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HUMAN HEALTH HAZARD AND RISK DUE TO ORGANOCHLORINES IN URBAN SOILS FROM CENTRAL INDIA

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INTRODUCTION

Due to their toxicity, bioaccumulation and persistence;PCBs, HCH and DDT are global concern and have been listed as priority pollutants and as persistent organic pollutants (POPs). Soil has been identified as a sink for a wide range of hazardous pollutants, and can play an important role in the global fate and distribution of OCs through volatilization, degradation and leaching. Studies have indicated that soils contaminated with OCs have a direct influence on public health via ingestion, inhalation, or dermal routes (Morraet al. 2006).

India is the fourth largest pesticide producer in the world with totalproduction of 81,000 metric tons (MT)in 2010-11. The annual pesticide consumption in India was approximately 42,000 MT. Government of India withdrewthe use of DDT and HCH in agriculture since 1989 and 1997, respectively, and restricted for onlypublic health purposes in accordance with guidelines of Stockholm Convention on POPs. However, PCBs have never been produced in India till date, but has beenused in industrial applications. There aresome recent reportson organochlorines in soil samples from various parts of India(Kumar et al. 2011, 2013a, 2014b,c, 2015).But, literature on organochlorines in environmental samples is rare for Central India.Therefore,HCH isomers, DDT isomers and 28 PCB congenersmeasuredin urban soils from central India for the assessment ofhuman health risk in accordance with health risk assessment guidelines.

Fig. 1. Map showing study area and sampling locations in Central India

MATERIALS AND METHODS

Study area (26o22’ N and 78o18’ E) is a located in Madhya Pradesh near Agra in central India with approximately population of 1.2 million, and surrounded by designated industrial areas. Temperature during summers ranges above 29.4°C in the region with relatively very low humidity and frequent mild dust storms. The winter season temperature remains low and remains between 15 and 18°C.

Forty eight soil samples collected from different locations in 2012 (Figure 1). Air dried soil samples(~20g)were extracted with mixture of acetone-hexane (1:1 v/v) in ultrasonic water bath,filtered through Whatman No 41 filter paper (process was repeated twice)and concentrated (~2mL) using a rotary evaporator (Eyela, Tokyo, Japan). Multifunctional silica column chromatographywas used for clean-up (Kumar et al. 2014c). Clean sample extracts were analysed for pesticides and PCBs using gas chromatograph with different operating conditions.Analysis of HCH and DDT compounds was carried out using Perkin Elmer gas chromatograph (Clarus 500, USA) equipped with an electron capture detector (ECD, 63Ni) and Elite-1 fused silica capillary column (25 m x 0.20 mm with 0.33 µm film thickness). However, PCBs was quantified using Shimadzu gas chromatograph (Shimadzu SPD 2010, Japan) equipped with an Electron Capture Detector (ECD, 63Ni) andHP-5MS fused silica capillary column (60 m x 0.25 mm x 0.25 µm film thickness).

Required quality control analysis was performed with the inclusion of five level calibration curves with the r2 value of 0.999, analysis of procedural blanks (analytes concentrations were <MDL ‘method detection limit’), random duplicate samples (standard deviation <10%) and random calibration verification (standard deviation <10%).Limit of detection (LOD) was obtained using signal to noise ratio (s/n >3) and calculated by multiplying standard deviation from spiked sample with 3 (tstudents value for eight replicates at 99% confidence level).

Thestatistically calculated detection limit for OCs was 0.01 µg kg-1. Matrix spiked recoveries rangedbetween 88 - 115% (± 5.5 - 9.4 %) (Kumar et al 2014c). The toxicity of dioxin-like PCBs (dl-PCBs) as toxic equivalent quotient (TEQ) was assessed bymultiplying the concentration with the corresponding 2,3,7,8-tetra-chlorodibenzo-p-dioxin (TCDD) relative toxic equivalent factors (TEFs) assigned by World Health Organization (WHO) (Van den Berg et al. 2006). Incidental ingestion of soils

contaminated withOCs was considered as the main pathways of life-long exposure for humans. Human exposure to OCs and the consequent health risk was estimated following recommended guidelines. For this study, human health risk assessment was reported for human adults and children with average body weight of 60 kg and 35 kg, respectively, considering the exposure with OCs contaminated soils for all the days in a year during their life span of 70 years and 12 years, respectively. Human exposure to OCs and the consequent health risk was estimated following recommended guidelines (USEPA 1989). The lifetime average daily dose (LADD), non-cancer risk as hazard quotient (HQ) and incremental lifetime cancer risk (ILCR) were estimated by using following equations:

LADD (mg kg-1 day-1) = (Cs x IR x F x EF x ED)/(BW x AT)

HQ = LADD/RfD

ILCR =LADD x CSF

Where, Cs is concentration of individual pollutant in the soil (mg kg-1), IR is the ingestion rate of soil (100 mg day-1 for adult and 200 mg day-1 for children), F is the unit conversion factor, EF is exposure frequency, ED is the life time exposure duration, BW is the body weight, AT is the averaging time for carcinogens (EF x ED days). CSF and RfD is cancer oral slope factor and reference dose, respectively for individual compound (mg/kg/day).

RESULTS AND DISCUSSIONS

Concentrations of organochlorines in soil

The concentration of ΣOCPs (ΣHCHs + ΣDDTs) in soil ranged between <0.01 – 29.5 µg kg-1with an average value of 10.3µg kg-1. The concentrations of DDTs were comparatively higher than HCHs. The observed concentration of ΣHCH and ΣDDT in soils ranged between <0.01 – 2.54 µg kg-1 and1.30 – 27.41µg kg-1with themean value of 1.80 ±0.91µg kg-1 and 8.77 ±7.82µg kg-1, respectively. Their contribution of α-HCH, γ-HCH, p,p'-DDE, o,p'-DDT and p,p'-DDT, accounted for 9.5%, 9.4%, 18.6%, 20.5% and 42%%, respectively of ΣOCPs.Comparatively higher concentration of p,p'-DDE (degradation product) can be explained by transformation of parental compounds present in the soil to DDE through aerobic degradation.The concentrations of Σ28PCBs ranged between <0.01 – 62.8µg kg-1 with themean value of 15.2±16.2 µg kg-1. Among 28 PCB congeners, dominant congener wereCB-18, CB-49, CB-77, CB-37, CB-74, and CB-70with their contributionof18.7%, 18.1%, 13.0%, 7.5%, 7.4% and 6.4%, respectively forΣ28PCBs. Congener CB-70, CB-77, and CB-18 were most detected congeners with their detection frequency of 93.8%, 68.8%, and 62.5%, respectively. However, the ΣTEQfor dl-PCBs in studied soils ranged from<0.01 to 38.03 ng-TEQ kg-1 with the mean of 4.57±11.74 ng-TEQ kg-1.Non ortho-PCB congeners, particulary PCB-126 and PCB-169 were the sole contributor of TEQ and accounted for >99% to ΣTEQ.

Fig. 2. Concentration of HCH and DDT in soils

Fig. 3. group homolog of PCBs in soils

Possible sources of organochlorines in soil

The pooled ratio of α/γ-HCH ranged between 0.7 – 2.4 with the mean value of 1.3,reflects combined use of lindane and technical HCH. However, the pooled ratio of DDT/DDE ranged 1.1-7.3 with an average of 3.7, suggested the recent contamination of soil with DDT. Due to higher vapor pressure,the volatilization of o,p-DDT in the atmosphere is much higher than p,p-DDT, however, p,p-DDT degrades to other metabolites in a tropical environment.These observations suggest mixed contamination from past and ongoing usage of DDT coupled with the long-range atmospheric transport (LART) tendency of DDT under tropical climate (Chakraborty et al. 2015).Technical DDT and HCH havebeen banned in agriculture,but, restricted their use by Government of India for public health programmes.

As per PCBshomolog patterns in this study,3CBs (42%) and 4CBs (49%) were the dominant homolog with their total contribution of >91% to ΣPCBs. Average concentration of 3CBs, 4CBs, 5CBs, 6CBs and 7CBs was 6.9 µg kg-1, 7.1 µg kg-1, 1.6 µg kg-1, 2.3 µg kg-1 and 1.5 µg kg-1, respectively.Similar PCBs homolog pattern have been reported for other environmental samples from India (Chakraborty et al. 2013; Kumar etal. 2013b, 2014a). PCB congeners in the ambient environment partitioned into the gaseous phase containing lower chlorinated congeners (Cl ≤ 6), and particle phases with higher chlorinated congeners (Cl ≥ 7) (Wang et al., 2011). The observed PCB homolog pattern for Gwalior soils may have originated from the atmospheric transport and deposition from industrial sites (Wilckeet al. 2006).It has been reported that PCBs released to the environment as unwanted by-products from combustion of chlorine containing waste, selected chemical processes involving organochlorines, such as PVC (polyvinyl chloride) manufacturing. Other possible sources arecombustion process ofwaste recycling,industrial activities and automobile could be the major contributor to PCBs. Soils with open

fire activities may have higher concentrations of PCBs.During the winter season, burning of mixtures of waste,consisting painted wood, plastics and garden wastes may produce relatively large amount of dl-PCBs (Park et al. 2009).

Human health and Ecotoxicologicalrisk assessment

The daily intake of total organochlorines (ΣPCBs+ΣHCHs+ΣDDTs) and health risk for human adults and children through soil was calculated and presented.The average LADD (mg kg-1 d-1) of ΣOCs through soils was 2.1x10-8 and 7.2x10-8, respectively for human adults and children in study area of central India. Their corresponding average non-cancer risk (HQ) was 1.0x10-2 and 3.6x10-2, and cancer risk (ILCR) was 7.9x10-8 and 2.7x10-7, respectivelyfor human adults and children.These, observed daily intake of ΣOCs and their non-cancer risk and cancer risk were lower than stipulated ADI and acceptable risk distribution range. Therefore, study suggested that present levels of organochlorines (HCH, DDT and PCBs) in soils implicit low health risk to human population in this study area.

Fig. 4. LADD, HQ and ILCR to humans due to ΣOCs (ΣOCPs+ΣPCBs) through soil

Environmental guidelines for HCH, DDT and PCBs in soils have yet not been established in India. Therefore, recommended soil quality guidelines from Canada government and National Oceanography and Atmospheric Administration (NOAA), USA were applied for the assessment of ecotoxicological health effect of HCH, DDTand PCBs in this study. The observed concentrations levels of HCH, DDT and PCBs in the soils of studied area in central Indiawere lower than the recommended guideline values for the protection of environmental and human health. Further, on the basis of HCH and DDT concentration in soil, study area may be classified as low polluted.

CONCLUSIONS

Study shows the low concentration of organochlorines, which were lower than recommended guideline values. Possible sources of HCH and DDT were combined contamination from past and ongoing usage of lindane and DDT coupled with the long-range atmospheric transport (LART). However, PCB homolog pattern shows the PCBs sources from the atmospheric transport, deposition from industrial sites and from combustions activities of biomass and chlorinated chemicals.

Lifetime average daily intake of organochlorines for human adults and children through soil were lower than stipulated acceptable daily intake and reference doses for HCH, DDT and PCBs. Consequently, their probabilistic cancer risk and non-cancer risk was lower than acceptable risk. Due to lack of data on dietary intake of organochlorines in India, we cannot give total daily intake. However, from this study, we can suggest that the daily intake and health risk due to organochlorines through soils for human adults and children residing in Gwalior, India was extremely low.

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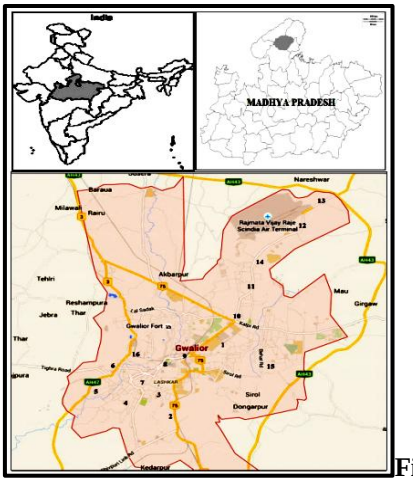

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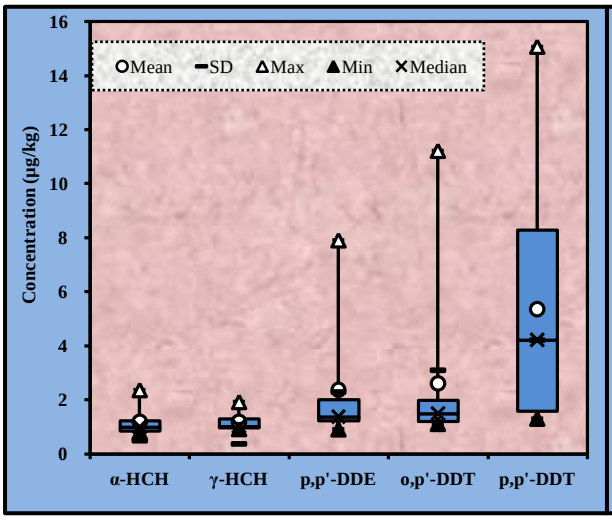

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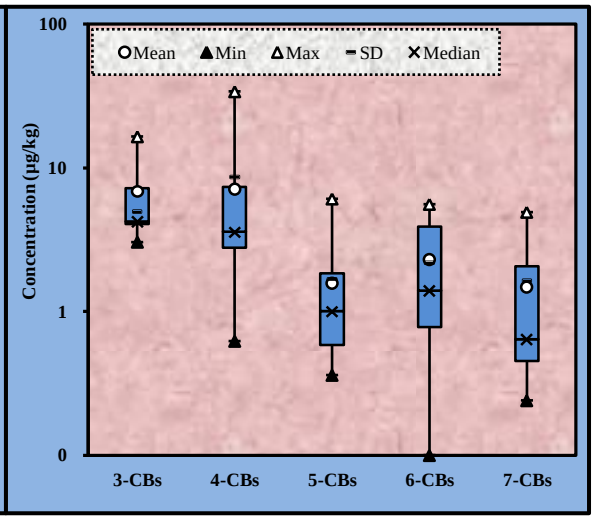
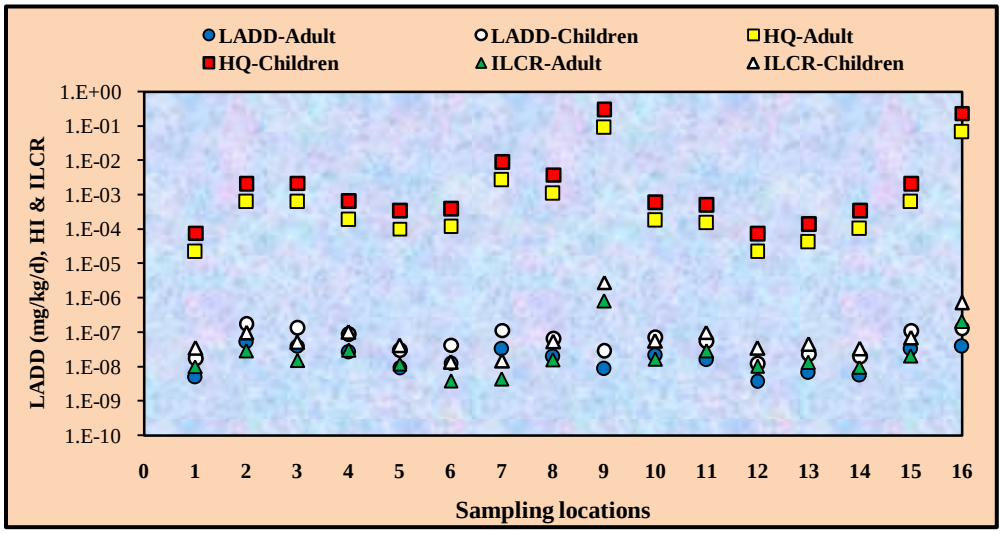


Fig. 3. group homolog of PCBs in soils



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