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Accumulation and distribution of persistent organochlorine pesticides and their contamination of surface water and sediments of the Sabarmati River, India

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Original Article

Abstract

Pesticides are chemical substances used to control pests in an effort to increase crop production and quality, and food storage. The levels of pesticides in different environmental compartments, such as water, soil, agricultural foods, and products of animal origin, have become a relevant issue. In this study, the levels of pesticide residues in Sabarmati River of Gujarat, India, have been investigated using surface water and sediment samples as a case study to find the extent of contamination and accumulation in the River. Thus, 3 organochlorine pesticides (OCPs), namely dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), and endosulfan, and their isomers were analyzed in the River through gas chromatography (GC) (Shimadzu, 2010) using an electron capture detector (ECD). The present research is very vital and holds a great significance for a developing nation like India. There is a lack of such studies in India and a similar study has not been carried out on the Sabarmati River since 1998. In some cases detected concentrations were higher than the standard set by the Indian Bureau of Standards as well as theEuropean Union. ∑OCP residues detected in surface water and sediments samples of the Sabarmati River ranged between below detection limit (BDL) and 392.71 µg/l and BDL-1393.81 ng/g.

KEYWORDS: Organochlorine Pesticides Residue, Analytical Determination, Gas Chromatography

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Introduction

Dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH) and endosulfan are very dangerous chemical substances and have been banned, but some farmers still use these substances to control pests. Some factories also produce organochlorine pesticides (OCPs). OCPs are very toxic and they may affect the biota and human consumers.[1] An epidemiological study has shown OCPs to be a potential risk factor for liver, breast, prostate, and testicular cancer, and lower sperm count in humans.[2] In 1993, DDT residues in excess of 100 mg/kg were reported in dried fish taken from rice fields in Bangladesh.[3] The present research is vital and holds a great significance for a developing nation like India. There is a lack of such studies in India and a similar study has not been carried out on the Sabarmati River, India, since 1998. Rivers in India are an important source of water supply and unfortunately are exposed to pesticide pollution. Therefore, it is very important to monitor water quality in terms of the presence of pesticides prior to its distribution in the society. In Ahmedabad, near the Sabarmati river, approximately 7 pesticide producing industries are situated. Many pesticide manufacturers and industries illegally dump their wastes directly into the river. A

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potential pathway for adverse effects of pesticides is via hydrologic systems, which supply water to natural ecosystems. Water is one of the primary ways through which pesticides are transported from an applied area to other locations in the environment. According to the guidelines of the World Health Organization (WHO), a concentration level of up to 2000 ng/l of HCH and DDT in drinking water is considered safe for humans and other living bodies.[4] There was a report of poisoning due to pesticides in India in Madhya Pradesh in 1967-68 where 12 people were affected and over 12 people died due to high levels of HCH.[5] A case study in Uttar Pradesh (India) in 1978 reported poisoning and death due to HCH in 250 and 4 individuals, respectively.[5]

The main objective of this study was to present a general overview of the existence of different pesticides in various locations of the respective river. This study was undertaken due to the necessity of monitoring pesticide residues in the river system, after the ban on the use of these pesticides, in order to assess any health/ecological risks. The study shows that the amount of OCPs found in agricultural areas is higher than that found in industrial and residential areas. Pesticides applied on soil eventually find their way to the aquatic system, thus, contaminating it. OCPs can persist in soil and water for several years, and subsequently, become accumulated in aquatic biota.[6].

Materials and Methods

All solvents (HPLC grade) were purchased from SD Fine-Chem Limited (SDFCL). Dichloromethane (DCM), acetone, hexane, sodium chloride (AR grade), and sodium sulphate (AR grade) were procured from SDFCL. Analytical standards of 4, 4′ DDT, endosulfan, and HCH were purchased from Sigma-Aldrich Laborchemikalien GmbH. The standard solutions (1.0 µg/ml) of organochlorine pesticides alone or in combination were prepared in hexane. Millipore Milli-Q purified water was used throughout the experiment.

The study area and sampling locations were identified based on the possible potential for water contaminations by pesticides. Sample collection was performed in two different phases. In phase I, samples were collected during May 2011, May 2012, and May 2013 to check the levels of pesticide residue in succeeding years and weather the concentration of pesticide gradually increased or decreased. In phase II, sampling was performed during January 2013, May 2013, and September 2013 to check the variation in levels of pesticides due to season in the Sabarmati River, Ahmedabad, Gujarat, India (Figure 1).

The Sabarmati River is located in Western India. It is one of the largest rivers of north Gujarat and originates from Dhebar Lake in Aravalli Range of the Udaipur District of Rajasthan and meets the Gulf of Cambay of the Arabian Sea. The millions of liters of 'treated' effluent water of 3,365 units of Vatva, Odhav, and Naroda pumped into the river by the Gujarat Industrial development corporation (GIDC) Mega pipeline at the Vasana-Narol Bridge near Ahmedabad. These effluents are 15 times more polluted than the accepted norms. The sampling locations were selected closer to the places where intensive agricultural and industrial activities are carried out. Surface water and sediment samples were collected from 8 sampling locations of the Sabarmati River because many industries are situated in nearby areas.

The river water (144 samples) and sediment (144 samples) samples were collected and analyzed once in each season (summer, monsoon, and winter) during the study period. The river water samples (2 l) collected from midstream of the river (40 cm below the surface) in high purity glass bottles were transported to the laboratory, refrigerated at 4 °C, and analyzed for residues of OCPs. The sediment samples collected in the polyethylene bags, approximately 500 g, were transported to the laboratory and pebbles, shells, and vegetable matter were removed, and the samples were air-dried at room temperature. The air-dried samples were then grounded with pestle and

mortar and sieved to 200-250 British Standard Sieve (BSS) mesh size. The samples were collected approximately between 0–50 Km ranges of the Sabarmati River.

For the extraction of OCPs, 10 g sediment samples were obtained from each location.[7] Then, 7 ml of 0.2 M NH_4Cl solution was added to the 10 g dried sediment samples. A mixture of 100 ml hexane:acetone (1:1) was used as a solvent to extract pesticides through overnight shaking for 12 hours on reciprocal or wrist action shaker at 180 rpm. The extract was carefully decanted through activated Florisil column (2-3 cm), and the sediments were washed twice with 25 ml hexane:acetone (1:1). The eluate was washed with 200 ml water, and then, aqueous layer was extracted again with 50 ml hexane. Finally, the hexane layer was washed with 100 ml water, and then, evaporated until dry with a vacuum rotary evaporator. The concentrated extract was then passed through a chromatographic column [30 cm x 10 mm internal diameter (i.d.)] containing 2 g Florisil (lower) and 1 g sodium sulphate (upper) which is pre-wetted with hexane: acetone (1:1). OCPs were eluted with 25 ml hexane: acetone (1:1). Solvent evaporation was performed using a rotary evaporator and final volume of solvent was adjusted to 5 ml, which is used for gas chromatographic analysis. All sediments were analyzed for HCH, DDT, and endosulfan.

NaCl (10 g) was dissolved in 1000 ml of water sample and kept in a separating funnel with a stopcock on a vertical stand. Then, 60 ml of DCM (dichloromethane) was added to the separating funnel and the separating funnel was shaken for 2-3 minutes. Next, the produced gas was released by opening the stopcock and the separating funnel was replaced on the stand in its original position. The organic layer was then separated and passed through a bed of anhydrous sodium sulphate and the extract was collected in a round bottom flask (RB). The whole process was repeated by adding 30 ml DCM twice and passing the whole extract through a bed of sodium sulphate. Evaporation, near to dryness, was performed using a rotary evaporator. The residue was extracted with acetone: hexane mixture (1:9) and heated until it evaporated almost to dryness. Subsequently, a mixture of acetone: hexane (1:9) was added until the residue reached 1 ml, and then, it was used for GC analysis.[8]

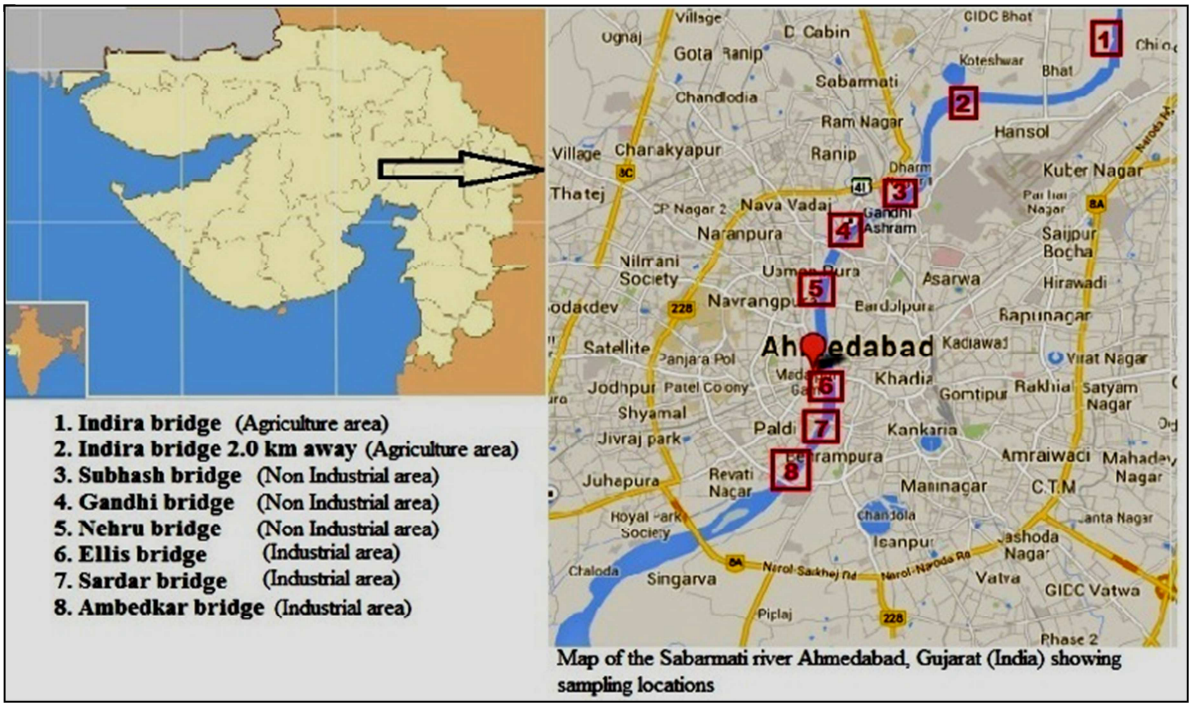

Figure 1. Map of the Sabarmati River Ahmedabad, Gujarat

Stock standard solutions (1000 µg/ml) were prepared individually by dissolving the appropriate quantity of pesticide in hexane. Working standard solutions (10-100 ppm), as per requirement, were prepared from pesticide stock solution in hexane. The obtained solutions were stored in a refrigerator at 2-8 ˚C. The pesticide residues were analyzed using a gas chromatograph (GC 2010, SHIMADZU) equipped with an auto sampler and supported by an electron capture detector (ECD) and GC solution software. This detector allows the detection of contaminants at trace level concentration in the lower ppb range in the presence of a multitude of compounds extracted from the matrix to which this detector does not respond. A 30 m x 0.25 mm i.d. x 0.25 µm fused silica capillary column was used for the chromatographic separation of pesticides. Nitrogen was used as the carrier gas and make up gas and the injection technique was in the split mode. Injector temperature was set at 270 ˚C and a volume of 1 µl of each sample was injected. The column flow was set at 0.7 ml/minute and detector temperature was set at 300 ˚C. The limit of detection (LOD) and limit of quantification (LOQ) for OCPs were 0.001 µg/l and 0.002 µg/l, respectively (Table 1).

Table 1. Pesticide residue limits (Bureau of Indian Standards)

Pesticides	Limit (µg/l)	Rt (minute)
α-HCH	0.01	7.60
ß-HCH	0.04	8.40
γ-HCH	2.00	8.65
δ-HCH	0.04	9.47
o,p-DDT	1.00	22.61
p,p-DDT	1.00	24.91
α-endosulfan	0.40	18.12
ß-endosulfan	0.40	21.76

HCH: Hexachlorocyclohexane; DDT: Dichlorodiphenyltrichloroethane

Results and Discussion

The present study has been undertaken to find the extent of pesticide contamination and accumulation in the Sabarmati River. Moreover, attempts have been made to check the presence of banned pesticides like DDT, HCH, and ndosulphan. All processes were performed in triplicate. The basic statistics of ∑OCPs at different sites in sediment and water samples of the Sabarmati River during the study period is summarized in table 2.

Hexachlorocyclohexane (HCH)

The solubility of lindane (γ-HCH) in water is 10 mg/l. The WHO classifies lindane as a "moderately hazardous" pesticide. The United States Environmental Protection Agency (USEPA) (2005) has reported that lindane does not contaminate drinking water in excess of the agency's level of concern. However, exposure to large amounts of linden can negatively affect the nervous system, producing a range of symptoms from headache and dizziness to convulsions, and very rarely death.[9] In water and sediment samples of the Sabarmati River collected from the Indira bridge, residual concentration of ∑HCH ranged from below the detection limit (BDL) to 8.59 µg/l and BDL to 1494.62 ng/g, respectively. In water samples collected from 2 km away from the Indira Bridge, ∑HCH residue concentration ranged from BDL to 194.93 µg/l. Nevertheless, the detected concentration of ∑HCH in sediment samples was BDL-1372.2 ng/g. Similarly, in water samples taken from the Ellis Bridge, ∑HCH residue concentration ranged from BDL to 169.44 µg/l, where as in sediment samples, it ranged from BDL to 4.22 ng/g. In water samples collected from the Nehru Bridge, ∑HCH residue concentration was in the range of BDL-232.59 µg/l. In the sediment samples, α-HCH and δ-HCH concentrations were in the range of BDL-5.65 ng/g and BDL-14.21 ng/g, respectively. In water samples taken from the Gandhi Bridge, residues of ∑HCH concentration was in the range of BDL-107.45 µg/l, and in sediment samples, isomers of HCH were not detected. Similarly, in water and sediment samples taken from the Subhash Bridge, residual concentration of ∑HCH ranged between BDL and 46.36 µg/l, and BDL and 15.45 ng/g, respectively. In water and sediment samples collected from the Sardar Bridge, ∑HCH residue concentration ranged from BDL to 11.07 µg/l, and BDL to 34.76 ng/g, respectively. In water samples taken from the Ambedkar Bridge, residual concentration of α-HCH was in the range

of BDL-5.09 µg/l, while others were not detected. In sediment samples, α-HCH and δ-HCH concentrations were in the range of BDL-3.84 ng/g and BDL-12.25 ng/g, respectively.

Table 2. Basic statistics of organochlorine pesticides (OCP) residues in water and sediment samples of the Sabarmati River

Pesticides	Water (µg/l)			Sediment (ng/g)		
	Range	Mean ± SD	Median	Range	Mean ± SD	Median
Indira Bridge						
α-HCH	BDL-0.95	0.87 ± 0.09	0.89	BDL-64.52	52.97 ± 11.51	52.90
ß-HCH	BDL-2.34	2.34 ± 0.16	2.34	BDL-524.62	512.98 ± 12.01	513.72
γ-HCH	BDL-1.60	1.41 ± 0.16	1.34	BDL-845.58	836.52 ± 10.30	838.68
δ-HCH	BDL-3.70	3.27 ± 0.30	9.82	BDL-59.90	58.54 ± 1.25	58.30
o,p-DDT	BDL-0.07	0.03 ± 0.03	0.03	BDL-0.51	0.46 ± 0.05	0.49
p, p-DDT	BDL-0.05	0.02 ± 0.02	0.02	BDL-0.02	0.01 ± 0.01	0
α-Endosulfan	BDL-0.07	0.02 ± 0.03	0.01	BDL-0	0 ± 0	0
ß-Endosulfan	BDL-0.08	0.03 ± 0.03	0.04	BDL-0	0 ± 0	0
Indira Bridge 2 km away						
α-HCH	BDL-0.08	0.03 ± 0.04	0.02	BDL-155.32	148.36 ± 7.60	149.52
ß-HCH	BDL-0.06	0.02 ± 0.03	0.01	BDL-41.52	38.37 ± 3.24	38.58
γ-HCH	BDL-4.58	4.53 ± 0.03	4.52	BDL-1120.84	1088.02 ± 33.09	1088.59
δ-HCH	BDL-190.21	189 ± 0.85	189.62	BDL-54.52	45.91 ± 8.06	44.69
o,p-DDT	BDL-65.52	65.03 ± 0.42	64.89	BDL-21.53	14.95 ± 6.18	14.08
p,p-DDT	BDL-80.51	79.55 ± 1.12	79.84	BDL-0.02	0.00 ± 0.01	0
α-Endosulfan	BDL-14.52	14.14 ± 0.54	14.39	BDL-0.04	0.01 ± 0.02	0
ß-Endosulfan	BDL-37.23	36.61 ± 0.83	36.95	BDL-0.02	0.01 ± 0.01	0.01
Ellis Bridge						
α-HCH	BDL-0.43	0.41 ± 0.02	0.42	BDL-4.21	3.58 ± 0.68	3.69
ß-HCH	BDL-7.04	7.01 ± 0.03	7.02	BDL-0	0 ± 0	0
γ-HCH	BDL-160.55	155.96 ± 4.22	155.12	BDL-0	0 ± 0	0
δ-HCH	BDL-1.42	1.24 ± 0.22	1.32	BDL-0.01	0.0 ± 0.00	0.01
o,p-DDT	BDL-0.04	0.02 ± 0.02	0.02	BDL-3.02	2.78 ± 0.24	2.79
p,p-DDT	BDL-0.02	0.01 ± 0.01	0.01	BDL-0.02	0.01 ± 0.01	0.01
α-Endosulfan	BDL-0.06	0.02 ± 0.03	0.02	BDL-0.65	0.45 ± 0.20	0.46
ß-Endosulfan	BDL-0.04	0.02 ± 0.02	0.02	BDL-5.25	3.83 ± 1.27	3.47
Nehru Bridge						
α-HCH	BDL-0.02	0.01 ± 0.0	0.01	BDL-5.65	4.72 ± 1.05	4.49
ß-HCH	BDL-5.19	5.05 ± 0.20	5.15	BDL-0	0 ± 0	0
γ-HCH	BDL-225.85	224.52 ± 1.89	225.38	BDL-0	0 ± 0	0
δ-HCH	BDL-1.53	1.33 ± 0.32	1.51	BDL-14.21	13.30 ± 0.84	13.15
o,p-DDT	BDL-0.08	0.03 ± 0.04	0.02	BDL-14.25	12.60 ± 1.70	12.71
p,p-DDT	BDL-0.03	0.01 ± 0.02	0.01	BDL-12.94	11.69 ± 1.08	11.18
α-Endosulfan	BDL-0.08	0.07 ± 0.01	0.07	BDL-7.98	6.83 ± 1.04	6.58
ß-Endosulfan	BDL-0.03	0.01 ± 0.04	0.01	BDL-10.25	9.64 ± 0.64	9.69
Gandhi Bridge						
α-HCH	BDL-0.39	0.37 ± 0.04	0.39	BDL-0	0 ± 0	0
ß-HCH	BDL–3.03	2.88 ± 0.25	3.02	BDL-0	0 ± 0	0
γ-HCH	BDL-103.99	102.22 ± 1.88	102.42	BDL-0	0 ± 0	0
δ-HCH	BDL-0.04	0.02 ± 0.02	0.02	BDL-0	0 ± 0	0
o,p-DDT	BDL-0.05	0.01 ± 0.03	0.01	BDL-0	0 ± 0	0

Table 2. Basic statistics of organochlorine pesticides (OCP) residues in water and sediment samples of the Sabarmati River (Continue)

Pesticides	Water (µg/l)			Sediment (ng/g)		
	Range	Mean ± SD	Median	Range	Mean ± SD	Median
p,p-DDT	BDL-0.03	0.01 ± 0.01	0.02	BDL-0	0 ± 0	0
α-Endosulfan	BDL-0.04	0.01 ± 0.02	0.01	BDL-0	0 ± 0	0
ß-Endosulfan	BDL-0.04	0.02 ± 0.02	0.02	BDL-0	0 ± 0	0
Subhash Bridge						
α-HCH	BDL-0.04	0.02 ± 0.02	0.02	BDL-0	0 ± 0	0
ß-HCH	BDL-0.82	0.74 ± 0.10	0.79	BDL-0	0 ± 0	0
γ-HCH	BDL-44.72	44.37 ± 0.59	44.71	BDL-0	0 ± 0	0
δ-HCH	BDL-0.78	0.77 ± 0.01	0.77	BDL-15.45	11.50 ± 3.62	10.74
o,p-DDT	BDL-0.06	0.03 ± 0.03	0.04	BDL-0	0 ± 0	0
p,p-DDT	BDL-0.08	0.03 ± 0.04	0.02	BDL-0	0 ± 0	0
α-Endosulfan	BDL-0.02	0.01 ± 0.01	0.01	BDL-4.54	3.44 ± 1.09	3.41
ß-Endosulfan	BDL-0.06	0.02 ± 0.03	0.02	BDL-0	0 ± 0	0
Sardar Bridge						
α-HCH	BDL- 0.15	0.13 ± 0.01	0.14	BDL-15.94	14.68 ± 1.11	14.25
ß-HCH	BDL-6.35	6.22 ± 0.20	6.32	BDL-3.87	2.68 ± 1.05	2.33
γ-HCH	BDL-4.07	3.92 ± 0.21	4.02	BDL-0	0 ± 0	0
δ-HCH	BDL-0.5	0.37 ± 0.15	0.40	BDL-14.95	12.56 ± 2.31	12.41
o,p-DDT	BDL-0.04	0.02 ± 0.02	0.02	BDL-9.87	8.72 ± 1.00	8.31
p,p-DDT	BDL-0.05	0.02 ± 0.02	0.03	BDL-11.54	10.43 ± 1.22	10.6
α-Endosulfan	BDL-0.06	0.02 ± 0.03	0.01	BDL-1.85	1.51 ± 0.42	1.65
ß-Endosulfan	BDL-0.04	0.02 ± 0.02	0.02	BDL-10.22	9.41 ± 0.78	9.35
Ambedkar Bridge						
α-HCH	BDL-5.09	5.03 ± 0.04	5.02	BDL- 3.84	2.58 ± 1.17	2.39
ß-HCH	BDL-0.09	0.05 ± 0.04	0.06	BDL-0	0 ± 0	0
γ-HCH	BDL-0.07	0.04 ± 0.03	0.05	BDL-0	0 ± 0	0
δ-HCH	BDL-0.06	0.02 ± 0.03	0.01	BDL-12.25	12.16 ± 0.08	12.17
o,p-DDT	BDL-0.02	0.01 ± 0.01	0.01	BDL-14.1	13.34 ± 0.71	13.25
p,p-DDT	BDL-0.06	0.03 ± 0.03	0.04	BDL-20.61	19.63 ± 0.48	19.67
α-Endosulfan	BDL-0.06	0.02 ± 0.03	0.02	BDL-2.98	2.79 ± 0.27	2.90
ß-Endosulfan	BDL-0.08	0.04 ± 0.04	0.04	BDL-14.6	14.09 ± 0.84	14.54

BDL: Below the detection limit; HCH: Hexachlorocyclohexane; DDT: Dichlorodiphenyltrichloroethane; SD: Standard deviation

The comparison of the residues of OCPs between different sampling sites showed that the location 2 km away from the Indira Bridge had the maximum concentration of these persistent compounds (1393.22 ng/g in sediment). However, this concentration was 392.71 µg/l in water sample. The high concentration of OCPs in this area is due to the fact that this is an agricultural area and two pesticide industries are situated near this location. Nevertheless, the concentration of OCPs at the Ambedkar Bridge (water sample) was lower (5.53 µg/l in water). However, sediment samples taken from the Gandhi Bridge had no detectable amount of OCPs (Figure 2).

As shown in table 3, the concentration of ∑HCH increased during the study period. As compared to residual concentration of ∑HCH in 2011, it has gradually increased in succeeding years. This is evidence of the use of HCH until today. This study has been performed mostly for Indian rivers like Gomti River (Uttar Pradesh), Kaveri River (Tamil nadu), Ganga River (Uttar Pradesh), Hugli River (Kolkata), Kuano River (Uttar Pradesh), and Yamuna River (Haryana-

Delhi). The level of ∑HCH ranged from 5.08 to 232.127 µg/l in water and BDL to 1494.62 ng/g in the sediments of the Sabarmati River. Gomti River showed lower concentration of ∑HCH (0.00163-0.368 µg/l) in water and (BDL-155.17 ng/g) sediments.[10] Ganga River also showed lower levels of ∑HCH in water (BDL-99.517 µg/l).[11]

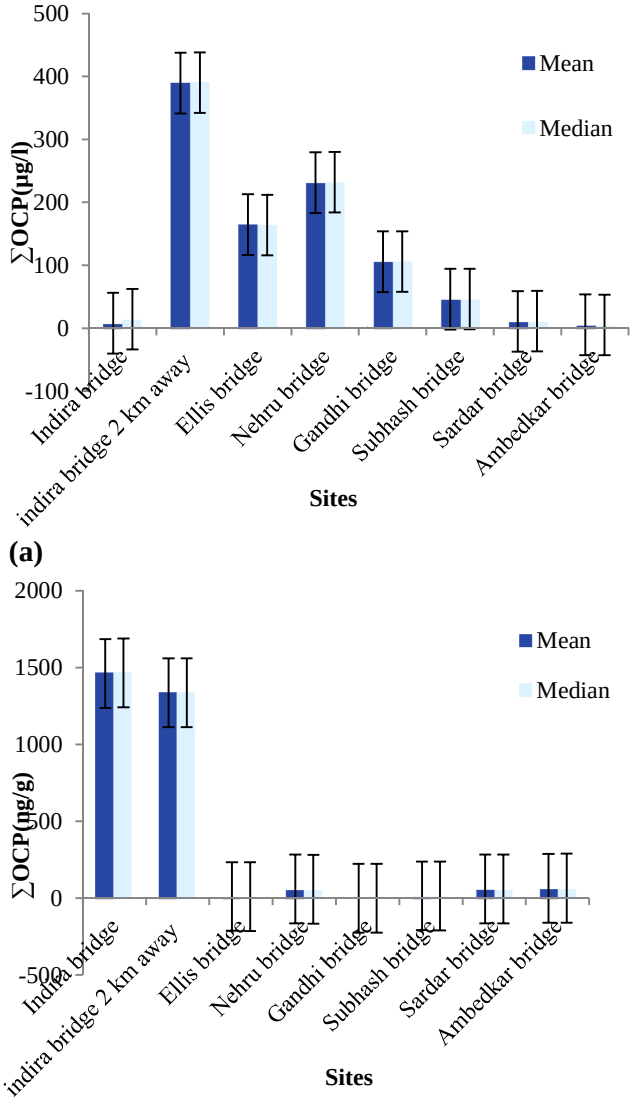

Figure 2. ∑ organochlorine pesticides (OCPs) (OCPs) residues in the (a) water and (b) sediments of the Sabarmati River

The concentration of ∑HCH in the Kaveri River ranged from 4.35 to 158.4 ng/g,[12] which is lower than the concentration found in our study. In surface water, levels of lindane (γ-HCH) were found to be in the range of 0.01-0.43 µg/l, which is less than that in the Hugli River, Kolkata.[13] The total concentration of HCH in the Kuano River ranged from 0.0008 to 0.020 µg /l[14], and in the Yamuna River from 0.01276 to 0.5934µg/l.[15] In the water samples of the Sabarmati River, the concentration of ∑HCH residues are relatively higher than that found in the Pearl River estuary (0.039–0.282 µg/l).[16] In the rivers of Taiwan and Mar Menor Lagoon, these values are lower than that of the Minjiang River estuary.[17] In this study, it can be said that HCH has the predominant residue concentration in the Sabarmati River. In rivers in the Southern part of Okinawa, in Japan, the highest concentration of HCH detected in water samples was 0.049 µg/l,[18] which is lower than our results. In sediments, the concentration level of HCH detected range from 0.44 to 17.9 ng/g in the West Central coast of India in the rabian Sea.[19] HCH is a widespread contaminant that has entered the environment through its manufacturing, use as a pesticide, and its formation as a by-product during production of a variety of chlorinated compounds.

Dichlorodiphenyltrichloroethane (DDT)

In water and sediment samples collected from the Indira Bridge, residual concentration of ∑DDT ranged from BDL to 0.12 µg/l and BDL to 0.52 ng/g, respectively. In water and sediment samples collected from 2 km away from the Indira Bridge, the ranges of residual concentration of op-DDT and pp-DDT were BDL-65.52 µg/l and BDL-80.51 ng/g, and BDL-21.53 µg/l and BDl-0.02 ng/g, respectively. In sediment samples taken from the Ellis Bridge, residual concentration of ∑DDT was 3.04 ng/g. In sediment samples collected from the Nehru Bridge, residual concentration of op-DDT and pp-DDT ranged from BDL to 14.25, and BDL to 12.94 ng/g, respectively. In sediment samples collected from the Sardar Bridge, residual concentration of ∑DDT was 19.15 ng/g.

In sediment samples collected from the

Ambedkar Bridge, residual concentration of op-DDT and pp-DDT ranged between BDL and 14.1, and BDL and 20.61 ng/g, respectively. In the remaining samples received from the Subhash and Gandhi Bridges, no residual concentrations of DDT isomers were detected. As shown in table 3, concentration of ∑DDT decreased during the study period. As compared to residual concentration of ∑DDT in 2010, it has gradually decreased in succeeding years. This may be due to the ban on the use of DDT. In this study, the range of residue levels of op-DDT and pp-DDT were BDL-65.52 and BDL-80.51 µg/l in water samples, and BDL-21.53 and BDL-0.02 ng/g in sediment samples from the Sabarmati River. This range was BDL-0.0688, BDL-0.01376 µg/l in water samples and BDL-345.66, BDL-206.12 ng/g in sediment samples of the Gomti River.[10] In surface water, levels of DDT were found to be 0.03-0.65 µg/l in the Hugli River, Kolkata,[13] which is lower than that found in the Sabarmati River. In the Kuano River of Uttar Pradesh, total DDT concentration ranged from 0.0002 to 0.003 µg/l,[14] which is lower than that in the Sabarmati River.

The level of ∑DDT concentration in the Sabarmati River water (BDL-144.54 µg/l) is higher than that found in the Ganga River (0.14-66.51 µg/l),[11] Yamuna River (0.07-0.72 µg/l),[15] Minjiang River estuary (0.04-0.23 µg/l),[17] and water supply of El-Haram (2.30-61.00 µg/l).[20] The level of ∑DDT concentrations in the sediments (BDL-108.48 ng/g) of the Sabarmati River are higher than those reported in the sediments of the Minjiang River estuary (1.6-13.1 ng/g dry weight). However, in the case of Haihe and Dagu Drainage rivers, ∑DDT concentration ranged between 0.32 and 80.18 ng/g, and 3.60 and 83.49 ng/g dry weight, respectively.[21]

Table 3. Concentrations of organochlorine pesticides (OCP) in sediments (ng/g) of the Sabarmati River, Ahmedabad, India

Location	OCPs	2011	2012	2013
		Mean ± SD	Mean ± SD	Mean ± SD
Site-1	∑HCH	7.69 ± 18.93	548.60 ± 13.81	1461.01 ± 35.07
	∑DDT	nd	nd	0.47 ± 0.06
	∑endosulfan	nd	nd	nd
Site-2	∑HCH	42.00 ± 18.93	498.21 ± 17.01	1320.66 ± 51.99
	∑DDT	87.40 ± 34.98	17.51 ± 7.14	14.95 ± 6.19
	∑endosulfan	21.21 ± 8.16	9.12 ± 3.14	0.02 ± 0.03
Site-3	∑HCH	nd	nd	3.58 ± 0.68
	∑DDT	6.00 ± 34.98	3.53 ± 0.01	2.79 ± 0.25
	∑endosulfan	3.93 ± 8.16	1.93 ± 0.02	4.20 ± 81.47
Site-4	∑HCH	13.02 ± 18.93	15.69 ± 3.93	18.02 ± 1.89
	∑DDT	49.3 ± 34.98	20.09 ± 2.08	24.29 ± 2.78
	∑endosulfan	16.27 ± 8.16	15.50 ± 0.09	16.47 ± 1.68
Site-5	∑HCH	nd	nd	nd
	∑DDT	nd	nd	nd
	∑endosulfan	nd	nd	nd
Site-6	∑HCH	6.15 ± 18.93	8.19 ± 3.02	11.50 ± 3.62
	∑DDT	nd	nd	nd
	∑endosulfan	nd	nd	3.44 ± 1.09
Site-7	∑HCH	25.16 ± 18.93	30.15 ± 17.02	29.92 ± 4.47
	∑DDT	33.90 ± 34.98	25.56 ± 12.03	19.15 ± 2.22
	∑endosulfan	10.40 ± 8.16	9.14 ± 2.02	10.92 ± 1.20
Site-8	∑HCH	10.28 ± 18.93	8.15 ± 0.04	14.74 ± 1.25
	∑DDT	60.50 ± 34.98	51.52 ± 11.09	32.97 ± 1.19
	∑Endosulfan	17.50 ± 8.16	nd	16.88 ± 1.11

HCH: Hexachlorocyclohexane; DDT: Dichlorodiphenyltrichloroethane; SD: Standard deviation; nd = not detected; OSP: Organochlorine pesticides

In the rivers in Taiwan the level ranged between 0.21 and 8.81 ng/g in dry weight.[22] In the Ogba River (Nigeria), op-DDT and pp-DDT levels ranged between 0.67 and 0.71 and 0.73 and 0.75 µg/l, respectively.[23] The range of concentration of DDT in sediments detected were 7.01-179.10 ng/g in the West Central cost of India in the Arabian Sea.[18] In sediments of the Sabarmati River, the residue levels of op-DDT and pp-DDT were higher than those in the sediments of the Qiantang River (op-DDT: 0.28-9.61 ng/g, pp-DDT: 0.46-22.78 ng/g).[24] The range of ∑DDT concentration was BDL-146.71 µg/l in water and BDL-108.48 ng/g in sediment samples of the Sabarmati River. DDT has been banned for agricultural use in 1989, but it is still used in public health sectors for malaria control.[25]

Endosulfan

The concentration level of ∑endosulfan in water and sediment samples obtained from 2 km away from the Indira Bridge ranged from BDL to 51.75 µg/l and BDL to 0.06 ng/g, respectively. In water and sediment samples collected from the Ellis Bridge, residual concentration of ∑endosulfan ranged from BDL to 0.10 µg/l and BDL to 5.90 ng/g, respectively. The concentration level of ∑endosulfan residues in the water sample obtained from the Nehru Bridge ranged from BDL to 0.11µg/l, whereas it ranged from BDL to 18.23 ng/g in the sediment sample. ∑endosulfan residues in sediment samples obtained from the Subhash Bridge ranged from BDL to 4.54 ng/g. In the Sardar Bridge, the concentration level of ∑endosulfan residues in sediment samples ranged from BDL to 12.07 ng/g. The concentration level of ∑endosulfan in sediment samples taken from the Ambedkar Bridge ranged from BDL to 17.58 ng/g. In the Gomti River of India, ∑endosulfan ranged from BDL to 0.094 µg/l in water samples, and BDL-1.00 ng/g in sediment samples; this is lower than the concentration of endosulfan (BDL-51.75 µg/l) in the Sabarmati River. In Hindon River Uttar Pradesh, India, endosulfan concentration range from 9.2 to 23.5 µg/l.[26] In this study levels of α-endosulfan (BDL-14.52µg/l) and ß-endosulfan (BDL-37.23µg/l) metabolites are higher than the concentration range of α-endosulfan in water (BDL-0.739 µg/l) and in sediment samples (35.5-50.47 ng/g). Nevertheless, the range of β-endosulfan level was BDL-0.157 µg/l in water and 34.40-303.09 ng/g in sediment samples of the Ganga River.[27] The levels of α-endosulfan (0.00146-0.0961 µg/l) and ß-endosulfan (0.00549-0.135 µg/l) found in the water of Pearl River estuary was relatively low (Table 4).[28]

Table 4. Comparison of organochlorine pesticides (OCP) concentrations in sediment samples from various locations in the world

Location	∑DDTs	∑HCH	References
Sabarmati River, India	nd-34.71[f]	nd-1494.62[***]	Present study
Gomti River, India	1.63-368.70[**]	nd-155.17[***]	Malik et al.[10]
Kaveri River, India	0.69-4.85[**]	4.35-158.4[*]	Rajendran and Subramanian[12]
Haihe, China	0.32-80.18[**]	1.88-18.76[***]	Yang et al.[21]
Qiantang River, China	1.14-100.20[**]	8.22-152.1[***]	Zhou et al.[24]
Manzala Lake, Egypt	0.20–5.17[£]	nd-3.42[***]	Barakat et al.[29]
Peacock River, China	0.10-1.54[**]	0.13-6.58[***]	Chen et al.[30]
Scheldt River, Belgium	6.6-27.60[ſ]	nd[*]	Covaci et al.[31]
Ebro River, Spain	0.85-9.03[§]	0.001-0.026[€]	Fernandez et al.[32]
Chaohu Lake, China	0.30-31.00[£]	0.2-1.8[***]	Liu et al.[33]
Mekong River, Vietnam	nd-110.00[ſ]	nd-1.3[*]	Minh et al.[34]

nd = not detected; [*]Sum of α-,β-, and γ-HCH; [**] Sum of p,p'-DDE,p,p'-DDD,o,p'-DDT, and p,p'-DDT'; [***]Sum of α-,β-,γ-, and δ-HCH; [£] Sum of o,p'-DDE,p,p'-DDE,o,p'-DDD,p,p'-DDD,o,p'-DDT, and p,p'-DDT; [€]Sum of α- and γ-HCH; [§]Sum of dichlorobenzophenone,p,p'-DDE,p,p'-DDD, and p,p'-DDT; [ſ] Sum of p,p'-DDE,p,p'-DDD, and p,p'-DDT; [f] Sum of o,p'-DDT and p,p'-DDT; HCH: Hexachlorocyclohexane; DDT: Dichlorodiphenyltrichloroethane

Samples were collected in January 2013, May 2013, and September 2013. As observed in figure 3, 404883 µg/l ∑OCPs was found in water sample during the summer which is very high compared to the other seasons. During winter, the concentration of ∑OCPs was lower compared to other seasons. During the monsoon season, heavy water flow causes erosion of river sediments and their resuspension into the river water column, and thus, the pollutants sorbed on the sediment particles may be diluted by runoff.

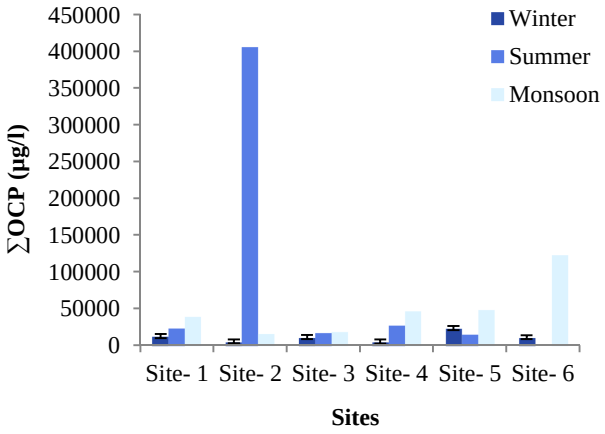

Figure 3. Seasonal variations of ∑ organochlorine pesticides (OCPs) residues in the Sabarmati River

The river flow, during the winter, becomes normalized and the river system starts to stabilize with the settling of eroded sediments. However, during summer, the river system is under stabilized conditions except in the case of some man-made disturbances or other activities like bathing, swimming, and boating. Thus, the biota and aquatic flora and fauna also fluctuate with the changing concentration of organochlorine pesticides. The same results were reported by Kouzayha et al. for Lebanon's water resources.[35] They reported that variation in pesticide concentration follows seasonal patterns, this may be due to the timing of agricultural activities and pesticide applications in addition to the runoff condition.[35]

Conclusion

The present study provides information on the current contamination status of the Sabarmati River located in the Ahmadabad city of Gujarat, India. During the study period, all samples from the Sabarmati River showed the presence of pesticide residue, specifically HCH, which is present in high concentrations. This suggests that the water of this river is not safe for drinking purpose and is harmful for aquatic life. DDT and endosulfan pesticides were also present in all the above samples. Organochlorine pesticides are one of the major environmental pollutants. Moreover, many pesticide manufacturers and industries dump their wastes directly into this river illegally. It also enters into natural waters through percolation and runoff and from urban city sewage sites. Even though the use of these OCPs are restricted and banned in India according to Section 5 of the Insecticide Act, 1968, they are still detected in water of the studied river, which shows that they are still in use for agriculture or industrial purposes. Hence, these levels indicate that the Sabarmati River receives intermittent inputs of organochlorine pesticides, which are the main cause of the pesticide pollution of this river. Assessment of the river water and sediment contamination in this study reflects that sediment and water are contaminated with OCPs. This may have toxic effects on biota and also humans who are consuming the water of this river.

Conflict of Interests

Authors have no conflict of interests.

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