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Assessment of Pesticide Residues in Sediments Collected from River Ravi and its Tributaries between its stretches from Shahdara to Balloki Headworks, Pakistan

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Abstract:

Contaminated bed sediments of fresh water bodies have a potentiality of polluting and rendering the water unfit for aquatic life. Though Pakistan has banned on the use of Organochlorine and Nitrogen containing pesticides, but no proper attention is being paid on the continuous monitoring and assessment of these banned pesticides to make sure that these banned pesticides are not in practice. Levels of selected organochlorine and nitrogen containing pesticides residues were assessed in sediments collected from eighteen sampling sites of River Ravi and its tributaries by GC-ECD method. All sediments samples were found contaminated with varying concentrations of pesticides residues, however levels of pesticides were below the tolerance limits suggested in national and international standards. Endosulfan was the predominant organochlorine pesticide residue in all sediment samples, while Carbofuran was found in least amounts as compared with other pesticides. After Degh fall and After Hudiara nulla fall river sampling sites were found severely contaminated while, among tributaries Degh fall and Hudiara drain were found highly severely contaminated with DDT, DDE, Endosulfan and Carbofuran. Constant monitoring programs are needed to be initiated to reform the present situation.

Key words: Sediments, Organochlorine, Endosulfan, Carbofuran, GC-ECD

1. INTRODUCTION

Use of banned pesticides is still continued not only in Pakistan but also continued all over the world as a number of recent works support the presence of pesticides in biota especially in aquatic life such as in Ghana-Africa (Ntow, 2005); Vietnam (Hung and Thiemann, 2002); China (Hauzheng *et al*., 2007) and India (Kaur *et al.*, 2008). There are benefits of using pesticides, but they also have drawbacks of potential toxicity to many other non-target species including man, fish, and other aquatic fauna (Gilden *et al.*, 2010). From the areas of applications, these pesticides find their way to nearby aquatic bodies through leaching and cause contamination of surface as well as ground water (Mahboob *et al*., 2011). Soil acts as main reservoir for pesticides due to its potential to serve as filter, buffer, and storage for a large number of chemicals including pesticides. These properties of soil are exhibited with the help of its active carbon (Burauel and Bassmann, 2005). Contaminated soil acts as potential source for the contamination of water, flora and fauna (especially fish) and finally man due to its top position as consumer in majority of food chains, so man is severely affected (Abrahams, 2002). Srivastava and Vidyarthi (2002) found that in aquatic ecosystem, compounds such as pesticides with low water solubility and high lipo-solubility are forced to seek organic lipid containing material. Though pesticide residues are present in all food but fatty foods are more susceptible for pesticide residues such as meat, butter, and milk, etc (Mahboob *et al*., 2011).

2. MATERIALS AND METHODS

The stretch of River Ravi from Shahdara to Balloki Headworks is 72 Km long (Rauf *et al*., 2009). To find out the Dichlorodiphenyltrichloroethane (DDT), Dichlorodiphenyldichloroethylene (DDE), Endosulfan and Carbofuran sediment samples were taken for one year on fortnightly basis from ten sampling sites along right and left banks of River Ravi viz River site **(R):1**= Shahdara Bridge downstream, Right bank (R B), **R:2**= Shahdara bridge downstream, Left bank (L B), **R:3**= After Farrukhabad nulla fall (R B), **R:4**= After Bakar mandi Nulla (L B), **R:5**= Before Degh fall (R B), **R:6**= Before Hudiara drain (L B), **R:7**= After Degh fall (R B), **R:8**= After Hudiara drain (L B), **R:9**= Balloki Headworks upstream (R B), **R:10**= Balloki Headworks upstream (L B) and eight effluent discharging tributaries of River Ravi viz tributary **(T):1**= Toll tax Nulla, **T:2**= Farrukhabad Nulla, **T:3**= Munshi hospital nulla, **T:4**=Taj Company Nulla, **T:5**= Bakar Mandi Nulla, **T:6**= Qadir Abad Link Canal, **T:7**= Hudiara drain and **T:8** = Degh Fall, respectively.

All sampling sites were further divided into five sub sample sites within 100 m of each sampling site so that a systemic composite soil sample can be obtained. Soil samples were taken with the help of steel pipe of 2 inch diameter. Steel pipe was pressed with pressure through water column to obtain a soil layer of approximately one foot. Soil samples obtained from all five sub-sampling sites were mixed thoroughly to prepare a composite soil sample. Three composite soil samples were obtained from each sampling site. These composite soil samples (each 1 kg) were then packed in properly labeled plastic bags, and transported to Research Laboratory, Department Wildlife and Fisheries, Government College University, Faisalabad. In laboratory, composite soil samples were air dried, grinded to homogenized and sieved through a screen (mesh size 3mm) to remove large particles. The extraction, clean up and determination of DDT, DDE, Endosulfan, Endosulfan sulfate, Carbofuran and Cartap in sediment samples was done by following the method described by Nafees and Jan (2009). Gas Chromatograph with electron capture detector having nitrogen (N_2) at the flow rate of 30-32 ml/minute was used with variable temperature arrangements (Injector temperature (220ºC); Oven temperature 150ºC maintained for 4minutes, then raised to 290ºC at a rate of 8ºC/ minute, and then hold for 10 minutes; Detector temperature: 300ºC). Gas Chromatograph was turned on for the detection and quantification of pesticides and 1 µl aliquot of concentrated elute was injected. Residue peak(s) of elute (s) injected was identified on the basis of retention time. Height/area of residue peak(s) was measured, and residue amount of test solution was determined, by comparison to the Height/area obtained from a known amount of appropriate reference/standard solution in the chromatograms.

2.1 Statistical Analysis of Data:

Data on pesticide residue concentrations was analyzed by using "ANOVA" (Two factor completely randomized design) and DMR tests to find out statistical differences among various parameters (Steel *et al*., 1996).

3. Results

DDT contamination in river bed sediments showed significant differences among different sampling sites. Annual mean concentration of DDT fluctuated between the minimum of 0.221±0.0022 µg/g at Bakar Mandi Nulla fall (LB) and maximum of 0.257±0.0021 µg/g at After Degh fall (RB) river sampling sites, respectively. Mean DDE concentration in river soil samples was the minimum (0.187±0.0028 µg/g) at Bakar Mandi Nulla fall (LB), while maximum (0.215±0.0036 µg/g) was detected at After Degh fall (RB) river sampling sites, respectively. The soil samples collected from Shahdara bridge (LB) river sampling site had the mean minimum concentration of Endosulfan (0.287±0.0024 µg/g). The maximum Endosulfan concentration was detected as 0.314±0.0041 µg/g at After Degh fall (RB) river sampling site followed by a concentration of 0.304±0.005 µg/g at After Hudiara Nulla fall (LB) sampling sites, respectively. Carbofuran contamination in river soil samples showed significant variations at majority of sampling sites with the mean minimum concentration of 0.162±0.0028 µg/g which was recorded at Bakar Mandi Nulla fall (LB), while maximum concentration of 0.199±0.0055µg/g was observed at After Degh fall (RB) river sampling sites (Table 1). Fluctuations in toxicity levels of pesticides in river sediments are depicted in figure 1.

Among the tributaries, Toll tax nulla exhibited the minimum annual mean concentration of 0.235±0.0037 µg/g of DDT and Hudiara drain showed maximum annual mean concentration of 0.274±0.0044 µg/g of DDT respectively. Mean DDE concentration was minimum (0.204±0.0028 µg/g) and maximum (0.240±0.0066 µg/g) in samples collected from Toll tax Nulla site and Degh fall nulla sampling sites, respectively. Mean minimum concentration of Endosulfan (0.289±0.0040 µg/g) was detected in sediments' samples collected from Toll tax Nulla. Sediments' samples taken from Hudiara drain had the mean highest Endosulfan contamination level of 0.331±0.0068 µg/g followed by a concentration of 0.329±0.0073 µg/g detected in samples collected from Degh Fall. Mean minimum concentration of Carbofuran (0.149±0.0023 µg/g) in Toll tax Nulla, while its maximum concentration of 0.208±0.0080 µg/g was recorded in Degh Fall respectively (Table 2). Toxicity levels of pesticides in tributaries sediments are shown in figure 2.

4. Discussion

The present study revealed that pesticide toxicity level of River Ravi stretching from Shahdara to Head Balloki is due to the pesticide toxicity levels of its tributaries. These tributaries carry a huge burden of concentrated industrial, domestic and agricultural waste substances and pour them as such into main River water. However, Degh fall and Hudiara drain discharge maximum pesticide contaminated water into River Ravi. Unfortunately, before the fall of these tributaries into the River, no treatment for the removal or breakdown of pollutants is done (Ahmad, 1993; CEWRE, 1997; Farhan and Samia, 2000; Farhan, 2001, Rauf *et al*., 2009 and Tehseen *et al*., 1994). To understand

the fate and behavior of persistent agrochemicals, bed sediments of aquatic ecosystems should be routinely sampled and pesticide residues present in them (if any) should be determined to monitor the extent of aquatic contamination and accumulation characteristics of pesticides in aquatic flora and fauna (Farshid *et al*., 2012).

In the current research study, after Degh Fall (RB) and after Hudiara nulla fall (LB) river sampling sites were found severely contaminated by pesticides as endorsed from the soil samples of Hudiara drain and Degh fall respectively, which were found severely contaminated with DDT, DDE, Endosulfan and Carbofuran. It was also observed that a number of industrial effluents enter into Degh fall nulla from a number of textile mills, leather processing units, tanneries, chemical, oil, ghee, rayon and paper processing units. While Hudiara drain receives industrial untreated effluents, raw sewage and waste water from India and Pakistan and pours its contents into River Ravi. A number of studies in Pakistan (Bano and Siddique, 1991; Jabbar *et al*., 1993; Tehseen *et al*., 1994; Sanpera *et al*., 2002; Tariq *et al.,* 2006) have detected the agrochemicals especially organochlorine pesticides in soils/sediments sampled from different areas of Pakistan. These studies point out that main cause of high pesticide contamination level of soil/sediments collected from water reservoir bodies are agricultural runoff, industrial effluents, and seepages lagoons around these water reservoir bodies. From soil/sediments, pesticides slowly go on breakdown and ultimately released in to ground or surface water to contaminate it (Stephenson and Solomon, 1993). When fish is harvested in water that is exposed to varying amounts of industrial chemicals, pesticides and toxic elements, then these contaminants may accumulate in fish at level that can cause illness; concern for these contaminants primarily focuses on fish harvested from freshwater estuaries, near-shore costal water rather than from open sea. Pesticides used near aquaculture operations may also contaminate fish (Davis, 1961; Froese *et al*., 1998; Zaranko *et al*., 1997; Zia *et al*., 2009). It is hoped that findings of this study could be used as an early warning so that fish and top consumers especially the humans can be saved from the carcinogenic, teratogenic and mutagenic effects of Organochlorine and nitrogen containing pesticides. These findings may be helpful for higher authorities to take appropriate measures to reduce the entry of potent sources of these Organochlorine pesticides into River Ravi.

5. Conclusion:

Sediments of River Ravi have a potentiality of polluting and rendering the water unfit for aquatic life and wastewater discharge without treatment into main River should be banned and there must be an effluent treatment facility near to discharge points to control the ever increasing pollution load on the local environment. Awareness should be developed in people through the print and electronic media so that they may realize the harmful effects of pesticides and stop/reduce their use. Currently, a constant monitoring program needs to be initiated to reform the present situation.

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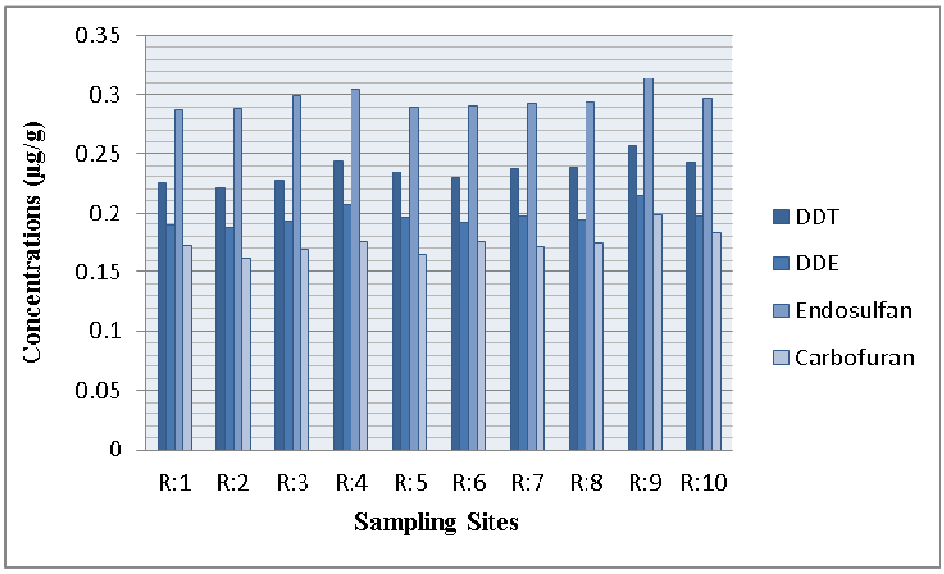

Figure 1: Pattern of Pesticide fluctuations in the River Ravi sediments during the study period

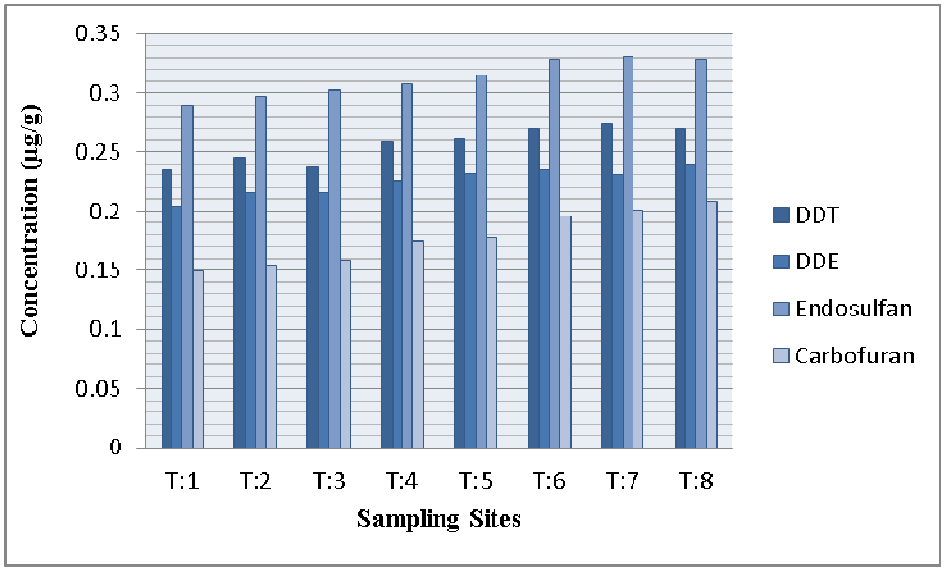

Figure 2: Pattern of Pesticide fluctuations in the tributaries sediments during the study period

Table 1: Analysis of Variance on Pesticide concentrations in the River Ravi sediments during the study period

S.O.V	D.F	F-Values			
		DDT	DDE	Endosulfan	Carbofuran
Month	11	119.71**	246.77**	327.85**	480.96**
Sampling Sites	9	340.11**	135.84**	113.35**	180.85**
Month x Site	99	7.36**	4.79**	6.05**	8.50**

** = Highly Significant (P<0.01)

Standard Error	DDT	DDE	Endosulfan	Carbofuran
Months	0.0006	0.0008	0.0009	0.0008
Sampling Sites	0.0006	0.0007	0.0008	0.0008
Months × Sites	0.002	0.0025	0.0027	0.0027

Comparison of Means

Sampling Stations	Means (µg/g) ± SE			
	DDT	DDE	Endosulfan	Carbofuran
Shahdara Bridge (LB)	0.225±0.0024 G	0.189±0.0022 F	0.287±0.0024 F	0.172±0.0049 D
Bakar Mandi Nulla fall (LB)	0.221±0.0022 H	0.187±0.0028 F	0.288±0.0033 F	0.162±0.0028 G
Before Hudiara Nulla fall(LB)	0.227±0.0009 F	0.192±0.0032 E	0.299±0.0039 C	0.169±0.0024 E
After Hudiara Nulla fall(LB)	0.244±0.0019 B	0.207±0.0036 B	0.304±0.0046 B	0.176±0.0035 C
Balloki Headworks (LB)	0.235±0.0014 D	0.197±0.0020 C	0.290±0.0033 E	0.165±0.0022 F
Shahdara Bridge(RB)	0.229±0.0025 E	0.191±0.0020 E	0.291±0.0028 E	0.176±0.0052 C
After Farrukhabad Nulla (RB)	0.238±0.0010 C	0.198±0.0021 C	0.293±0.0031 D	0.171±0.0041 DE
Before Degh fall (RB)	0.239±0.0009 C	0.194±0.0033 D	0.294±0.0027 D	0.175±0.0037 C
After Degh fall (RB)	0.257±0.0021 A	0.215±0.0036 A	0.314±0.0041 A	0.199±0.0055 A
Balloki Headworks (RB)	0.243±0.0015 B	0.198±0.0024 C	0.297±0.0030 C	0.183±0.0043 B

Means sharing similar letters in column are statistically non-significant (P>0.05).

Table 2: Analysis of Variance on Pesticide concentrations in Tributaries sediments during the study period

		F-Values			
S.O.V	**D.F**	**DDT**	**DDE**	**Endosulfan**	**Carbofuran**
Month	11	640.86**	640.86**	783.34**	302.20**
Sampling Sites	7	180.67**	180.67**	417.15**	665.49**
Month x Site	77	7.13**	7.13**	6.64**	16.89**

** = Highly Significant (P<0.01)

Standard Error	**DDT**	**DDE**	**Endosulfan**	**Carbofuran**
Months	0.0011	0.0011	0.001	0.0011
Sampling Sites	0.0009	0.0009	0.0008	0.0009
Months × Sites	0.0031	0.0031	0.0027	0.003

Comparison of Means

Means sharing similar letters in column are statistically non-significant (P>0.05).

	Means (µg/g) ± SE			
Tributaries	**DDT**	**DDE**	**Endosulfan**	**Carbofuran**
Toll tax Nulla	0.235±0.0037 G	0.204±0.0028 F	0.289±0.0040 G	0.149±0.0023 H
Farrukhabad Nulla	0.245±0.0014 E	0.216±0.0039 E	0.297±0.0042 F	0.153±0.0014 G
Munshi hospital Nulla	0.238±0.0044 F	0.216±0.0059 E	0.302±0.0054 E	0.159±0.0022 F
Taj Company Nulla	0.259±0.0037 D	0.225±0.0068 D	0.307±0.0046 D	0.175±0.0034 E
Bakar Mandi Nulla	0.261±0.0031 C	0.232±0.0061 C	0.315±0.0052 C	0.178±0.0032 D
Qadir Abad Link Canal	0.270±0.0046 B	0.235±0.0060 B	0.329±0.0059 AB	0.196±0.0041 C
Hudiara drain	0.274±0.0044 A	0.231±0.0067 C	0.331±0.0068 A	0.201±0.0064 B
Degh Fall	0.269±0.0031 B	0.240±0.0066 A	0.329±0.0073 B	0.208±0.0080 A