RESIDUES OF PERSISTENT ORGANOCHLORINE PESTICIDES IN SOILS FROM VARIABLE CROPPING PATTERN AGRICULTURE AREAS

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ABSTRACT

This paper presents the levels of organochlorine pesticides in agricultural soils from national capital region, Delhi. Among OCPs HCH, DDT endosulphan and dieldrin ranged between <0.01-94.73 ng g^{-1}, <0.01-15.79 ng g^{-1}, <0.01-7.57 ng g^{-1} and <0.01-2.38 ng g^{-1}, respectively. α/γ HCH ratio was 4.00 indicates technical HCH usage. The ratio of *p,p'*-DDT/ *p,p'*-DDE and *p,p'*-DDT/∑DDT reflect the contamination by aged DDT or conversion of DDT isomers. Pesticides contamination levels were lower than soil quality guideline values stipulated by Canada, However, pesticides in agricultural soils is a matter of concern for future food chain accumulation and human health so; regular investigation of pesticide residues is recommended on soil health and contamination levels.

INTRODUCTION

Several pesticides are used in modern agricultural production to meet the need for abundant, safe and affordable food and fiber. Although the use of pesticides has led to increased agricultural production but their use has also been associated with several concern, including risk to human health and environment. These are persistent in the environment and are known to accumulate in soil, sediment, plants, animals, and human beings (Kannan *et al*. 1995).

Soil is an important sink in pollution cycling; however, it can also act as a contributor of persistent pollutants to the atmosphere, especially of semi volatile compound in warm climates (Dalla Valle *et al*., 2005). The fate of pesticides in soils with different cropping land use have been extensively studied worldwide (Viet *et al*. 2000; Kumar *et al*. 2008; Senthil Kumar *et al*. 2009).

Country's pesticide production is about 85,000 metric tons and, about 3700 metric tons (t) are annually used in India, against 182.5 million hectare of land where 70% accounts for DDTs, HCHs and OPPs (Kumar *et al.* 2008). The consumption of pesticides in India is comparatively low (only 3.75% of global consumption) (Gupta 2005). The present study was undertaken to investigate the level of organochlorine (OCP), organophosphate (OPP) pesticides and herbicides, in intensive agriculture soils of national capital region (NCR) of India.

MATERIALS AND METHODS

Sampling

50 samples from agriculture areas with different cropping pattern in national capital region (NCR, Delhi) were collected for the study of organochlorines in soils. Approximately 1 Kg. soil of upper layer collected using

stainless steel auger in clean wide mouth amber glass bottle. After collection, samples were transported to laboratory and kept at -20^{0}C until further extraction.

Extraction and cleanup

10-15 g wet sample was mixed with diatomaceous earth and extracted 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 100^0 C. The extracts were concentrated to 2.0 ml using Rotatory Vacuum evaporator (Eyela, Japan). Moisture content was determined to report data on dry weight basis.

The column chromatography was performed to remove interfering organic and polar species. Glass column (300X10 mm) was packed with 10 g silica gel and 5.0 g anhydrous sodium sulphate. The column was pre-rinsed with n-hexane. Sample was loaded with three rinsing and eluted with hexane and dichloromethane. The eluted dichloromethane extract containing OCPs was concentrated to 1.0 ml using Turbovap (Caliper, USA) and, Rotatory Vacuum evaporator (Eyela, Japan).

Instrumental analysis

Separation and Quantification of organochlorines (OCPs) was carried out using GC (Perkin Elmer, Clarus 500) with autosampler equipped with an Electron Capture Detector (ECD, ^{63}Ni), on fused silica column 25 m x 0.20 mm id Elite-1 (0.33 µm particle of 5% diphenylpolysiloxane and 95% dimethylpolysiloxane). The column oven temperature was initially maintained at 170^o C and programmed to 220^{o}C (7^{0}C min^{-1}) and again ramped to 250^{o}C at 5^{o}C min^{-1} and held for 6.86 min. The injector and detector temperature were maintained at 250^{o}C and 350^{o}C respectively. Purified nitrogen gas was used as carrier at the flow rate of 1.0 ml. min^{-1}.

Analytical quality control

Certified reference standards (Sigma Aldrich,USA) were used for calibration of the instruments. The concentrations of analyte were determined by comparing the peak area of the samples and five level calibration curves of the standards. The correlation coefficient of calibration curves were ranged from 0.9980 to 0.9990. The peak identification was conducted by the accurate retention time of each standard. Appropriate quality assurance/ quality control (QA/QC) analysis was performed including a method blank processing along with the samples to check any loss or cross contamination during the sample processing (analyte concentrations were <MDL 'method detection limit'), random duplicate samples (Standard deviation <5), calibration curves with the r^2 value of 0.999, and matrix spike recovery 100±22%. The results of the analysis are reported in ng g^{-1} dry -weight (dry wt.) basis. A reporting limit of > 0.01 ng g^{-1} was taken for calculation. Levels below reporting limit or below MDL (<0.01 ng g^{-1}) were taken as zero (0) in the calculations.

RESULTS AND DISCUSSIONS

The observed concentrations of OCPs are shown in **Table 1**. ∑HCH alone accounts 88% and, was dominant pollutants with a mean of 11.19±3.15 ng g^{-1} concentration followed by DDTs, endosulphan, dieldrin and aldrin, 1.15 ng g^{-1}, 0.27 ng g^{-1}, 0.14 ng g^{-1} and <0.01 ng g^{-1}, respectively. α-HCH is the predominant contaminant among all organochlorine isomers followed by γ-HCH, *p,p'*-DDE, *p,p'*-DDT, β-endosulphan and dieldrin. It has been widely recognized that HCH is available in two formulations: technical HCH and lindane. Technical HCH

contains isomers in the following percentage: α, 55-80%; β, 5-14%; γ, 8-15%; δ, 2-16%; ε, 3-5% (Qui *et al.*, 2004), and Lindane contains >90% of γ-HCH. The composition of HCH isomers in the present study reveals α=72% and γ=16% indicates technical HCH usage. The ratio of α–HCH to γ–HCH has been used to identify the possible HCH source. In this study the ratio of α-HCH to γ-HCH isomers (α/γ ratio) was 4.00, reflects the use of technical formulation in the study area. The technical mixture of HCH produced and used in India until it was banned in 1997, and lindane formulation are registered for use in public health practices to control vector borne diseases and for pest control in selected crops.

Table 1: Concentration of organochlorine pesticides in agriculture soils (ng g^{-1} dry wt.)

Name of compound	Range		Mean±SE*	%**
	Min	Max		
α-HCH	<0.01	76.22	9.17±2.75	71.89
γ-HCH	<0.01	18.51	2.02±0.53	15.86
α/γ HCH	**<0.01**	**8.83**	**4.00±0.46**	**-**
∑HCH	<0.01	94.73	11.19±3.15	87.75
Aldrin			<0.01	
Dieldrin	<0.01	2.38	0.14±0.07	1.12
α-endosulphan			<0.01	
β-endosulphan	<0.01	7.57	0.27±0.17	2.08
∑endosulphan	<0.01	7.57	0.27±0.17	2.08
p,p'-DDE	<0.01	12.26	0.61±0.25	4.77
o,p'-DDT	<0.01	1.41	0.07±0.04	0.58
p,p'-DDT	<0.01	3.94	0.47±0.13	3.70
***p,p'*-DDT/ *p,p'*-DDE**	**<0.01**	**2.30**	**0.22±0.08**	**-**
***p,p'*-DDT/∑DDT**	**<0.01**	**1.00**	**0.44±0.06**	**-**
∑DDT	<0.01	15.79	1.15±0.35	9.05
∑OCP	**<0.01**	**94.73**	**12.75±3.13**	**100.00**

***SE=standard error (SD/√n), **percent of ∑OCPs**

In this study the observed mean concentration of DDT isomers was *p,p'*-DDE (0.61 ng g^{-1}), *o,p'*-DDT (0.07 ng g^{-1}) and *p,p'*-DDT (0.47 ng g^{-1}). In the present study the amount of *p,p'*-DDT volatilized from the soil surface may be relatively small compared to *o,p'*-DDT. After the DDT applications were discontinued, much of the DDT may be converted to *p,p'*-DDE (Baxter, 1990). Higher concentration of *p'p*-DDE has been interpreted as a result of DDT conversion to *p,p'*-DDE by UV radiation after prolong exposure in the environment (Atlas and Giam, 1988). The residence time of *p,p'*-DDT could be estimated using the ratio of *p,p'*-DDT to ∑DDTs. The *p,p'*-DDT/∑DDTs ratio for technical DDTs was reported to be 0.77 (WHO, 1989). The mean ratio of *p,p'*-DDT to ∑DDTs in present study was 0.44, which indicates that these areas have not been sprayed with DDTs more recently. The ratio of *p,p'*-DDT and *p,p'*-DDE can be used to estimate whether recent inputs of technical DDT

exist. Generally, a ratio of 0.33 or less is considered as aged mixture, while a relatively high *p,p'*-DDT/*p,p'*-DDE ratio implies a recent input. In this study the ratio of *p,p'*-DDT/*p,p'*-DDE was 0.22 (mean) so, it is anticipated that the inputs of aged mixture of DDTs existed in the study area.

Endosulphan alone accounts for over 10% of the total insecticide consumption in India. Endosulphan consists in two isomers, α and β, in the ratio of 7:3. Endosulphan is toxic to aquatic organisms particularly fishes (USEPA, 1980) and classified as a class II component (moderately hazardous) by the World Health Organization (1984). In the present study the sum of endosulphan ranged from <0.01 to 7.57 ng g^{-1} with the mean of 0.27 ng g^{-1}. The α- isomer of endosulphan was not detected at any of the locations while β-endosulphan was detected at selected locations with the mean concentration of 0.27±0.17 ng g^{-1}. Similarly contamination of soils by drins cannot be ignored, where aldrin was absent at all locations and dieldrin was found to be 0.14±0.07 ng g^{-1} mean concentration.

CONCLUSION

Pesticide contaminations were lower than soil quality guideline values. The study shows that technical HCH are still in used in the study area and DDTs contamination in this region reflects the recent use of DDT and degradation of older DDT. The pesticides in agricultural soils are a matter of concern for future food chain accumulation and human health so; regular investigation of pesticide residues is required on soil health.

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