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Organo Chlorine Pesticides in the Sediment of River Yamuna, Agra, India

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Abstract: *High concentration of pesticides was found in the sediment of river Yamuna. This can be attributed to the excessive use of pesticide in agriculture and health purpose. The distribution of various organochlorine pesticides in the sediments from 12 sampling sites reveals a wide range of fluctuation. Results indicated that although these pesticides are banned in India but still used by farmers due to their cheap costs.*

The distribution of pesticide is not found uniform and they did not follow a single pattern. It may be due to the physico-chemical properties of pesticide as well as the sediment properties. Further, hydrophobicity and persistence of these pesticides increases the accumulation in sediments. The main sources of pesticides in sediments are agricultural runoff, aquaculture activities and atmospheric deposition. The isomeric composition of HCH reveals a heterogenic nature of distribution in the sediments. This may be relative to isomerization of HCHs during the processes of transport and transformation in an aquatic system. The T-HCH ranges from 274 to 405 µg/Kg in the sediment of river Yamuna, Agra, in which α-HCH was 188±56 µg/Kg in the upstream cis Yamuna and 150±2 µg/Kg in the cis Yamuna downstream, while γ-HCH was 84±13 µg/kg in the upstream and 101±19 µg/Kg downstream of cis Yamuna. But the concentration of α-HCH was 173±5 µgm/kg at upstream and 165±34µgm/kg at downstream, whereas γ-HCH was 92±20µgm/kg in upstream and 93 ±12 µgm/kg at downstream trans Yamuna sediment at Agra. γ-HCH and α-HCH were found higher in concentration at many places and has a good relation with a composition of technical grade HCH, which contains 70% α-HCH and 14 % γ-HCH, rest is β and δ isomers. Further, (isomers of α, β and δ are observed to contribute about 33-74%, 28.5% and 26-50% respectively, to the total HCHs. A-HCH has higher values of Hennery Law constant and vapour pressure than β and γ-HCH, indicating greater efficiency by atmospheric transport of α-isomer than other isomers). These factors may account for the α-isomer existing in all samples.

1. Introduction

The major sources of contamination of natural waters with pesticides include direct application of the insecticides runoff from agricultural fields, discharges of waste water from fecal and urban drains, disposal of containers and equipment washing etc. The pesticides applied may find their way to water resources through runoff sedimentary transport or leaching into ground water during rainfall irrigation. According to World Bank, current estimates for population growth indicates that the human population of the region will double in the next 20-40 years, while global demand for dwindling water resources will continue to rise at almost twice that rate. In India, overall, water demand will increase from 552 BCM to 1050 BCM by 2025, which will require the use of all available water resources in the country. Of the present water usages, 92.94% is devoted to agriculture; already six of India's twenty major river basins fall below the water scarcity threshold of 1000 cubic meters per year with five more basins to added to the list within the next three decades. The rapid increase in agro-chemical use in the past five decades has contributed significantly to the pollution of both surface and ground water resources. The factors, which influence the persistence of pesticide in water, are solubility, bottom mud, organic matter, temperature and pH. Chlorinated pesticides are known to drift over thousands of kilometers and even they are found in the water melted from Antarctic snow. Since most of the rivers empty in sea, the cumulative effects of contaminants in seawater are high. It was estimated that about 25% of pesticides used on land ultimately drift in seawater.

2. Pesticide Residues in Sediments

It was observed that pesticide often become absorbed into organic matter present in mud and sediment. Sediments conserve important environmental information (Van Gunter, et.al., 1997) and are increasingly recognized as both a carrier and a possible source of contamination in aquatic system. Pollutants are transferred between the sediment and overlying water which are in a state flow of dynamic balance effected by the tidal flow, the bed sediment and suspended sediment in water is continuously falling to the river bed to become part of the bed load while the bed erodes and become suspended sediment simultaneously. In this processes the suspended sediment may absorb the pollutants in water and deposit them on the bottom and the bed sediment may release the pollutant from the bottom during resuspention by the tide and waves (Liu, C et.al, 2003). There is also an interchange of pesticide between the sediment and the water depending on equilibrium conditions. Pesticides do not remain their site but after entering aquatic environment, affecting abundance and diversity of non-target species producing complex affects on the altering tropic interactions (Rand et.al, 1995). Further, many pesticide eventually end up in groundwater and transformation products may remain for years (Belfroid, et.al., 1998). The eventual fate of pesticide in sediment depends upon differences in chemical and physical properties of insecticides, chemical and physical properties of water and sediment, climate and biology. The pesticides are organic hydrophobic pollutants, which tend to stay in the sediment.

A total of Pesticide were registered for use in India (Anon, 2002). During 1999-2000, India used about 46,195 MT of technical grade pesticides to cover 182.5 million hectares of cultivated area. India accounts for one third of pesticide poisoning annually.. Present status of chlorinated hydrocarbons pesticide and their derivatives in India are shown in table 2. It is estimated that about 25,000 MT of chlorinated pesticides were used annually in India and DDT accounted for 40% of this group. HCH and DDT account for 2/3rds of the total consumption of pesticides in the country. DDT is mainly used to control the vectors of Kala-Azar and malaria. Inevitably, traces of DDT reach the river. To control the vector the vector of Kala-Azar , i.e., the sand fly 2191.582 metric tones of DDT was sprayed only in the year 2001-02 (www.cseindia.org). State wise consumption of different class of pesticides as a product with medicinal qualities that curve the ailments of their crops, and because of this misconception, farmers in Southeast Asia, 31% viewed all insects as pests and 80%applied pesticides when discovered any type of pest.

In Agra region rabi and kharif are the major crops, and a total of 2, 34190 kg (Table-1) pesticides is used only for agricultural. Besides it approximately 2000kg is used for health purposes. Additionally, although many of the farmers introduced pest resistant seeds strains in to their fields, their spraying levels continued to remain constant (Science News, 1994).

3. Result And Discussion

Lindane belongs to the organochlorine (OCI) pesticide class. It is discovered independently by imperial chemical industries in Britain and in France in 1942. This is one of the oldest classes of pesticides, and only few OCLs are still in use today. There are three major subclasses of OCL psticides: diphenyl aliphatics, cyclodienes, and hexachlorocyclohexanes (HCHs). The well –known pesticide DDT belongs to the first class. The HCH subclass is not so much a class as the collection of the five isomers of HCH: alpha (α), beta (β), gamma (γ),delta (δ), and epsilon (ε). Only the gamma isomer has strong insecticidal properties [Angerer et. al., 1983]. This is the isomer named lindane. It is a strong contact and stomach poison and exhibits fumigant properties also. It doesn't cause much "tainting". It also called gammexane, benzenehexachloride (BHC). The use of lindane is restricted by the corresponding environmental protection agencies of many countries; it can be applied only by certified pesticide applicators. Lindane production involves the purification of technical grade HCH (16%α-HCH, 7%β-HCH, 45% γ-HCH) to a 99.8% pure product. The α-HCH and β-HCH, isomers (which have a half-life of seven to eight years) are metabolized, but γ-HCH is metabolized much faster than (its half-life is less than one day); therefore, most metabolites recovered in urine originate from the gamma isomer (i.e., lindane). The most common human metabolites observed are 2, 3, 5-trichlorophenol, 2, 4, 6-trichlorophenol, and 2, 4-dichlorophenol [Anereret.et.al., 1983] .

Lindane has been used to control a wide variety of insect pests in agriculture, public health, and medicinal applications. It is available as a suspension, emulsifiable concentrate, fumigant, seed treatment, wettable and dustable powder, and ultra-low-volume (ULV) liquid. The chemical identity of lindane and HCH isomers is shown in fig.1 summarizing their physical and chemical properties.

3.1. HCH and their Isomers

The HCH levels of HCH isomers in sediment are shown in Table 3. The isomeric composition of HCH reveals a heterogenic nature of distribution in the sediments. This may be relative to isomerization of HCHs during the processes of transport and transformation in an aquatic system. The T-HCH ranges from 274 to 405 µg/Kg in the sediment of river Yamuna, Agra, in which α-HCH was 188±56 µg/Kg in the upstream cis Yamuna and 150±2 µg/Kg in the cis Yamuna downstream, while γ-HCH was 84±13 µg/kg in the upstream and 101±19 µg/Kg downstream of cis Yamuna. But the concentration of α-HCH was 173±5 µgm/kg at upstream and 165±34µgm/kg at downstream, whereas γ-HCH was 92±20µgm/kg in upstream and 93 ±12 µgm/kg at downstream trans Yamuna sediment at Agra. γ-HCH and α-HCH were found higher in concentration at many places and has a good relation with a composition of technical grade HCH, which contains 70% α-HCH and 14 % γ-HCH, rest is β and δ isomers. Further, (isomers of α, β and δ are observed to contribute about 33-74%, 28.5% and 26-50% respectively, to the total HCHs. A-HCH has higher values of Hennery Law constant and vapour pressure than β and γ-HCH, indicating greater efficiency by atmospheric transport of α-isomer than other isomer (Iwata, et. al. 1994). These factors may account for the α-isomer existing in all samples.

These findings are contrast to Rajendran, et al. 2005. They found higher concentration of β and δ-HCH than α and γ-HCH. According to them, isomerization of α to β-HCH and its persistence with respect to microbial degradation, low solubility and volatility are the main reasons for higher concentration of β and δ-HCH. But these findings resemble to Pandit et al 2001 and Zhau et al 2001. Therefore, these findings in present study suggesting fresh input of HCH in these sediments. The ratios of α-HCH/γ-HCH were well below > 4 at all samples than those in the technical mixtures (4-7) (Table 4.14), implies the use of lindane in this region.

HCH causes neurochemical alteration in the brain, behavioral alteration in adult animals, and in the offspring of animal exposed to HCH. Decreased no. of red and white blood cells and haemoglobin has been reported in rats following repeated administration of HCH or technical grade HCH. Most HCH isomers were shown to increase cytochrome P-450 contents and the associated enzymes in rodents and also produce liver necrosis and degeneration with higher doses and HCH produced immuno suppression in mammals. β-HCH induced liver tumours in mice, and technical grade HCH induced liver tumours in mice; inconclusive results have been obtained with an HCH, and negative results were obtained in HCH. In genotoxicity assays, HCH isomers exhibited no genotoxic activity or weak activity at best. Adverse reproductive effects have been observed in male and female laboratory animals orally exposed to γ-, β-, or technical grade HCH (www.atser.cdc.gov/toxprofiles/tp43-cl.pdf)

Table1. *Total Consumption of Pesticides in Agra district during 2003-04*

Category	Crop	Agricultural Unit (Kg or Liter)	Cooperative Unit (Kg or Liter)	Private Unit (Kg or Liter)	Total (Kg or Liter)
Insecticide/dust &granules	Kharif	4861	-	26000	30861
	Rabi	3609	-	47015	50624
Insecticide Liquid	Kharif	370	-	6350	6720
	Rabi	927	-	46036	46923
Fungicides	Kharif	456		4190	4646
	Rabi	3812	-	65290	69102
Weedicides	Kharif	245	-	4773	5018
	Rabi	1433	-	17795	19228
Rodenticides & fumigant	Kharif	10	-	60	70
	Rabi	11	-	947	958
				Total	234190

Table2. *State wise Consumption of pesticide in India*

States	94-95	95-96	96-97	97-98	98-99	99-01	01-02	02-03
A.P	9343	10957	8702	7298	4741	4054	3850	3706
Assam	432	316	300	284	284	260	237	181
Arunachal Pradesh	19	22	20	18	18	17	17	15
Bihar	1462	1383	1039	1150	834	832	890	1010
Gujrat	4985	4560	4545	4642	4803	3646	4100	4500
Goa	10	4	2	2	4	4	5	5
Haryana	5100	5100	5040	5045	5035	5025	5020	5012
H.P	280	300	300	200	276	385	311	380
J&K	50	108	63	78	75	26	4	98
Karnataka	3640	3924	3665	2962	2600	2484	2500	2700
Kerala	1384	1280	1141	602	1161	1069	1345	902
M.P	2771	1748	1159	1641	1643	1528	714	1026
Maharashtra	3647	5097	4567	3649	3468	3614	3135	3724
Manipur	25	41	31	20	31	21	14	9
Meghalaya	17	20	20	8	9	8	6	6
Mizorum	21	21	18	17	16	19	26	15
Nagaland	11	9	9	9	9	10	7	7
Orissa	1580	1293	885	924	942	998	1018	1134
Punjab	7300	7200	7300	7150	6760	6972	7200	7200
Rajasthan	3308	3210	3075	3211	3465	2547	4628	3200
Sikkim	20	26	16	16	15	0.16	2	3
Tamil Nadu	3394	2080	1815	1809	1730	1685	1576	3346
Tripura	12	25	22	19	16	17	16	88
U.P	7970	8	7859	7444	7419	7459	6951	6775
West Bengal	4370	4213	4291	3882	3678	3370	3180	3000
Andaman &Nicobar	10	7	9	4	5	5	4	4
Chandigarh	1	3	3	3	3	4	1	1
Delhi	58	76	61	65	64	62	58	60
Dadar &Nagar Haveli	5	7	4	4	4	2	4	5
Daman & Diu	1	1	1	1	1	1	2	1
Pondicherry	130	118	115	81	71	70	58	57

Table3. *Mean concentration of HCH and its isomers (in µg/kg) in the sediment of river Yamuna*

S.S	α-HCH	β-HCH	γ-HCH	δ-HCH	Total
Cis Yamuna (Upstream)					
AG1	135	37	81	19	274
AG2	181	38	99	12	331
AG3	248	48	73	35	405
Average	188±56	41±6	84±13	22±11	337±65
Downstream					
AG4	152	50	83	11	298
AG5	149	51	99	9	310
AG6	150	38	120	15	323
Average	150±2	47±8	101±19	11±3	310±12
Trans Yamuna (Upstream)					
AG7	168	44	80	14	307
AG8	175	39	116	19	350
AG9	177	50	82	14	323
Average	173±5	44±6	92±20	15±3	327±21
(Downstream)					
AG10	143	44	79	14	280
AG11	205	44	101	13	364
AG12	149	34	99	15	298
Average	165±34	40±6	93±12	14±1	314±43
Overall Average	176±31	44±5	94±15	18±7	328±37

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