Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

Vol. 7	No. 4	pp. 593-596	2008

Original Research Paper

Determination of Pesticide Residues in Some Agricultural Water Samples by Gas Chromatography

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Key Words:
Pesticide residues
Water pollution
Agricultural water
Gas Chromatography

ABSTRACT

Experiments were conducted to determine 18 pesticide residues in water samples collected from irrigated agricultural farmlands around Mysore city, Karnataka, India. The samples were analysed by gas chromatography consisting of electron capture detector to look for organochlorine pesticides (OCPs) and flame photometric detector for the determination of organophosphorus pesticides (OPPs). Seven pesticides were detected in water samples namely aldrin, dieldrin, a-HCH, b-HCH, g-HCH, 2,4-DDD and endosulfan-1. All the detected pesticides in water samples were in low concentrations. Pond and bore well water samples had no pesticide residues. Among organochlorine pesticides, present in farm water samples, a-HCH and g-HCH were more frequently found followed by 2,4-DDD. No organophosphorus pesticide residues were detected in any water samples.

INTRODUCTION

Intensive agricultural practices often include the use of pesticides to enhance crop yields. However, the improvement in yield is sometimes concomitant with the occurrence and persistence of pesticide residues in soil and water (Ware & Whitacre 2004). Water contains pesticide residues in agricultural fields. The crops too would pose threat to human health if such water is used for growing crops. Fortunately, the consumption of pesticides in India is one of the lowest in the world. India uses 0.5 kg/hectare pesticide compared to 7.0 kg/hectare by USA, 2.5 kg/hectare by Europe, 12 kg/hectare by Japan and 6.6 kg/hectare by Korea. However, increased use of pesticides has caused economic, environmental, health and social problems in India (Rajendran 2003). Water solubility and adsorption to soil are important factors in determining pesticide tendency to move through the soil profile with infiltrating water, and over the soil with runoff (Dem et al. 2007). To understand the potential of pesticide movement towards groundwater or in runoffs, pesticide properties, application factors, soil and site conditions must be evaluated. Rainfall, irrigation practices and evapotranspiration will also significantly influence the pesticide movement in water. In India DDT and BHC were the two major chemicals used in agriculture and public health programs. Although, now partially banned, they are still very much in use because of their wide spectrum of activity and ready availability at low cost (Karanth 2002). As an organochlorine insecticide, DDT and its metabolites have been detected in a wide variety of environmental media including groundwater (ATSDR 2000, DHHS 2002 and Zhou et al. 2001). Organophosphorus and organochlorine pesticides are widely used in Indian agriculture. Unfortunately, most of them are recalcitrant to biodegradation and toxic even at very low levels. Therefore, accurate monitoring of the hazardous substances is essential for the health of the Indian population.

The studies conducted by different countries have confirmed the contamination of water by pesticide residues. The DDT was the main contaminant detected in soil and water samples of Banjul and Dakar in West Africa (Manirakiza et al. 2005). A study on surface water quality in Ivory Coast demonstrated the occurrence of organochlorine pesticides at low concentrations (Wandan & Zabik 1996). In Mali, eight pesticides were detected in water samples collected from four cotton-producing areas. All the detected pesticides in water had concentrations below our established quantification limit except for atrazine (Dem et al. 2007).

In India, an Indo-Dutch study has shown alarming levels of pesticides in Yamuna water supplies to Delhi. The organochlorine pesticides like aldrin, BHC, DDT and dieldrin were detected in the range of 0.001-1.064 µg/L (Agarwal 1997). Organochlorine residues were detected in the sediments of River Ganga. Of the various organochlorines detected, g-HCH, aldrin, dieldrin and heptachlor epoxide were more frequently present (Ahmad et al. 1996). In New Delhi, out of 5 top brands and other less popular brands of drinking water tested for 12 organochlorine pesticides and 8 organophosphorus pesticides, most of the bottled water samples were contaminated with pesticide residues. The levels, however, were lower than the raw water. Although agricultural pesticide use is increasing in Mysore, but no information is available on the specific concentrations and types of pesticides in Mysore city agricultural water.

MATERIALS AND METHODS

Water samples were collected from various parts of Mysore city during January to March 2007. The samples were stored at a 4°C in a refrigerator and all were extracted within 7 days using liquid-liquid partition (LLP). Each sample (1-L) was poured through a folded filter paper and measured in a graduated cylinder (1-L) before transfer to a separating funnel. Sodium sulphate (10 g) was added to the separating funnel and dissolved by shaking. The water-sodium sulphate mixture was extracted with dichloromethane (3 × 100 mL), and after each separation, the upper organic layer was collected in a separate beaker and the lower aqueous layer was again extracted with 100 mL of dichloromethane. The combined dichloromethane layers were reduced in volume on a rotary evaporator to about 5 mL. The crude extracts were cleaned up by florisil column chromatography. Glass columns (40 cm × 1.1cm i.d.) were packed from the bottom with a glass wool plug, 8 cm of deactivated florisil and 4 cm anhydrous Na_2SO_4 to remove excess oil, fat and moisture contents respectively. The packed column was prewashed with 50 mL of petroleum ether. The extracts were transferred to the column and eluted with 200 mL petroleum ether mixed with diethyl ether (85:15). The combined extracts were reduced almost to dryness and the final volume was reached to 5 mL with GC grade solvent. No additional cleanup was needed and the water extracts were subjected to GC analysis.

A Shimadzu 14B GC unit, OV 17 column and electron capture detector (ECD) was used to analyse organochlorine pesticides, and flame photometric detector (FPD) for the analysis of organophosphorus pesticides. Pure analytical grade pesticide standards were used for GC analysis as reference standards. The temperature programs of GC were: injector 230°C, column 220°C and detector 260°C. Ultra pure nitrogen gas was used as carrier gas (flow rate 40 mL/min) and zero air and ultra pure hydrogen were used as flame source for FPD detector (flow rate 60 mL/min). CR-6 chromatographic data processor was used to record the chromatograms, and peak areas were used to calculate the pesticide residues in the sample comparing with the technical standard pesticides.

RESULTS AND DISCUSSION

Pesticides considered for the monitoring study are given in Table 1, and occurrence and range of pesticide residues in Table 2. The suitable GC condition is very important for better separation and sensitivity of the analyte. Analysis of samples by gas chromatography identified no pesticide residues in most of the water samples. It is evident that some of the agricultural waters in Mysore city have pesticide residues, but not above the permissible limits.

Eight pesticides were detected in the water samples: aldrin, dieldrin, a-HCH, b-HCH, g-HCH, 2,4-DDD and endosulfan-1. For the pesticides detected, g-HCH was detected in 30 % of the samples, followed by 2,4-DDD and a-HCH (each 20 %). A comparative picture reveals that the water samples collected from east of Mysore contain less pesticide residues than the waters tested from other sites. Among the organochlorines, isomers of HCH were more frequently detected. Although DDT was not detected in any of the samples, one of its metabolites, 2,4-DDD, was detected. Endosulfan was present in only one sample. No organophosphorus pesticides were detected in the samples. The highest concentration of a-HCH and g-HCH were 0.002 and 0.0093 mg/L respectively, which were detected in agricultural water samples. Maximum concentration of 0.0012 mg/L was detected for 2,4-DDD in an agricultural water sample. All the pond and bore well water samples in the study area were completely free from pesticide residues.

It is believed that residues in the selected sites are the main sources for the contamination of pesticide residues in water bodies. In some cases, water drawn from industrially polluted fields and heavily pesticide sprayed agricultural lands are responsible for the presence of the pesticide residues in these samples. Agricultural use as well as pesticides applied for other than agricultural uses, like outdoor industrial uses, may also contaminate agricultural waters. As pesticide residues in runoff water move from sites of application to natural or man-made water bodies, leaching and runoff soil conditions are two main reasons for changes in water residue concentrations over time. There seems to be a possible relationship between the amounts of pesticides found in the water samples with that of the amount of pesticides consumed in the district.

The concentrations detected for OCPS residues were below the detection limits reported in some sources (Manirakiza et al. 2005). DDD found in the environment might have resulted from the pesticide application for other than agricultural uses, specifically for vectors. Of the eight pesticides detected in water samples, all had low concentrations and only trace of g-HCH was detected in a surface water sample. The results of this study suggest that contamination by pesticides in the Mysore district is not as severe as might be anticipated. However, this study was limited to samples collected from a small number of agricultural water bodies in only one phase of the growing season. Further studies in other agricultural areas of Mysore district are needed in order to assess the levels of pesticide residues in Mysore city agricultural water resources.

ACKNOWLEDGMENT

The authors thank Dr. Akmal Pasha, Mr. Vijaya Shankar and Mr. V. Lalith Kumar of CFTRI, Mysore for their valuable support, help and suggestions throughout the research work.

Table 1: Pesticides considered for the monitoring study.

NO.	Name of the pesticide	NO.	Name of the pesticide	NO.	Name of the pesticide
1	Aldrin	7	Heptachlor	13	4,4-DDT
2	a-HCH	8	Heptachlor epoxide	14	Endosulfan-1
3	b-HCH	9	2,4-DDD	15	Endosulfan-2
4	Dieldrin	10	2,4-DDT	16	Atrazin
5	Endrin	11	4,4-DDD	17	Methoxychlor
6	g-HCH	12	4,4-DDE	18	Dimethoate

Table 2: Pesticide residues (mg/L) in different agricultural water samples collected from Mysore city.

	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10
Pesticide residues	Pond	Bore well	Agri. water	Agri. water	Pond	Agri. water	River	Bore well	Agri. water	Drinking water
Aldrin	ND	ND	0.0035	ND	ND	ND	ND	ND	ND	ND
a-HCH	ND	ND	ND	ND	ND	0.0013	ND	ND	0.00007	ND
b-HCH	ND	ND	ND	ND	ND	0.0513	ND	ND	ND	ND
Dieldrin	ND	ND	0.0077	ND	ND	ND	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
g-HCH	ND	ND	0.0093	ND	ND	ND	0.00127	ND	0.00229	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor ep.	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-DDD	ND	ND	ND	0.001	ND	ND	ND	ND	0.257	ND
2,4-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4,4-DDD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4,4-DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4,4- DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endosulfan-1	ND	ND	ND	0.00006	ND	ND	ND	ND	ND	ND
Endosulfan-2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Atrazin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dimethoate	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND: Non detectable; Agri. Water - Agricultural water; Heptachlor ep. - Heptachlor epoxide

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