Pak. J. Bot., 41(4): 1981-1987, 2009.

ANALYSIS OF PESTICIDES RESIDUES OF RAWAL AND SIMLY LAKES

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Abstract

Water samples were collected from the locations of Rawal and Simly lakes. Analysis of pesticide residues in water samples was done GC/ECD through Turbochrome hardware/software system. From the collected samples, 21 pesticides were analyzed and categorized in organophosphates, organochlorines and pyrethroids. In Rawal Lake samples average concentration of fenitrothion, 2, 4-DDT and diazinone was higher while in Simly Lake, the average concentration of 2, 4-DDT, diazinone and 4, 4-DDT was higher. The benefit of the study is awareness of general public about the risk of pesticides contaminating water, the toxicity of pesticides that have the potential to enter the aquatic system and the discussion of possible consequences of pesticide bioaccumulation of the food chain.

Introduction

The environment and the human health are closely interrelated. Pollution caused by many pesticides is more harmful as they are slowly biodegradable and persist in the eco-system for a very long period of time. In the present scenario, pesticides have become a necessary part of the agricultural husbandry. The continuous use of pesticides in agriculture has revealed potential to reach ground water. The harmful residues that remain on edible portion of crops and the amount which reach water bodies, has become the cause of great concern .The problem is aggravating day by day as they move up in the food chain and being at the top of the food chain, man is most susceptible to them (Bakore *et al*., 2004). The use of chemicals to control pests has been practiced for centuries; however, agro-chemicals came into use in Pakistan in 1954. In 1989, the sale and distribution of pesticides was transferred from the public to the private sector, which brought about a fivefold increase in pesticide consumption in one year. Almost 80% of total pesticides are used on cotton plants; the remainder is applied to other crops such as paddy tobacco, fruits and vegetables (Jan *et al*., 2002; Tariq *et al*., 2006). Organophosphorus (OP) and organochlorine (OC) pesticides are widely used in agriculture as insecticides leave residues to varying extents in agricultural produce such as vegetables and fruits. Due to pesticides toxic properties and potential risk to consumers, their residues in food commodities is an issue of public concern and controlled by legislation (Kin *et al*., 2006). In Pakistan, drinking-water supplies are generally obtained from surface water sources (such as rivers, canals or lakes) or the underground aquifers. The quality of surface water is deteriorating as a result of the disposal of untreated municipal and industrial wastewaters and saline drainage effluent from agricultural areas (Aziz, 2005). Sanpera *et al*., (2003) used colonial water birds as bio-indicator of pollution levels in selected wetlands of Pakistan. Similarly, impaired physiological behavior and mortality of fish are subtle indicators of the presence of toxic pollutants in aquatic environment (Singh *et al*., 1998). When a sudden fish killing in

Rawal lake, Islamabad occurred during mid June 2004, it caught the attention of print and electronic media as well and an initiative was taken to analyze pesticides residues by Ahad *et al*., (2005). Similar studies were taking place in 2007 for the verification of pesticides residues in Rawal lake as well in Simly lake, Islamabad. Characterized by toxicity, stability, and recalcitrance to degradation in natural environments, many organochlorine pesticides (OCPs) are described as persistent organic pollutants (Zhang *et al*., 2006).

Materials and Methods

Sample collection: The areas selected for the present study of pesticides are Rawal and Simly Lakes. Rawal Lake is one of the greatest reservoirs of freshwater for the residents of Rawalpindi. The Pakistan Environment Protection Agency (EPA) reports that water in the lake is highly contaminated, largely because of human activities in the catchments of the Lake. An examination of water samples taken from the Rawal Lake revealed that the biological oxygen demand of the lake had jumped up to an alarming level of 680 milligram per litre, which was far below the standard for safe water (Malik, 2007). Simly Lake is major water source for residents of Islamabad. The Simly Lake is located 20 km from Islamabad towards North.This water reservoir is recognized as the cheapest source of fresh drinking water for the city. According to IUCN it stores not only the perennial flow from the springs of the Murree/Patriata mountain aquifer but also a considerable part of floodwater of the Soan River (Anon., 2005).

Three water samples were collected from the sites (Old Murree road, Korang canal and Spillway) of Rawal Lake and Simly Lake (Moaza canal, source, filtration plant) in May 2007.

Preparation of water samples bottles: Water samples were collected in thoroughly rinsed glass bottles (2L). Prior to the collection of the water sample, water volume of 100ML was allowed to enter the bottle by immersing the bottle in the body of water. The lid was placed on the bottle and then, rinsed. The water contents were discarded in a way that would not disturb the sample about to be taken. Rinsing step was repeated for two or more times. The bottle was reimmersed in the water and allowed it to fill the top of the bottle to minimize the head space. Bottle was sealed with screw on lid. All the samples were collected through the same procedure. After collection, the samples were transported to the laboratory. The extraction of collected samples was done by liquid extraction (Ahad *et al*., 2005). First distilled water (1000ml) was measured with the help of graduated cylinder and poured in a separating funnel (2L) fixed in stand. Dichloromethane (25ml) was added with the help of dispenser flask. The separating funnel was closed by placing the lid on it. The separating funnel was shaken gently (not vigorously) in to and fro motion so that the solvents mixed well. Mixing was repeated three times. The gases were removed out from the separating funnel each time by opening the stopper. The separating funnel was kept in stand for 10 minutes to separate the two phases and the lower oily layer was collected in a round bottom flask through a small funnel having small cotton wool plug and anhydrous sodium sulphate in its opening. Sodium chloride was added with the help of pasture pipette for efficient separation. Addition of Dichloromethane (25ml) and separation of lower organic layer was repeated three times. Propylene glycol and Ethyl acetate (1:1) solution (10 drops) were added to the round bottom flask. The extract was evaporated on rotavapour at 55°C

under vacuum and optimum rotation speed to dryness. For ultimate dryness nitrogen or air stream over activated charcoal was used. After complete dryness, n-hexane (1400µl) was added to round bottom flask and was rotated in hands symmetrically. It was transferred to glass vial with the help of posture pipette. Volume was made up to mark. This is known as reconstitution or clean up. The sample was ready for analysis on Gas Chromatograph (GC) (Ahad *et al.,* 2005). All the glass vials were labeled to prevent the mixing of samples. Collected water samples were analyzed on Perkin Elmer gas chromatograph (66942A) coupled with (ECD-Ni^{63}), electron capture detector. The column used was Silicon methyl (capillary type). Water samples were removed from the refrigerator before analysis. The GC was switched on for 24 hours before analysis. When system became ready, 1µLof the sample was taken in Hamilton syringe avoiding air bubble and injected through split less mode into the gas chromatograph under specific conditions.

Results and Discussion

Diazinon, heptachlor, parathion-methyl, fenitrothion, 2, 4'-DDD, 4, 4'-DDE, 2,4'-DDT and a-cypermethrin were analyzed in Korang canal water sample. Alpha-HCH, lindane, diazinon, heptachlor, parathion-methyl, endosulfan-I, 2,4'-DDD, 4,4'-DDE, 2,4'-DDT, Azinphos-methyl, a-Cypermethrin were detected in old Murree road water sample. In Spillway water sample alpha-HCH, heptachlor, 2,4'-DDD, 4,4'-DDE, 4,4'-DDT, azinphos-methyl, Cyfluthrin (Baythroid), a-Cypermethrin and esfenvalerate were present (Fig. 1).

In analyzed water samples of Rawal Lake average concentration of fenitrothion, 2, 4-DDT and diazinone was higher. The pesticide residues are believed to have originated from agricultural or household uses. The villages of Bhara Kahu, Malpur, Bani Gala and Noorpur Shahan are situated close to the Rawal Lake. A number of housing colonies, residential areas are coming up in the Rawal Lake catchement area without any consideration that this will adversely affect the quality of water coming into Rawal Lake (Pakistan Environment Protection Agency, Ministry of environment, 2004). In analyzed water samples of old Murree road endosulphan (0.72ug/l) was present in higher concentration and was more than the standard of European Union (0.25) (Fig. 2). The sources of contamination in the point of old Murree roads are human settlements, recreational and agricultural activities in the residential areas of lake. Rawal Dam has built on the Korang river, water samples were collected from Korang canal and analyzed results shows that in Korang canal water samples 2, 4-DDT (2.14ug/l) was present in higher concentration which is greater than EU standards (1.65) of pesticide residues in water. There are approximately 170 poultry farms situated around the Rawal Lake and disposal of their waste in the lake catchment area. Some basic arrangements for disposal of poultry wastes have been made but these are unlikely to significantly delay or prevent the inflow of pollutants into the lake (Pakistan Environment Protection Agency, Ministry of environment, 2004). So, improper disposal of poultry waste may contaminate the water of Korang canal.

In water analysis of spillway, fenitrothion (2.32ug/l) and esfenvalerate (0.22 ug/l) were present in higher concentration as compared to standard of EU (1.18 & 0.01). Agriculture is done in small patches of land in the fields. The excess irrigation water is drained out through Nullahs and enters in to the lake. The use of pesticides and herbicides in agriculture is a source of toxic pollution. These toxic chemicals are washed away by streams and enter the Rawal Lake. (Anon., 2004). Similar study has been conducted by Ahad *et al*., (2005) and they reported the presence of pesticides residues in Rawal Lake.

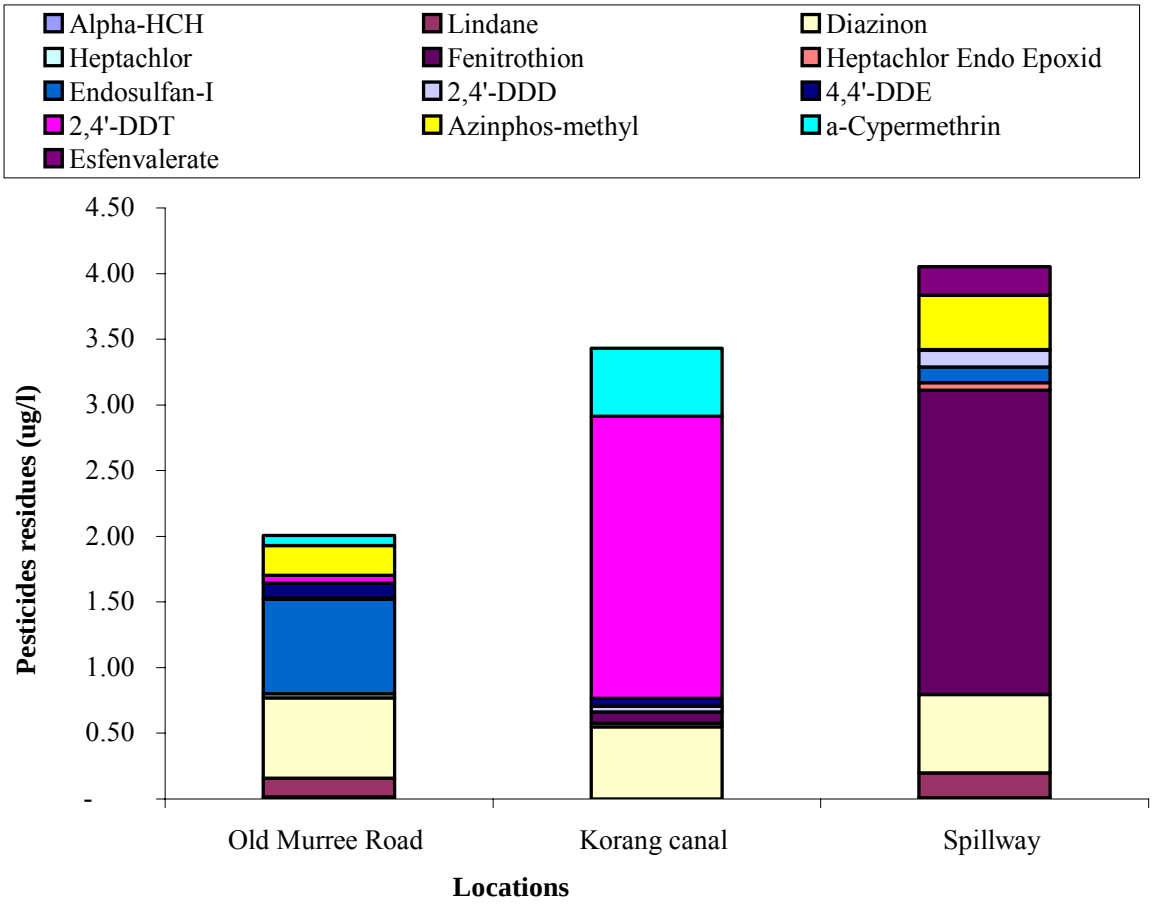

Fig. 1. Concentration of pesticides residues in Rawal lake samples.

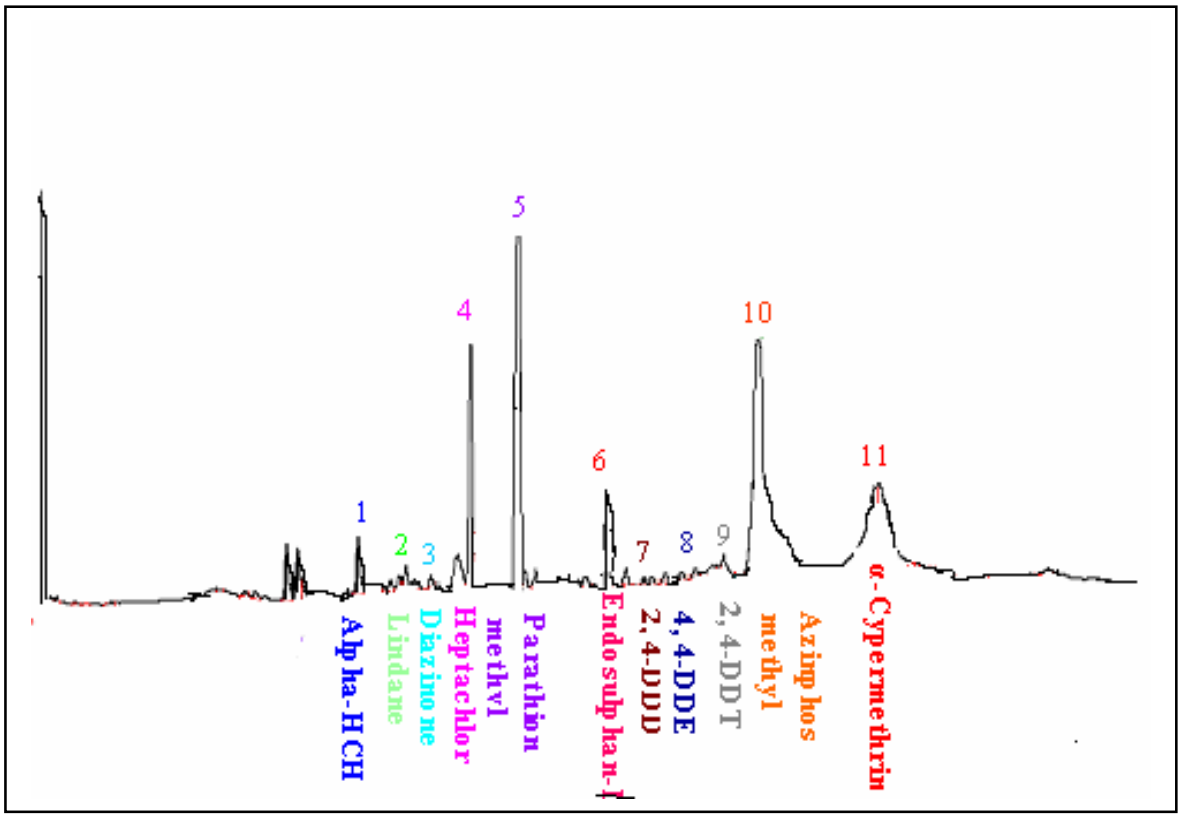

Fig. 2. Typical chromatogram of water samples collected from old Murree roadside of Rawal Lake, Islamabad.

They reported some pesticides i.e., parathion methyl, fenitrothion, azinphos methyl and alpha-cypermethrin. According to Ahad *et al*., (2005) the concentration of pesticides residues was higher than European Union (EU) standards. The pesticides may enter into water body by the activities of anglers or fish catchers who had dropped the pesticides intentionally to the lake for catching fish (Ahad *et al*., 2005). The sum of organophosphates (∑3.2) was highest in Rawal dam as compared to organochlorines and pyrethroids. The presence of alpha-HCH, lindane, diazinon, parathion methyl, fenitrothion, endosulphan 1, 2, 4-DDD, cyfluthrin in Moaza canal water samples was found. Alpha-HCH, lindane, diazinon, heptachlor, parathion methyl, heptachlor endo epoxide, endosulphan 1, 2,4-DDD, 4,4-DDE, 2,4-DDT, 4,4-DDT, azinphos methyl, cyfluthrin, esfenvalerate and deltamethrin were present in source water (Fig. 3).

In filtration plant alpha-HCH, lindane, diazinone, parathion methyl, heptachlor endo epoxide, 4,4-DDE, 2,4-DDT, 4,4-DDT, azinphos, methyl, cyfluthrin, alpha-cypermethrin and esfenvalerate were present. The results of pesticide residue analysis of Simly Lake showed that the average concentration of 2, 4-DDT (0.96ug/l), diazinone (1.81ug/l) and 4, 4-DDT (0.80ug/l) were within the accepted MRLs (Maximum Residue Limits) (1.65, 1.51, 1.37). The sum of organophosphates (∑3.61) were highest in Simly dam and pyrethroids were lowest (∑1.12). The possible reasons may be non-professional agricultural practices in the villages of Shah Bagh, Phulgarah town, Pind Baigwal, Athal and Moaza Dhakhoin which are situated close to Simly Lake.

In Moaza canal analyzed water sample, alpha-HCH (0.84ug/l), endosulphan (0.66ug/l) were present in higher concentration and were more than standards (0.47, 0.25). There may be possibility that harmful contaminants may reside in Simly Lake through Soan Nullah that falls into lake. From the source water collected sample, diazinone (3.55ug/l), azinphos methyl (1.79ug/l), deltamethrin (1.47ug/l) were in higher concentration as compared to European Union standards (1.51, 0.97, 0.81). The highest contamination level of pesticides in water may be as a result of accidental spillage of chemicals (Ahad *et al.,* 2000). In filtration plant analyzed sample 2, 4-DDT (2.87ug/l) 4, 4-DDT (2.39ug/l) and fenitrothion (2.06u/l), 2, 4-DDD (0.23ug/l), azinphos methyl (1.54ug/l) were present in greater concentration than tolerance limits of (EU) European Union. (1.65, 1.37, 1.18, 0.07, 0.97). Residue analysis of filtered water reveals that the activated carbon filter of filteration plant that is meant for removing organic contaminants is not working properly and needs to be changed (Fig. 4). The benefit of the present study is the better understanding of causes of detioration of water quality due to pesticide residues and developing strategies to minimize the losses caused by residues. The data generated may be utilized by further researchers for taking appreciate measures against the threat of water pollution and for the formulation of water quality standards or guidelines for pesticide residues in Pakistan.

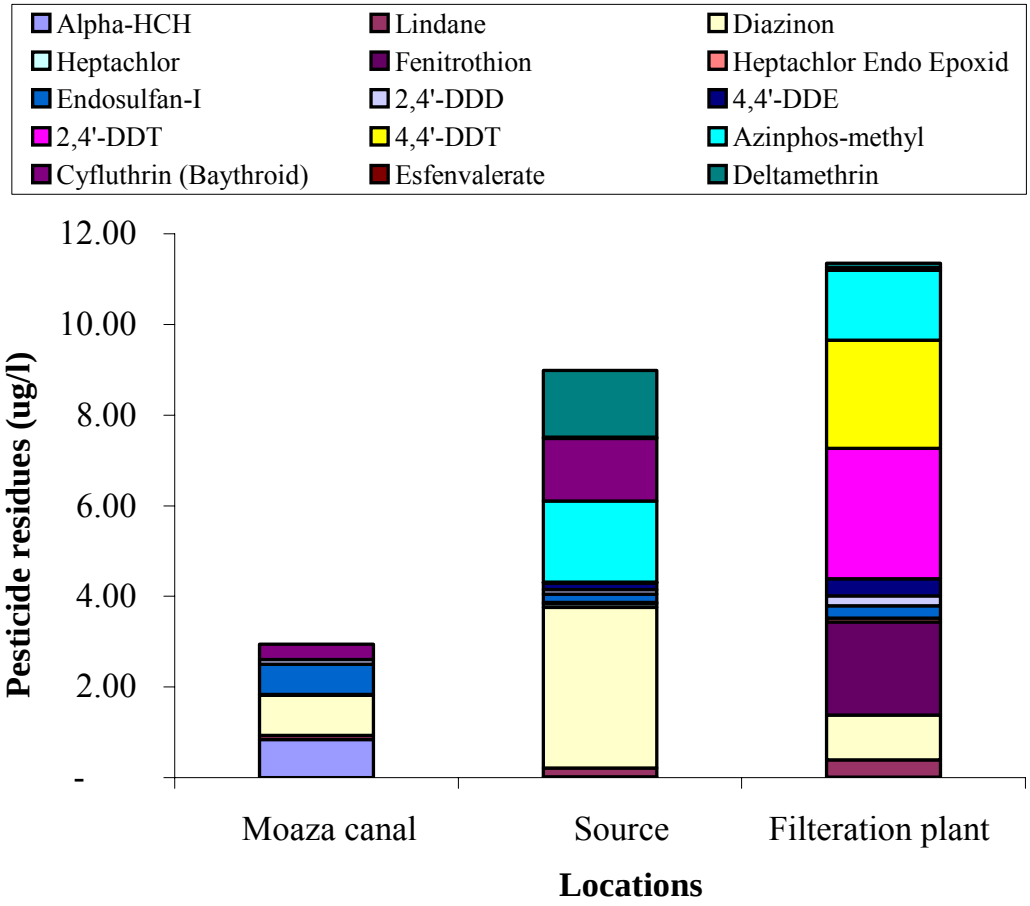

Fig .3. Concentration of pesticides residues in Simly lake samples.

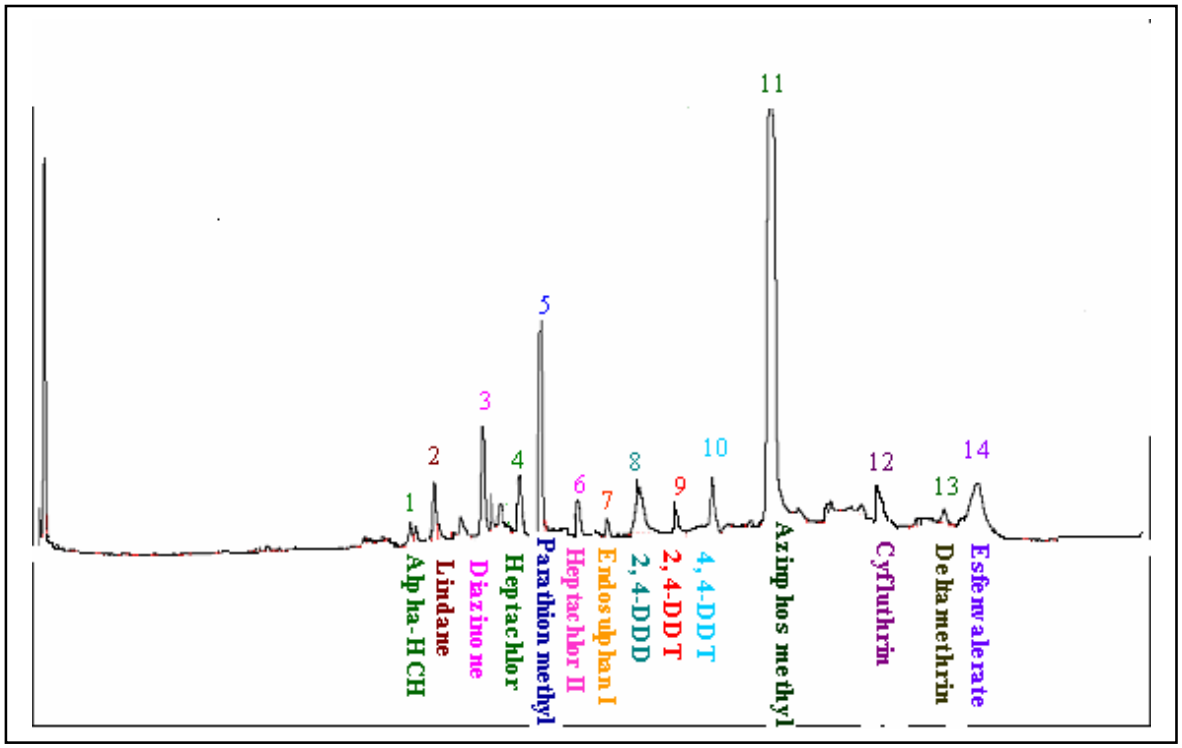

Fig. 4. GC/ECD chromatogram of water samples collected from Simly Lake, Islamabad.

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(Received for publication 13 September 2008)