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Pesticide Residues in Cropland Soils and Shallow Groundwater in Punjab Pakistan

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Pesticide application has become an essential component of modern day agriculture. However, the uncontrolled and excessive use of pesticides creates environmental pollution problems by contaminating soils and shallow groundwater (Perry et al., 1988 and Bouwer, 1991).

The pesticides used at present are mostly synthetic organic compounds. The principal processes that influence their potential for loss from soil to groundwater are volatilization (and subsequent diffusion), decomposition, retention by the soil, and transport by water. Some organic pesticides, such as chlordane, DDT and dieldrin, decompose very slowly and may persist for years. These pesticides, however, are of little concern as groundwater contaminants from agricultural use because they are relatively insoluble in water and are retained strongly by the soils. The principal mechanism by which pesticides are transported from soil to groundwater is downward percolation of water containing dissolved pesticides. An Environmental Protection Agency (EPA) official has estimated that as many as 50 of the more than 1,000 registered pesticides possess the potential for detection in groundwater under conditions conducive to downward movement.

In Pakistan pesticide usage started in 1954. The pesticide consumption has increased from 906 m ton a.i. in 1981 to 5296 m ton a.i. (with a market price of Rs. 4581 million) in 1990 at a rate of 40% per annum. Insecticides make up 85% of the total pesticides and herbicides as 6% (Jabbar and Inayatullah, 1990). In all 91% goes directly to soil or plantations. Upto 75% of insecticides are used on cotton crop alone and the rest is used on crops like rice, sugarcane, maize, vegetables etc. Whereas pesticide residues had been reported in the vegetable and other edible crops (Ilahi, 1985 and N.I.H., 1984) the subject of groundwater contamination has not so far been studied in Pakistan. Since introduction of canal irrigation system in 1886 Punjab has been the main agricultural area of Pakistan. Faisalabad (Central Punjab) is an agriculture intensive city mainly irrigated by canal waters. Wheat, sugarcane, cotton and maize are the major cash crops in addition to fodder crops, vegetables and fruit trees. The water table in the area is between 12-80 feet. Because of the long history of the agrochemical usage and higher water table there is a great possibility of shallow groundwater contamination by these pollutants.

MATERIALS AND METHODS.

For groundwater pollution study Samundri area, District Faisalabad, has been picked

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because of higher water table condition and long history of agrochemical usage. The project area is 30 km south of Faisalabad and is bounded by latitude 30°45' to 31°05'N and longitude 72°45' to 73°00'E, giving total coverage of 700 sq kms. Topographically the area is almost flat with elevation change from 540' in south to 567'(above sea level) in the north. The water table depth varies from 10 feet to more than 40 feet.

For the study of shallow groundwater contamination by pesticides drinking water samples were taken from the hand pumps drawing water from the depth of 30-45 feet. Seven samples were taken from the cotton growing area of Faisalabad and 3 samples were also collected from the chemical (pesticide) industrial area of Kala Shah Kaku, Lahore. Leaching of agrochemicals is controlled by the amount of excess water required for evapotranspiration and nature of compound. Soil contamination by pesticides and possible downward leaching was assessed in the study area by drawing soil samples at 1, 2, and 3 feet depths with the help of auger. The samples were shade dried to a constant weight before analysis.

All chemicals used in the study were AR grade and solvents were redistilled in an all glass system before use. Each sample was processed in triplicate to check reproducibility of results.

Each sample of water and soil was intimately mixed and extracted separately as follows. 10 g of each water sample was extracted thrice with 100+25+25 ml n-hexane according to the method of Zweig and Sherma (1974). Three extracts were then combined and concentrated down to approx. 0.5ml in a rotary vacuum evaporator at 40°C and taken up in a graduated 5 ml test tube for gas chromatographic analysis. A control sample was processed in a similar manner. No clean up was considered in this case. Each soil sample (75g) was extracted thrice with 100+50+50 ml of n-hexane:acetone 2:1 v/v. The mixtures in each case was intimately mixed for 3 hours on an electrical shaker and the contents filtered. The three different portions of the extract were then combined and concentrated down to about 2 ml in a rotary vacuum evaporator at 40°C for clean-up. 5g Florisil, 60/100 mesh (BDH, England), activated at 600°C for 3 hours and 0.5 g activated charcoal (Merck Art.2183) were weighed in a 100 ml beaker. A slurry was prepared with 15% ether in petroleum ether and transferred on to a 200mm x 10mm i.d. glass column continuously tapped to obtain a uniformly compact column packing. Anhydrous sodium sulphate (0.25 g approx.) was added on top of the column bed and the concentrated extract was then quantitatively transferred to the column which was eluted with 15% ether in petroleum ether. 200 ml eluate was collected. It was then concentrated down to 2 ml in a rotary vacuum evaporator for gas chromatic analysis.

The pesticide residue analysis were carried out using Gas Liquid Chromatography. Varian AG GC-3600 gas-liquid chromatograph equipped with ^{63}Ni electron capture detector was used in conjunction with data system DS-651. The following operating parameters were employed:

Glass column 2 meter long x 2 mm i.d. packed with a mixture of 1.5% OV-17 + 1.95% OV-210 on 80-100 mesh chromosorb W-HP. Temperatures: Injector 225°C, column oven 200°C, detector 250°C, Attenuation 64, Range 10, nitrogen carrier gas flow, 30 ml/minute. The detector was linear in the range of 0.001-1.0 ng and 0.01-2.0 ng for chlorinated and phosphorus containing pesticides respectively. Pyrethroid analysis was similar except changes in temperarure conditions. Injector 270°C, column oven 250°C, detector 300°C. The detector was linear in the range of 0.005 to 1.0 ng. In order to further confirm our results, all cleaned-up sample extracts were run through another GL column as well consisting of 3% OV-17 on 80-100 mesh chromosorb W-

HP. All other GL parameter remained unchange. Results obtained by both the GC columns were similar and comparable.

Each cleaned up sample extract was analyzed by gas chromatography alongwith its insecticde standard (Analytical grade supplied by the manufacturers) in n-hexane using 1ul injections. Results were evaluated by comparing the peak heights of sample extracts with those of relevant insecticide standards. A control sample processed in an analogous manner did not show any interfering peak that might be attributed to the studied compounds. Results of analysis of soil and water samples are presented in Tables 2 and 3. Each figure in the table is the average of three replicates.

RESULTS AND DISCUSSION.

In the study area three major crops receive pesticide cover (Table 1). Sugarcane used to be treated by endrin during 60's and 70's. Since the ban on endrin the pesticide application has been minimized to Nuvacron, Azodrin and Kerosine oil (for termites only). 47% of the surveyed farmers are applying insecticides. Mechanical weeding in wheat is still the most favored practice, however, since last 4-5 years Arelon and Dicuron is being applied by about 47% of the surveyed farmers to control weeds in wheat. A single application in the form of spray is applied. Cotton is the crop which receives the bulk of insecticides. Nearly 90% farmers in the area use insecticide spray to control insect pests. The extensive insecticide application on cotton had started around 1982, soon after the transfer of pesticide business to private sector. The farmers are using fresh insecticides, and recommended doses are applied per schedule rather disregarding infestation level. Only 40% farmers surveyed responded affirmative that advisory service was available and that again from the pesticide company representatives. Almost all farmers were unanimous that Government agencies were not providing full advice to the farming community. The number of applications of pesticides on cotton were 4 by 13%, 4-5 by 7%, 5 by 40%, 5-6 by 33% and 6 by 7%. In other words 80% farmers are applying insecticides as 5-6 spray per season. The main insecticides in use are: Monocrotophos, Cypermethrin + Profenofos, Cypermethrin, Dimethoate, Fenpropathrin, Cyhalothrin, and Fenvalerate.

An assessment of the hydrologic factors, agricultural factors and chemical factors that may effect the leaching of agricultural chemicals to groundwater was conducted to evaluate the extent and severity of agricultural chemical contamination of groundwater resources.

Table 1. Cumulative (%) data on pesticide usage

Plant protection measures adopted	%	Advisory service	%
Yes	88	Yes	40
No	12	No	60
Mechanical weeding in Wheat	100	Use fresh pesticides	100
Herbicides in wheat	47		
Insecticides in cotton	89	No of insecticide	
Insecticides in sugarcane	47	Sprays on cotton	
		4	13
Pesticide application		4-57	7
- according to schedule	100	5	40
- recommended dose	100	5-6	33
		6	7
Spray as mode of application	100		

The agricultural activity based heavily on the usage of pesticides to increase crop yields has proved to be a potential source of groundwater contamination. The shallow groundwater in Samundri area drawn from a depth of 30-40 feet is contaminated with pesticide residues (Table 2). Monocrotophos is detected in the range of 0.04 to 0.06 ppm, cyhalothrin in the range of traces to 0.0002 ppm, and endrin is present in the range of 0.0001 to 0.0002 ppm.

A number of reports are available on the groundwater contamination by pesticides in developed countries. In USA pesticides have been detected in groundwater in many locations (Hallberg, 1986, and Younos and Weigmann, 1988), however, the only report on drinking water contamination in Pakistan focuses on cattle drinking water in Karachi (Parveen and Masud, 1987). These authors analyzed 79 samples. The study revealed contamination of ten samples with chlorinated pesticides or their metabolites. Six samples were found to contain r-BHC in the range of 1.0 to 16.4 ppb, one contained p,p'-DDT in traces. In two samples p,p'-DDE was found to be present in traces. Aldrin and dieldrin were present in one sample in quantities from 2.0 to 31.5 ppb, respectively.

Table 2. Pesticide contamination of shallow groundwater

Insecticides	No. of samples*	Range (ppm)	Average (ppm)
Monocrotophos	3	0.04-0.06	0.05
Cyhalothrin	4	Traces-0.0002	0.00005
Endrin	3	0.0001-0.0002	0.00017
Non	3	-	-

* = Water was drawn from hand-pumps at 10 different sites.

The soil of Samundri in cotton growing area is contaminated with pesticide residues (Table 3). Monocrotophos is detected in the top 1 foot soil in the range of 0.3331 to 0.6429 ppm. Cyhalothrin is present in top 1 foot in the range of traces to 0.1932 whereas dimethoate was detected at one site at a concentration of 0.3858 ppm. The pyrethroids fenvalerate, cypermethrin and organophosphate profenofos are present in traces in the top 1 foot layer. The organochlorine insecticide residues of aldrin, dieldrin, endrin, p,p'-DDT and its metabolites p,p'-DDD and p,p'-DDE are detected in the lower 2 to 3 feet layers of the soil. Their concentrations varies from traces to 0.0096 ppm. In fact all the studied soils have been contaminated by varying amounts of different pesticides residues. As the most recently used insecticides were not found in the lower depths of the soil the analysis was not further carried out.

Studies on the pesticide residues in soil and environment have always lagged behind in Pakistan due to financial constraints and lack of proper laboratory facilities. The ones which have appeared so far are cited below. The Pesticide Research Laboratories, PARC, Karachi is continually monitoring pesticides in food commodities and environment, however, Baig (1985) presented a detailed report. The reported studies were carried out during 1978-1985. In the first instance, the p,p'-DDT under semifield conditions of 5-7 sprays was found to be 0.8 - 1.3 ppm in cotton seed oil. Moreover, the cotton seed oil from aerially sprayed cotton contained 0.18 - 0.92 ppm of DDE an metabolite of DDT. These values were below the FAO/WHO limits of 0.5 - 5.00 for DDT and metabolite, like DDE. One notable thing was that these experiments were carried out about 10 years ago when DDT was used abundantly, secondly after processing of cotton seed oil a further decline was expected due to processing loss.

The study was inconclusive as it did not look into situation in market products i.e. vegetable oil and "ghee" manufactured from cotton seed oil.

Table 3. Pesticide contamination of farming land*

Insecticides	No. of sites	Depths (feet)		
		1	2	3
Monocrotophos	2	0.3331-0.6429	-	-
Cyhalothrin	2	Traces-0.1932	-	Traces
Dimethoate	1	0.3858	-	-
Fenvalerate	1	Traces	-	-
Profenofos	3	Traces	0.0007	-
Cypermethrin	2	Traces	-	-
Aldrin	4	-	0.0013-0.0018	0.0004
Dieldrin	4	-	0.0031-0.0096	Traces-0.0103
Endrin	3	-	0.0002-0.0006	Traces-0.0004
p,p'-DDD	3	-	Traces-0.002	Traces
p,p'-DDE	4	-	Traces-0.002	0.001-0.0037
p,p'-DDT	2	-	Traces	Traces-0.0002

* Soil samples were collected from 5 different sites.
The results are given as ppm.

In second study random sampling of soil from agricultural areas of Punjab and North West Frontier Province (NWFP), where DDT was in use for decades, was undertaken. Up to 0.6 ppm were detected in the rice fields around Kala Shah Kaku, and 0.2 - 0.59 ppm in sugarcane and tobacco fields of NWFP and in the orchards of Bhalwal. These levels of DDT were not considered to be a matter of great concern unless their seepage into water.

Carefully controlled studies by Hussain and his group (1988) at Nuclear Institute for Agriculture and Biology, Faisalabad using sandy loam soils have indicated that most of the applied DDT is retained by the top 5 cm layer. Movement down to 10 cm and 15 cm is very slow. This may be due to the fact that DDT is water insoluble. However, their important finding was that half life dissipation for DDT in laboratory was 890 days but under field conditions the half life was 110 days in irrigated and 112 days in rainfed soils. This trend is in conformity with other tropical and sub-tropical countries and has implication that DDT is degradable. Maybe, but there are other possibilities.

Breakdown of organic pesticides in soils beyond that involving reactions with water is attributed to micro-organisms and catalytic effects of soils. Pesticides such as dalapon, 2,4-D, malathion and parathion that breakdown rapidly (50% decomposition in 2 weeks or less under favorable conditions) are not likely to be detected in groundwater. Some organic pesticides such as DDT and dieldrin decompose very slowly and may persist for years. These pesticides, however, are not of concern as groundwater contaminants from agricultural use because they are relatively insoluble in water and are retained strongly by soils. The decomposition (loss of 75 to 100% of the biological activity) of different classes of pesticides in soil varies. Studies under agricultural conditions with normal rates of application have shown various organophosphate and carbamate insecticides to persist for 1-12 weeks, and chlorinated pesticides from 2-5 years.

Tinsley (1979) noted that the 50% decomposition times for certain pesticides increased in the order malathion, diazinon, and DDT. Depending upon the experimental conditions wide differences in the absolute values were found. For example, the 50% decomposition time for DDT was 240 days in a tropical environment, 3840 days in a temperate environment and 33 days in a laboratory test done in the absence of free oxygen. The 50% decomposition times were greater when measured in subsoil samples than in surface soil samples, presumably due to lesser microbial activity in the sub-soil samples.

To conclude the insecticides have reached the shallow aquifer. The soils are loaded with the pesticide residues which are a constant threat to public health and to the environment. The occurrence of potentially toxic hazardous chemicals in groundwater/drinking water, even in low concentrations, is of real concern because of the potential for long term and wide-spread exposure to public. At the present time, only relatively shallow aquifers are affected. However, this may simply be a function of time when the deeper aquifers will also be contaminated.

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REFERENCES.

Baig MMH (1985) Digest of activities of Federal Pesticides Research Laboratory, Pakistan Agricultural Research Council, Karachi.

Bouwer H (1991) Agricultural chemicals and groundwater quality. Modern Agriculture September, 1991 pp 33-42.

Hallberg G R (1986) Overview of agricultural chemicals in groundwater. In Proc. Conf. Agr. Impact on Groundwater. Nat. Well Water Assoc., Dublin, Ohio.pp 1-63.

Hussain A, Trimzi H, Babar Z (1988) Studies on the degradation, dissipation and persistence of DDT in a sandy loam soil under laboratory and field conditions. Proc. Third (Final) FAO/IAEA research coordination meeting on the fate of persistent pesticides in the tropics, using isotope techniques, January 25-29, 1988, Bangkok, Thailand.

Ilahi A (1985) Study of the level of insecticide residues in food and feed stuffs. Final technical Report (1984-1985). University of Agriculture, Faisalabad.

Jabbar A, Inayatullah C, (1990) Environmental considerations of pesticide production and usage in Pakistan, RENPAP Gazette, 1(1):15-24.

NIH (1984) Food contamination study and control in Asia and Far East. Report of National Institute of Health, Islamabad.

Perry CA,Robbins FV, Barns PL (1988) Factors affecting leaching in agricultural areas and assessment of agricultural chemicals in the groundwater of Kansas. Water Resources Investigation Report 88-4104, U.S. Geological Survey, Lawrence, Kansas. pp 1-55.

Parveen Z, Masud SZ (1988) Organochlorine pesticide residues in cattle drinking water. Pak. J. Sci. Ind. Res. 31:53-56.

Tinsley IJ (1979) Chemical concepts in pollutant behavior. John Wiley and Sons, New York. pp 1-265.

Younos TM, Weigmann DL (1988) Pesticides in groundwater data base. 1988 Interim Rpt. U.S. Environmental Protection Agency. Washington D.C.

Zweig G, Sherma J (1974) Pesticides, Plant Growth Regulators and Food Additives, Vol 7. Academic Press Inc., London. pp 13-50.

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