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Persistent Organic Pollutants and Pesticide Residues in Seasonal Waters of Rural Bangladesh

S. Hasan*, K. A. Rabbani, M. L. Rahman and M. A. Hossain
School of Environmental Science & Management, Independent University, Bangladesh, Dhaka, Bangladesh

***Abstract*—Despite their worldwide ban, Persistent Organic Pollutants (POPs) and other organochlorine pesticides are widely in use in developing countries including Bangladesh. The presence of POPs has been indicated in different matrices, such as poultry, fish, vegetables, lake water etc. This study detected POPs and organochlorine pesticides (HCB, O, P`– DDT, DDD, 4, 4`-DDT, and α-HCH, β-HCH, and δ-HCH) in water samples from and around agriculture fields. The water samples were analyzed using Gas Chromatograph equipped with an Electron-Capture Detector (GC-ECD). The highest extractable concentration among all the DDT analytes was $121.793X10^{-2}$ μgL^{-1} of 4, 4`-DDT. Among the HCH analytes, δ-HCH was present in all the samples. There is serious concern whether these bioaccumulative substances have now found their way into the fatty tissues of human body.**

INTRODUCTION

Widespread use of organochlorine pesticides in agriculture, inspite of their known harmful effects, is causing serious concern about human health and environment [1]-[5]. Some of these have been banned worldwide due to their persistence and bioaccumulative nature [6], [7]. One such group of organochlorines has been classified as Persistent Organic Pollutants (POPs). In May 1995, United Nations Environment Program (UNEP) has recognized the POPs as an imminent danger for human health and made a short list of twelve POPs, commonly known as dirty dozen [8]. POPs resist degradation by physical, chemical, biological, and photolytic processes [6]. In some cases, when breakdown does occur, it creates chemicals that are hazardous [9]. POPs' persistence and semi-volatile nature enables them to be transported by air, water or other means to remote regions where they have never been used or released. After their release into the environment, they travel in multiple cycles of evaporation, transport by air and condensation [10]. Various studies all over the world have shown the presence of a large variety of POPs in different matrices, such as water, air, fish, soil, solid wastes, human tissues etc [11]-[16]. POPs' health effects include cancer, neurological, behavioral, immunological, birth defects and reproductive discrepancies, in humans and other animal species [3], [4], [17]-[20].

Six more chemicals including isomers of hexachlorocyclohexane (HCH) and polyaromatic hydrocarbons (PAHs) have been added to the dirty dozen, in the negotiations of UNECE Convention on Long Range Transboundary Air Pollution (LRTAP) for a protocol on POPs [21], [22]. HCH isomers (α, β, γ and δ-HCH) are also harmful, persistent and bioaccumulative [23]. Due to its extensive use as insecticide, all living organisms are at a risk of HCH exposure. Isomers of HCH act as stimulants and δ central nervous depressants [24]. Due to its lipophilicity and persistence, isomers of HCH frequently accumulate in human adipose and breast tissues. [24]. Human studies have shown that exposure to HCHs is linked to cancer, Parkinson's, Alzheimer's, reproduction and fertility disruption, etc. [23] – [25]

Despite their worldwide ban, POPs and HCH pesticides are widely used in developing countries, especially South Asian countries [26]. Agriculture plays an important role in the lives of Bangladeshi people. The major crops grown in the country are rice, wheat, jute, potato, sugarcane, vegetables and tea [26]. Greenpeace has reported that there have been stockpiles of POPs in Bangladesh and these are available in markets under different names and brands. Greenpeace has found DDT, dieldrin, heptachlor along with other harmful chemicals openly sold in markets of Bangladesh [27]. According to a study conducted by a local NGO named Environment and Social Development Organization (ESDO), POPs are still widely used and released to the environment across the country. [26] There have been DDT stockpiles in different districts stored as buffer stocks which are contaminating the environment. The major concentration of these hotspots in Bangladesh has been found in Dhaka city and the surrounding areas namely Gazipur, Narshingdi, Narayanganj, and also in Chittagong, Khulna, Sylhet and Barishal. Some recent studies have found DDT in lake, pond and hand tube well water of the Dhaka metropolitan city area and also in dry fish and vegetables like cauliflowers [28], [29]. HCB is a widespread contaminant that has entered the environment through its past manufacture and use as a pesticide. HCB is also formed as a by-product during production of a variety of chlorinated compounds.[30]

No recent studies have been done in Bangladesh on the prevalence of HCH in the environment. HCHs have been found in water samples in previous studies conducted worldwide. [31]-[34]

This paper focuses on the quantitative detection of POPs and HCHs in water samples collected from inside and around agricultural fields. The concentrations of POPs and HCHs were determined using GC-ECD, the standard method for detecting organochlorine pesticides in water. [34]

MATERIALS AND METHODS

Sampling Area

The sample areas chosen were located around Dhaka city, the capital of Bangladesh. The sample areas for this study are Gazipur, Rupganj and Kaliganj.

Sampling

The procedures for sampling, extraction and clean-up were followed according to established methods. [35]. Fifteen water samples from and around rice, jute and sugarcane fields were collected immediately after the monsoon season. Samples were collected in the season when farmers apply pesticides and there was stagnant water. Out of the total 15 samples, 9 were collected from the ditch situated right beside the crop fields. The rest 6 samples were collected from the stagnant water present inside the rice, sugarcane and jute fields.

Samples were collected directly in pre-cleaned plastic sample bottles. Care was taken not to disturb the surface of the soil layer while collecting the samples. The water samples were not filtered to separate suspended particles because the suspended particles, especially fat particles, could contain POPs in them. Samples were kept below 4ºC until analysis. The pesticide standards were purchased from Sigma-Aldrich with the purity of 99.8%. All other chemicals, solvents and reagents used in this study were of analytical grade.

500 ml of each water sample was taken in a separating funnel and 50g of sodium chloride was added. The content was extracted three times with 50 ml of n-hexane. 30 g of anhydrous sodium sulphate was added to the combined extracts. The extracts were filtered and the water-free organic layer was taken in an evaporation flask. The volume was carefully reduced to about 0.5 – 1.0 ml by evaporation, never allowing the temperature to exceed 69°C. The sample was cleaned up with 2 ml of 95 - 97% pure sulphuric acid saturated with cyclohexane. The mixture was left for separation and the upper phase was taken for analysis in a gas chromatograph.

C. Analytical Methods

Gas chromatographic analyses were carried out on a Shimadzu Model 2010 Gas Chromatograph equipped with a ^{63}Ni electron capture detector with ultra pure nitrogen gas (99.9%) as the mobile phase. Chromatographic determinations were carried out using a 30 m x 0.53 mm x 3.00 µm dimethyl siloxane capillary column (DB-624) manufactured by J & W. The operating conditions were as follows: injection mode was splitless; injection port temperature was 210.0 °C; detector temperature was 300.0°C; column temperature was raised from 240.0°C to 260.0°C. Peak areas were used as the basis for quantification. Standard solutions of HCB, O, P`– DDT, DDD, 4, 4`-DDT, and α-HCH, β-HCH, and δ-HCH were made from double distilled, deionized water. The concentration in samples was expressed in μgL^{-1}.

RESULTS AND DISCUSSION

The purpose of this research was to evaluate the prevalence of organochlorine pesticides like POPs and HCHs in water samples. Table I shows the area from where samples were collected; the kind of crops that were being cultivated; also indicates whether the samples were collected from an adjacent ditch or from the stagnant water present inside the crop fields.

Table I: Sample Sites

No.	Area	Kind of Crops	Source
1	Rupganj	Jute, Sugarcane	Adjacent ditch
2	Rupganj	Jute, Sugarcane	Adjacent ditch
3	Rupganj	Rice	Adjacent ditch
4	Gazipur	Rice	Adjacent ditch
5	Gazipur	Rice	Water from Field
6	Kaliganj	Jute	Water from Field
7	Kaliganj	Jute	Water from Field
8	Rupganj	Rice	Adjacent ditch
9	Kaliganj	Jute	Water from Field
10	Rupganj	Jute, Sugarcane	Adjacent ditch
11	Rupganj	Rice	Water from Field
12	Rupganj	Sugarcane	Adjacent ditch
13	Rupganj	Sugarcane	Adjacent ditch
14	Rupganj	Jute	Adjacent ditch
15	Rupganj	Sugarcane	Water from Field

The concentration of HCB, O,P`DDT, DDD, and 4,4`DDT detected in the samples are shown in Table II.

Table II: Concentrations of POPs in Water Samples from Agricultural Fields

No.	Concentration (μgL^{-1} x 100)			
	HCB	O,P`DDT	DDD	4,4`DDT
1	0.352	ND	ND	8.655
2	0.985	43.362	ND	58.496
3	ND	ND	ND	ND
4	1.584	ND	5.871	105.113
5	10.297	5.000	5.000	10.206
6	0.530	ND	8.279	112.219
7	11.010	2.927	3.690	56.816
8	1.344	ND	ND	65.242
9	0.767	ND	4.837	91.653
10	0.191	ND	7.626	47.530
11	0.371	ND	7.778	121.793
12	ND	9.345	ND	49.812
13	ND	ND	ND	2.873
14	0.014	ND	ND	ND
15	0.096	0.349	ND	10.868

Note. ND : Below detection limit

Thirteen of the fifteen samples were found to contain 4, 4` DDT with concentrations ranging from $2.873X10^{-2}$ to $121.793X10^{-2}$ $\mu gL^{-1}$. It is known that the major component (77%) of the commercial DDT used as pesticide is the 4,4` isomer. [36] It can be speculated from the results that commercial DDT is being used in almost all our sample sites. Twelve samples contained HCB with concentrations ranging from $0.096\ X10^{-2}$ to $11.010X10^{-2}$ μgL^{-1}. DDD was found in 7 samples and their concentration ranged from $3.690\ X\ 10^{-2}$ to $8.279\ X\ 10^{-2}$ μgL^{-1}. O, P` DDT was found in only 5 samples and the concentrations varied from $0.349X10^{-2}$ to $43.362X10^{-2}$ μgL^{-1}. Almost all the samples had atleast one of the three isomers of DDT in them. The

presence of these DDT isomers is an indication of the continued use of POPs in agriculture.

The concentrations of HCHs detected in the samples are shown in Table III.

Table III: Concentrations of HCHs (μgL^{-1}) in Water Samples from Agricultural Fields

No.	Concentration (μgL^{-1} x 100)		
	α-HCH	β- HCH	δ-HCH
1	ND	ND	7.703
2	29.133	3.673	56.662
3	ND	0.775	2.429
4	ND	0.421	49.525
5	ND	ND	10.117
6	ND	ND	51.790
7	ND	ND	45.653
8	ND	ND	13.781
9	ND	ND	100.386
10	ND	ND	30.567
11	ND	ND	79.486
12	ND	ND	24.892
13	0.295	0.574	3.158
14	ND	0.018	0.955
15	0.056	ND	8.954

Note. ND: Below detection limit

All the fifteen samples contained δ-HCH at concentration ranging from $0.955X10^{-2}$ to $100.38X10^{-2}$ μgL^{-1}. Seven samples had δ-HCH concentration at a higher value than the standard value set by the European Union [16]. α-HCH and β-HCH were not as common. β-HCH was found in only 5 samples and their concentration ranged from $0.018X10^{-2}$ to $3.673X10^{-2}$ μgL^{-1}. The three samples that did contain α-HCH, were all collected from Rupganj area.

All the samples collected had atleast one of the seven organochlorine pesticides present. No sample showed the presence of all seven target pesticides, but sample number 2, collected from Rupganj area, showed the presence of six of the seven target pesticides.

CONCLUSION

The analyzed results of this study indicates the use of organochlorine pesticides like HCB, DDT, α-HCH, β-HCH, δ-HCH in agriculture of the country. In most of the cases, the samples with higher concentrations were those that were collected from inside the fields. Further studies can be carried out in larger and more targeted sample areas with all POPs and other significant organochlorine pesticides. Since POPs have higher affinity to sediments and fats compared to water, studies should be conducted involving these matrices. Worldwide studies have found HCB, DDT and α, β, γ- HCH in human blood, breast milk and adipose tissues, but so far no study seems to have been carried out in Bangladesh. Various food and agricultural crops can also `be analyzed for POPs and HCH. As the present study found existence of POPs and HCHs in surface water, chances of groundwater contamination should also be addressed.

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