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Residues of organochlorine insecticides in water and sediment from Ramgarh water reservoir, Jaipur, Rajasthan

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Abstract
In the present study we investigated the residues of HCH and its isomers (α,γ, and β), dieldrin, heptachlor, p,p'-DDT and its metabolites in water and sediment of the reservoir with the help of gas-chromatograph. The residues of γ-HCH were found in most of the water samples, while dieldrin in sediment samples. The mean concentration of p,p'-DDT was found maximum in water samples followed by γ-HCH, dieldrin, p,p'-DDD, β-HCH, p,p'-DDE, heptachlor, and α-HCH. However, the mean concentration of p,p'-DDE was found maximum in sediment samples followed by p,p'-DDD, p,p'-DDT, dieldrin, β-HCH, γ-HCH, α-HCH, and heptachlor. The monthly variation was found significant in mean concentration of HCH and its isomers, heptachlor, p,p'-DDT and its metabolites, in water samples. However, the HCH and its isomers varied significantly in sediment. The monthly variation, of organochlorine pesticide in water and sediment, showed the use of pesticides in different time intervals for different purposes in the catchment area of the reservoir.

Keywords: Organochlorine pesticide, water, sediment, gas chromatograph

Introduction
In India, the use of pesticides, in controlling vector borne disease and in agriculture; started in the year 1948. Since then different categories of pesticides are in continuous use. The organochlorine pesticides, like DDT and BHC, were among them. The indigenous production of DDT and BHC began in 1954. By 1958, India was producing over 5000 metric tone (MT) of five basic pesticides. The production reached a volume of about 60000 MT per annum in mid-eighties. The total installed capacity was at over 139300 tones and the formulation capacity installed in the organized sector was about70000 MT in term of technical grade material during 1997-98. The production of pesticides was lower in year 1997-98 as compared to 1996-97, because of phasing out the production of BHC by March 31st, 1997 (Mathur and Tannan, 1998) [1].

Till date tonnes of pesticides have been dumped on the soil for variety of purposes and the water, soil and sediment are becoming the ultimate sink for the pesticide (Kumar *et al.*1995, Jaffe *et al*.1995, Ahmed *et al*.1996, Dua *et al*.1996, Kumari *et al*.1996, Abbassy *et al*. 1999 and Erkmen *et al*. 2013) [2-8]. The OCPs are long-lived compounds that become concentrated as they move through food chain. They have the toxic effect on animal reproduction, development, and immune system. The OC are also called as Persistent organic pollutants (POPs), Bioaccumulative chemical of concerns (BCCs) and Persistent Toxin that Bioaccumulate (PTBs).

The presence of organochlorines pesticides in various edible commodities was of great concern because of their adverse effects on non-target organisms. Therefore, there was a need of surveillance to find out the extent of exposure of residues of organochlorine insecticides. The determination of OCPs residues in water and sediment samples can provide valuable data to determine extent of exposure.

Ramgarh water reservoir is situated 30 km from Jaipur City (popularly known as pink city) in Northeast direction. Besides being as the source of potable water for inhabitants of Jaipur, this reservoir was also used for fish breeding. It is an irrigation dam and receives water from a perennial river Bhanganga. Anthropogenic activities such as agriculture along the river and in the vicinity of reservoir might be considered as source of pollutants like pesticides and heavy metals to the aquatic ecosystem of the reservoir.

However, there has been a lake of monitoring for trace organic pollutants in this area. Therefore, the aim of this study was to evaluate monthly variation of the residues of OCPs and their metabolites in water and sediment samples collected from the reservoir.

Materials and Methods

Collection and storage of samples

Samples of water and sediment were periodically collected from three sites of Ramgarh reservoir from October 1996 to September 1997. One-liter, pre hexane washed, borosilicate glass bottles were used for collection of water; and samples of bed sediment were collected in polythene zip lock bags and carried to the laboratory for extraction of pesticides.

Extraction of organochlorine insecticides

Water samples

Organochlorine insecticides were extracted in n-hexane (HPLC-grade) (here onwards hexane) by liquid-liquid partitioning method prescribed by APHA (Franson, 1995) [9]. Unfiltered water sample was taken in separatory funnel having saturated sodium chloride and hexane. After clear separation of layer, the lower aqueous phase was transferred into the second separatory funnel of same capacity and extracted twice with hexane and was kept on standing until the clear separation of layers. The combined hexane layers was washed with distilled water in the first separatory funnel. The hexane extract was then collected in beaker and subjected to column chromatograph clean up.

From sediment

The samples of sediment were air-dried and were transferred into conical flasks having solvent mixture of hexane: acetone (1:1). After intermittent shaking, the mixture was filtered into separatory funnel fitted with filter paper no.1. The content in the conical flask was again extracted with solvent mixture, and filtered. The combined extract was shacked with 2 percent sodium chloride to remove acetone. After the clear separation of layers, the lower layer was shaken with hexane for two minutes. Hexane layer was transferred into the first separatory funnel and the combined extract was washed with of distilled water, and hexane layer after the separation was subjected to column chromatograph clean up.

Clean up of Extract

The interfering pigment from water and sediment were removed by filtering the hexane extract through a glass column plugged tightly with glass-wool, anhydrous sodium sulfate and deactivated alumina. The filtrate was collected in a stoppered glass tube and was evaporated to dryness by a flash rotatory vacuum evaporator, keeping the water bath temperature between 45-50 °C

The cleaned up extracts were stored at 4 °C for further analysis on Gas Chromatograph.

Qualitative and quantitative determination of organochlorine insecticide.

Prior to estimation of insecticides, the Gas Chromatograph was calibrated with pesticide standards. The cleaned up and dried extracts were estimated qualitatively and quantitatively by HP 5890 series II Gas Chromatograph coupled with HP 3396 A Integrator.

Instrument Parameters

The experimental conditions prescribed by EPA 608 (Chang and Sanders, 95) [10] for gas chromatograph were followed.

Injection Parameters: - Temperature-250 ºC, Volume injected-1 µl, Pneumatics- Splitless, Purge delay-1 min., Carrier gas-Nitrogen (ultrapure), Head pressure-10 psi, 2.4 ml/min. constant flow.

Oven Parameters: - Initial Temperature- 80 °C (1 min.), Ramps- 1st ramp-30 °C /min.to9 °C. 2nd ramp-6 °C /min. to 300°C, Final temperature-300 °C (2.0 min.).

Detector Parameters: - Electron capture detector (ECD) with Ni^{63}, Temperature-330 °C

Columns: - Capillary column –1st: HP (methyl silicon gum), 10m x 0.54mm x 2.65µm

2nd:Ultra-2(Crosslinked5%PhMesilicon)25mx

0.32mm x .025µm film thickness.

Types of insecticides identified by *GC:* HCH and its isomers (α,γ and β), dieldrin, heptachlor, and p,p'- DDT and its metabolites (DDD&DDE).

Analysis of Variance (ANOVA) was applied to find out monthly variation in distribution of residues of organochlorine insecticides in water and in bed sediment.

Results and Discussion

In Water

The water and sediment samples of reservoir were found to have the residues of OC pesticide during study time (fig.1&2). The mean total residues of OC in water ranged from 0.5 to2.8 $\mu g.ml^{-1}$. The mean concentration of γ-HCH was 0.3±0.05 $\mu g.ml^{-1}$(range ND-1 $\mu g.ml^{-1}$) in water and present in 90 percent of samples with maximum concentration observed in the month of July. The maximum concentration of total HCH was observed in the month of July and it constituted 34 percent of total residues. The common use and persistence may be a reason of the high frequency of γ HCH in water. Also the bacterial activity and ultra violet radiation in water column may isomerise α and β HCH to γ HCH (Lenardon *et al.* 1984) [11]. The variation in HCH and its isomers may be due to microbial population, chemical degradation or photodegradation.

The residues of p,p'- DDT and its metabolites constituted highest percentage in water (46) of total residues of OC pesticide. The residues of p,p'- DDT was present in 80 percent of water samples followed by γ HCH, with a maximum average concentration found in October. The residues of p,p'- DDD was found in 63 percent of water samples with average of 0.2 $\mu g.ml^{-1}$ and found in maximum concentration in December, and for p,p'- DDE it was maximum in April.(fig-1)(Table-1).

In water the concentration of HCH and its isomers, heptachlor, p,p'-DDE and p,p'-DDD varied significantly (p<0.05) (Table-3). Since, p,p'-DDT is known to undergo metabolic conversion by dehydrochlorination reductive dechlorination and oxidation (Matsmura, 1985) [12], the p,p'-DDE and p,p'-DDD encountered in the present study might be due to such metabolic processes.

The residue of dieldrin was detected in 61 percent of water samples, constituted 14 percent of total organochlorine residues. The concentration of dieldrin didn't vary significant monthly. The residue of heptachlor constituted 7 percent of total organochlorine residues with a frequency distribution of 30 percent (Table-1) in the present investigation. The maximum average quantity of heptachlor was observed in the month of November.

The accumulation of pesticides despite its low solubility in water, in aquatic environment may be attributed to the total organic carbon (TOC) and dissolved organic carbon (DOC) in waters (Johnson-Logan *et al.*1992) [13].

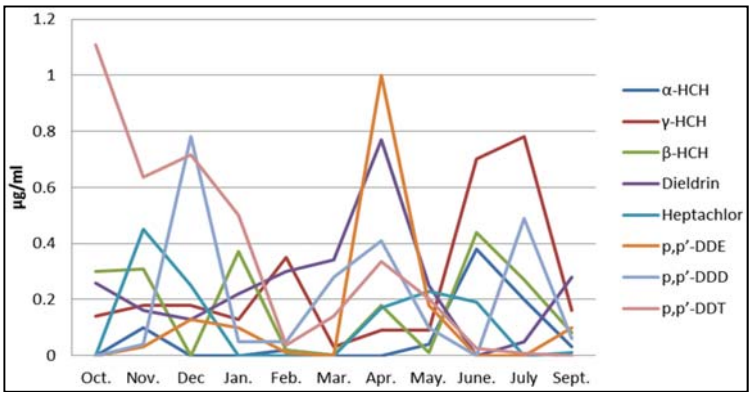

Fig 1: Monthly variation of OC pesticide residues in the water of reservoir

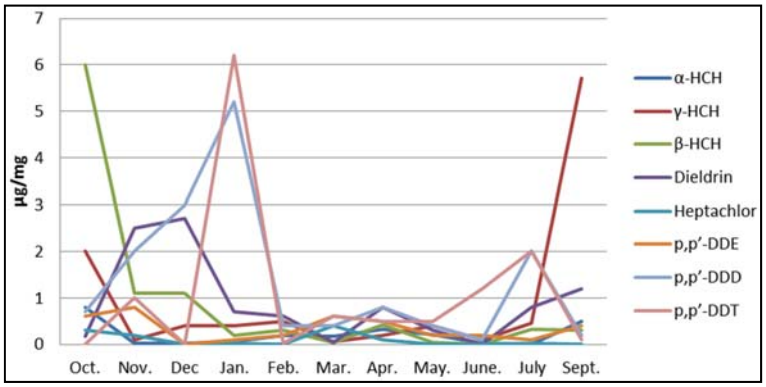

Fig 2: Monthly variation in residues of OC pesticide in the sediment of reservoir

Table 1: Summary of OC pesticides residues in water samples of Ramgrarh water reservoir.

Insecticide (µg/ml)	Mean ± SEM	Range	%occurrence	Month with maximum concentration
α-HCH	0.1±0.02	ND-0.52	61	June
γ-HCH	0.3±0.05	ND-1.1	91	June
β-HCH	0.2±0.1	ND-4.14	73	November
Dieldrin	0.2±0.2	ND-2.3	61	April
Heptachlor	0.01±0.02	ND-0.06	30	November
p,p'-DDE	0.13±0.06	ND-2.0	55	April
p,p'-DDD	0.21±0.05	ND-0.87	63	March
p,p'-DDT	0.4±0.17	ND-1.7	81	October

Table 2: Summary of OC pesticides residues in sediment samples of Ramgrarh water reservoir.

Insecticide (µg/mg)	Mean±SEM	Range	%occurrence	Month with maximum concentration
α-HCH	0.2±0.05	ND-1.07	73	October
γ-HCH	0.5±0.11	ND-1.9	91	October
β-HCH	0.9±0.39	ND-8.2	81	October
Dieldrin	0.9±0.28	ND-5.3	96	November
Heptachlor	0.1±0.05	ND-0.77	32	March
p,p'-DDE	0.3±0.08	ND-1.5	82	November
p,p'-DDD	1.4±0.49	ND-10.5	81	January
p,p'-DDT	1.0±0.39	ND-7.23	67	January

Table 3: The monthly variation in residues of OC pesticide on applying ANOVA

Insecticide	Water	Sediment
α-HCH	*P*<0.05*	*P*<0.05*
γ-HCH	*P*<0.05*	*P*<0.05*
β-HCH	*P*<0.05*	*P*<0.05*
Dieldrin	NS	NS
Heptachlor	*P*<0.05*	NS
p,p'-DDE	*P*<0.05*	NS
p,p'-DDD	*P*<0.05*	NS
p,p'-DDT	NS	NS

*Significant
NS-not significant

In Sediment

Sediment may be considered as a more stable base for contamination studies and can identify pollution source that could escape detection by water surveillance alone (Forstner and Wittmann 1979) [14]. Monthly variation in the level of organochlorine pesticide residues the sediment of Ramgarh reservoir is presented in fig-2. The mean total residues of OC pesticides ranged from 1.0 to 13.0 µg/g (dry weight) during study period.

Total HCH concentration accounted for about 35 percent of total residue concentration. The active γ- isomer was present in 90 percent, with maximum mean concentration of in

October (Table-2). The α HCH, γ HCH and β HCH accounted for 4 percent, 17 percent and 15 percent of total residue of OC pesticides, with frequency distribution of 72, 90, and 81 percent respectively.

Total HCH ranged from 0.1- 8.5μg.ml^{-1}, with average of 2 μg.ml^{-1}. The maximum quantity of this was observed in October and in following months a declining trend has been found up to June (fig-2), thereafter an increasing trend in the concentration was observed up to September. The monthly variation in distribution of α HCH and γ HCH and β HCH in sediment were found significant (p<0.05).

The residues of heptachlor, constituted nearly 2 percent of total residues with frequency distribution of 32 percent. The maximum average quantity of heptachlor was observed in March and minimum in July. The monthly distribution of heptachlor was not found significant(Table-3). The mean residue of dieldrin was 0.9 μg.ml^{-1}, constituted 15 percent of total residues and found in 96 percent of samples. The maximum concentration was observed in November and minimum in June (fig-2). The monthly distribution of dieldrin in bottom sediment was not found significant (Table-3).

The residues of p,p'-DDT and its metabolites constituted maximum part (47 %) of residues. The p,p'- DDE was found in 82 percent of samples followed by p,p'- DDD (81 percent) and p,p'- DDT (67 percent). The maximum mean concentration of p,p'-DDE was observed in November. However, monthly variation in distribution of p,p'-DDT and its metabolites were not significant (Table-3).The concentration of residues of OC pesticide in sediment was more than in water samples. The organic matter contents in sediment (Renet *et al* 1986) [15] and low solubility of OC in water could have been the main factors of organic contamination in sediment. However, in the present work organic phase in the sediment was not determined.

Lichtenberg (1970) [16] studied Organochlorine pesticide contamination in different river of US. Reich *et al* (1986) [17] reported the residues of OCs in Northern Alabama ecosystem. Cova *et al* (1990) [18] focused on toxicological aspect of pesticide chemical interaction in drinking water. Poissant and Koprivnjak (1996) [19] studied fate of atmospheric concentration of α and γ HCH in Quebec, Canada. Rajendran and Subramanian (1999) [20] reported chlorinated pesticide residues in surface sediment of river Kaveri, India. Dua *et al* (1996) [5] and Kumari *et al.* (1996) [6] reported organochlorine insecticides in various ponds of India. Abbassy *et al* (1999) [7] showed organochlorine pesticide and polychlorinated biphenyls in the water of Nile, Egypt.

Conclusion

Organochlorine pesticides (technical HCH and DDT) have extensively used in India due to their wide spectrum application. The residue of OC pesticide can move thousand kilometers from the point of release through atmosphere as gases and aerosols. Water can provide a means of transporting from one place to another. Water and soil becomes the ultimate sink for most of the contaminants. The indiscriminate use, and due persistent properties, these compounds were found in water and sediment of Ramgarh reservoir. The seasonal variation in the distribution of residues of OC pesticide reflected their use. The behaviour of residues in water and sediment is of great concern, since disappearance, persistence or partial transformation of such compounds may helpful in determining the target affectivity and the non-target effects.

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