Secretary of Central Pollution Control Board for guidance and providing the necessary facilities and infrastructure in the National Reference Trace Organics Laboratory to conduct the present work.

References

1. IARC (International Agency for Research on Cancer). (2006). Monogaraphs 92
2. ATSDR (Agency for Toxic Substances and Disease Registry) (2005); Toxicological profile for HCHs. http://wwwatsdrcdcgov/toxprofiles/tp43html.
3. ATSDR (2008); Toxicological profile for DDT, DDE, and DDD. US Public Health Service, Atlanta, GA.
4. Morra P, Bagli S and Spadoni G. (2006). *Environ Int*. 32:444-454.
5. Kaur S, Senthilkumar K,Verma VK, Bhupander Kumar, Sanjay Kumar, Katnoria JK, Sharma CS. (2013); Archives of Environmental Contamination and Toxicology (in press).
6. USEPA (1989); Risk Assessment Guidance for Superfund. Human Health Evaluation Manual (Part A).
7. Senthilkumar K, Kannan K, Subramanian AN, Tanabe S. (2001); *Environ Sci Pollut Res* 8: 35-47.
8. Willett L, Ulrich EM, Hites HA. (1998); *Environ Sci Technol* 32(15): 2197-207.
9. Senthilkumar K, Kannan K, Sinha RK, Tanabe S, Giesy JP. (1999); Environ Toxicol Chem 18: 1511-20.
10. Talekar NS, Sun LT, Lee EM, Chen JS. (1977); *J Agric Food Chem* 25: 348-352.
11. USEPA (2012); http://wwwepagov/reg3hwmd/risk/human.
12. NOAA (1999); HAZMAT REPORT 99-1, Updated Feb 2004.
13. CCME (Canadian Council of Ministers of the Environment) (2008); http://www.ec.gc.ca/ceqg-rcq.
14. CCME (2010); In: Canadian environmental quality guidelines, 1999, Vaughan St., Winnipeg, Canada.
15. . Maliszewska-Kordybach B. (1996); *Appl. Geochem* 11:121–127.
16. Wang X, Wang D, Qin X, Xu X. (2008); *J Environ Sci* 20:1090–6.