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Pesticide Residues in Rawal Lake, Islamabad, Pakistan

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Pesticides not only do their intended job, but may also adversely affect non-targeted beneficial species. Ultratrace levels of pesticides now exist in every segment of the environment. Pesticide residues have been reported at places like North Pole snow (Jensen et al. 1969) and rain water in USA (Peakall 1976) and UK (Wheatley and Hardman 1965) far from the sites of their application. The open water sources like rivers and reservoirs are more vulnerable to pesticide contamination through agriculture and municipal run-off, accidental spillage and unintentional dumping or deliberate criminal contamination of water sources. Mohamed et al. (1984) reported very high levels of parathion-methyl in sea water, sediments and various fish species at Port Said in Egypt after spillage of 1 MT of the insecticide due to collision of two ships. Miliais (1993) detected lindane in Iliki Lake in Greece while Ang et al. (1989) have reported 22.3% drinking water samples contaminated with pesticide residues mainly with dieldrin in Australia. Legrand et al. (1991) monitored 38 pesticides in various surface and groundwater sources in France, and atrazine and simazine were found to be the most frequently detected pesticides. Similarly, the presence of atrazine, alachlor and carbofuran has been reported in well water samples from central Maine, USA (Bushway 1992). Yukio Hirai and Tomokuni (1989) reported the presence of chlordane in water and sediments of rivers around Saga City, Japan. Furthermore, DDT and HCH compounds have been reported in ponds and drinking water of Haryana, India (Kumari et al. 1996).

In Pakistan climatic conditions favor insect pests like white fly, jassids, aphids, bollworm and fruit flies (Baloch and Haseeb 1995). For their control pesticides have been used ranging from 24,868 MT in 1994 to 112,928 MT in 2004 (MINFAL 2004). This usage has resulted, among others, residue concerns in food chain and environmental compartments in the country (Ahad et al. 2000; Jabbar et al. 1993; Parveen and Masud 1988). Sanpera et al. (2003) used colonial water birds as bio-indicators of pollution levels in selected wet lands of Pakistan. Similarly, impaired physiological behavior and mortality of fish are subtle indicators of the presence of toxic pollutants in the aquatic environment (Singh et al. 1998). Accordingly, when a sudden mass fish killing in Rawal Lake, Islamabad occurred during mid June 2004, that caught the attention of print and

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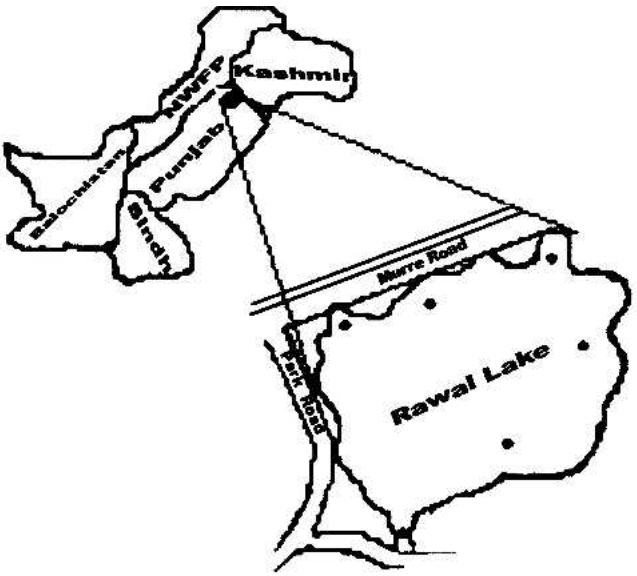

Figure 1. Map of the area showing sampling locations (•).

electronic media as well, an initiative was taken to analyze its water samples for toxic pesticide residues. The findings are discussed in this paper.

MATERIALS AND METHODS

Rawal Lake was constructed in east of the capital city, Islamabad, thirty seven years ago (Ahmed 2005). It has a catchment area of 275 km^2 with a live storage capacity of 5.30 x 10^7 m^3. The lake is fed by 4 major and 43 small tributaries. Major polluting sources are 360 poultry sheds, car washes, recreational activities and human settlements in Bhara Kahu, Malpur, Bani Gala and Noorpur Shahan (PEPA 2004). After passing through the filtration plant of the Water and Sanitation Agency (WASA), Rawal Lake supplies drinking water to 1.5 million people in Rawalpindi, the 4th congested city in the country (PCO 2005). On June 15, the Lake water temperature was 33.5°C and volume was 1.85 x 10^7 m^3 while on August 8, the volume was increased to 2.47 x 10^7 m^3 (*Record book of WASA, Islamabad*).

The instrument used in this study was a Perkin Elmer Autosystem Gas Chromatograph (GC) equipped with an electron capture detector (ECD-Ni^{63}), nitrogen phosphorus detector (NPD), narrow bore fused silica capillary column (P.E. No. N931-2414, methyl 10% phenyl silicone, 17 mm, 0.32 i.d., 0.5 mm o.d., 0.5µ film thickness) and Turbochrom4® data analysis hardware/software system. Moreover, a nitrogen generator (Peak Scientific), Sartorious balance (JS-110, Y.M.C. Co. Ltd. Japan) and rotavapor (R-114, Buchi, UK) were also used in this

study. The analytical pesticides standards were purchased from Riedel-de Haën AG Seelze, Germany. Their stock solutions and required working dilutions were prepared in ethyl acetate. Other solvents and reagents used in this study were purchased from Merck, Kock-light Ltd. and Pharmacos Ltd., UK.

Initially four water samples from Rawal Lake were sent to our laboratory for pesticides residues analysis. These samples were collected from four sites viz. (1) Korang canal (2) Old Murree road (3) Rawal Lake spillway and (4) Banni Gala side on June 28, 2004. Since the sample sizes were less than required for analysis, samples from sites 2 and 4 and sites 1 and 3 were pooled and labeled as sample-A and sample-B, respectively. The samples were found to be highly polluted, hence follow-up sampling was done on August 4-5, 2004 from the following locations (1) Stream, Diplomatic enclave (2) Korang canal (3) Picnic spot, Old Murree road (4) Banni Gala, hill side (5) Banni Gala, village side (6) Filtration Plant, inlet (7) Filtration Plant, after chlorination (8) WASA residential colony (Figure 1). The water samples were collected in pre-washed 2.5 L glass bottles and fortified with 10 mL dichloromethane in order to stop biological activities. The samples were transported to the laboratory and processed immediately.

A liquid-liquid extraction procedure (Ahad et al. 2000) was adopted for extraction of pesticides from water samples. One litter of water samples was extracted with 75 mL of dichloromethane in a separatory funnel. The funnel was kept in a stand until two distinct phases were formed. The lower organic layer was collected in a round bottom flask over a small cotton wool plug and anhydrous Na_2SO_4. A few drops of propylene glycol in ethyl acetate (1:1) solution and 3-4 glass beads were added. The contents were evaporated on a rotavapor at 40°C under vacuum and optimum rotation speed. To achieve complete dryness a nitrogen stream was used. The contents were reconstituted in 1 mL ethyl acetate for analysis on GC/ECD under the following operational conditions: carrier (nitrogen) flow rate 12 mL/min (21 psi), makeup flow rate 21 mL/min., injector (splitless mode) and detector temperatures 220°C and 350°C respectively, initial oven temperature, 80°C (2 min.), ramped to 250°C (2 min.) at the rate of 10°C/min. One µL of the samples was injected with a 10 µl Hamilton syringe by the solvent flush injection technique.

RESULTS AND DISCUSSION

The retention times for standard insecticides under the above mentioned conditions were found to be: dichlorvos (2.93), lindane (8.67), parathion-methyl (10.17), fenitrothion (10.76), malathion (11.10), alpha-endosulfan (12.14), azinphos-methyl (15.90), fenpropathrin (17.65), cyhalothrin (17.76), alpha-cypermethrin (18.10), esfenvalerate (18.97) and deltamethrin (19.55) (Figure 2). First of all, a mixture of the standard solutions was injected into GC followed by a sample injection to identify qualitatively the analytes of interest on the basis of their respective retention times. The rest of the efforts i.e. Calibration, determination of LOD and percent recoveries, were then restricted to the detected four pesticides of interest.

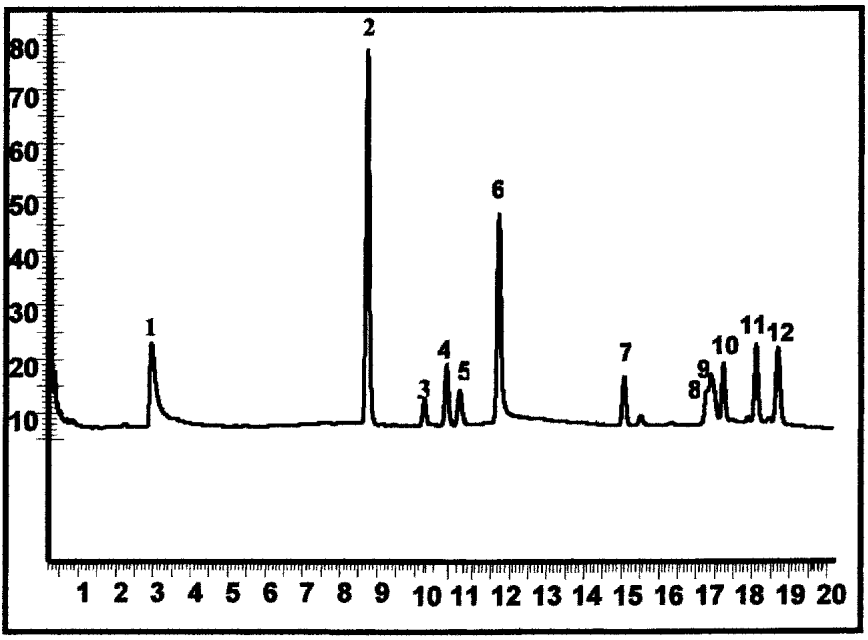

Figure 2. GC/ECD chromatogram of standard pesticides in ethyl acetate. (Legend: 1. Dichlorvos, 2. Lindane, 3. Parathion-methyl, 4. Fenitrothion, 5. Malathion, 6. α-Endosulfan, 7. Azinphos-methyl, 8. Fenpropathrin, 9. Cyhalothrin, 10. α-Cypermethrin, 11. Esfenvalerate, 12. Deltamethrin)

For statistical evaluation of overall method's efficiency, 1 L of distilled water was spiked with the target pesticides at three concentration levels approximately equivalent to 0.05, 0.1 and 0.2 µg/L of each compound keeping in view the European Economic Union (EEC) limits of 0.1 µg/L. The compounds were quantified on the basis of their respective peak areas. The %recoveries were found to be in the range from 79.5 ± 0.87 to 97.8 ± 0.98. No corrections were made for recoveries while calculating the concentrations in the samples. The limit of detection for parathion-methyl, fenitrothion, azinphos-methyl and alpha-cypermethrin were 0.019, 0.038, 0.057 and 0.068 µg/L, respectively that were calculated with SuperCalc™ (Version 5.00A, Copy right 1998, Computer Association International, Inc.). Method blank and calibration standards were analyzed with each set of samples. The overall status of pesticide residues found in individual samples has been summarized in Table 1. As far as samples collected in June (peak time of fish fatality) are concerned, the sample-B (Korang canal + Spillway) and sample-A (Old Murree road + Banni Gala) were found to be respectively 86 and 35 times more contaminated than EEC standards of 0.5 µg/L for total pesticides residues in drinking water. On average, the contribution of parathion-methyl, fenitrothion, azinphos-methyl and α-cypermethrin to the measured overall pesticides pollution of Rawal Lake was 8, 22, 26 and 44 percent, respectively.

Table 1. Pesticide residues (μg/L) in water samples collected from Rawal Lake, Islamabad in June and August 2004.

Sampling location	Pesticide residues (μg/L)				
	Pm	Fe	Am	Ca	Total
Old Murree road + Banni Gala	2.24	5.27	2.48	7.66	**17.65**
Korang canal + Spillway	2.71	8.3	13.28	18.76	**43.05**
Diplomatic enclave stream	0.08	0.19	0.06	0.78	**1.11**
Picnic spot, old Murree road	0.1	0.3	1.99	4.03	**6.42**
Korang canal	0.44	1.02	12.85	13.98	**28.29**
Banni Gala, village side	0.99	1.64	1.86	5.69	**10.18**
Banni Gala, hill side	0.62	1.03	1.45	6.65	**9.75**
Filtration Plant, inlet	0.38	0.62	3.32	5.82	**10.14**
Filtration Plant, after chlorination	0.05	0.15	2.67	0.22	**3.09**
WASA residential colony	0.02	0.08	1.82	0.21	**2.13**

(Legend: Pm Parathion-methyl, Fe Fenitrothion, Am Azinphos-methyl, Ca Cypermethrin-α)

In August eight samples were collected and analyzed. This time the lake volume was increased up to 2.47×10^7 m^3 and was muddy due to onset of monsoon rains. The total pesticide load had reduced by 64% from 30.35 μg/L to 11.15 μg/L as per expectation because of the dilution and degradation factors. For individual compounds 96, 90, 50 and 97 percent reduction was recorded in parathion-methyl, fenitrothion, azinphos-methyl and alpha-cypermethrin levels, respectively. However, the overall concentration was still approximately 22 times higher than EEC standards. These concentrations, after receiving treatments in Water and Sanitation Agency (WASA) filtration plant, were further reduced by a factor of 81%. However, the water supplied to general public still had pesticide residues approximately 4-fold higher than EEC standards for drinking water (Figure 3). As indicated earlier, the major pollutants were azinphos-methyl and alpha-cypermethrin. Azinphos-methyl is an organophosphate while alpha-cypermethrin is a synthetic pyrethroid having the LC_{50} of 20 μg/L and 2.8 μg/L for trout fish, respectively (Tomlin, C. 1994). The solubility of these two compounds in water favors their low mobility and adsorption to suspended soil particles and sediments. However, the surfactants being used for bathing, clothes and automobile washings decrease the surface tension of water and make the compounds available for biological activities.

In the absence of other relevant data like pesticide residues in sediments or fish tissues, or monitoring of cholinesterase inhibition in fish, the mass killings of fish in June 2004 can't be fixed on pesticide residues alone. However, it can be ascertained that elevated water temperature (33.5°C), decreased quantity of water (1.85×10^7 m^3 as compared to total capacity of 5.30×10^7 m^3) and the presence of pesticide residues along with other expected pollutants had eventually led to fish deaths.

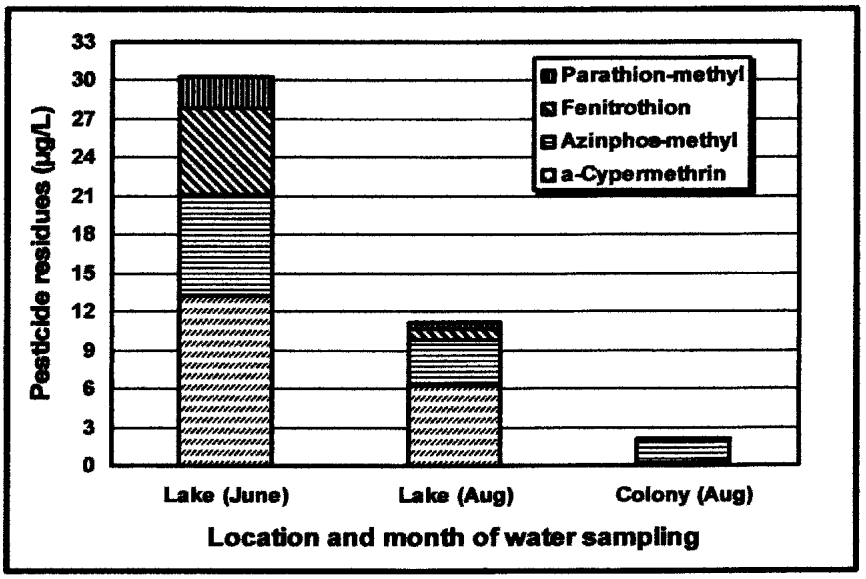

Figure 3. Average pesticide residues (µg/L) in water samples collected from Rawal Lake, Islamabad before and on onset of monsoon rains in 2004.

The role of pesticide pollution in this event can be demonstrated by the selective killing of Silver Carp while Black Cat fish were not affected. The LC_{50} of pesticides under investigation are not available for the subject species. The LC_{50} of a pesticide varies from species to species for instance azinphos-methyl has LC_{50} of 0.02 and 0.12 mg/L for rainbow trout and golden orfe respectively (Tomlin, C. 1994). Thus the Silver Carp may be more susceptible to the pesticides under consideration than other species.

Since this lake provides municipal water to Rawalpindi Cantonment area, hence the presence of pesticides above the Maximum Allowable Concentration (MAC) set by EU is a matter of great concern. Consequently our team surveyed the watershed area to find out the sources of these pesticides. The agriculture in this area is limited to maize, wheat and some fruit orchards. There are few small pesticide retailers in the area and the pesticide usage is nominal. Wastes from Murree, poultry farms and surrounding residential areas do come to the lake but the pesticides being detected are not meant for use in public health sector. Moreover, the pesticide run off can also be ruled out because of the drought like situation in June. The two options left with are, either some one had dumped expired pesticide in Korang canal or some miscreants had thrown away pesticides intentionally to the lake for catching the fish or other unknown intentions. In this regard the Chief Commissioner, Islamabad has taken some quick and positive decisions to avoid such a situation in future (Bobarik Virk. 2004).

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