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Determination of Organophosphorous Pesticide Residue in Water Samples using Gas Chromatography-Electron Capture Detector

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Most wastewater contains pollutants, which may deteriorate the quality of receiving water bodies and harm associated aquatic life. Pesticides contamination to water systems have received particular attention during the last few years. Organophosporous pesticide residue values in surface water samples from Deg Nallah are reported in this study. The samples were extracted with 15 % methylene chloride in hexane and analyzed on a gas chromatograph equipped with an electron capture detector using capillary column. Contamination levels in all sites were found to be below the maximum acceptable concentration (MAC) as described by National Environmental quality standards (NEQS) Pakistan. High-resolution gas liquid chromatographic (HR-GLC) analysis of the to water samples, detected diazinon, dichlorvos, mevinphos, dimethoate, methyl parathion, malathion, fenitrothion, chlorpyriphos, endosulfan, prothiopos, profenophos, ethion and T-BHC at trace level.

Key Words: Gas chromatography-Electron capture detector, Water pollution, Organophosphates.

INTRODUCTION

Pesticides contamination to water systems have received particular attention during these last few years. More than 700 pesticides are approved for use around the world, many of which are suspected to endocrine disrupts. Other pesticides, though no longer used, persist in the environment where they bioaccumulate in the flora and fauna. Pesticides with toxic to nature, have become an important class of water pollutants today. Even if these compounds are present only in very low concentrations, they are hazardous because some species of aquatic life are known to concentrate them 100-fold or more. There is no predictable safe level for pesticides in waters where food chain can occur[1]. Pakistan uses insecticides in agriculture and for control of vector-born diseases in the public health sector. These insecticides find there way into the water systems through leaching, channeling, direct spillage and wind drift. In addition to this, pesticides can be introduced to the canals in runoff and by direct spraying of: (1) insecticides for the control of insects and (2) herbicides for the control of terrestrial and aquatic weeds. Currently organophosphates (insecticides) are used since most of the organochlorides insecticides have been banned because of toxicity, persistence and bioaccumulate in the environment[2].

Many pesticides, particularly those with low solubility, show a tendency to bioaccumulate in organisms[3] and thus, can be harmful and toxic to aquatic organisms when present in water or sediment even in very low concentrations. Organisms may bioaccumulate pesticides from either water, food or sediments and their tissue may accumulate, in time, concentrations several orders of magnitude higher than the aqueous concentrations of the compounds. Many of the effects of bioaccumulation are complex and unknown[4]. Many pesticides have been shown to be potentially toxic, carcinogenic and mutagenic[5]. However, less information is available on the sources, fates and effects of pesticides in aquatic environments than for many other water-quality constituents. Pesticides may also have negative effects on aquatic ecosystems, which may directly affect human health. For example, high concentrations of herbicides flushed to surface water during spring runoff may adversely affect the growth and survival of aquatic plants, which are essential food sources and breeding grounds for aquatic organisms[6]. The widespread use of toxic pesticides has created a need for their monitoring in water systems. Gas chromatographic (GC) methods are common methods for analysis of pesticide residue using electron capture detector[7].

Deg Nallah which is polluting the nearby residential areas and the river Ravi, is an important stream. It originates from Kashmir passes through district Sialkot, Narrowal and then enters the district Sheikhupura. This natural stream has discharged[8] varying from 0.1 to 70 m^3/d. It crosses the G.T. Road at about 22 Km from Lahore and eventually crosses through residential colonies *e.g.*, Zia Abad, Rayan Pura, Hakeem Abad, Sharif Pura and Kala Pind. Ultimately, Deg fall in to the river Ravi down stream of Lahore at *ca.* 192 Km. The climate of the area is semi-arid, sub-tropical and continental and is characterized by intense hot summer and cold winter. Temperature variations within respective seasons are not much more. Mean annual rainfall is 493 mm[9].

EXPERIMENTAL

To investigate pollution levels in Deg Nallah, based on the initial survey, four sampling points were selected for the collection of water samples. The first sampling point was selected up stream behind the railway bridge, one kilometer before mixing of industrial discharge from Kalashakaku industrial area. The second sampling point was selected just after mixing of industrial discharge from Kalashakaku industrial area. The third sampling point was selected two kilometer before mixing of industrial discharge from Mandiali paper mills (Pvt.) Ltd. and fourth sampling point was selected after mixing of industrial discharge from Lahore-Sheikhupura road industrial units linked with Deg Nallah *e.g.*, Mandiali paper mills (Pvt.) Ltd.

The significance of a chemical analysis depends, to a large extent, on the sampling. An ideal sample is one which is both valid and representative. For present water analysis three principal types of sampling procedures were employed, spot or grab sampling, composite sampling and integrated sampling. It is essential to protect the collected water samples from changes in composition and deterioration with aging due to various interactions. The preservation of water samples were carried out according to standard method for examination of water and waste water[10].

Extraction of samples were carried out using 15 % methylene chloride in hexane. After vigorous shaking sample was poured into a 2-L separatory funnel. Sample bottle was rinsed with 60 mL 15 % methylene chloride in hexane, then this solvent was poured in to separatory funnel and shacked vigorously for 2 min. After separation of two phases, water phase was drained from separatory funnel into sample bottle and carefully poured organic phase through a 2 cm OD column containing 8 to 10 cm of Na_2SO_4 into a Kuderna-Danish apparatus fitted with 10 mL concentrator tube. Sample was poured bake into separatory funnel and extraction procedure was repeated for thrice. Na_2SO_4 was washed with several portions of hexane and drained well. Kuderna-Danish was fitted with a three-ball Synder column and volume was reduced to about 7 mL in a hot water bath (90 to 95 ºC). At this point all the methylene chloride present in the initial extracting sample had been distilled off. After cooling concentrator tube from Kuderna-Danish apparatus was removed, ground glass joint was rinsed and extracted sample was diluted to 10 mL with hexane[10].

Gas chromatographic analysis of extracted pesticide sample was carried out using Perkin Elmer, auto system, gas chromatograph equipped with ECD. The solvent flush injection technique was used. The other analysis conditions were as, column (methyl silicon 25 m × 0.53 mm), initial oven temperature 50 ºC, ramp rate 5 ºC/min, final oven temperature 175 ºC, initial and final holdup time were 3 and 9 min, respectively and detector temperature was 250 ºC. Moisture free pure nitrogen at a flow rate of 5 mL/min was used as carrier gas. The identification of various pesticide was done by comparison with the chromatogram of mixture of standards. The quantification was done by a chromatography station for Windows (CSW32) data handling software (Data APEX LTD., The Czech Republic). The pesticide composition was reported as a relative percentage of the total peak area.

RESULTS AND DISCUSSION

The analysis was carried out in triplicate and the data is reported as mean ± SD[11].

TABLE-1
% COMPOSITION OF VARIOUS ORGANOPHOSPHOROUS PESTICIDES AT SELECTED SITES OF DEG NALLAH

Sr.#	Pesticide	Sampling point # 1		Sampling point # 2		Sampling point # 3		Sampling point # 4	
		$\overline{X}$	SD	$\overline{X}$	SD	$\overline{X}$	SD	$\overline{X}$	SD
1	Diazinon	0.027	0.003	0.036	0.007	0.034	0.006	0.031	0.036
2	Dichlorvos	0.036	0.007	0.058	0.008	0.004	0.003	0.018	0.003
3	Mevinphos	0.019	0.002	0.010	0.002	0.025	0.007	0.030	0.005
4	Dimethoate	0.066	0.010	0.075	0.005	0.060	0.010	0.072	0.012
5	Methylparathion	0.109	0.009	0.085	0.008	0.085	0.010	0.160	0.029
6	Malathion	0.116	0.047	-	-	-	-	-	-
7	Fenitrothion	0.150	0.022	0.129	0.025	0.126	0.025	0.145	0.035
8	Chlorpyriphos	0.017	0.004	0.109	0.015	0.005	0.002	0.005	0.003
9	Endosulfan	0.015	0.001	0.126	0.032	0.002	0.001	-	-
10	Prothiophos	0.014	0.004	0.028	0.003	0.004	0.002	0.010	0.001
11	Profenophos	0.130	0.021	0.082	0.006	0.120	0.019	0.160	0.021
12	Ethion	0.016	0.002	0.022	0.002	0.044	0.005	-	-
13	T-BHC	0.020	0.001	-	-	0.029	0.008	0.034	0.006

$\overline{X}$ = mean value; SD = standard deviation.

The compounds are listed (Table-1) along with corresponding peak and their % constituents. At sampling point # 1, among various organophosphorous pesticides found, diazinon, dichlorvos, mevinphos, dimethoate, methyl parathion, malathion, fenitrothion, chlorpyriphos, endosulfan, prothiophos, profenophos, ethion and T-BHC (peak # 1 to 13) showed a % composition of 0.027, 0.036, 0.019, 0.066, 0.109, 0.116, 0.15, 0.017, 0.015, 0.014, 0.130, 0.016 and 0.020 %, respectively. At this point, fenitrothion showed a maximum % composition of 0.15 % while prothiophos detected with least % composition *i.e.* 0.014 %. At sampling point # 2, diazinon, dichlorvos, mevinphos, dimethoate, methyl parathion, fenitrothion, chlorpyriphos, endosulfan, prothiophos, profenophos and ethion (peak # 1 to 11) with % composition of 0.036, 0.058, 0.010, 0.075, 0.085, 0.129, 0.109, 0.126, 0.028, 0.082 and 0.002 %, respectively were detected. Highest % composition at this point showed by fenitrothion and least by mevinphos. While malathion and T-BHC were not detected at this point. At sampling point # 3, diazinon, dichlorvos, mevinphos, dimethoate, methyl parathion, fenitrothion, chlorpyriphos, endosulfan, prothiophos, profenophos, ethion and T-BHC (peak # 1 to 12) organophosphorous pesticides detected were, with % composition of 0.034, 0.004, 0.025, 0.060, 0.085, 0.126, 0.005, 0.002, 0.004, 0.12, 0.044 and 0.029 %, respectively. Malathion remain undetected at this point. At sampling point # 4 various organophosphorous pesticide detected with % compositions 0.031, 0.018, 0.030, 0.072, 0.16, 0.145, 0.005, 0.010, 0.160 and 0.034 % were diazinon, dichlorvos, mevinphos, dimethoate, methyl parathion, fenitrothion, chlorpyriphos, prothiophos, profenophos and ethion (peak # 1 to 10), respectively. Malathion, endosulfan and T-BHC were not detected at this point. At the end it was concluded that, contamination levels in all sites were below the maximum acceptable concentration (MAC) as described by the National Environmental Quality Standards (NEQS) Pakistan.

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