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DETECTION OF ORGANOCHLORINE PESTICIDES IN WATER SAMPLES AND THEIR RISK ASSESSMENT TO THE RESIDENTS OF DISTRICT NOWSHERA KPK, PAKISTAN

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ABSTRACT

Organochlorine Pesticides (OCPs) are the preserving pollutant in water which attracts the attention of chemists worldwide for several years. In this study OCPs provide a detailed data regarding concentrations, bioaccumulation and risk assessment. For this aim, 32 samples were collected from District Nowshera from surface and ground water.

The most well analyzed pesticides in water samples detected were Heptachlor, Dieldrin,γ-BHC,4,4'-DDE, Chlorpyrifos, p,p'-DDD and o,p'-DDD. However, other pesticides such as o,p'-DDT, and 4,4'-DDT, were found in trace amount. However Dieldrin was found in 06 samples having concentration of 0.023 μg L^{-1}and0.029 μg L^{-1} in surface and ground water respectively.

To assess the possible adverse effects of organochlorine pesticides in surface and ground water samples in the Nowshera District, the health risk assessments of detected pesticides were also traced-out. It can be concluded that the water of Nowshera district may also have carcinogenic effects due to heptachlor and dieldrin. In most groundwater samples, the risk of cancer in children and adults through drinking water for heptachlor, aldrin and dieldrin was greater than the acceptable risk level recommended by the US Environmental Protection Agency for carcinogens (1×10^{-6}).

Keywords: Organochlorine Pesticides, Gas Chromatography- Electron Capture Detector, Solid Phase Extraction, Health Risk Assessment

INTRODUCTION

The uses of pesticides in most developing countries are turning into a genuine environmental pollution such as water and habitat contamination and ecosystem disruption. Generally, Pesticides cause adverse effects especially to the people contact with them in their daily lives. In developing countries, most farmers are illiterate and unaware about the safety use of pesticides. Thus unsafe application and contact with agrochemicals have negative health impacts on farmers, chemical applicators on commercial farms and on small-holder farms **[1]**.

Pesticides are the chemical substances intended to stop, terminate, or to reduce the special effect of a pests. Pest is basically an organism that is harmful to human beings and yields such as livestock. They have an inhibitory effect on basic biogeochemical processes due to varying degrees of exposure. Epidemiological studies have shown resistance to neurological diseases **[2]**, carcinogenic **[3]** geno-toxic **[4]** and reproductive effects on human health. Common pesticides include natural biological compounds, metals, fuel products and various non-naturally components such as organophosphates and chlorinated hydrocarbons **[5]**. Pesticides are used in modern agricultural technology and can be used for organisms which are harmful to human health **[6]**.

The presence of pesticides in the groundwater is highly toxic although the original components of pesticides and their other degradation byproducts are found in large number in groundwater since mid of 1900.About 2.5 billion kilograms pesticides are used every year worldwide **[7]** and sale figures show that the number is getting higher **[8]**.

In order to protect crops in Pakistan, different pesticides are used. In the past two decades, national pesticide the use of pesticides have increased by 11.6%, but on the other hand, there has been no significant progress in the production of large quantities of pesticides **[9]**. (Khan, 2010). Cotton is a major source of exports and play an important role on the economy of country and it has access to a large number of pesticides, accounting for more than 80% of Pakistan's total use **[10]**. The use of pesticides in cotton crop have tripled, representing the largest use of pesticides **[11]**. This study concentrated on measurement of organochlorine pesticides due to agricultural activities in District Nowshera, Khyber Pakhtunkhwa Pakistan, where organochlorine pesticides are applied for agricultural purposes.

MATERIALS AND METHOD

32 samples were collected from various parts of Nowshera district. 16 samples of surface water were collected from Zwanikhel, Bara banda, Rashakai, Khairabad, Shaidu, Mohibbanda and Azakhel and 16 samples of ground water were collected from industrial area Risalpur, Marble city, Amankot and Inzari. Qualitative and quantitative data were collected using various techniques including questionnaire, on-farm observations and interviews from water experts, agrochemical dealers and agricultural experts, laboratory analysis of water and sediments samples.

Water Sampling

The attention was focused on sampling from wells, hand pump or wells installed nearby heavily sprayed fields of cotton, rice and tobacco, in order to measure the pesticides contamination in drinking and surface water. All the water samples collected from tobacco and vegetable belt of district Nowshera, Khyber Pakhtunkhwa, Pakistan.

Standard and Reagents

Analytical standards of various selected pesticides (purity > 99%)were purchased from Supelco sigma Aldrich (Germany). 5 ppm standard stock solutions were prepared from solid standard (Supelco, USA) such as γ-BHC, Chlorpyrifos, o,p'-DDD,p,p'-DDD, o,p'-DDT, p,p'-DDT, Aldrin and Dieldrin. Than fresh working solutions of various concentrations 0.05, 0.1, 0.5, 1.0 and 1.5 ppb were prepared for the calibration curve.

Extraction of Pesticides from Water

The pesticides concentrations present in contaminated water samples are very low and well extraction method is needed to determine their contamination in water matrixes. For the extraction of pesticides from water samples, several methods are available. More recent method is solid phase extraction (SPE) and solid phase micro-extraction (SPME), which are preferred because it causes less pollution and also small amount of solvent is needed. SPE is used to isolate analytes of interest from aqueous matrix or extracts of solid matrices like soil, sludges, food samples etc. SPE is based on selective adsorption and desorption of components dissolved in a solvent (mobile phase) by solid (stationary phase) through which sample is passed **[12]**.

After sample collection, the water samples were filtered from Whattman filter paper (size 125mm) in order to remove large and undissolved substances from samples. The filtrates were again passed from 0.45µm micron filter paper (Sartolon Polyamid, Germany) using filtration assembly. Solid phase extraction (SPE) analyses through gas chromatography method were used for the identification of various pesticides in water samples. 100 ml of each sample was passed through the SPE cartridge (Supelclean ENVI-18 SPE cartridge). Then 3 ml methanol was passed through SPE cartridge to collect pesticides residues in clean vials. The aliquot was dried by the stream of nitrogen and re-dissolved in 1mL HPLC grade methanol for analysis by GC-ECD3 ml methanol and 5ml distill water were passed to clean the SPE cartridge for further samples treatment.

Effective Condition for GC-ECD

The Gas Chromatography with Electron Capture Detector (GC-ECD), Agilent technology, United State of America (USA), was conditioned before the water sample analysis to keep the injector, oven and detector at temperature 260˚C, 280˚C and 300˚C, respectively. Nitrogen (99.999% purity) gas was used at a flow rate of 1ml min^{-1}. 1.5µL of each treated sample was injected into the injector of the GC-ECD. The column used was HP-5 (5%-diphenyl-95%-dimethylpolysiloxane, 30 m x 0.25 mm-i.d and 0.25 µm) thickness. The running time of each sample was 25 minutes.

Health Risk Assessment Model

The procedure to guess the natural surroundings and possibility of opposing health effect in human beings who expose to chemicals in polluted environmental means, at present or in the future known as health risk assessment. People exposed to organochlorine pesticides through different ways, but oral contact way is reflected is most significant one **[13-14]**. In the present study, health risk assessment model derived from United State Environmental Protection Agency is assess to calculate the cancer causing and non-cancer causing danger for children and adults using the ground water as a source of drinking **[15]**.

Health risk Assessment through daily ingestion of OCPs

To calculate human exposure to contaminants chronic daily intake (CDI) is used **[16]**, and is calculated as.

CDI = (C × IR× EF × ED) / (BW × AT) (1)

C = chemical concentration in water (mg l^{-1}); IR = water ingestion rate (l day^{-1}) (for children: IR = 1.0; for adults: IR = 2.0); EF = the exposure frequency (350 days $year^{-1}$); ED = exposure duration year) (for children: ED = 6; for adults: ED = 70); BW = body weight (kg) (for children: BW = 14; for adults: BW = 60); AT = average lifespan (days) (for children: AT = 2190; for adults: AT = 25,550

Cancer Risk or Carcinogenic risk (R)

Carcinogenic risk (R) is calculated by the following formula **[17]**;

$$R = CDI \times SF \quad (2)$$

where CDI is the chronic daily intake from the oral exposure route (mg kg^{-1} per day), SF is the slope factor of the contaminant via oral exposure route [(mg kg^{-1} per $day)^{-1}$].

Hazard quotient (HQ) indices or non-cancerous risk

Hazard Quotient (HQ) is calculated by the following formula:

$$HQ = CDI / R_f D \quad (3)$$

Where, R_fD (mg/kg/day) = Reference Dose. The values of slope factor and reference dose for OCPs are obtained from the US EPA Integrated Risk Information System **[18]**.

RESULTS AND DISCUSSIONS

Surface and underground water samples were collected from various region of Nowshera district. Total of 32 samples were collected at a distance of about 3-5 kilometer. Organochlorine standard solutions of various concentrations of 0.05, 0.1, 0.5, 1.0 and 1.5 ppb, were prepared for calibration curves. An aliquot (1.5 μL) of each concentration was injected into the Gas chromatography (GC-ECD) and the responses recorded. A calibration curve was constructed by plotting the concentration against their respective peak areas and good linear correlation was found in the range (R^2: 0.9973- 0.9998). The presence of each pesticides found in water samples were confirmed by matching the retention time of the peak with the retention time of standards of chlorinated pesticides. **Figure 1** show the Chromatogram and peaks of various analyst of standard solution measured in the water samples.

The results of detected organochlorine pesticides in surface water and ground water samples are summarized in **Table 1**. 16 surface water samples were tested for 09

OCPs residues. Various water samples were found contaminated with different pesticides. The pesticides detected in the samples are Aldrin, 4,4'-DDT, o,p'- DDD, γ-BHC p,p'-DDD, chlorpyrifos, dieldrin o,p'-DDT, p,p'-DDT and heptachlor in most of the water samples.

In 16 surface water samples of district Nowshera (Table 2),03 samples found contaminated with γ-BHC, 06 samples with heptachlor, 04 samples with chlorpyrifos, 02 Samples with aldrin, 06 samples with dieldrin, 03 samples with o,p'-DDD, 02 samples with p,p'-DDD, 03 samples with o,p'-DDT and 03 samples with 4,4'-DDT with a maximum concentration of 0.025, 0.115, 0.2, 0.018, 0.023, 0.027, 0.029, 0.019 and 0.099 µg L^{-1} respectively.

However, in 16 ground water samples of district Nowshera, γ-BHC contamination found in 03 samples, heptachlor in 02 samples and chlorpyrifos in 03 samples, with a maximum concentration of 0.019, 0.11and 0.281 µg L^{-1} respectively. Similarly, aldrin contamination found in 02 samples, dieldrin in 05 samples, o,p'-DDD in 03 samples, p,p'-DDD in 2, o,p'-DDT and 4,4'-DDT in 01 samples with a maximum concentration of, 0.12, 0.029, 0.015, 0.012 , 0.01 and 0.008, µg L^{-1} respectively.

Health risk Assessment through daily ingestion of OCPs

The risk of cancer and non-carcinogenicity of pesticides detected for children and adults was estimated according to the Health risk assessment model (IRIS, 2010; USEPA, 2010). Two scenario were implemented, the first being the consideration of raw surface water consumption and the second is most realistic the ground water used for drinking.

The cancer risk assessment for selected OCPs such as γ-BHC, Heptachlor, Aldrin, p,p'-DDD, Dieldrin, and p,p'-DDT was estimated by taking the tested surface water samples **(Table 2)**. The risk for the rest of organochlorine pesticides was not calculated because no slope factors are available.

Non-Carcinogenic Risks or Hazard Quotient (HQ)

The Hazard Quotient for the most commonly detected six pesticides is given in **Table 2**. The Hazard Quotient was estimated to be less than 1, then it has no adverse health effect, and if the hazard quotient was higher than 1, then it has adverse health effect. Each Hazard Quotient

was lower than 1 and the highest value in surface water was 4.11×10^{-2}, which indicated that surface water was relatively safe. The Highest Hazard Quotient value has observed in surface water sample of

Amankot Nowshera for Aldrin in the case of risk assessment for children when considering the high concentration. The second highest Hazard Quotient value for children was also detected in Sample Bara banda District Nowshera which is 3.15 × 10^{-2} for dieldrin. However in ground water the maximum value detected was 27.4 × 10^{-2} for Aldrin. The highest HQ value was observed in ground water of Misribanda District Nowshera for Aldrin when considering a high concentration in case of children risk assessment.

These results indicate that pesticides in surface water in the Nowshera area pose a potential low risk to humans.

Carcinogenic Effect

In surface water Possible carcinogenic effect of Dieldrin, Aldrin, Heptachlor,4,4'-DDT, 4,4'-DDD, and γ-BHC have been reported. However, the concentration of the 06 OCPs in the surface water of Nowshera district had a varied range, the levels of the health risk caused by 06 organochlorine pesticides groups either for children or for adults through surface water have also increased. Summary statistics for the health risk for adults and children is shown in **Table 2**. The maximum carcinogenic risks for adults were 1.039 ×10^{-6} for γ-BHC, 16.541 × 10^{-6} for heptachlor, 9.781 × 10^{-6} for Aldrin, 11.763 × 10^{-6} for dieldrin, 1.076 × 10^{-6} for 4,4'-DDT and 4,4'-DDD has a lowest value 0.222 × 10^{-6}than the parametric value of 1.0 × 10^{-6} recommended by USEPA.

However, for children, maximum cancer risk from surface water were 2.226 ×10^{-6} for γ-BHC, 35.445 × 10^{-6} for heptachlor, 20.959× 10^{-6} for Aldrin, 25.206 × 10^{-6} for dieldrin, 2.306 × 10^{-6} for 4,4'-DDT and 0.477 × 10^{-6} for 4,4'-DDD which is lower than the parametric value of 1.0 × 10^{-6} recommended by USEPA.

While in ground water carcinogenic effect of Aldrin, 4,4'-DDT, Dieldrin, Heptachlor, 4,4'-DDD, and-BHC have been reported **(Table 3)**. For adults, the maximum cancer risks from ground water were 0.789 ×10^{-6} for γ-BHC, 15.822 × 10^{-6} for heptachlor, 65.206 × 10^{-6} for Aldrin, 14.831 × 10^{-6} for dieldrin and 0.092 × 10^{-6} for 4,4'-DDD, 9.20548 × 10^{-6} , and 0.0867 × 10^{-6} for 4,4'-DDT. The 03 OCPs such as γ-BHC, 4,4'- DDD, and 4,4'- DDT has the lowest parametric value of 1.0 × 10^{-6} recommended by USEPA. However, the maximum cancer risk for children from ground water were 1.692 × 10^{-6} for γ-BHC, 33.904 ×10^{-6} for heptachlor, 33.904 × 10^{-6} for Aldrin, 31.781 × 10^{-6} for dieldrin, 0.198 × 10^{-6} for 4,4'-DDD, 0.186 × 10^{-6} for 4,4'-DDT. The highest carcinogenic risk for adults from ground water is 65.206 × 10^{-6} for Aldrin and for children is 33.904 $\times 10^{-6}$ **(Table 3)**.

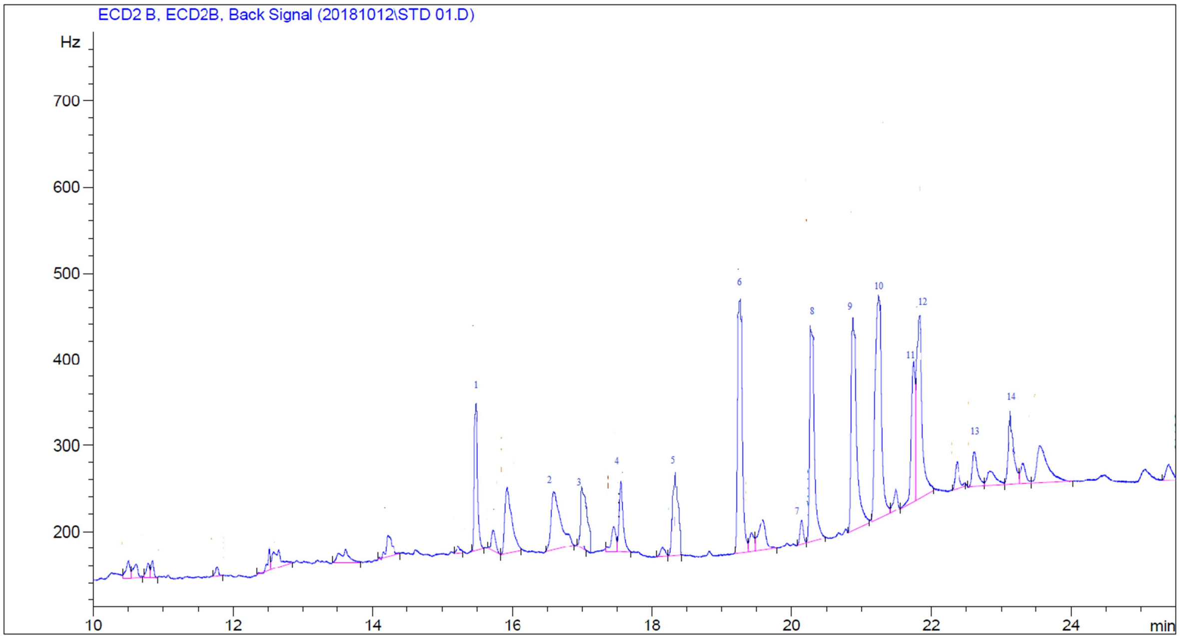

Figure 1: Chromatogram peaks identification of standard solution: (1) α-BHC; (2) β-BHC; (3) γ-BHC; (4) δ-BHC; (5) heptachlor; (6) aldrin; (7) heptachlor epoxide; (8) γ-chlordane ; (9) α-chlordane (10) endosulfan I;(11)4,4'-DDE; (12) dieldrin; (13) endrin; (14) endosulfan II

Table 1: Summary of selected pesticides contamination in surface and ground water samples of District Nowshera

Pesticide	SF/[(mg kg^{-1} per $day)^{-1}$]*	R_fD/(mg kg^{-1} per day)*	Cancer risk (10^{-6})		Hazard quotient (10^{-2})	
			(for children)	(for adults)	(for children)	(for adults)
γ-BHC	1.3	3.0E-4	2.226	1.039	0.571	0.266
Heptachlor	4.5	5.0E^{-4}	35.445	16.541	1.580	0.735
Aldrin	17	3.0E^{-5}	20.959	9.781	4.110	1.920
Dieldrin	16	5.0E^{-5}	25.206	11.763	3.150	1.470
4,4'-DDD	0.24	2.0E^{-3}	0.477	0.222	0.099	0.046
4,4'-DDT	0.34	5.0E^{-4}	2.306	1.076	1.360	0.633

Table 2: Health risks cause by OCPs for children and adults in the Nowshera district through surface water

No	Compound	Total samples tested		Contaminated samples		Range (µg L^{-1})	
		Surface water	Ground water	Surface water	Ground water	Surface water	Ground water
1	γ-BHC	16	16	03	03	Nd - 0.025	Nd - 0.019
2	Heptachlor	16	16	06	02	Nd - 0.115	Nd - 0.11
3	Chlorpyrifos	16	16	04	03	Nd - 0.2	Nd - 0.281
4	Aldrin	16	16	02	02	Nd - 0.018	Nd - 0.12
5	Dieldrin	16	16	06	05	Nd - 0.023	Nd - 0.029
6	o,p'-DDD	16	16	03	03	Nd - 0.027	Nd - 0.015
7	p,p'-DDD	16	16	02	02	Nd - 0.029	Nd - 0.012
8	o,p'-DDT	16	16	03	01	Nd - 0.019	Nd - 0.01
9	4,4'-DDT	16	16	03	01	Nd - 0.099	Nd - 0.008

Table 3: Health risks summary cause by OCPs for children and adults in Nowshera district through ground water

Pesticide	SF/[(mg kg^{-1} per day)$^{-1}$]*	R_fD/(mg kg^{-1} per day)*	Cancer Risk (10^{-6})		Hazard Quotient (10^{-2})	
			(for children)	(for adults)	(for children)	(for adults)
γ-BHC	1.3	3.0E-4	1.692	0.789	0.434	0.202
Heptachlor	4.5	5.0E^{-4}	33.904	15.822	1.51	0.703
Aldrin	17	3.0E^{-5}	33.904	65.206	27.4	12.8
Dieldrin	16	5.0E^{-5}	31.781	14.831	3.97	1.85
4,4'-DDD	0.24	2.0E^{-3}	0.198	0.092	0.0411	0.0192
4,4'-DDT	0.34	5.0E^{-4}	0.186	0.087	0.110	0.0511

CONCLUSIONS

This study assumed that organochlorine pesticides effect in District Nowshera is influenced by the driving forces which manifests in expansion of agricultural activities. These drivers trigger pressure in the form of water pollution in the selected areas, thus causes water pollution. The state of water degradation in these areas reduced living organisms in aquatic environment, increased concentration of chemicals from the surrounding to the first organism in the aquatic environment by the process known as bio-accumulation and ultimately destruction to the health of human beings.

To reduce severity of the effects, various mitigation measures should be undertaken. The study suggests the following measures: management and monitoring of the surface and ground water, education and encouragement of farmers for using safe equipment’s during spraying of pesticides, application of the right choice of pesticides to the crops, appropriate amount of fertilizers to the crops and refrain from use of prohibited pesticides like Heptachlor, Dieldrin, DDT and Aldrin. In Nowshera district the pesticides found in the surface water samples were γ- BHC, heptachlor, Chlorpyrifos, Aldrin, Dieldrin, o,p'- DDD, p,p'- DDD, o,p'- DDT, and p,p'- DDT with highest concentration of 0.025, 0.115, 0.2, 0.018, 0.023, 0.027, 0.029, 0.019 and 0.099, µg L^{-1} respectively. However the pesticides found in groundwater of district Nowshera were γ-BHC, Heptachlor, Chlorpyrifos, Aldrin, Dieldrin, o,p'- DDD, p,p'- DDD, with extreme concentrations of 0.019, 0.11, 0.281, 0.012, 0.029, 0.015, and 0.012, µg L^{-1} respectively. However, o,p'-DDT, and p,p'-DDT were found in few samples.

The concentrations of 09 OCPs were measured and their health risks assessment were calculated. Mostly cancer risk caused by Heptachlor, Dieldrin and Aldrin for adults and children through ground water was higher than the acceptable risks level (1×10^{-6}) suggested by United State

Environmental Protection Agency for carcinogens. This study investigated that the present concentrations of organochlorine pesticides in water have a serious carcinogenic risk to the local residents in most of the sites of district Nowshera, specially to children. It means that water in the selected areas is not suitable for drinking purpose. It is essential to stop fresh input of these OCPs in the water.

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