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SURVEY OF PESTICIDE RESIDUES IN SOILS AROUND MYSORE CITY

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ABSTRACT

A survey was conducted to examine the pesticide residues in some soil samples collected from irrigated agricultural farmlands around Mysore city, Karnataka, India. These samples were analysed by gas chromatography consisting of electron capture detector (ECD) to analyse the organochlorine pesticides (OCPs) and flame photometric detector (FPD) for analysis of organophosphorus pesticides (OPPs). OCPs consist of hexachlorocyclohexane (HCH), endosulfan, DDT and its metabolite DDE which were detected in all the soil samples, and their total concentration range from > 64.27µg/g to 4504.18µg/g. Among all the pesticides, endosulfan had the highest concentration, followed by HCH with an order of endosulfan > HCH > DDE > DDT. The regional concentration of residues was as follows: east > west > south > north. DDT residues were absent in western part of the city and the concentration of other pesticides except endosulfan was quite low. DDT concentrations indicate no new input or very low new applications of this pesticide in these soils, while the high concentration of endosulfan may show new input of pesticides like dimethoate, malathion, parathion, monocrotophos, fenoprop etc. in these farmlands. No detectable organophosphorus pesticides were found in the soil samples. The main source of contamination was related to human activities, such as agricultural chemical applications.

INTRODUCTION

Agriculture affects the environment through many complex physical, chemical and biological processes. Although application of agrochemicals is desirable to farm management, it can cause some undesired effects to the environment. At present, more than 10,000 different pesticides are widely used throughout the world. Their annual consumption in India is about 100,000 tons, currently used on 25% of the total cultivated area. Due to the continuous and uncontrolled use of highly persistent pesticides, residue problems have become quite alarming, especially in developing countries.

Organochlorine pesticides are ubiquitous and persistent, and are extremely toxic to non-target populations of living beings. In India, DDT and HCH are the two major chemicals used in agriculture and public health programmes. More than 600,000 tons of HCH and 270,000 tons of DDT have been added to the environment since their respective introductions in 1949 and 1952 (Karanth 2000). Although, officially chloroorganic pesticides have ceased to be applied in many parts of the world, in India some of them like DDT and lindane are still applied as pesticides.

DDT, an organochlorine insecticide, for a long time was used in agriculture and silviculture (Fry 1995) but currently is licensed almost exclusively for vector control at least in 24 countries (WHO 2001). DDT and its metabolites have been detected in a wide variety of environmental media, including soil, sediments, surface and groundwater, air, animal and plant tissues, food and also in working and domestic environments (ATSDR 2000, DHHS 2002, Zhou et al. 2001).

Hexachlorocyclohexane (HCH), an organochlorine insecticide, and its all isomers are toxic compounds. Endosulfan, as a chlorinated cyclodiene insecticide, is used on food, non-food and forage crops as well as for wood preservation and in home gardening products. It may be found in formulations with other active ingredients such as dimethoate, malathion, methomyl, triazophos, parathion and petroleum oils (Herrmann 2003).

The studies conducted in different countries, have widely confirmed the serious contamination of soil by pesticide residues. A study carried out in Mali, West Africa, showed the presence of pesticide residues in soils collected from four cotton-producing areas. Pesticides were detected in 77% of the soil samples and included p,p-DDT and its breakdown products, endosulfan-I, endosulfan-II and endosulfan sulphate (Jean et al. 2007).

The analysis of some soil samples in northern Portugal revealed the presence of persistent pesticides, parent compounds and degradation products such as endosulfan, DDE, DDD and alachlor (Goncalves et al. 2006). The results obtained from an analytical study in Hong Kong showed that the concentration of HCH, DDT and their isomers are predominant contaminant substances in soil samples (Zhang et al. 2006). In Australia, the soil analysis confirmed the contamination of soil samples by a range of pesticides especially with triazin herbicides (Ying et al. 2004). In Spain, OCPs such as HCH and DDT were detected at levels ranging from moderate to severe pollution in stream sediments even though they were banned a few decades ago (González et al. 2005).

In Tanzania, analysis of some soil samples distinguished that DDT and HCH were dominant in all samples (Kishimba et al. 2003). In USA, an analysis of soil samples collected from 30 farms in Alabama, Louisiana and Texas showed presence of DDT, Chlordanes, dieldrin and HCH (Bidleman et al. 1999-2000). In India, a survey carried out on surface sediment samples collected from the mouth of Hugli estuary in the vicinity of Sundarban mangrove environment showed the residues of HCH, α-endosulfan, endosulfan sulphate, DDT and pp'-DDE. The concentration of these compounds was quite low. The literature review indicates that there is a basic lack of information about the presence of pesticide residues in the soil of Mysore area.

MATERIALS AND METHODS

Soil samples were collected from irrigated agricultural farmlands characterized by different agricultural crops around Mysore city (Fig.1 and Table 1). Since top soil shows a wider spectrum and higher concentrations of pesticide residues, soil samples were collected from 5-30 cm below the soil surface. In fact, each sample was representative of five points within farmland, in that they were collected from five separate points, mixed well, and only one sample was finally chosen.

The internationally accepted standard analytical method was followed for analysis of pesticide residues in soils. 50g of each sample was weighed and added with ammonium chloride solution (NH_4Cl), followed by acetone and shaken well for 20 minutes. Then 50 mL of petroleum ether was added and kept in a shaker for overnight.

After filtering by Whatman No. 1 filter paper, 50 mL of acetone was added again to each soil sample and was filtered again. To remove excess solvents, Rotary Flash Evaporator (rpm-100, temp. 45-50°C) was used. The crude extracts were cleaned up by florosil column chromatography. Glass columns (40 cm × 1.1-cm i.d.) were packed from the bottom with

Table 1: Description of samples, around Mysore city, India, 2007.

Soil sample No.	Type of cultivation	Sample location
1	Paddy	West
2	Coconut	North west
3	Brinjal	West
4	Coffee	South west
5	Lentil	East
6	Corn	East
7	Sugarcane	North
8	Bean	North
9	Mulberry	South
10	Onion	South

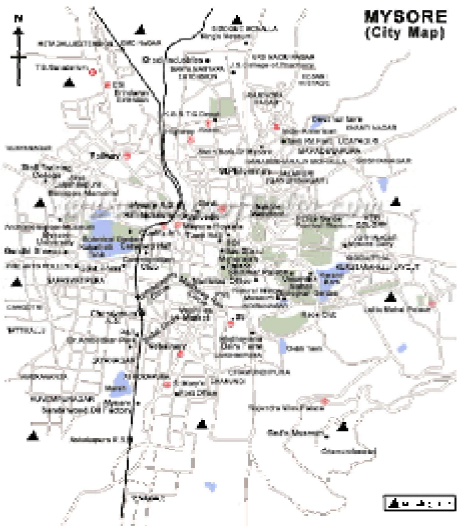

Fig. 1: Sampling sites around Mysore city.

a glass wool plug, 8 cm of deactivated florosil and 4 cm anhydrous Na_2SO_4 were used to remove excess oil, fat and moisture contents. The packed column was prewashed with 50 mL of petroleum ether. The extracts were transferred to the column eluted with 160 mL petroleum ether mixed with diethyl ether. The combined extracts were evaporated almost to dryness and the final volume was reached to 5 mL with GC grade solvent. Anhydrous sodium sulphate was added to remove the traces of moisture if any, before injecting the sample to GC.

A Shimadzu 14B GC unit, OV 17 column and electron capture detector (ECD) was used to analyse organochlorine pesticides and flame photometric detector (FPD) was used for the analysis of organophosphorus pesticides. Pure analytical grade pesticide standards were used for GC analysis as reference standards. The temperature programmes of GC were as follows: Injector 230°C, Column 220°C, Detector 240°C.

Ultra pure nitrogen gas was used as carrier gas (flow rate 40 mL/min) and zero air and ultra pure hydrogen was used as flame source for FPD detector (the flow rate was 60 mL/min). CR-6 chromatographic data processor was used to record the chromatograms and peak areas used to calculate the pesticide residues in the sample comparing with the technical standard pesticides.

RESULTS AND DISCUSSION

Analysis of samples by gas chromatography identified organochlorine residues in all the soil samples (Table 3). Paddy and lentil soils showed the highest occurrence in the region including large quantities of endosulfan. The mean pesticide residue concentrations detected in each sample ranged from 16.06µg/g to 1501.39µg/g. The HCH residue levels ranged from not detectable (limit of detection = 0.1µg/g) to 11.98µg/g. Endosulfan residues were generally the highest in the soil samples (Table 4). The maximum detected concentration for endosulfan was 4497.60µg/g in a lentil crop soil in the east side of the city, followed by 2643.60 µg/g in a paddy farmland in west. DDE was detected in all samples and its maximum concentration was 3.09µg/g. In contrast, DDT was not found in 50% of crop soils, especially in west side of the city and its maximum concentration was 1.45µg/g in the

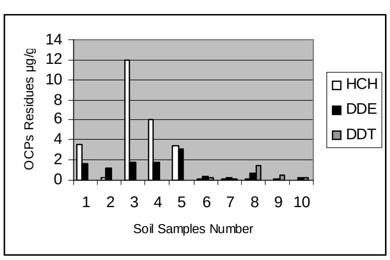

Fig. 2: Amounts of pesticide residues found in soil samples around Mysore city.

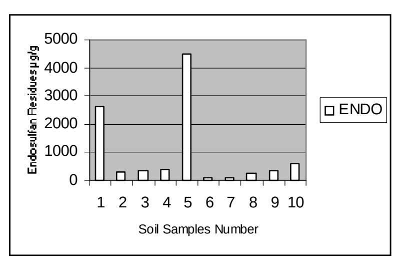

Fig. 3: Amounts of endosulfan residues found in soil samples around Mysore city.

Table 2: Some physico-chemical characteristics of soil samples collected around Mysore city.

Sample No.	pH	W.H.C (%)	Lime content(%)	Ca^{++} (mg/kg)	Mg^{++} (mg/kg)	Na^{+} (mg/kg)	K^{+} (mg/kg)
1	8.29	40	9.59	4.80	0.729	37.4	9.5
2	7.40	52	9.84	3.24	0.997	35.6	9.6
3	8.62	46	8.61	4.56	0.656	30.8	9.3
4	7.97	50	7.87	2.925	0.998	32.1	8.2
5	7.78	64	9.84	2.805	0.798	33.2	8.8
6	8.28	54	8.36	3.326	0.632	39.5	13.5
7	7.43	56	9.34	3.647	0.462	61.8	9.0
8	8.16	58	9.59	2.605	0.608	31.1	3.8
9	8.31	44	9.10	4.008	0.972	30.8	5.8
10	7.28	58	8.61	2.805	0.753	21.3	2.3

Table 3: OCPs residues concentration (pico grams & nano grams) identified in the soil samples around Mysore city.

Soil sample No.	HCH(pg)	Endosulfan(ng)	DDE(pg)	DDT(pg)
1	29.08	22.03	13.6	0
2	2.32	2.43	10.38	0
3	99.99	2.98	14.34	0
4	49.99	3.31	15.09	0
5	29.08	37.48	5.08	0
6	0.68	0.53	3.19	1.75
7	0.68	0.76	2.33	0.62
8	1.07	2.07	5.88	12.16
9	0.28	2.47	1.41	4.18
10	0.56	5.07	2.47	1.55

Table 4: OCPs Quantitative analysis of residues identified in the samples around Mysore city.

Soil samples No.	HCH (ppb)	Endosulfan (ppb)	DDE (ppb)	DDT (ppb)
1	3.5616	2643.6	1.632	0
2	0.2427	291.6	1.2456	0
3	11.9880	357.6	1.7208	0
4	5.9988	397.2	1.8108	0
5	3.4896	4497.6	3.0967	0
6	0.0816	63.6	0.3828	0.210
7	0.0826	92	0.2796	0.075
8	0.1284	248.4	0.7056	1.459
9	0.0340	357.1	0.1692	0.453
10	0.0067	609.3	0.2964	0.186

north. The concentrations of HCH, DDT and DDE in the sampling areas, however, were quite low (Fig.2). The concentration range for endosulfan was > 63.60 to 4497.60µg/g (Fig.3) and for total residues was from > 0.43µg/g to 13.70µg/g in each sample. In these samples, the estimated mean amount of total organochlorine pesticide residues except endosulfan was 2.28µg/g. For endosulfan residues it was 955.80µg/g. No organophosphorus pesticide residues were found in the samples.

The persistence (DT50) of organochlorine pesticides varies from 50 days to 30 years (Lee 2003, Tomlin 2002). Residues of organochlorine pesticides from new and historical use were detected in Mysore area. The concentrations detected for OCPs residues (except endosulfan) were below the detection limits reported in some sources (Wan et al. 2005). DDT found in the environment might have resulted from historical use as a general insecticide when large quantities of DDT were directly applied to agricultural soils (ATSDR 2000) specifically for vector control (Vieira et al. 2001, Torres et al. 2002). On the other hand, agricultural applications of DDT are highly persistent in the environment with a reported half-life of 2 to 15 years (Howard et al. 1991). Routes of loss and degradation include runoff, volatilization, photolysis and biodegradation (aerobic and anaerobic). These processes generally occur very slowly.

India, for many years, was a major consumer of the pesticide such as BHC (Li 1999), which is in fact a technical mixture of HCH isomers, and its concentrations in the Indian population are among the highest in the world (Allsopp et al. 1995, 1998). However, India banned the use of technical HCH in 1997 (Kalra et al. 1999). Therefore, It seems that the HCH detected represent a long-term contamination resulting from earlier applications. Although the pesticides found in the soils at 10 sites were generally similar, they tend to be higher in the eastern and western parts of Mysore city, followed by the south and north zones. Except endosulfan, the concentrations of other organochlorine pesticide residues were quite low in the crop soils around Mysore city. Endosulfan which is normally used for the control of many agricultural pests may be recommended to replace with alternative, newer organophosphate pesticides (Verrine et al. 2004) since persistence of pesticides in soils and sediments, in general, is particularly influenced by the chemical properties of the pesticide, and soil and sediment characteristics etc. (Table 2).

Organophosphorus pesticides are known to undergo both biotic and abiotic transformations in soils and water, so they easily degrade in environment and the rate of degradation is affected by pesticide application rate and many environmental variables, such as temperature, pH, moisture and redox potential (Jianhang Lu 2006). These are the major reasons for not getting organophosphorus pesticide residues in the soil samples analysed.

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