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Bioaccumulation and Ecological risks of Organochlorine Pesticides in Water Sediments and Fish from Mahi river, Vadodara, Gujarat, India

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Abstract

Environmental pollutions by pesticides of inland water have been a worldwide issue, since most of these compounds are very persistent, bio-accumulative and poisonous. Pesticides could allot to the components of the environment, such as water, sediment, and accumulate in the biota. The side effects of pesticides could be serious and chronic. In this study, we have investigated the levels of selected pesticides such as DDT (dichlorodiphenyltrichloroethane), HCH (hexachlorocyclohexane) and Endosulphan in surface waters, sediment and fish samples by gas chromatography of the Mahi river of Vadodara, India which was passed out in several periods from 8 pre-determined positions. Organochlorine pesticide (OCPs) concentration level in sediment is pointedly different from that of water and fish tissue, which had the maximum residual concentration. Detected pesticide residues are generally higher than specific limit of 0.01 µg/l by USEPA for pesticides of aquatic life-cycle; therefore, possess an ecological risk to the ecosystem and consequently human health.

Keywords: Organochlorine pesticides, gas chromatography, river water, sediments and fish.

Introduction

The study of environmental pollutants and their metabolites in other compartments of the environment have been recently used to determine the risk posed by this kind of contaminants to ecosystem[1]. Pesticides residues are widely distributed in river, lakes and estuaries. So, it is significant to identify the residual contamination, distribution, and possible ecological risk of pesticides in water, sediments and bio-aquatic system[2]. In this study, the investigation of accumulation and circulation of organochlorine pesticides (OCPs) contamination level in Mahi River, Gujarat, India. Persistent pesticides are widely used as insecticides on vegetable crops around the agriculture area of the river. Distribution of pesticides is carried out in fish may pose a risk to these organisms and then to their consumers including humans[3]. The residues of DDT and HCH have been detected in man and his environment the world over.

However, by assessment maximum concentration point of these residues have been described in human blood, fat, and milk samples in India[4]. Investigation of bottled water and other soft drinks passed out by the Centre for Science and Environment, New Delhi exposed very high substance of pesticideresidues[5]. Various types of skin problems as well as pigmentation on the exposed parts have been described in workers handling pesticides[6]. This study therefore is targeted at identifying the pollution level of the water ecosystem of Mahi River and to assess the potential risk for the people. The present study investigated the accumulation and supply of organochlorine pesticide residues contamination in different samples such as water, sediments and fish collected at eight different sites (figure-1).

Material and Methods

River's water, sediment and fish were collect between January 2012 and January 2013 from the Mahi River, Vadodara Gujarat, India (figure-1). The Mahi river is situated in western India, it rises in the western vindhyarange, just south of Sardarpur, and it flows northward through Madhya Pradeshstate. Mahi river enters Rajasthan state and then turns southwest to flow through Gujarat state through the north of Vadodara city outskirts and then enters the Arabian Sea by a wide estuary past Khambhat after about a 580 km course. It is popularly described as Mahisagar due to the vastness of the river.

Sample collection: All the chemicals and reagents are purchased from SD Fine-Chem Limited (SDFCL) and all the solvents are HPLC grade. The water samples were collected in high purity (1 liter) brown glass bottles from 8 different location of Mahi River, Gujarat region for a period of 1 year and refrigerated at 4˚C until analysis. The study was done in 8 locations of Mahi river namely Fajalpur, Vasad, municipal corporation, Khandi, Kherda, aproximetly 2 km away from Kherda, Rajupura and Jalampura (1,2,3,4,5,6,7 and 8). A total 140 samples analyzed, in which 60,60 and 20 samples are of river water, sediments and fish samples respectively (table-1).

For sediment sample collection, the samples were collected in polyethylene air tied bag, approximately 250 g, were transported to the laboratory and pebbles were removed and then sediment samples were air-dried at room temperature. Air –dried samples were then grounded with pestle-mortar and sieved. Fish samples were caught by fisher man, approximately 500 gm, from different sites at the same time as water and sediment sampling.

The soft parts of fish samples were removed and then a muscle tissue sample was taken from the dorsal muscle and kept in ice box. Mahi river regions samples were collected from agriculture, industrial and residential area. Variation of pesticide in surface water, sediment and fish sample affording to timing of pesticide applications related to sampling intervals have been observed.

Table-1
Sample collection and season variations in Mahi River Vadodara, Gujarat

Season	Water	Sediment	Fish
Winter	20	20	-
Summer	20	20	-
Monsoon	20	20	20
Total samples	60	60	20

Sample preparation: Extraction of OCPs from water sample 10 g of sodium chloride was taken in a separating funnel and dissolved sodium chloride in 1000 ml of water sample. Shaken the separating funnel for 1-2 min and separating funnel is allowed to stand for few minutes. Added 60 ml of dichloromethane (DCM) in separating funnel and again shaken and kept on stand. The organic layer was then separated and passed through anhydrous sodium sulphate bed and collected the organic layer in a round bottom flask (RB). The whole process was repeated by extracting twice with 30 ml DCM and passed the whole extract through sodium sulphatebed. The extract was evaporated near to dryness with the help of rotary evaporator.

The eluate was evaporated to dryness and dissolved in acetone-hexane (1:9) for GC analysis[7]. Determination and distribution of the pesticides residues in sediment sample, performed using the method of AOAC (1976)[8]. In a conical flask taken, 10 g of sediment sample was mixed with 7 ml of 0.2M NH_4Cl and added 100 ml hexane: acetone (1:1) and overnight shaken for 12 h.

Figure-1
Showing Sample collection site of water, sediments and fish sample from Mahi River Gujarat, India

The eluate was carefully decanted through activated florisil column. Sediment was washed twice with 25 ml hexane: acetone (1:1), and eluted with 200 ml of water. Aqueous layer was extracted again with 50 ml hexane and hexane layer was washed with 100 ml of water. Evaporated until dry with vacuum rotary evaporator. The eluate was passed through a chromatographic column, containing 2 g florisil (lower) and 1 g sodium sulphate (upper) which is pre wetted through hexane: acetone (1:1). Pesticides were eluted with 25 ml hexane: acetone (1:1) and all evaporation was performed using a rotary evaporator and finally made 5 ml volume with solvent, which is used for gas chromatographic analysis, For extraction of fish sample a 10 g sample of cut tissue from the muscle was grounded with activated sodium sulfate until a homogeneous mixture was obtained. The mixture was transferred in to conical flask and added 100 ml of solvent (n-hexane: dichlorometane 1:1) and was overnight shaken for 12 h on reciprocal or wrist action shaker[9]. Extract of OCPs residues in sediment, water and fish were analysed by gas chromatograph Shimadzu 2010. The condition and parameter are given below in Table-2.

Table-2
Analytical procedure for detection of organochlorine pesticides residues by gas chromatography

Detector	FID
Colum	silica capillary
Carrier gas	Nitrogen
Injector temperature	270 °C
Column flow	0.7 ml/ min
Detector temperature	300°C
Injected volume	1 µl
Limit of detection (LOD)	0.001 µg/l

Results and Discussion

The concentration level of hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) residues in water, sediments and fish samples from Mahi river Gujarat and assessments with other studies are shown in (tables- 3, 4 and 5) respectively. HCH and DDT residues were noticeable in all three types of samples at eight sampling sites (table-1). The comparison of the residues of ∑HCH and ∑DDT between different sampling sites is shown in table-6. This study results were and compared mostly with Indian rivers like Gomtiriver (Uttar Pradesh), Kaveri river (Tamilnadu), Ganga river (Uttar Pradesh), Hugli river (Kolkata), Kuano River (Uttar Pradesh) and Yamuna river (Haryana-Delhi). We have also compared with rivers of other countries, like Tonghui River (china), Kucukmenderes River (Turkey) and Ebro River (Spain). In water, sediment and fish samples collected from the Mahi River, concentration level of ∑HCH ranged from BDL-4042.95 µg/l, (table-3) BDL –to 1450.10 µg/l (table-4) and BDL- 962.89 µg/l (table-5), respectively. ∑HCH in water (0.22-28.58 µg/l) and sediments (0.001- 0.026 ng/g) showed lower concentration in Ebro River[10]. Sabarmati River also showed lower level of ∑HCH in water sample, ranged from BDL- 232.59 µg/l[11]. The concentration level of ∑HCH in Kaveri River ranged from 4.35 to 158.4 ng/g[12], which is lower than the concentration detected in our research. The total concentration of HCH residues in the Kuano river ranged from 0.0008 to 0.020 µg/l[13], and in the Yamuna river ranged from 0.0127 to 0.593 µg/l[14]. In Tonghui river the concentration level of ∑HCH in water and sediments ranged from 70.12 to 992.6 µg/l and 0.06-0.38 respectively[15], this levels are also lower concentration than found in our study. In Kucuk Menderes River, Turkey, the highest contamination of HCH found in water was 187 to 337 µg/l which is lower than our study[16].In this study HCH has the predominant residue concentration in the Mahi River. HCH referred to as benzene hexachloride BHC is a combination of different isomers generally α, β and γ-HCH .These compounds have been used as insecticide and is the most hazardous. β- HCH is the generally symmetric and stable isomer; it is also persistent in nature. β- HCH is excluded five times more slowly from the body than other isomer and has higher capability to accumulate in the fat tissue than lindane[17,18]. HCH is the mostly used and widely distributed in fresh water systems, which eventually pass onto human through consumption of drinking water and fish[19].

Table-3
Concentration level of organohlorine pesticides residues in water sample of Mahi River:

Sites	Mean ± SD					
	Summer		Winter		Monsoon	
	HCH	DDT	HCH	DDT	HCH	DDT
S 1	940.47±64.50	223.28±69.84	4042.95±1464.93	4352.63±0	838.07±78.98	274.39±9.40
S2	1133.93±132.60	221.77±39.49	135.59±12.76	0±0	915.92±26.03	160.79±9.80
S3	754.16±94.64	210.26±46.30	7.88±1.50	0±0	673.15±43.55	235.30±48.78
S4	1077.09±169.17	203.44±39.60	7.81±4.73	0±0	723.99±54.64	180.67±5.12
S5	693.84±19.03	135.00±41.74	156.85±9.61	0±0	569.66±103.54	238.55±53.45
S6	369.25±49.97	153.09±35.63	58.62±2.73	0±0	812.08±43.53	148.67±27.43
S7	788.95±39.74	270.69±20.89	153.32±10.63	0±0	578.80±31.44	260.24±39.98
S8	710.30±64.22	228.21±35.81	261.63±56.53	0±0	465.36±43.02	177.81±11.66

Table-4
Concentration levels of organochlorine pesticides in sediment sample of Mahi River

Sites	Mean± SD					
	Summer		Winter		Monsoon	
	HCH	DDT	HCH	DDT	HCH	DDT
S1	154.48±29.04	48.96±8.43	1085.57±283.94	822.72±57.75	134.56±12.51	20.26±1.01
S2	858.41±43.33	146.63±10.92	1316.79±158.65	367.52±154.62	879.88±8.02	14.37±1.86
S3	1146.96±8.22	164.03±13.20	1450.10±104.48	0±0	137.42±9.18	0±0
S4	133.08±9.10	352.46±43.51	1198.30±64.04	161.93±18.51	661.63±111.98	4.46±4.02
S5	449.09±27.61	14.79±3.54	861.10±47.36	382.51±59.56	782.01±15.62	159.14±13.11
S6	128.93±8.30	160.03±14.28	326.19±17.62	0±0	248.46±7.14	167.53±20.26
S7	683.92±28.56	0±0	660.32±23.25	47.40±2.38	16.21±3.87	281.52±34.44
S8	146.70±11.46	702.45±12.67	214.19±25.94	134.27±13.34	250.44±6.69	64.29±20.40

Table-5
Concentration levels of organochlorine pesticides residues in fish sample of Mahi River

Sites	Mean± SD	
	Monsoon	
	HCH	DDT
S 1	597.50±53.20	850.30±21.45
S2	962.89±14.90	655.01±14.97
S3	424.68±44.83	267.70±65.64
S4	221.23±18.87	159.65±12.47
S5	160.30±11.23	351.69±32.27
S6	865.86±17.23	115.38±7.61
S7	333.19±48.38	24.48±3.09
S8	47.27±1.38	659.41±18.04

Table-6
Calculations of HCH and DDT substances in the water and sediments sample from Mahi River with those from other region worldwide

Location sites	∑HCH		∑DDT		References
	Water	Sediments	Water	Sediments	
Mahi River, India (2012-2013)	ND-4042.95 µg/l	ND-1450.10 µg/l	ND- 4352.63 µg/l	-	Present study
Sabarmati River India, (2011-2013)	ND-232.59	ND-1494.62	ND-146.03	ND-34.71	[10]
Gomti River India, (1996-1999)	0.02-4846.0	0.1-1650.0	ND-4578.0	ND-509.0	[11]
Tonghui River, China (2002)	70.12-992.6	0.06-0.38	18.79-663.3	0.11-3.78	[12]
Kucuk Menderes River, Turkey (2000-2002)	187-337	ND	ND-120	ND	[13]
Ebro River, Spain (1995-1996)	0.22-28.58	0.001-0.026	1.97-6.77	0.85-9.03	[14]

The concentration level of ∑DDT was detected, ranged from BDL to 4352.63 µg/l, BDL- 4352.63 µg/l and BDL-850.30 ng/g in water, sediment and fish samples of Mahi River respectively. When we compare the concentration of ∑DDT residues contamination in different river, like Sabarmati River the concentration level of ∑DDT residues in water and sediment ranged from BDL-146.03 µg/land BDL-34.71ng/g respectively[10]. In our study a high level of concentration of ∑DDT residues was found compared to other sites. Table-6 showed the comparisons of concentration level of HCH and DDT substances in the water and sediments samples from different rivers. DDT is very toxic substance for human and aquatic system, so government has banned this substance. DDT is sprinkled in the public health sector for malaria vector control. The World Health and Food and Agriculture Organizations have established standards for residue limits in food, consumption water supplies, as well as distribute products such as fish, fruits and horticultural produce [20].

Conclusion

The present study showed that high concentration of HCH pesticide is detect in water, sediment and fish samples of Mahi River, Vadodara. DDT pesticide is present in some of the above samples but in less concentration. These levels indicate that Mahi River takes intermittent inputs of organochlorine pesticides which are the main issue to the pesticide contamination of Mahi River. The levels found in water, sediment and fish also support the fact that the concentration of OCPs will be more in river water, since most of pesticides have more solubility in water and will be washed away from sediments. Assessment of the river water, sediment and fish contamination in this study reflects that sediment and fish are polluted with OCPs and toxic effect may occur to biota and also humans will suffer those who are consuming fish from Mahi River. In this study HCB was the predominant residue in the total sample. So this proposes that further studies should focus on the potential bioaccumulation of organochlorine pesticides in aquatic system and hazards connected with their consumption.

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