

Technical note

Determination of insecticide residues in groundwater of Mardan Division, NWFP, Pakistan: A case study

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Abstract

Insecticide residue values in groundwater samples from Mardan Division, North-Western Frontier Province, Pakistan, are reported in this paper. The samples were extracted with dichloromethane and analysed on a gas chromatograph equipped with an electron capture detector (ECD-⁶³Ni) using a capillary column. Contamination levels in all sites were found to be below the maximum acceptable concentration (MAC) set by the European Community (EC), except for three sites namely Amber, Swabi (0.82 µg/l), Lahore Shakh, Chota Lahore (0.50 µg/l) and Madras Kalay, Mardan (0.64 µg/l). Correlation between water depth and insecticide residues was ill-defined. Loss in recovery due to the matrix effect was found to be 10 to 20%.

Introduction

Pakistan uses insecticides for food production and for control of vector-borne diseases in the public health sector. Here the insecticide levels have increased from 665 M.T. a.i. in 1980 to 24868 M.T. a.i. in 1994 (Agricultural Statistics of Pakistan, 1994-1995). These insecticides can find their way into the groundwater through leaching, channelling (downward percolation), direct spillage and wind drift. Insecticide residues in drinking- and groundwater of developed countries like the USA (Bushway et al., 1992; Molto et al., 1991), France (Legrand et al., 1991), Australia (Ang et al., 1989) and Denmark (Felding, 1991) have been reported. In Pakistan, Parveen and Masud (1988) have detected some chlorinated insecticides in cattle drinking water from Karachi while Jabbar et al. (1993) reported monocrotophos, cyhalothrin, and endrin in shallow groundwater of Faisalabad, the cotton-growing area of the country. Results of insecticide residue analyses of groundwater or drinking-water samples from the areas of North-Western Frontier Province (NWFP) have so far not been reported.

Currently organophosphate (OP) insecticides are used since most of the organochloride (OC) insecticides have been banned because of their toxicity, persistence and bioaccumulation in the environment (Molto et al., 1991). Tobacco, sugar-cane and maize are the main crops of Mardan Division where substantial amounts of insecticides per cropping season are applied. The widespread use of toxic insecticides has created a need for their monitoring in water, soil and food commodities of this area. Illiteracy in farmers, indiscriminate use and adulterated insecticides pose a potential threat to local inhabitants. In this study insecticide residues in groundwater of Mardan Division were determined. Twelve sites were sampled. These sampling points are indicated in Fig. 1.

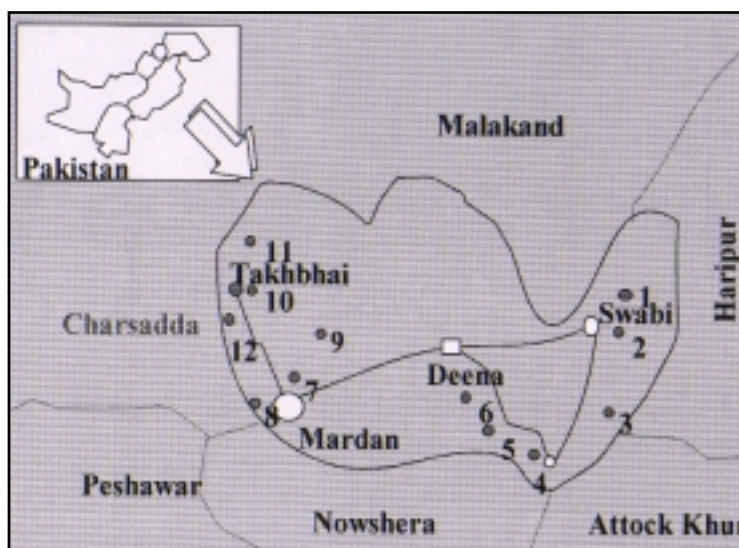


Figure 1

Groundwater sampling sites in Mardan Division, NWFP, Pakistan

Reagents

Insecticide standards, dichlorvos, mevinphos, dimethoate (99.9%), gamma-BHC (99%), methyl parathion (99.2%), fenitrothion, chlorpyrifos, endosulfan (99.5%) and profenphos were supplied by the Danish Institute of Plant and Soil Sciences, Department of Weed Control and Pesticide Ecology, DK-4200 Slegelse, Denmark and the Tropical Agricultural Research Institute (TARI), PARC Karachi. GPR grade dichloromethane (BDH), HPLC grade ethyl acetate (BDH) and anhydrous Na₂SO₄ (Riedel-deHaën) were used.

Apparatus

A gas chromatograph, Autosystem, Perkin Elmer, equipped with ⁶³Ni electron capture detector (ECD), splitless injector, capillary

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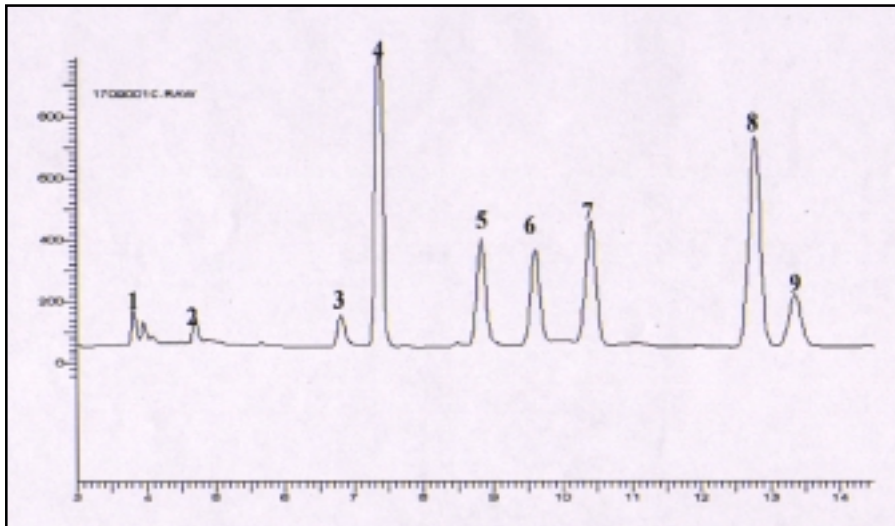


Figure 2
Chromatogram of
standard insecticides

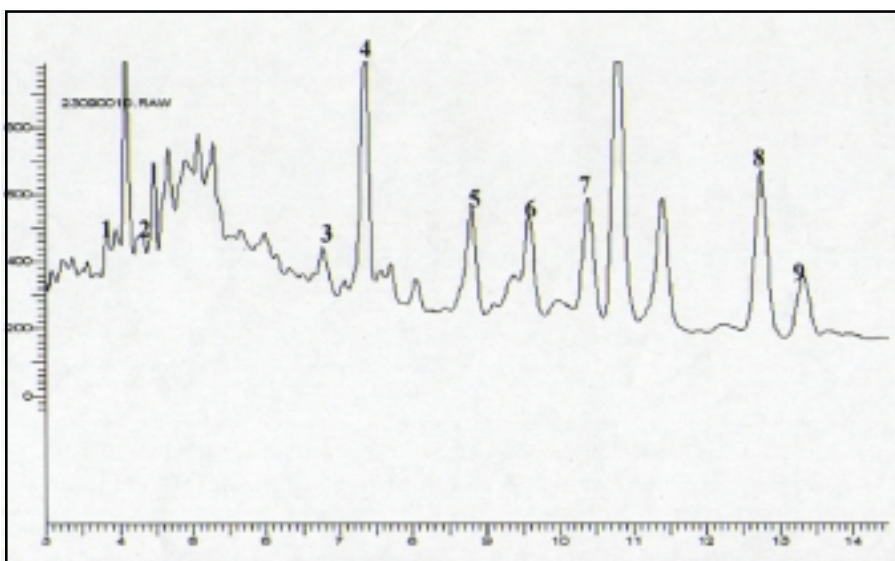


Figure 3
Chromatogram of
distilled water spiked
with 0.1 µg of each
insecticide

column (methyl silicon, 25 m, 0.53 mm i.d., 2.0 µm film thickness) and Turbochrom hardware/software system was used in the study. A rotavapor, R114, Buchi, was used for evaporating solvent from the sample.

Water sampling

Groundwater samples were collected in 2 l pyrex glass bottles in duplicate from wells, tube wells and hand pumps from different depths ranging from 3.6 to 5.1 m below the surface in different localities of Mardan Division (Fig. 1). Each sample was spiked with 1 ml of dichloromethane on-site in order to avoid biological degradation. The sealed bottles were immediately transported and stored in an airconditioned room till further use.

Sample preparation

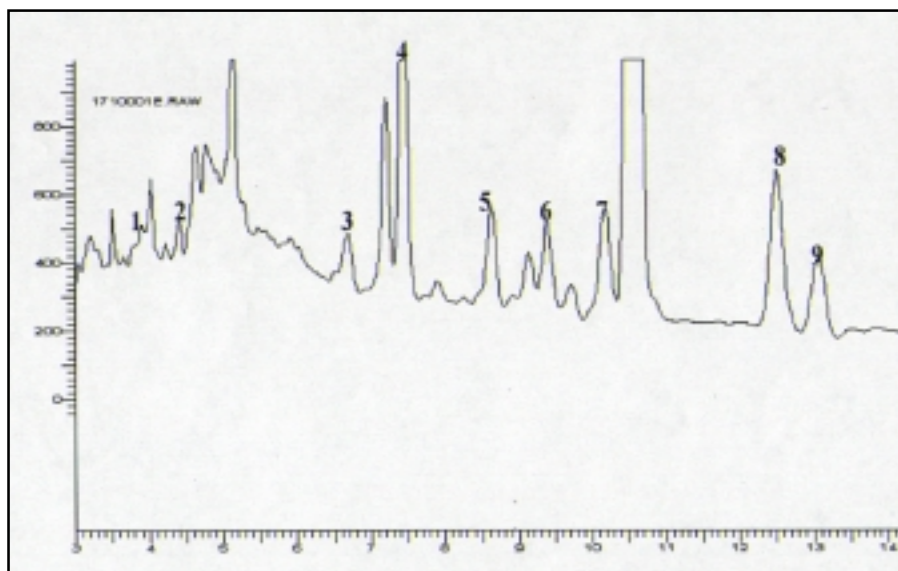
All the samples, 1 l each, were extracted with dichloromethane (25 ml) in a separating funnel. The lower organic layer was collected over cotton wool and an anhydrous Na₂SO₄ bed in a 100 ml round bottom flask. A few drops of 10% propanediol in ethyl acetate and 3 to 4 glass beads were added. It was concentrated

to dryness in a rotavapor at 40°C. An air stream over activated carbon was used to get rid of traces of the solvent. The completely dry samples were reconstituted with ethyl acetate in a 1 l volumetric flask. The extracts were stored in a refrigerator at 4°C until gas chromatographic analysis. The same extraction procedure was adopted for control and per cent recovery experiments. The distilled water (in volumes of 1 l) used was spiked with 0.00, 0.05, 0.1 and 1.0 µg of each insecticide.

Analysis

All the standards and samples were analysed using a gas chromatograph equipped with ⁶³Ni electron capture detector, splitless injector, capillary column and Turbochrom hardware/software system. The solvent flush injection technique was used. The temperature programming was: detector temperature 300°C, oven temperature 60°C (0.5 min), 30°C/min to 180°C (0 min), 4°C/min to 280°C (17 min). The components were identified on the basis of relative retention times and quantified on the basis of peak area using software based on Miller and Miller statistics (1993).

Figure 4
Chromatogram of
water sample
spiked with 0.1 µg
of each insecticide



Results and discussion

The chromatogram of standard insecticides is shown in Fig. 2. Retention time (tr), relative retention time (Rtr) and response factors (Rf) for different insecticides were calculated using gamma-BHC as a reference. Per cent recovery of each insecticide at different spiking levels (0.05, 0.10 and 1.0 µg/l) is given in Table 1 and the representative chromatogram for a spiking level of 0.1 µg/l is shown in Fig. 3. A general trend of decrease in per cent recovery with increase in spiking level was observed. It may be due to detector linearity or saturation at higher doses (Mattick and Portch, 1985). The optimum spiking level is regarded to be 0.1 µg/l because 1.0 µg/l gives very poor recovery and an 0.05 µg/l spiking level is shown to be inconclusive. In order to check the effect of the matrix on per cent recovery of insecticides from water, 1 l of different samples was spiked with 0.1 µg of each insecticide. Figure 4 shows the chromatogram of a groundwater sample collected from Baja, Swabi (Site 2 on Fig. 1) which was spiked with 0.1 µg/l of each insecticide. The results were compared with those obtained for distilled water. It has been found that about 10 to 20% loss in recovery occurs due to the matrix being present in water samples. Table 2 summarises insecticide residues which were detected in 12 groundwater sources from Mardan Division, NWFP, Pakistan.

Total insecticide residues range from 0.2 µg/l to 0.82 µg/l (Table 2). Insecticide contamination levels at three sites namely Amber, Swabi (0.82 µg/l), Lahore Shakh, Chota Lahore (0.50 µg/l) and Madras Kalay, Mardan (0.64 µg/l) exceed the maximum acceptable concentration (0.5 µg/l) set by the EC for total insecticide concentration in water. For 9 of the 12 source points one or more insecticides exceed the MAC of 0.1 µg/l for an individual insecticide. It is also noted that Site 3 (Amber, Swabi) has four individual insecticides exceeding the MAC of 0.1 µg/l. This may be due to wind drift during application or direct spillage since the Rahat (an open Persian well) from where the sample was taken, is situated in a freshly sprayed tobacco field. Empty insecticide containers were washed on the bank of the Rahat Well during sampling.

Higher residue concentrations for individual insecticides, especially dichlorvos, mevinphos and profenphos, at other localities may also be due to direct spillage since the contamination level is independent of the water depth. Mevinphos residue is high in most

TABLE 1
RECOVERY (%) OF INSECTICIDES FROM DISTILLED WATER

Insecticides	Spiking level		
	0.05 µg/l	0.1 µg/l	1.0 µg/l
Dichlorvos	180	40	23
Mevinphos	320	230	88
Dimethoate	100	50	74
Methyl parathion	100	60	30
Fenitrothion	40	50	34
Chlorpyrifos	60	60	26
Endosulfan	60	50	23
Profenphos	100	70	76
T-BHC	60	50	11

of the samples studied. This may be due to its abundant application in the area and or to its long half-life period of 35 d in a neutral environment (Tomlin, 1994).

Conclusion

Insecticide pollutants have found their way into groundwater. Whether this is due to leaching and/or other groundwater transport processes, or whether this is due to irresponsible insecticide handling practice, is not known. We recommend that on-going monitoring be continued to determine trends of insecticide residue levels. We also recommend that further studies be carried out to determine the pathways of insecticide contamination in groundwater. Insecticide user education is essential as very poor practices were observed, i.e. washing of used insecticide containers at the Rahat Well.

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TABLE 2
INSECTICIDE RESIDUES ($\mu\text{g/l}$) IN GROUNDWATER MARDAN DIVISION, NWFP, PAKISTAN

Insecticide	Sampling stations											
	Swabi			Chota Lahore			Mardan			Takhbai		
	1	2	3	4	5	6	7	8	9	10	11	12
Dichlorvos	0.10	0.09	0.08	0.09	0.08	0.06	0.04	0.45	0.03	0.16	0.03	0.04
Mevinphos	0.19	0.09	0.17	0.21	0.09	0.05	0.11	0.08	0.12	0.06	0.15	0.22
Dimethoate	0.01	0.00	0.15	0.00	0.00	0.02	0.02	0.02	0.01	0.00	0.01	0.00
Methyl parathion	0.01	0.01	0.06	0.01	0.00	0.01	0.05	0.03	0.01	0.01	0.01	0.01
Fenitrothion	0.00	0.00	0.20	0.01	0.00	0.00	0.06	0.03	0.01	0.01	0.00	0.01
Chlorpyriphos	0.00	0.01	0.01	0.02	0.00	0.03	0.00	0.01	0.00	0.01	0.01	0.00
Endosulfan	0.00	0.00	0.02	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01
Profenphos	0.02	0.02	0.13	0.16	0.02	0.06	0.01	0.02	0.01	0.17	0.02	0.10
Total	0.33	0.22	0.82	0.50	0.20	0.23	0.30	0.64	0.19	0.42	0.23	0.39

References

- AGRICULTURAL STATISTICS OF PAKISTAN GOVT. (1994-1995) Pakistan, MINFAL, Economic wing, Islamabad. 157 pp.
- ANG C, MELEADY K and WALLACE L (1989) Pesticide residues in drinking water in the North Coast region of the New South Wales, Australia, 1986-87. *Bull. Environ. Contam. Toxicol.* **42** 595-602.
- BUSHWAY RJ, HURST HL, PERKINS LB, TIAN L, GUIBERTEAU C, YOUNG BES, FERGUSON BS and JENNINGS HS (1992) Atrazine, alachlor and carbofuran contamination of well water in central Maine. *Bull. Environ. Contam. Toxicol.* **49** 19.
- FELDING G (1992) Leaching of atrazine into groundwater. *Pestic. Sci.* **35** 39-43.
- JABBAR A, ZAFAR MASUD S, PARVEEN Z and ALI M (1993) Pesticide residues in cropland soils and shallow groundwater in Punjab, Pakistan. *Bull. Environ. Contam. Toxicol.* **51** 268-273.

- LEGRAND MF, COSTENTIN E and BRUCHET A (1991) Occurrence of 38 pesticides in various French surface and groundwaters. *Environ. Toxicol.* **12** 985-996.
- MATTICK LR and PORTCH S (1985) *Analytical Chemistry, Instrumentation and Maintenance. A training Manual and Aid.* BARC, Bangladesh.
- MILLER JC and MILLER JN (1988) *Statistics for Analytical Chemistry* (2nd edn.) Ellis Horwood, Chichester. 227 pp.
- MOLTO JC, PICO Y, FONT G and MANES J (1991) Determination of triazines and organophosphorus pesticides in water samples using solid-phase extraction. *J. Chromatogr.* **555** 137-140.
- PARVEEN Z and MASUD SZ (1988) Organochlorine pesticide residues in cattle drinking water. *Pak. J. Sci. Ind. Res.* **31** 53-56.
- TOMLIN C (1994) *The Pesticide Manual, A World Compendium.* BCPC, (10th edn.).