INT. J. BIOL. BIOTECH., 2 (3): 641-646, 2005.

OCCURRENCE AND DISTRIBUTION OF PESTICIDES IN UNDERGROUND WATER OF MALIR RIVER CATCHMENT AREA : A PRELIMINARY STUDY

M. Ali Khan[1], N. Ahmed Khan[2] and Omme Hany[1]

[1]*Institute of Environmental Studies, University of Karachi, Karachi-75200, Pakistan*
[2]*Department of Geology, University of Karachi, Karachi-75200, Pakistan*

ABSTRACT

The concentrations and spatial distributions of various pesticides levels were investigated in underground water collected from ten stations from Malir River catchment area. The pesticides analysed were Aldrin, Cypermethrin, DDE, Dieldrin, DDT and Malathion. The concentrations of these pesticides are relatively significant at some stations. Their continuous accumulation in underground water of aquifers is a source of potential environmental threat which is responsible for serious health implications.

Keywords: Malir River, pesticides, pollution, underground water

INTRODUCTION

The use of synthetic organic chemicals such as pesticides and other agricultural chemicals have increased many folds during the past few decades and have brought about revolutionary change in the alleviation of world food problems. More than 75000 individual compounds and 35000 formulations are being used since 1945 and today they represent a massive percentage to which man is exposed directly or indirectly (Forget, 1991).

Pesticides have been used extensively for the last 25 years and are generally considered to be persistent in nature (Freed, 1987). There are more than hundred pesticides in common usage. Many of them are available in several formulations or under several trade names. These pesticides are commercially classified according to the properties of the active ingredients as either selective or non-selective.

The WHO estimates that 500,000 pesticides poisoning cases occur annually in the world and that 170 are fatal (5000 deaths/year), (Rosenstock *et al*, 1991; Mcloughlin and Belleinger, 1993).
Pesticides that are soluble in both water and fats are usually taken up more quickly by man and animals as the traces of these pesticides along with their metabolites and breakdown products are ubiquitously present in abiotic and biotic environment (Tiel, 1972).

Pesticides are also suspected to play a causative role in the alteration of sexual development in the wild life species (Soto *et al.* 1994; US-GAO, 1987; Mot and Synder, 1987). In Pakistan about 254 metric tons of pesticides formulations were used which increased to 16,226 metric tons in 1976-77and their use increased exponentially in the last decade (Baloch, 1985; Ahmad, 1987; Naqvi, 1994). However, the data related to migration of agricultural pesticides to ground water of Pakistan is scanty (Tariq, *et al.*, 2004).

District Malir lies between 24°45' to 25° 37' north latitudes and 67° 06' to 67° 34' east longitudes and is bounded on the north by Dadu district, on the south by Thatta district and Arabian sea, on the east by Dadu and Thatta districts and on the west by Karachi south, Karachi Central, Karachi East, Karachi west and Lasbala district of Balochistan province. Malir district has a variegated topography, ranging in height from below the datum level in south along the tidal swamps and mud flats of Ibrahim Hyderi and Bin Qasim coastal strips to the maximum of 525 meters above the mean sea level at Mol escarpment in Sindh Kohistan. In the upper reaches the two main effluents of Malir are Khadeji Nadi and Mol Nadi, which have their catchments basins in Sindh Kohistan in a synclinal fold between the main Kirthar range and its off shoot branches. Malir river, ephemeral in nature, flows in the district. This river is constituted from two major tributaries, Mol and Khadeji and smaller tributaries of Konkar, Thaddo and sukkhan.

The whole Malir river is rain fed and hence most of the cultivation is dependent upon the ground water reservoirs. The fertile land of Malir has played a vital role in the agro economy of Karachi. This area served as the main local source of fruits and vegetables for the people of Karachi. Malir river and its tributaries maintain a huge underground reservoir of water (Kazmi and Ghori, 1994). Although, the water is being used for domestic and agriculture purposes but no quantitative data is available pertain to its public health quality. Khan *et al* (2005) reported the underground water characteristics of Malir river catchment area based on some preliminary investigations.

So far no intensive survey has been conducted to demonstrate the pesticide pollution profile of Malir River catchment area. The aim of the present study was to determine the level of pesticide pollution in underground water, which serves as the most extensive source of water not only for agriculture but also for human consumption.

MATERIALS AND METHODS

The study was conducted during February and December 2004. Water samples were collected from 10 different sampling stations along the catchment area of Malir River. At different sampling stations the depth of water varied significantly from 1.0 to 7.5 meters. Samples were brought to the laboratory within two hours of collection, processed accordingly and analyzed for the pesticides (APHA, 1995) commonly available in the market. Table 1 and Fig 1 represent the sites for sample collection from Malir River catchment area.

Collection of water samples

For the collection of water samples sterilized glass bottles of 2-litre capacity were used. The samples were collected in such a way to avoid floating materials and were analysed according to the procedures as mentioned in Standard Methods for the Examination of Water and Wastewater (APHA, 1995).

Table 1. Malir River sampling sites along with the associated activities.

S. No.	Sampling stations	Coordinates	Sampling sites	Associated activities
1.	ST-1	67.17 E 25.00 N	Mol river (down stream)	Agriculture, squatter settlement
2.	ST-2	67.28 E 25.04 N	Mol river (upstream)	Agriculture squatter settlement
3.	ST-3	67.30 E 25.06 N	Khadeji river (upstream)	Agriculture squatter settlement
4.	ST-4	67.35 E 25.07 N	Khadeji river (upstream)	Barren land
5.	ST-5	67.38 E 25.12 N	Tributary of Sari Nadi (up stream)	Agriculture, squatter settlement
6.	ST-6	67.34 E 25.17 N	Sari Sing	Barren land
7.	ST-7	67.39 E 25.09 N	Tributary of Sari Nadi (Middle)	Barren land
8.	ST-8	67.35 E 25.06 N	Tributary of Sari Nadi (Middle)	Barren land
9.	ST-9	67.34 E 25.04 N	Tributary of Sari Nadi (down stream)	Agriculture, squatter settlement
10.	ST-10	67.23 E 25.01 N	Junction of Mol and Khadeji river	Agriculture, squatter settlement

Determination of pesticides

Sample Preparation

About 2 litres of water sample was condensed upto 25 ml on a water bath. The condensate was extracted with n-hexane thrice the quantity of sample in a separatory funnel. Approximately 25 ml sediment sample was extracted with n-hexane in a similar way using separatory funnel. In both the cases n-hexane extract was dried in a rotary

evaporator and sample was reconstituted in methanol (HPLC grade) and filtered through a membrane filter of 0.22 μm.

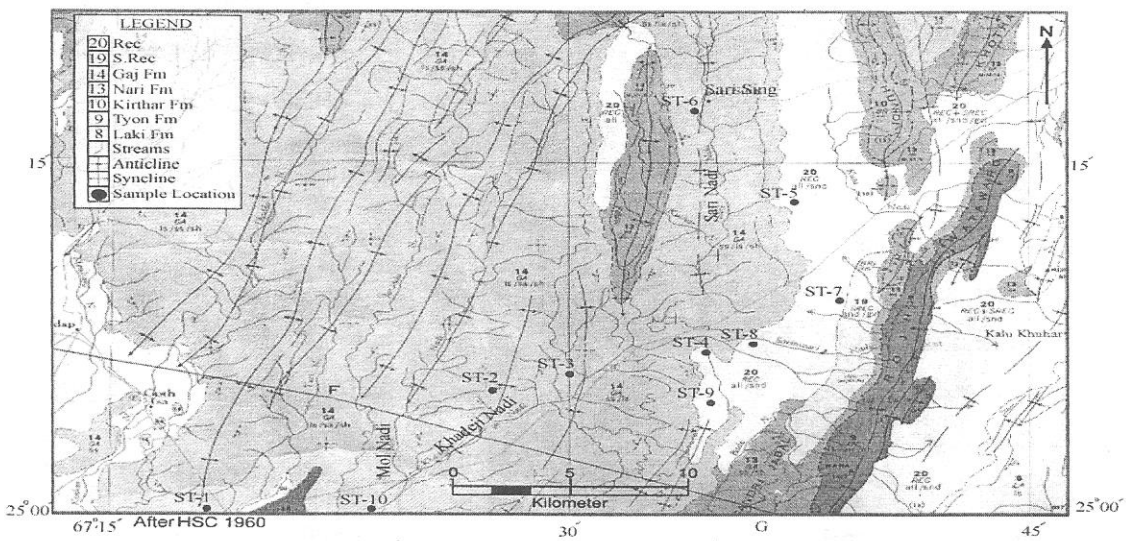

Fig. 1. Sites of sample collection of Malir river catchment area.

High Pressure Liquid Chromatography (HPLC)

The HPLC (Shimadzu, Japan) chromatographic system used in the present study consists of a solvent delivery pump LC-10AS, connected with an auto injector model SIL-6A and a rheodyne injection valve fitted with a sample loop (20 μl). A guard column filled with μBondapak C_{18} analytical waters μBondapak reversed phase column, effluents was monitored by using UV-detector (visible spectrophotometer detector SPD-10A). The output of the detector was connected to a chromatopack (CR6A).

Mobile phase consisted of methanol (Merck HPLC grade). The methanol was first distilled twice and further purified by filtration through Millipore filtration unit (0.2 and 0.4 μm Millipore filter; Micropore, Nylon). The filtered methanol was degassed prior to use by sonication.

The flow rate was adjusted at 1.5 ml/minute with total elution time of 12 minutes for each run. The column was flushed with deionized distilled water and methanol whenever required removing impurities and was allowed to equilibrate between runs.

RESULTS AND DISCUSSION

The results of pesticide analysis are reported in Table 3 and represented in Fig. 2,3,and 4.

From Table 3 it can be seen that samples of ST-2, ST-4, ST-5, ST-8 and ST-9 did not show any significant concentration of pesticide. However, Site 1 contained Aldrin, DDT, and Malathion in a concentration of 0.16, 0.15 and 0.17 mg/l respectively (Fig. 2). Similarly, S-3 showed the presence of Dieldrin (0.15mg/L), DDT (0.16mg/L) and Malathion (0.14 mg/L)as can be seen in the chromatogram presented in Fig.3. Only Malathion (0.16 mg/L) was present in the sample collected from the Site No.5 whose chromatogram is presented in Fig.4. The environmental impact of these pesticide residues and their effect on human health is a matter of much concern. Recent studies on the estrogen like behaviour of DDT and PCBs in human suggest the implication of these compounds in breast cancer (Carvalhado *et al.*, 1998). Carvalhado *et al.*, (1998) also reported the presence of DDT in planktons and in the marine bottom deposits in China. The presence of DDT indicates its past use and confirm the long term persistence in the environment.

Table 2. Chromatographic conditions.

S.No.	Parameters	Characteristics
1.	Separation (Experiment type)	Liquid chromatography
2.	Flow rate	1.5 ml/minutes
3.	Column	C_{18} (Reversed-phase column)
4.	Detection (Wave length)	220 n.m
5.	Temperature	Ambient
6.	Mobile phase	Methanol (MeOH 100%)
7.	Injection Volume	20 μl
8.	Chart speed	5 mm/minutes
9.	Attenuation	4
10.	Peak width	10
11.	Peak slope	500
12.	Peak width	10
13.	Peak minimum area	50000
14.	Stop time	12 minutes

Table 3. Pesticides concentration in ground water sample of Malir river catchment area

Sites	Pesticides mg/L						
	Aldrin	Cypermethrin	Deltamethrin	DDE	Dieldrin	DDT	Malathion
ST-1	0.16	Nil	Nil	Nil	Nil	0.15	0.17
ST-2	Nil	Nil	Nil	Nil	Nil	Nil	Nil
ST-3	Nil	Nil	Nil	Nil	0.15	0.16	0.14
ST-4	Nil	Nil	Nil	Nil	Nil	Nil	Nil
ST-5	Nil	Nil	Nil	Nil	Nil	Nil	0.16
ST-6	Nil	Nil	Nil	Nil	Nil	Nil	Nil
ST-7	Nil	Nil	Nil	Nil	Nil	Nil	Nil
ST-8	Nil	Nil	Nil	Nil	Nil	Nil	Nil
ST-9	Nil	Nil	Nil	Nil	Nil	Nil	Nil
ST-10	Nil	Nil	Nil	Nil	Nil	Nil	0.16

It is strongly felt that the concentration of these pesticides and their continuous accumulation in the underground water need to be addressed immediately. It is interesting to notice that the DDT which is banned all over the world is still being used in the present situation without knowing the fact that it can persist in the environment even for a very long period of time.

CONCLUSION

The study reveals that the underground aquifers are continuously receiving the agricultural runoff containing pesticides. Their persistent accumulation in the underground water is a potential environmental threat. It is suggested that a more extensive study of the underground water of Malir river catchment area need to be undertaken to elucidate their impact on the ecological environment.

evaporator and sample was reconstituted in methanol (HPLC grade) and filtered through a membrane filter of 0.22 μm.

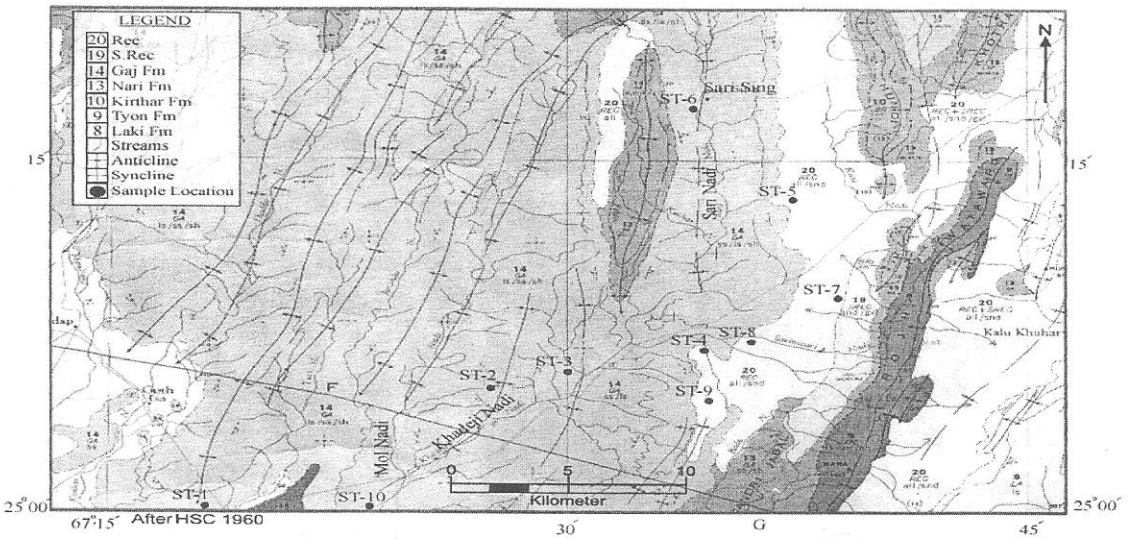

Fig. 1. Sites of sample collection of Malir river catchment area.

High Pressure Liquid Chromatography (HPLC)

The HPLC (Shimadzu, Japan) chromatographic system used in the present study consists of a solvent delivery pump LC-10AS, connected with an auto injector model SIL-6A and a rheodyne injection valve fitted with a sample loop (20 μl). A guard column filled with μBondapak C_{18} analytical waters μBondapak reversed phase column, effluents was monitored by using UV-detector (visible spectrophotometer detector SPD-10A). The output of the detector was connected to a chromatopack (CR6A).

Mobile phase consisted of methanol (Merck HPLC grade). The methanol was first distilled twice and further purified by filtration through Millipore filtration unit (0.2 and 0.4 μm Millipore filter; Micropore, Nylon). The filtered methanol was degassed prior to use by sonication.

The flow rate was adjusted at 1.5 ml/minute with total elution time of 12 minutes for each run. The column was flushed with deionized distilled water and methanol whenever required removing impurities and was allowed to equilibrate between runs.

RESULTS AND DISCUSSION

The results of pesticide analysis are reported in Table 3 and represented in Fig. 2,3,and 4.

From Table 3 it can be seen that samples of ST-2, ST-4, ST-5, ST-8 and ST-9 did not show any significant concentration of pesticide. However, Site 1 contained Aldrin, DDT, and Malathion in a concentration of 0.16, 0.15 and 0.17 mg/l respectively (Fig. 2). Similarly, S-3 showed the presence of Dieldrin (0.15mg/L), DDT (0.16mg/L) and Malathion (0.14 mg/L)as can be seen in the chromatogram presented in Fig.3. Only Malathion (0.16 mg/L) was present in the sample collected from the Site No.5 whose chromatogram is presented in Fig.4. The environmental impact of these pesticide residues and their effect on human health is a matter of much concern. Recent studies on the estrogen like behaviour of DDT and PCBs in human suggest the implication of these compounds in breast cancer (Carvalhado *et al.*, 1998). Carvalhado *et al.*, (1998) also reported the presence of DDT in planktons and in the marine bottom deposits in China. The presence of DDT indicates its past use and confirm the long term persistence in the environment.

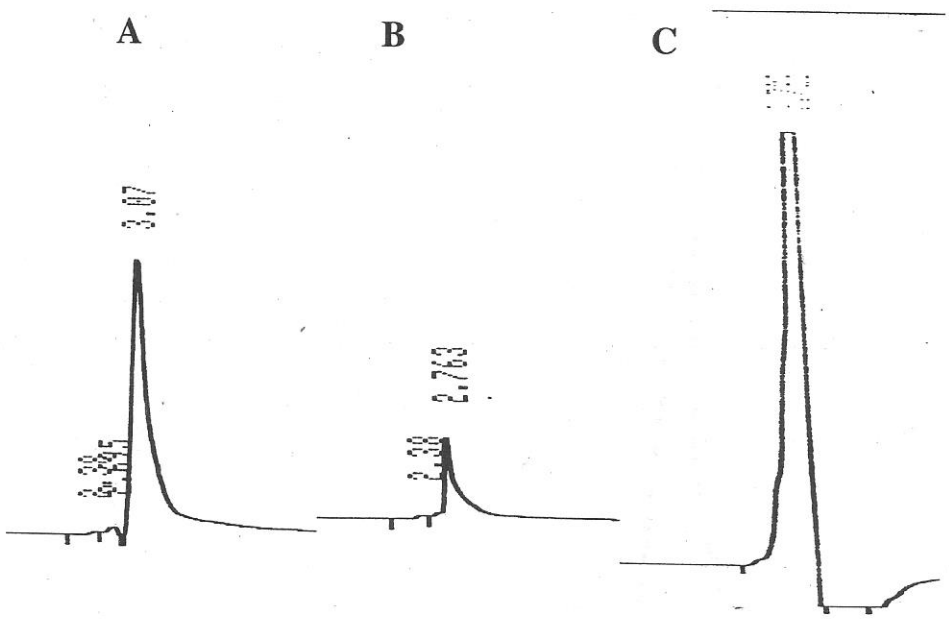

Fig.2. Chromatogram showing different concentration of pesticides at ST-1, A=Aldrin 0.16mg/L, B=DDT 0.15mg/L, C= Malathion 0.17mg/L.

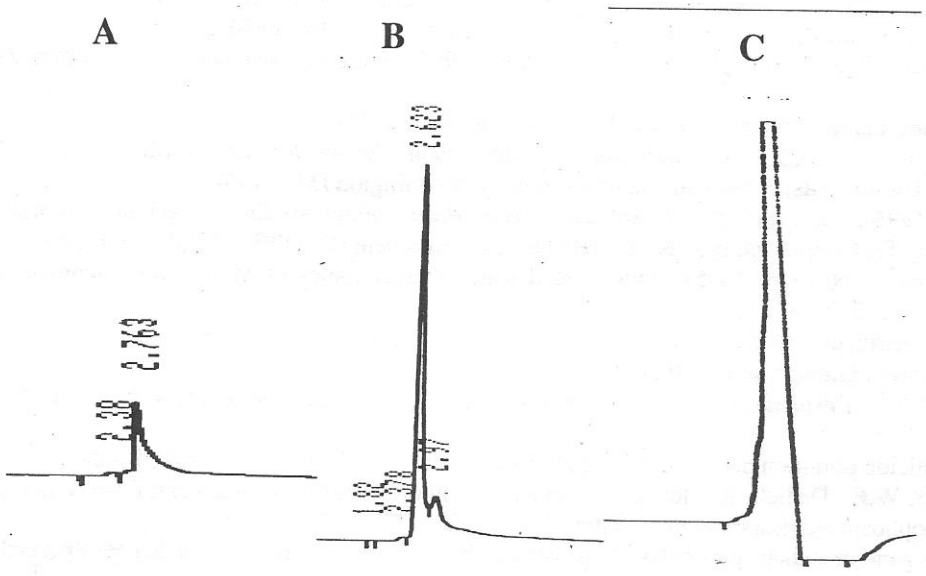

Fig.3. Chromatogram showing different concentration of pesticides at ST-3, A= DDT 0.16mg/L, B= Dieldrin 0.15 mg/L, C = Malathion 0.14 mg/L

REFRENCES

American Public Health Association (APHA), American Water Works Association (AWWA), Water Pollution Control Federation (WPCF) (1995). *Standard Methods for the Examination of Water and Wastewater.*

Ahmad, I. (1987). Hazards of increased pesticidal usage in Pakistan; suggestions to boost rice in a pesticide free environment. *Pak. J. Envt. Karachi. Supplement,* 48-51.

Baloch, U.K. (1985). Problems associated with the use of chemicals : 63-78. In: *Basic and Applied Mutagenesis with Special Reference to Agricultural Chemicals in Developing Countries.* (Amr. M. and Von Borstel, R.O. eds.) plenum Press, New York. : 441.

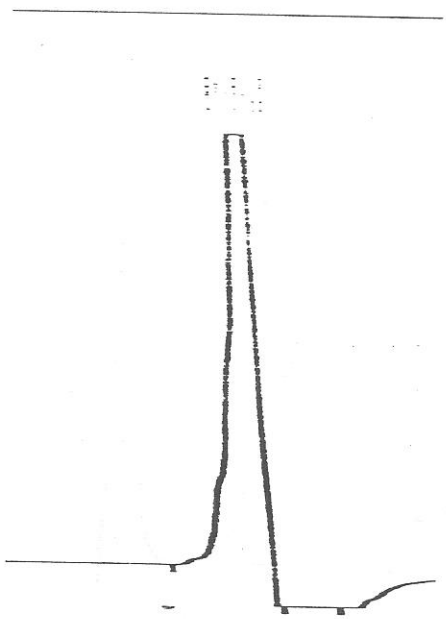

Fig.4. Chromatogram showing concentration of Malathion at ST-5 Malathion 0.16 mg/L

Byrne, D. H. and P.A. Kitos (1983). Teratogenic effects of cholinergic insecticides in chick embryos-IV. The role of tryptophan in protecting against limb determites. *Biochem. Pharmacol.*, 32: 2881-2890.

Carvalhado, F.P., D.D. Nhan, C. Zhong, T. Tavares and S. Klaine (1998). Tracking pesticides in the tropics. *IAEA Bulletin*, 40: 3.

Forget, G. (1991). Pesticides and third world. *J. Toxicol. Environ. Health*, 32: 11-31

Freed, V.H. (1987). Pesticides: Global use and concerns. In: *Silent Spring Revisited.* (Marco, G.J., R.M. Hollingworht and W. Durham eds) American Chemical Society, Washington D.C : 145-158

Kazmi, J. and S. Ghori (1994). *Sand and gravel excavation from Malir valley: An Environmental Appraisal for Desertification.* Society for Conservation of and Protection of Environment (SCOPE), Karachi, Pakistan.

Khan. N.A., M.A. Khan and S. Nassem (2005). Underground water characteristics of Malir river catchment area. *Int. Jour. Biol. Biotech.*, 2: 377-382.

Mcloughlin, J. and E.G. Bellinger (1993). *Environmental Pollution Control. An Introduction to Principles and Practice of Administration.* Graham and Trotman Ltd. London.

Mott, L. and K. Synder (1987). *Pesticide Alert. A guide to pesticides in fruits and vegetables.* Sierra Club. Books. San Francisco. p.179.

Naqvi, S.N.H. (1994). Pesticide pollution and problems produced by them. *Zoologica Pakistan*, 4: 59-65.

Rosenstock, L., M. Keifer, W.E. Daniell, R. McConnel and K. Claypoole (1991). Chronic central nervous system effects of acute organophosphate pesticide intoxication. *Lancet.*, 338: 223-227.

Saunders, D.S. (1991). Organophosphate pesticides: Neurotoxins threaten farm workers. Jour.N.I.H. Research. **3**: 21-24.

Smith, L.R. and M.T. Smith (1998). *Elements of Ecology. 4th Edition.* The Benjamin Cumming Publishing Company, CA-94025 USA.

Soto, A.M.; K.L. Chung and C. Sonnenschein (1994). The pesticides Endosulfan, Toxaphene and Dieldrin have estrogenic effects on human. *Environ. Health. Perspect.* 102 (4).

Tariq, M. I., S. Afzal and I. Hussain (2004). Pesticides in shallowground water of Bahawalnagar, Muzafargarh, D.G. Khan, and Rajan pur districts of Punjab, Pakistan. *Envt. Int.*, 30: 471:479.

Tiel, N.V. (1972). *Pesticides in Environment and Food. Environmental Quality and Safety.* Vol. 1. Academic Press Inc., New York. : 180-189.

US-GAO. (1987). *U.S. General Accounting Office Testimony. Federal Regulation of Pesticide Residues in Food.*

(Accepted for publication June 2005)