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DETERMINATION OF PESTICIDE RESIDUES IN GROUND AND SURFACE WATER SAMPLES AND PERCEPTION OF FARMERS ABOUT PESTICIDES IN SINDH

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ABSTRACT

The continuous monitoring of pesticide residues in our food, drinking water, environment and biosphere at large is needed for creating awareness for the trends of level of contamination and building up a data base upon which future plan could be decided. In this paper monitoring requirements regarding the instrumentations, valid sampling, analytical protocols and its purpose are discussed in detail. Twenty nine water samples were analyzed and 22 were found contaminated with detectable level of 5 pesticides. These samples were found contaminated in the range of 0.0005-0.054 µg/L. The percentage of detection of Chlorpyriphos, Malathion, Dimethoate, Cypermethrin, and Endosulfan was respectively 7%, 14%, 17.8%, 35.8% and 25%. However, none of the samples were found above their Maximum Acceptable Concentrate (MAC) i.e. 0.1µg/L and 0.5µg/L for single and number of insecticides respectively set by EEC (European Economic Commission). Moreover, a survey of farmers' perceptions in respect of effects on their health with pesticide exposure was conducted to find out farmers' perception for the use of pesticides and how these may affect on their health with, identification of key issues those are relevant to farmers' health for further training to increase farmer's awareness about the use of pesticides.

Keywords: Pesticides, Insecticides, Monitoring, Groundwater, Farmer's Perception

INTRODUCTION

It is almost impossible to apply pesticides in such a way that only the target pest is exposed. Nationally chemicals applied almost any where in the environment tend to be distributed to the entire surrounding environment. The rate and extent of this distribution is complex due to interaction among the physical and chemical properties of the pesticides, the methods of application, environmental conditions and management practices. In Pakistan, tremendous amount of agrochemicals are used in agriculture in order to meet the food requirements of burgeoning population. By mid sixties the pesticide consumption reached over seven thousand tons per annum, both for former East and West Pakistan which materialized green revolution in the country (Kafi and Baig, 1987). In 1980, the pesticides import, distribution and sale was transferred from public to private sector which brought about five fold increase in the pesticide consumption in subsequent year (Baloch and Haseeb, 1995). The pesticides consumption has risen four folds during the past decade (1981-90). By 1981, some 3677 metric tons (MT) of pesticides were used on the land and the amount has increased every year since then. In 1990 the consumption was 14742 MT of 4581 million rupees worth, which reached to 43219 MT of 9987 million rupees in 1996. This quantity reduced to a level of 20394 metric tons in 2006-07 (ESP-2007).

Among the total pesticides consumed in Pakistan, 86% were insecticides out of which 65% belonged to Organophosphorus group. Approximately 80% of the total pesticides being marketed in Pakistan were used on cotton and the rest on other crops like fruits, vegetables, paddy, tobacco and sugarcane etc (Kafi and Baig.1987). Roughly 85 to 90 percent of pesticides applied in agriculture never reach the target organism but disperse through air, water and soil. Such an abuse of pesticides not only drains our exchequer but also present a growing threat to the people and environment of Pakistan. Hence we are not only helping in degrading our soil but we are also destroying our environment and poisoning not only ourselves but our future generations.

Pesticide residues in drinking and ground water of developed countries like USA (Molto *et al*., 1991) and France (Legrand *et al*., 1991) have been reported. Maximum Acceptable Concentrate (MAC) for drinking water in most of the developed countries is not toxicologically based but fixed from the point of view that we do not want pesticides in our drinking water. In Pakistan, some chlorinated pesticides were found in cattle drinking water from Karachi (Parveen and Masood, 1988) while monocrotophos, cyhalothrin and endrin in shallow ground water in Samundari, Faisalabad (Jabbar *et al.*, 1993) and some commonly used pesticide residues in ground water of Mardan division (Ahad *et al*., 2000) was also reported. Recently Anwar *et al*. (2005) have reported the pesticide residues in the ground water of Bahawalpur division, Punjab.

MATERIALS AND METHODS

Ground water samples were collected from wells, tube wells and hand pumps from different depths ranging from 12-140 feet in different localities of Nawabshah, while surface water samples were collected from River Indus, Rohri Canal, Kinjher Lake and Haleji Lake. A total of 29 water samples were analyzed for pesticide residues Water samples were extracted with Liquid-Liquid Extraction technique (LLE) using the dichloromethane and insecticide residues were measured by Gas Chromatography (GC) with Flame Ionization Detector (FID). On the basis of retention time of standard pesticides (chlorpyrifos, malathion, profenofos, bifenthrin, fenvalerate, dimethoate, cyhalothrin, cypermethrin, endosulfan and monocrotophos) the water samples were integrated.

A survey of farmers' perceptions in respect of effects on their health with pesticide exposure was conducted. In this connection a questionnaire with closed and open question, was designed to collect data about farmer's socio-economic background, health status of family, perceptions of use of pesticides and health signs and symptoms from pesticide use. The survey was conducted in Sakrand, Daulatput and Nawabshah thesils of District Nawabshah, the cotton growing areas of Sindh, where heavy use of pesticides had been reported. The criteria for the sample population in the study areas were farmers who grew cotton or vegetables and used pesticides on their crops. Respondents were randomly selected using a snowballing technique in the field.

RESULTS AND DISCUSSION

The cotton growing areas in Pakistan receives heavy amount of pesticides. These pesticides can find their way in to ground water through leaching, channeling (downward percolation), and direct spillage and wind drift. Unwarranted optimism regarding the risk and even gross ignorance regarding some essential features is usually the case of serious problems that may develop. Pesticide with relatively high-water solubility, such as the herbicide atrazine, may have tendency to migrate to ground water. Moreover, the persistence of pesticide in soil and their adsorption to soil particles are of special importance in evaluating the potential transport of pesticide in the soil. Surplus of precipitation and soil organic matter contents are important environmental parameters of leaching.

Some results are being reported regarding the extraction and analysis of pesticides in water. The presence of 38 pesticides (19 herbicides, 7 insecticides and 12 fungicides) in various French surface and ground waters has been reported (Legrand *et al*., 1991). Seven multi-residue analytical techniques were developed to measure the pesticides at or below 100-ng/litre level of drinking water EEC directive. GC-MS and HPLC techniques were used. The use of Solid-Phase Cartridges (C_{18}) for routine large-scale extraction of several N-containing pesticides from well water has been discussed (Nash, 1990). It was found that more than 48 samples/day could be analyzed. Recovery efficiencies were found to be in the range of 77-99% with detection limits of 0.05 - 0.20 μg/litre. Runoff losses of azinphos-methyl and fenvalerate from sugarcane-insect IPM system to water and sediments has been reported (Smith *et al*., 1983). Octadecyl (C_{18})- bonded porous silica for the extraction of triazines and organophosphorus insecticides from natural water has been evaluated (Molto, *et al.*,1991). The results were compared to those obtained by liquid/liquid extraction. A solid phase extraction (SPE) and capillary GC procedure to extract and concentrate traces of selected pesticides from stream water has been reported (Novak and Watts, 1996). Solid Phase Extraction and immunoassay analysis of metolachlore in surface runoff and tile drainage has been compared (Gaynor *et al*., 1996). The concentrations of nine selected organonitrogen and organophosphorus pesticides in Chesapeake Bay, USA. Annual loads of organo- N/P pesticides were directly correlated with field application rates (Foster and Lippa, 1996). SPE and GC-MS techniques for the confirmation of chlorpyrifos contamination of water supplies in Saskatchewan, Canada, has been reported (Thompson and Treble, 1996). Solid Phase Extraction (SPE) and Liquid-Liquid extraction (LLE) techniques were validated for organophosphate insecticide residues in fortified drinking water sample at different spiking levels. The gas chromatograph equipped with Nitrogen Phosphorous Detector (NPD) was used for analysis. The methyl parathion at the spiking level of 1.6 μg/l was recovered to be 74% by LLE and 80% by SPE (Anwar *et al*., 2006).

A total of 29 water samples were analyzed and 22 were found contaminated with detectable level of 5 pesticides. These samples were found contaminated in the range of 0.0005-0.054 μg/L. The percentage of detection of chlorpyriphos, malathion, dimethoate, cypermethrin and endosulfan was respectively 7%, 14%, 17.8%, 35.8% and 25%. However, none of the sample was found above their MRLs (0.1μg/L and 0.5μg/L for single and number of insecticides respectively set by EEC (European Economic Commission). Whereas, six water samples were found free from tested insecticide. Percent recoveries in the control sample were calculated to be 90-130. Although, the pesticides measure were below the MRLs, but the groups of insecticide used in this area belong to highly hazardous (Ib) and moderately hazardous (III) classes categorized by WHO. Therefore, pesticides concentration found in water

samples may threaten the human and livestock health.

Table 1. Pesticide residues (μg L^{-1}) in ground and surface water samples collected from, Sindh, Pakistan.

S. Nos	LOCATIONS	PESTICIDES					
	Sample code	Chlorpyriphos	Malathion	Dimethoate	Cypermethrin	Endosulfan	Total
1	SK-1	0	0.0066	0	0.0018	0	0.0084
2	SK-2	0	0	0	0.003	0	0.003
3	SK-3	0	0	0	0.015	0	0.015
4	Sk-4	0	0	0	0	0.015	0.015
5	SK-5	0	0	0	0	0	0
6	SK-6	0	0	0	0	0.0009	0.0009
7	SK-7	0	0.0071	0	0	0	0.0071
8	SK-8	0	0	0.045	0	0	0.045
9	SK-9	0	0	0	0	0.0021	0.0021
10	SK-10	0	0	0.0044	0	0	0.0044
11	SK-11	0	0	0.007	0	0	0.007
12	DP-1	0	0	0	0.0156	0	0.0156
13	DP-2	0	0	0	0.004	0	0.004
14	DP-3	0.0015	0	0	0.0141	0.006	0.0216
15	DP-4	0	0	0	0	0	0
16	DP-5	0	0	0	0	0	0
17	DP-6	0	0.0025	0	0	0.005	0.0075
18	DP-7	0	0	0	0	0	0
19	NS-1	0	0	0.0455	0	0.0063	0.0518
20	NS-2	0	0	0	0	0	0
21	NS-3	0	0.0021	0	0	0	0.0021
22	NS-4	0	0	0	0.0026	0	0.0026
23	NS-5	0	0	0	0.0146	0.007	0.0216
24	NS-6	0	0	0.038	0	0	0.038
25	NS-7	0.00127	0	0	0	0	0.00127
26	RS-1	0	0	0	0	0	0
27	RC-1	0	0	0	0	0	0
28	KL-1	0	0	0	0.006	0	0.006
29	HL-1	0	0	0	0.0023	0	0.0023
	Detection	7%	14%	17.8%	35.8%	25%	*29(22)^{0}

*Sample analyzed (contaminated)$^{\text{Above MAC}}$

Note: Values are the mean of duplicate samples. Whereas, 0 stands for "pesticide not detected". Ground water samples codes stand for SK: Sakrund, DP: Daulatpur, NS: Nawabshah. The surface water collected form River Indus (RI), Rohri Canal (RC), Kinjher Lake (KL) and Haleji Lake (HL). MAC stands for Maximum Acceptable Limits.

FARMERS' HEALTH PERCEPTION

A survey of farmers' perceptions in respect of effects on their health with pesticide exposure was conducted. The objective of survey was: to find out farmers' perception for the use of pesticides and how they may affect on their health with, identification of key issues those are relevant to farmers' health for further training to increase farmer's awareness about the use of pesticides.

In this connection a questionnaire with closed and open questions, was designed to collect data about farmer's socio-economic background, health status of family, perceptions of use of pesticides and health signs and symptoms from pesticide use. The survey was conducted in three study areas: Sakrand, Daulatput and Nawabshah, Thesils of District Nawabshah; cotton growing areas of Sindh where heavy use of pesticides had been reported. The criteria for the sample population in the study areas were farmers who grew cotton or vegetables and used pesticides on their crops. Respondents were selected using a snowballing technique in the field. A total of 27 field workers were interviewed. The majority of farmers were found with the thinking that there was a strong correlation between pesticides used and their health condition and further pesticides could shorten their lifespan. They noticed that due to the pesticides usage their health became weaker and they fell sick more easily. Some farmers reported that sometime they could not spray pesticides because they felt dizzy and got headache when they smelled the spray solution. Amongst, the farmers who reported that there was a little affect on their health, 27% suffered from headaches and dizziness and 11.5% felt no symptoms at all.

It was reported that farmers often applied insecticides frequently in high doses on a single crop, continuously throughout the season without understanding the instructions on label and other protective measures. They also used pesticides admixture of different kinds of pesticides. They usually followed the instructions given by the pesticide sellers/dealers etc. Farmers (98%) used Triazophos+Deltamethrin (Deltaphos) Methamidophos (Sundaphos), Monocrotophos (Nuvacron) Cyhalothrin (Karate), Bifenthrin (Talistar), Deltamethrin (Decis), Endosulphos (Thiodan) Cypermethrin (Polytrin). 100% of them claim that they knew about the recommended dose and method of using pesticides. 35% reported that they adopted no precautionary measures while 65% used their shirt or any piece of cloth to cover their face during spraying. 57.6% reported that they did not smoke and eat during spraying and 50% did not drink during spraying. Not much consideration or importance was found given by 62% farmers to safe storage of used or filled pesticides bottles, correct dosage of chemical measured or the mixing of different brands together. When suffering from mild symptoms of nausea, headaches and dizziness. 88% respondents mentioned many remedies varied from consuming sugarcane, candy, lemon juice, honey solution and Lassi. 30.76% farmers reported for a private doctor called to cure them at home, and in more serious cases of poisoning 65.3% went to the civil hospital. 67.7% reported that pesticides had effects on birds, cows and goats. 65.3% admitted about the death incidence due to pesticides.

Effective monitoring requires considerable infrastructure and a set of validated sampling and analytical protocols to ensure that reliable data are generated. Besides Gas Liquid chromatography (GLC) or High Performance Liquid Chromatography (HPLC), the Enzymed Linked Immunosorbent assay (ELIZA) are being used. The purpose of monitoring is to provide feedback on contamination. This can reduce the risk to humans and livestock. The heath risks for the users of the wells for drinking water are tremendous. The cumulative effect of these pesticides result in ill health by blocking the calcium metabolism. The pesticide keeps on accumulating in the fat cells of human being. This results in the development of fatal diseases of brain, liver, kidneys arthritis and cancer. The severe effects of these toxicants might appear soon after their application but could also develop after lapse of many years. Some cause "Parkinson disease". Some are known to cause immense depression. Many of these disrupt hormone systems causing cancer of prostate, testes, breast and cervix. The endocrine disruptions are commonly observed among the effected human. Mughal and Rehman (1973) were probably the first in Pakistan who reported extremely high content of organochlorine in the fatty tissues of patient. There is an apparent association between high serum organochlorine pesticide level and the subsequent appearance of the hypertension and antihero-sclerotic cardio vascular disease. The continuous monitoring of pesticide residues in our food, drinking water, environment and biosphere at large is needed for creating awareness of pesticides contamination and building up a data base upon which future plan could be decided.

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