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Quantification of Pesticide Residues in Drinking Water in Different Areas of District Charsadda, Pakistan

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Abstract. Pesticides residues were determined quantitatively in drinking water samples collected from district Charsadda of the province Khyber Pakhtunkhwa, Pakistan employing GC-MS technique. The survey was conducted soon after the flood in 2010. Aldicarb (0.003 mg/L) was found only in C7, while residues of acetachlor (0.001 mg/L) was found in C8. Among the pesticides quantified Chlorpyrifos delivered highest amount of residues in C8, C9, C10, C11 and C12. Residues of *o*, *p′*-DDT were found higher in C1 to C6 than the permitted value (0.002 mg/L), while higher concentration of Pyridaben than the allowed value (0.0001 mg/L) was resulted in C1, C5, C6 and C14. Residues of Carbofuran, Atrazine, α-Endosulfan and Dieldrin, β-Endosulfan, Difenoconazole-1 and Difenoconazole-2 were not detected in any of the collected water samples. Concentrations of rest of the pesticides residues detected in water samples were within the permissible limits. The study revealed that water samples collected from district Charsadda are highly contaminated with pesticides, which is a health risk factor for the inhabitant of this areas.

Keywords: drinking water, pesticides residues, GC-MS, district Charsadda, flood 2010

Introduction

Pesticides play a fundamental role in green revolution by producing crops of good quality and quantity through the control of the insectivorous and herbaceous pests. On one side chemistry has proved to be of merit for the life but unfortunately on the other side, it has also brought some demerits. Among these some have threatened the long-term survival of major ecosystems by disruption of predator-prey relationships and loss of biodiversity. Pesticides have also produced numerous health problems (Hayat *et al*., 2010) like neurotoxicity (Karalliedde and Senanayake, 1999; Brown *et al*., 1989) and can result in gastrointestinal, cardiological, dermatological, respiratory, genito-urinary and musculoskeletal problems (Vial *et al*., 1996; Hueser, 1992). It has been shown that these chemicals are injurious to defense and endocrine systems (Luster and Rosenthal, 1993; Arlien-Soberg, 1992; Chambers, 1992).

The most commonly used technique for the extraction of pesticides from the complex sample is liquid-liquid extraction, which is carried out by mixing the aqueous phase with other immiscible organic solvents like ethyl acetate, dichloromethane and hexane. Various analytical procedures are employed for the analysis of pesticides including chromatographic techniques like GC and HPLC coupled to various detection systems. GC-MS is the method of choice which is a robust and routinely employed for pesticides analyses.

Contamination of drinking water after flood is a burning environmental issue and a health threat. Flood water can be contaminated with a variety of substances including pathogenic micro-organisms, automotive fluids, animal wastes, fertilizers, chemicals like pesticides etc. when surface water drained into the ground water carrying these contaminants. Contamination of drinking water with pesticides cause a number of health problems. Therefore, determination of pesticide residues in drinking water sources is important in order to take appropriate measures for the provision of safe drinking water to public and protection of public health.

Surface water contaminated with pathogenic micro-organisms and chemicals like pesticides and herbicides are the most alarming, when the surface water goes into ground water. The surface water drained the pesticides and herbicides into the drinking water resources making it highly contaminated and harmful for the human consumption. Hence, drinking water samples were collected from different areas of district Charsadda after the flood in 2010 for the evaluation of pesticides residues.

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This paper presents the results of pesticides residues determination in drinking water samples from different areas of district Charsadda of the province Khyber Pakhtunkhwa.

Materials and Methods

Chemicals and reagents. Ethyl acetate (GC grade) and dichloromethane (GC grade) were purchased from Fischer Scientific (Leicestershire, UK). Sodium sulphate anhydrous (analytical grade), potassium dihydrogen phosphate, HCl and sodium chloride (analytical grade) were obtained from Merck (Darmstadt, Germany). GC grade pesticide standards acetamiprid (>99%), acetochlor (>99%), atrazine (>99%), cypermethrin (>99%), dichlorvos (>99%) and pyridaben (>99%) were purchased from AccuStandard New Haven, CT, USA. Aldicarb (99.9%), alpha endosulfan (99.6%), beta-endosulfan (99.9%), chlorpyrifos (99.2%), cyhalothrin (99.7%), fenvalerate (99.8%), methamidophos (98.4%) and popachlor (99.5%) were procured from Sigma-Aldrich GmbH, Seelze, Germany. Carbofuran (98.5%), dieldrin (98.3%), methiocarb (98.5%), *o,p′*-DDD (99.6%), *o,p′*-DDT (99.5%) and *p,p′*-DDE (98.5%) were obtained from Dr. Ehrenstorfer GmbH Ausburg, Germany. Helium gas (99.9999%) was procured from Pak Gas (United Arab Emirates). Double distilled water was used through out this experimental work.

Preparation of pesticide standard mixture. The pesticides selected for the study were those which are most commonly sprayed in these areas as insecticides and herbicides, and are easily available in the form of standards. The data of the most commonly used pesticides in the area has been taken from the department of Agriculture Training Institute Peshawar, Khyber Paktunkhwa. For this study total of 21 pesticides were selected as shown in Table 1. Detail of the retention times, areas, concentrations and quantifying ion (m/z value) of each pesticide is tabulated in Table 1.

Stock solutions of the individual pesticides under study were prepared in methanol. For preparing working standard solution, appropriate volume from each individual pesticides solution was mixed together in a vial. 2 L of the standard mixture was injected into the GC column using auto injection system of GC-MS.

Samples collection. Samples from drinking water sources were collected from various places of districts Charsadda, which were under water for many days in flood 2010 in Pakistan. Samples were properly preserved at 4 °C until their use for experimental work.

Extraction of pesticides and preparation of samples. The official methods of analysis of AOAC International with some modifications was employed for the extraction of pesticides. One litre of water sample was adjusted to pH by adding phosphate buffer (pH 7). 100 g of NaCl was dissolved in this solution followed by the addition of 300 mL of ethyl acetate. The mixture was shaken for one hour at 200 rpm through shaker. After one hour, the mixture was poured into separating funnel and the layers were let to separate. The upper organic layer was collected in a round bottom flask. The lower aqueous layer was again extracted with 60 mL of ethyl acetate. The mixture was shaken for 15 min. Then the organic layer was separated and mixed with the first time collected layer. Organic layer was dried with sodium sulphate anhydrous. The solution was filtered and evaporated to dry residue through rotary evaporator. The dried residue was dissolved in 2 mL of dichloromethane. The solution was filtered through 0.45 m membrane filter and 2 L of this solution was injected into the GC column using auto injection system.

Table 1. GC-MS data of pesticides standard mixture

Name	R. Time (min)	Quantification ion (m/z value)
Aldicarb	3.86	68
Methamidophos	4.35	98
Dichlorvos	6.43	109
Carbofuran	7.27	164
Methiocarb	10.02	168
Propachlor	10.69	120
Cyhalothrin	11.76	198
Atrazine	12.24	200
Acetochlor	13.57	59
Chlorpyrifos	14.54	97
α- Endosulfan	16.17	241
p, p′-DDE	16.55	246
Dieldrin	16.69	79
β-Endosulfan	17.30	195
o, p′-DDD	17.36	235
o, p′-DDT	18.06	235
Acetamiprid	18.82	56
Pyridaben	20.92	147
Cypermethrin-1	21.74	181
Fenvalerate-1	22.60	125
Fenvalerate-2	22.85	125

Chromatographic separation of pesticides. A gas chromatograph from Shimadzu hyphenated to a mass spectrometer QP 2010 plus (Tokyo, Japan) equipped with an auto-sampler (AOC-20S) and auto-injector (AOC-20i) was used. Ultra high pure helium was used as carrier gas. All chromatographic separations were performed on a capillary column (DB-5ms; Agilent Technologies, CA, USA) having specifications: length; 30 m, i.d.; 0.25 mm, thickness; 0.25 µm. Other GC-MS conditions are: ion source temperature (EI); 280 °C, interface temperature; 280 °C, solvent cut time; 2 min. 2 µL of samples and standard were injected into the GC column. Injector was operated in a splitless mode. Injection temperature was 250 °C. The column temperature programme started at 50 °C for 1 min and ramped to 125 °C at the rate of 25 °C/min. The temperature was further increased to 220 °C at the rate of 10 °C/min and hold for 15 min. Total elution time was 37.5 min. MS was operated in single ion monitoring (SIM) mode. GC-MS solutions software provided by the supplier was used to control the system and to acquire the data. Identification and quantification of the compounds was carried out by comparing the mass spectra obtained with those of external pesticide mixed standard solution. Qualification of the peaks was further authenticated through standard mass spectra from the NIST Library (NIST 05).

Results and Discussion

Selection of sampling area and choice for pesticides. The samples were collected from different areas of district Charsadda, Pakistan.

Pesticide residues in drinking water samples. Standard maximum permissible values for pesticide residues in drinking water have been shown in Table 2. Quantities of pesticides under study in drinking water samples collected from different areas of district Charsadda are depicted in Table 3. Many pesticides were found in appreciable amounts in these samples. Among the pesticides studies, quantities of methiocarb obtained were 0.012, 0.019 and 0.016 (mg/L) in C5, C7 and C8, respectively. Cyhalothrin were found at the level of 0.013 and 0.016 (mg/L) in C1 and C3, respectively. In sample C8, 1.23 mg/L of chlorpyrifos was found while in C9, C10, C11 and C12 this analyte was obtained at the concentration of 0.030, 0.45, 0.41 and 0.91 (mg/L), respectively. In C1, C2, C3, C4 and C5 the concentration of *o,p′*-DDT found were: 0.028, 0.032, 0.025, 0.019 and 0.017 (mg/L), respectively. Appreciable amount of acetamiprid was detected in C1 and C2 samples as 0.013 and 0.016 (mg/L), respectively, while high amount of propachlor i.e., 0.012 mg/L was found in C11. In rest of the samples the pesticides quantified were either at the level of 0.01 (mg/L) or below. For some pesticides

Table 2. Standard maximum permissible values for pesticide residues in drinking water

Pesticide name	Maximum permissible limits (mg/L)	Reference
Aldicarb	0.01	(Hamilton *et al*., 2003; Jenkins, 1999)
Methamidophos	Data not available	
Dichlorvos	0.012	(Moermond *et al*., 2008)
Carbofuran	0.007	(Hamilton *et al*., 2003)
Methiocarb	0.035	(Jenkins, 1999)
Propachlor	0.09	(Jenkins, 1999)
Cyhalothrin	Data not available	
Atrazine	0.002	(Hamilton *et al*., 2003)
Acetochlor	0.14	(Jenkins, 1999)
Chlorpyrifos	Data not available	
α- Endosulfan	0.042	(Jenkins, 1999)
p, p′-DDE	0.002	(Hamilton *et al*., 2003)
Dieldrin	0.0002	(Hamilton *et al*., 2003)
β-Endosulfan	0.042	(Jenkins, 1999)
o, p′-DDD	0.002	(Hamilton *et al*., 2003)
o, p′-DDT	0.002	(Hamilton *et al*., 2003)
Acetamiprid	Data not available	
Pyridaben	0.0001	(Moermond *et al*., 2008)
Cypermethrin-1	Data not available	
Fenvalerate-1	Data not available	
Fenvalerate-2	Data not available	

Table 3. Concentration of pesticides in flood water samples collected from district Charsadda (C); LOQ: 0.001 (mg/L)

Name	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16
	(mg/L)															
Aldicarb	ND	ND	ND	ND	ND	ND	0.003	ND	ND	ND	ND	ND	ND	ND	ND	<0.001
Methamidophos	ND	ND	ND	ND	0.007	0.009	0.004	0.008	0.002	0.005	0.010	0.005	0.007	0.004	0.004	0.003
Dichlorvos	ND	ND	ND	ND	ND	ND	0.004	0.001	0.001	0.001	0.001	0.003	0.001	0.001	0.001	0.001
Methiocarb	ND	ND	ND	ND	0.012	0.008	0.019	0.016	0.007	ND	ND	ND	0.002	0.010	ND	ND
Propachlor	ND	ND	ND	ND	ND	0.003	ND	ND	0.002	0.002	0.012	0.010	ND	ND	<0.001	<0.001
Cyhalothrin	0.013	ND	0.016	0.007	0.009	ND	ND	ND	ND	ND	0.001	ND	ND	ND	ND	ND
Acetochlor	ND	ND	ND	ND	ND	ND	ND	0.001	ND	ND	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	ND	ND	ND	1.231	0.030	0.449	ND	ND	ND	ND	ND	ND
p, p′-DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.413	0.910	ND	ND	ND	ND
o, p′-DDD	ND	0.001	ND	ND	ND	0.001	0.001	ND	ND	ND	ND	ND	ND	ND	ND	ND
o, p′-DDT	0.028	0.032	0.025	0.019	0.017	0.002	ND	ND	0.001	0.001	ND	ND	0.001	ND	<0.001	<0.001
Acetamiprid	0.013	0.016	ND	0.001	ND	0.001	ND	0.001	0.002	ND	ND	ND	0.001	ND	ND	<0.001
Pyridaben	0.001	ND	ND	ND	0.001	0.001	ND	ND	ND	ND	0.003	0.001	ND	0.001	<0.001	<0.001
Cypermethrin-1	ND	ND	ND	ND	ND	0.002	ND	ND	ND	ND	ND	ND	ND	0.003	<0.001	<0.001
Fenvalerate-1	ND	ND	ND	0.001	ND	0.003	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fenvalerate-2	ND	ND	ND	ND	ND	0.004	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = not detected.

the data for their permissible limit in drinking water is not available as shown in Table 2.

Aldicarb (0.003 mg/L) was found only in C7 while residues of acetachlor (0.001 mg/L) in C8. Among the pesticides quantified chlorpyrifos delivered highest amount of residues in C8, C9, C10, C11 and C12. Residues of *o,p′*-DDT were found high in C1 to C6 than the permitted value (0.002 mg/L), while higher concentration of pyridaben was resulted in C1, C5, C6 and C14 than the allowed value (0.0001 mg/L). Residues of carbofuran, atrazine, α-endosulfan and dieldrin and β-Endosulfan were not detected in any of the water samples collected. Concentrations of rest of the pesticides residues detected in water samples were within the permissible limits.

Conclusion

From the data it is evident that the flood water has contaminated the drinking water sources especially in the severely flood hit KP areas like Charsadda. Therefore, proper measures should be taken to clean the drinking water from such contaminants. It is further suggested that preventive actions should be taken to avoid such occurrence in future.

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