

Original Research Article

Gas Chromatography-Mass Spectrometry Determination of Organophosphate Pesticide Residues in water of the irrigation canals in the North Zone, Tamil Nadu, India

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A B S T R A C T

Keywords

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COD;
DO;
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Residue;
Organo-phosphate (OP).

Pesticide residues of Organophosphates (OP) of most commonly used classes were monitored in the water samples collected from agricultural area in various places, Tamil Nadu. The samples were analyzed for DO, COD, BOD, and Phosphate as test parameters. The data obtained from the laboratory tests were compared based on the standard or recommended value. The dissolved oxygen level of Bhavani, Coimbatore, Pollachi, and Erode were 3.5mg/L^{-1} , 3.3mg/L^{-1} , 3mg/L^{-1} , 3.2mg/L^{-1} showed the significant decrease from the standard value of DO ($4\text{--}5\text{mg/L}^{-1}$). The BOD level of 4 places (Bhavani, Coimbatore, Erode, Pollachi) are 88mg/L^{-1} , 105mg/L^{-1} , 93mg/L^{-1} , 142mg/L^{-1} respectively, showed the significant variation from the standard value ($1\text{--}2\text{mg/L}^{-1}$). Same as to BOD, the COD concentration also significantly varies from the standard value of $1\text{--}10\text{mg/L}^{-1}$ to the highest value of 247mg/L^{-1} and the lowest value observed as 135mg/L^{-1} in the water samples of Bhavani. The standard value of phosphate is 0.5mg/L^{-1} , but the result showed that the phosphate level is more than the recommended concentration in the water samples. Occurrence and concentrations of pesticides residue detected in the water samples by GC-MS. Out of three insecticides namely Methyl parathion, Dichlorvos and Chlorpyrifos only two insecticides were detected except methyl parathion. Insecticides that were present in higher concentrations in the surface water were dichlorvos ($4.421\mu\text{g/mL}$) in S1 and ($1.229\mu\text{g/mL}$) in S4, where as in S3 chlorpyrifos was detected ($1.329\mu\text{g/mL}$) except methyl parathion in S2. This could be due to frequent usage of the above mentioned insecticides plus contamination could originate from the application sites.

Introduction

Pesticides are one of the many components used in modern agriculture. Pesticides are chemicals used to control or kill the pest species, which include plants, that are not required (Margni *et al.*, 2002). The world's pesticide production was valued at more than \$35.8 billion in 2006

and more than \$39.4 billion in 2007 (Grude *et al.*, 2011). In 2007, the total production increased due to increased usage of all types of pesticides (Grude *et al.*, 2011). The amount of pesticides used was estimated at 5.2 million tonnes in 2006. Uncontrolled use of pesticides in

agricultural and/or non-agricultural sectors accounted for the presence of their residues in various environmental matrices (ICPR 1991). Pesticides are used to increase crop yields, can be applied either directly or indirectly and their residue may accumulate not only in crops, but also in the soil surface water and other environmental matrices (Wesseling *et al.*, 1999).

Non-point-source contamination of surface water has emerged as an important environmental problem during the last decade. Although significant advances have been made in controlling point-source pollution, little progress has been accomplished in the area of nonpoint-source pollution of surface water. This is because of the seasonality, inherent variability and multiplicity of the origin of non-point- source pollution (Pereira and Hostettler,1993). Studies on pesticide contamination have been carried out throughout the world and have been documented (Pereira and Hostettler, 1993; Richards and Baker,1993; . Larson *et al.*, 1995). Since the 1940s, pesticide contamination of the environment has been given special attention by researchers (Richards and Baker, 1993; . Larson *et al.*, 1995).

Clean fresh water is considered the most important of all natural resources. But, surface water can be contaminated by domestic, industrial and agricultural waste, including fertilizers, pesticides etc. Several studies have demonstrated a positive correlation between concentrations of pesticides and land use practices (Pionke and Glotfelty, 1989; Holden *et al.*, 1992). Pesticides and other organic compounds can also be transported into the atmosphere by various processes (Albanis *et al.*, 1998). Once in the atmosphere, these compounds can be dispersed and

distributed to water and land surfaces, often at considerable distances from their origin (Goolsby *et al.*, 1992).

Materials and Methods

Study Area

Water samples from the Stream and irrigation system were taken from a hose plugged into a quick coupling connection on the golf course. Sampling was conducted when the irrigation system was active and made sure that the sample was free from stagnant water and was representative of the water actually being applied to the golf course and was collected in clean glass jars.

Surface irrigation water, samples were collected at several locations of North zone (S1-Coimbatore: Corn, S2- Erode: Tomato, S3 - Pollachi: Corn, S4 - Bhavani: Sugarcane) (Figure.1 & Table.1)

Biochemical analysis

The samples were analyzed for DO, COD, BOD, and Phosphate as test parameters. The data obtained from the laboratory tests were compared based on the standard or recommended value (Aneja, 2001).

Determine the Residues of Organo phosphate pesticide in water by GC-MS analysis

Experimental Design

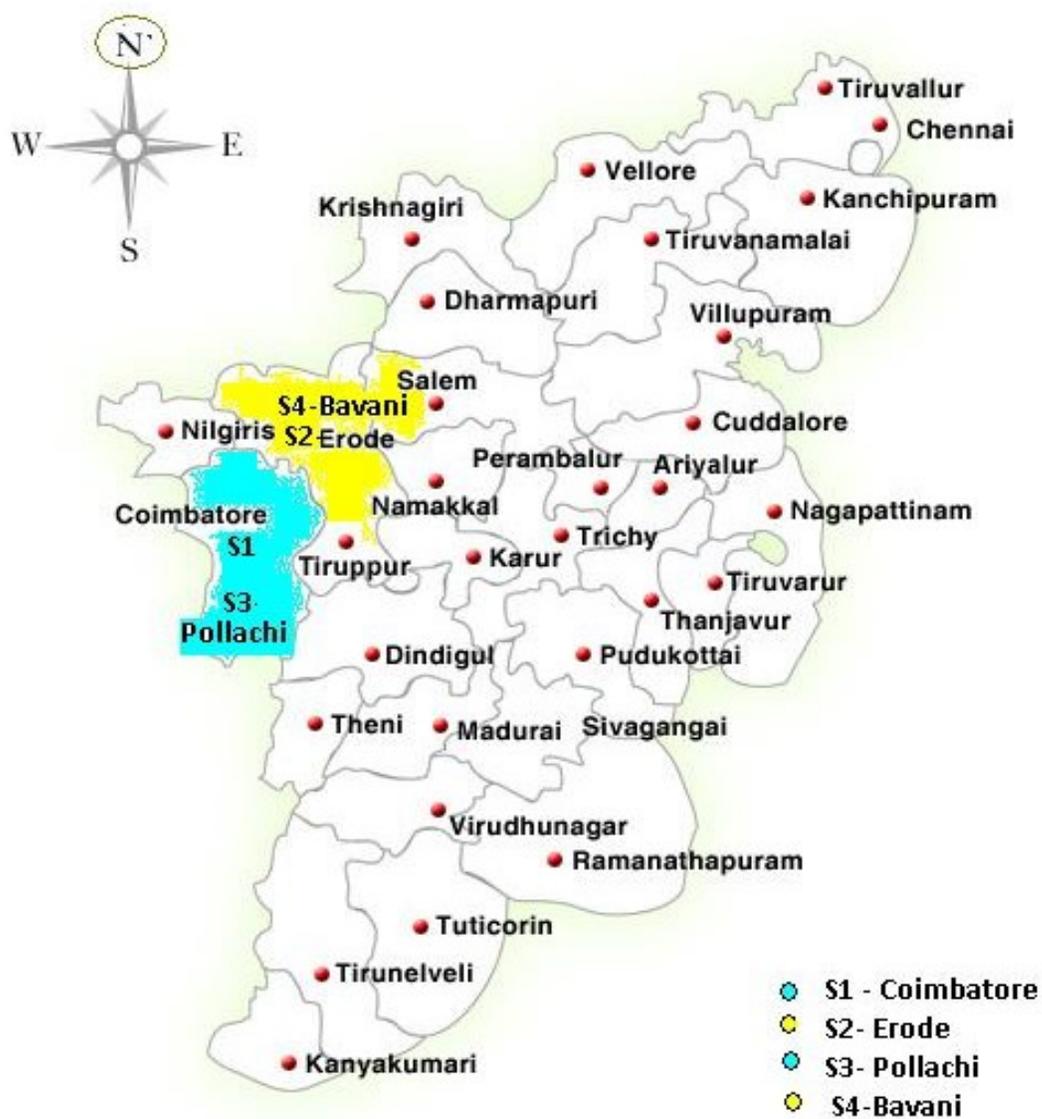
Sampling methodology

The sampling was focused on locations influenced by agricultural areas mainly from irrigation canal. The water was sampled by grab method into 2.5 L amber bottles by making several composite samples. Sampled sediment was collected in to a clean air tight plastic bottle on wet ice and later stored at -4°C prior to extraction.

Table.1 Location of Sampling

Stations	District	Place	Agri field
S1 & S4	Erode	Bhavani & Erode	Sugar cane & Tomato
S2 & S3	Coimbatore	Coimbatore & Pllachi	Corn

Figure.1 Map of Tamil Nadu showing location of sampling stations



Equipment

Gas Chromatograph used was Agilent GC MS – 6890/5975 and capillary column, 35 % phenyl methyl siloxane for MS; length 30 m; 0,32 mm I.D. & 0,25 µm film thickness. A 1-µl syringe (splitless) from Aglient Co. was used. Selection of analysed pesticides was done on the basis of pesticide use information provided by Ntow *et al.*, (2006).

Reagents

The analytical grade standards of insecticide (Dichlorvos-20%, Methyl parathion-76% and Chlorpyrifos-50%) were purchased from local market. All solvents (n-hexane, acetone, dichloromethane, di-ethyl ether) as well as other analytical materials used (anhydrous sodium chloride, Florisil) were of analytical grade quality obtained from Hi Media, Mumbai and the solvents double distilled to ensure purity.

Sample extraction and cleanup

Extraction and cleanup of the samples was followed according to the described protocol (NRI, 1991). 2 L of water sample was transferred into a separatory funnel and pH was measured. A 50 ml portion of 0.2 M disodium hydrogen phosphate buffer was added to the sample, and pH was adjusted to 7. The neutralized sample was treated with 100 g sodium chloride to salt out the pesticides from the aqueous phase. A 60 ml aliquot of triple distilled dichloromethane was added and shaken for 2 min while releasing pressure. The sample was allowed to settle for 30 min to enhance separation of the phases. The organic layer was collected in 250 ml Erlenmeyer flasks and stored at 4°C in a refrigerator. The extractions were repeated twice using 60 ml portions of dichloromethane, the organic phase

combined and cleaned by passing through florisil column topped with anhydrous sodium sulphate. Pesticide residues were sequentially eluted with 200 ml of 6%, 15% and then 50% diethyl ether in hexane. The elutes were combined and concentrated to near dryness using a rotary evaporator at 60°C, and reconstituted in 5 ml HPLC hexane for GC analyses (Safina Musa *et al.*, 2011).

Chromatographic analyses

Organophosphorus pesticide residues in the field sample were analyzed by Agilent GC MS – 6890/5975 at the Toxicology Research Laboratory, Department of Chemistry, Tirupur. The instrument was equipped with MSD (Electron Impact) detector and column type of (35 % phenyl methyl siloxane for MS; length 30 m; 0.32 mm, I.D. & 0,25 µm film thickness; temperature was programmed at 150 °C for 1 min to 250 °C at 8 °C/min to 290 °C at 3 °C/min Isothermal 5,00 min. Transfer line temperature 280 °C & Total run time is 34 min. The carrier (Helium) gas flow rate of 2 ml/min were applied. Sample analysis was carried out by injecting (Splitless) 1 µl sample size into the GC (Ntow *et al.*, 2006).

Result and Discussion

Biochemical analysis

Table 2 shows a analysis results of DO, COD, BOD and Phosphate level which compared with standard values.

Determine the Residues of Organophosphate pesticide in water by GC-MS analysis

Table 3 shows a summary of the occurrence and concentrations of pesticides residue detected in the water samples collected at the four sampling points in the irrigation canals Out of three insecticides

namely Methyl parathion, Dichlorvos and Chlorpyrifos only two insecticides were detected except methyl parathion. Insecticides that were present in higher concentrations in the surface water were dichlorvos (4.421µg/mL) in S1 and (1.229 µg/mL) in S4, where as in S3 chlorpyrifos was detected (1.329 µg/mL) except methyl parathion in S2 (Figure 2,3).

This study demonstrated clearly that the canal water in the agricultural fields was contaminated with specific pesticides (Methyl Parathion, Chlorpyrifos and Dichlorvos). The selected pesticides extracted from the water samples collected belonged to the organophosphate groups.

Out of three insecticides namely Methyl parathion, Dichlorvos and Chlorpyrifos only two insecticides were detected except methyl parathion.

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Table.2 Biochemical characteristics of irrigation canal water samples analysed

Parameters	Standard value (mgL ⁻¹)	Sugarcane (Bhavani) (mgL ⁻¹) station-1	Corn (Coimbatore) (mgL ⁻¹) station -2	Corn (Pollachi) (mgL ⁻¹) station-3	Tomato (Erode) (mgL ⁻¹) station-4
DO (mgL ⁻¹)	4-5	3.5	3.3	3	3.2
BOD (mgL ⁻¹)	1-2	88	105	93	142
COD (mg L ⁻¹)	1-10	135	210	175	247
Phosphate (mg/L ⁻¹)	0.5	24.50	19.50	14.25	18.20

Table.3 Summary of pesticide concentration detected in surface water from the four sampling sites in the Tamil Nadu agricultural area.

Location / Station	Insecticide	Limit of detection (µg/mL)	Maximum concentration (µg/mL)
S1	Dichlorvos	0.001*	4.421
S2	Methyl parathion	0.01*	ND*
S3	Chlorpyrifos	0.005**	1.329
S4	Dichlorvos	0.001*	1.229

Source: ** (Ismail *et al.*, 2012) , *(ICPR, 1991); *ND – Not detected

Figure.2 Mass Spectra of Dichlorvos and Chlorpyrifos

File :D:\RESULTS\Year\2013\MAY\13MY S1(PH) 21 05 2013.D
Operator :
Acquired : 21 May 2013 16:20 using AcqMethod CPSIA PHTHALATE METHOD.M
Instrument : GCMS
Sample Name :
Misc Info :
Vial Number: 2

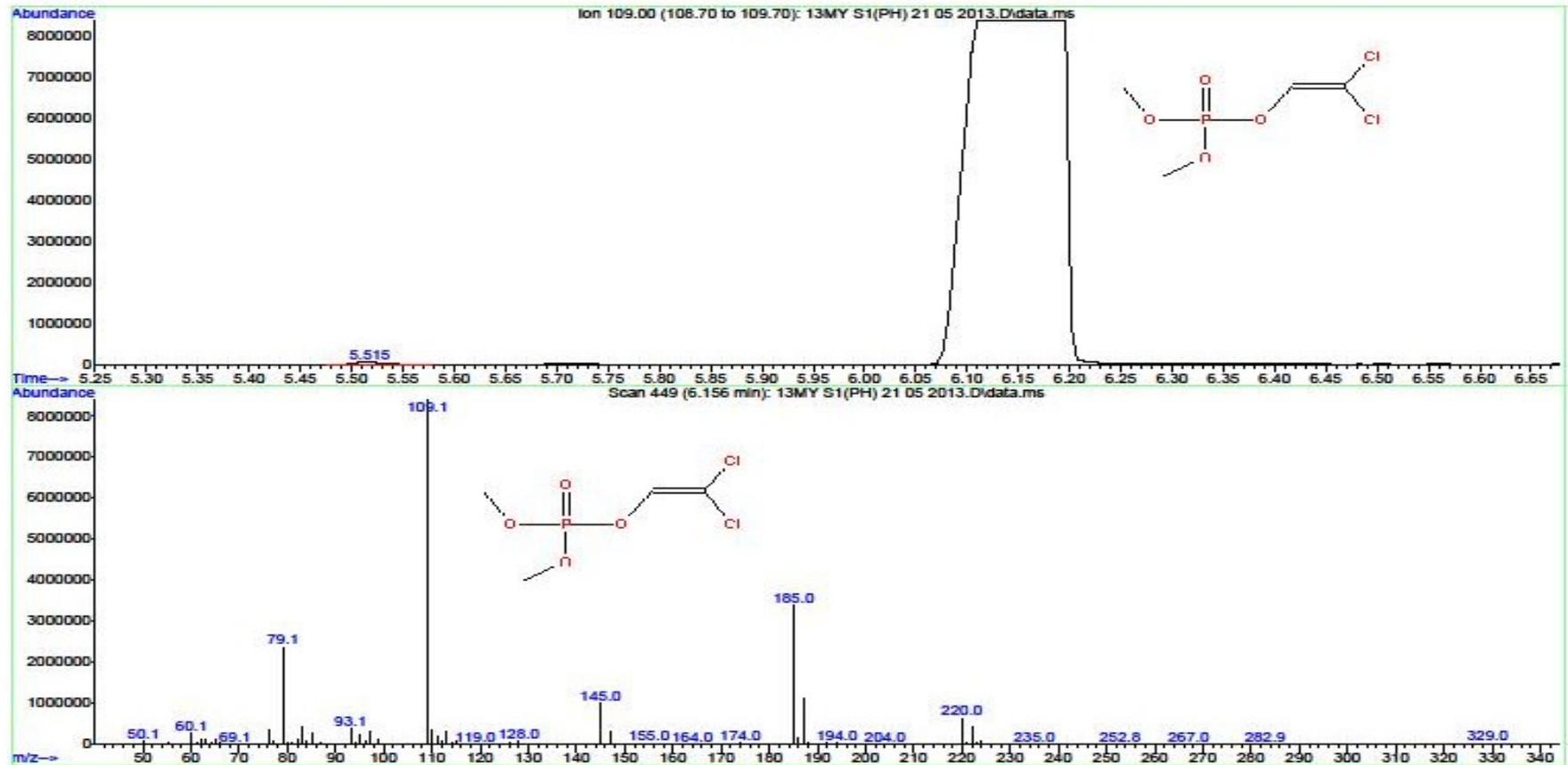
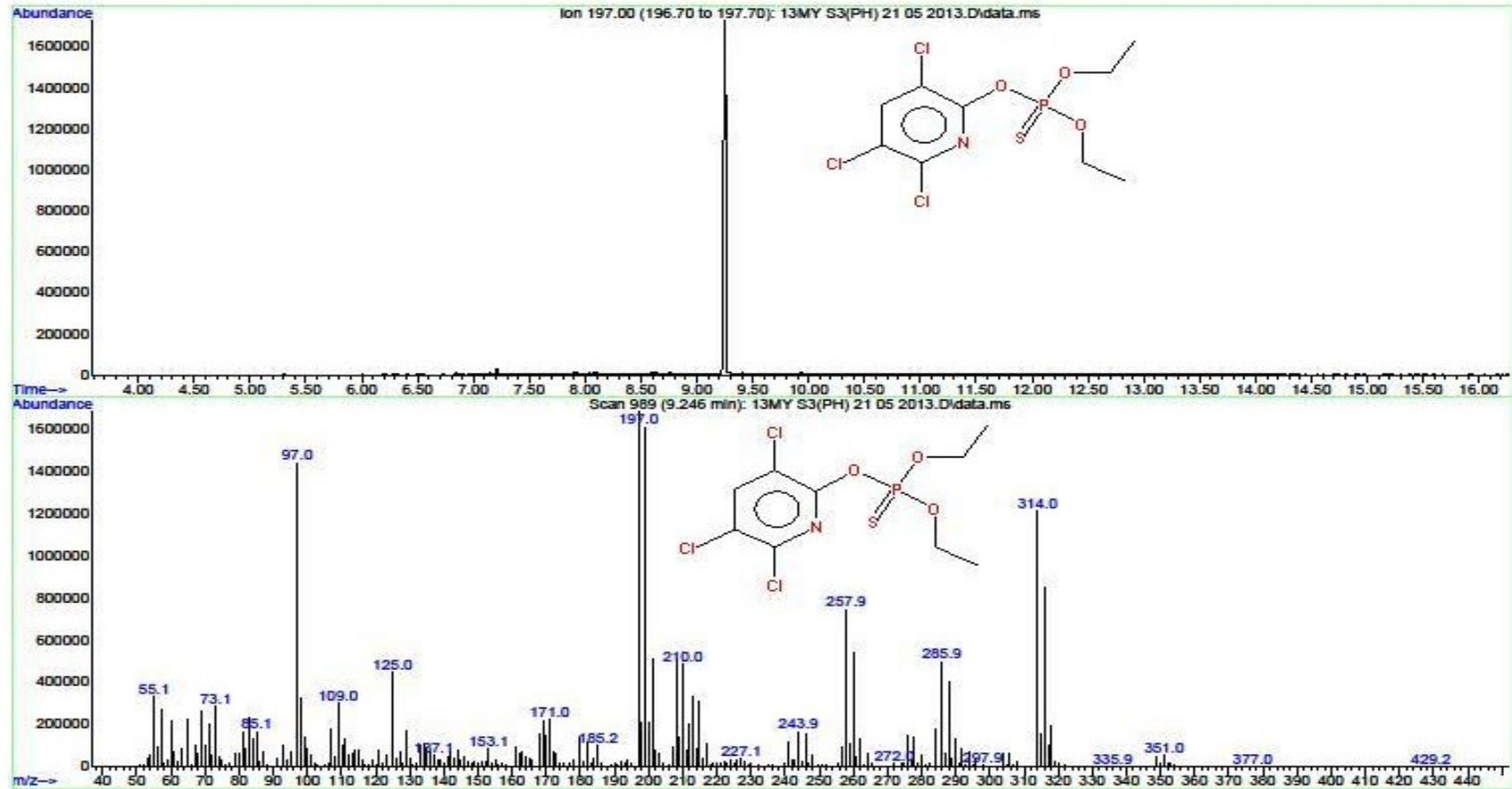


Figure.3 Mass Spectra of pesticide concentration detected in surface water

File :D:\RESULTS\Year\2013\MAY\13MY S3(PH) 21 05 2013.D
Operator :
Acquired : 21 May 2013 16:45 using AcqMethod CPSIA PHTHALATE METHOD.M
Instrument : GCMS
Sample Name:
Misc Info :
Vial Number: 3



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