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Organochlorines and Polycyclic Aromatic Hydrocarbons in the Sediments of Ganges River (India)

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Organochlorine (OC) insecticides have been extensively used in India since 1954 in agriculture as well as public health sector(Gupta 1986). The use of OCs which are banned or restricted in most developed countries are still being used in this country. The major factors responsible for detrimental effects on the environment from use of these chemicals are that they are very persistent, extremely toxic to fish, used more as preventive measures rather than cure in controlling insects and some of them were found to biomagnify in organisms (Edwards 1970). Their accumulation in low concentration in the body fat of mammals may pose health problems in long run (Metcalf 1977) and it has been reported that most Indians accumulate about 26 mg DDT in their body through food items. Polycyclic aromatic hydrocarbons (PAHs) are formed as a result of incomplete combustion of organic compounds but may also be synthesized by some bacteria, algae and plants (Andelman and Snodgrass 1974; Harrison et al. 1975). PAHs are on the USEPA and EC priority pollutants list since some PAHs are known or suspected carcinogens/mutagens. In surface waters, they are known to be strongly adsorbed on sediment clays (Strosher and Hodgson 1975) and other particles while their degradation in sediment also occur (Neff 1979). Therefore, during low stream flow, fluvial materials settle down and may contain concentrations of OCs and PAHs. Hence , it is necessary to include sediment in the determination of organic contaminants in surface waters.

No OC pesticides in the water samples of Hoogly estuary (Ganges in Bengal) were detected, however, particulate matter and sediments have been found to contain ppb levels of BHC and DDT residues (Joshi and Ghosh 1982). In another study, the concentration of DDT in water samples varied from 0.004-0.0000006 mg/l in 12 samples out of 35 samples analyzed (Haldar et al. 1989). In typical study conducted by the Geography Department (1990) of Aligarh Muslim University revealed that in the selected area (between Narora and Kannauj) of the Ganges plain, the OC pesticides used for crop protection was about 0.46 Kg/hectare. It has

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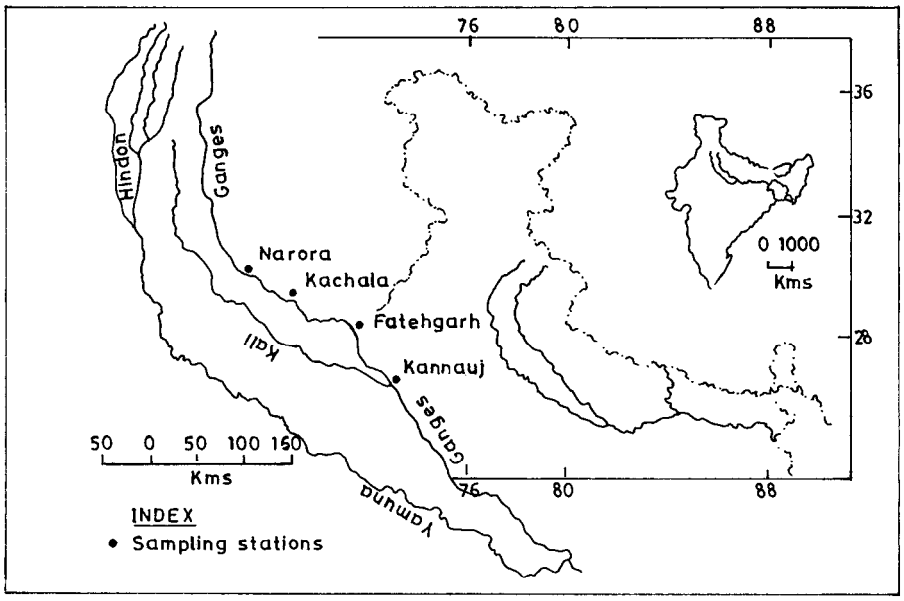

Fig. 1 - Showing Sampling Stations

been documented (Anon. 1985) that 40% of pollution in Ganges river was due to sewage discharge and 13% owing to chemical wastes released from factories. Several methods reported for analysis of PAHs and OCs in sediments and soil are by TLC (Poole et al. 1987) GC (Cooper et al. 1987) HPLC (Coover et al. 1978) GC and GC/MS (Hawthrone and Miller 1987) GC-MS-simca pattern (Vogt et al. 1987) GC-ECD, GC-FID (Malins et al. 1987) and simultaneous dual capillary column, dual detectors, followed by GC (Durell and Sauer 1990). The sediment samples from Ganges river collected in 1988-1989 were screened for the presence of OC pesticides and PAHs. GC-MS remained the choice of technique due to its sensitivity and ability to identify the compounds. Coupled GC-MS avoids interference which may occur in GC by using a separate method (other than retention time or volume) to identify compounds. A review of literature revealed that no work of this kind has been reported for Ganges river in Uttar Pradesh province so far.

The Ganges river flow through a distance of 2525 Km before its confluence with Yamuna river at Allahabad. The present study covers about 236 Km of the Ganges from Narora to Kannauj in Uttar Pradesh Province. Four sampling stations selected were Narora, Kachala, Fatehgarh and Kannauj. The river is considered to be relatively less polluted along this stretch due to comparatively less urbanization and industrial establishments, Figure 1 shows the sampling spots. The major source of pollution in the Ganges river along the belt under study is the domestic sewage discharge coming from densely populated settlements along the river bank and

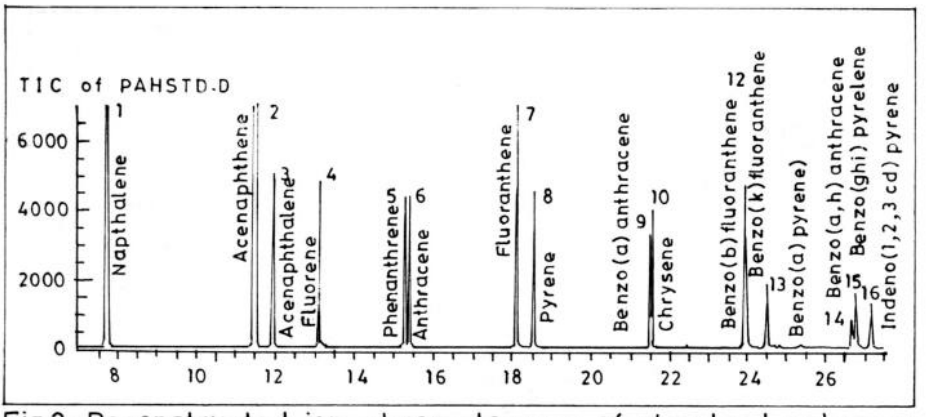

Fig.2-Reconstructed ion chromatogram of standard polyaromatic hydrocarbons

surface run off. However, no measurement could be made about the volume of waste discharge.

This paper refers to a monitoring programme for screening the OCs and PAHs concentrations in the Ganges river sediments. Further, to the Authors knowledge, it is the first effort carried out to monitor these organic contaminants in the reported region. There are only few reports available in the literature on the distribution of pesticides in Indian rivers, particularly Ganges.

MATERIALS AND METHODS

Hewlett-Packard Model HP-5880 gas chromatograph coupled with HP-5970 MSD and HP-7914 data system was used for the chromatographic separationand identification of OCs and PAHs. Fused silica column HP1, 13mX0.20mm I.D (0.33µ film thickness) interfaced directly to MS ion source was used for chromatographic separations. One µL sample was injected into the column using splitless mode with carrier gas (He) flow rate at 1.0 ml/min. Temperatures: Injector temperature 200°C, GC-MS interface temperature 280°C. Mass spectrometer was in Selected Ion Mode (SIM) with dwell time 100 ms/ion. Samples were also analyzed in the scan mode. Conditions: scan range m/z 50-500, scan threshold 15, solvent delay 2 min., dwell time 2 ms/ion. The identification of individual peak in the total ion chromatogram was done by HP-7914 data system having a NBS mass spectra library of about 40,000 compounds.

Fisher (Pesticide) grade methylene chloride was used after twice distilled in all glass apparatus. HPLC grade water was used for all extraction analysis in the laboratory. Analar grade NaOH and HSO_4 were used to make basic (pH>11.0) and acidic (pH<2.0) extractions. Granular anhydrous sodium sulphate of reagent grade was used after washing with acetone, hexane and finally with methylene chloride as drying bed after overnight heating at 250°C. Glassware was soaked in

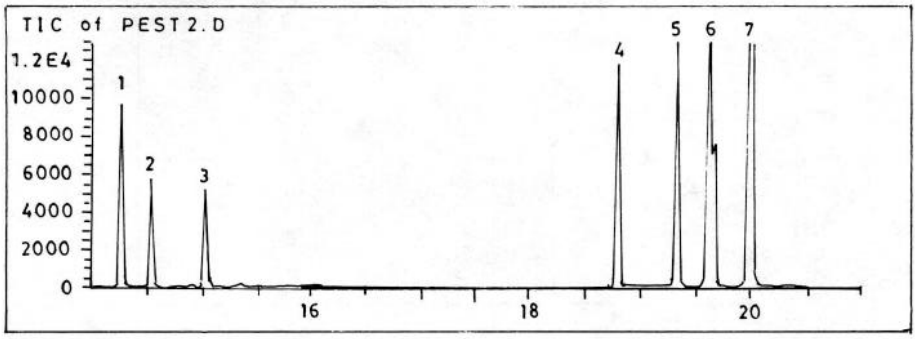

Fig. 3 - Computer reconstructed ion chromatogram of standard pesticides

Peaks: 1. α-BHC; 2. β-BHC; 3. δ-BHC; 4. Endosulfan-I & pp'DDE; 5. Endrin; 6. 4,4'DDD; 7. Endosulfan-II

chromate cleaning solution washed with water and rinsed with acetone and methylene chloride before use.

Commercially available Supelco Basel, (Switzerland) grade standards were used for the quantification and identification of OCs and PAHs.

The sediments collected from a depth of 15-20 cm of the surface from five places of each sampling station were transported to the laboratory in polyethylene bags where they were extracted as per U.S. Geological Surveys (1987) standard recommended procedures, The combined fraction from acid and base extractions was concentrated to 1.0 ml by Kunderna-Danish concentrator at a temperature of 60-65° C on water bath for 15 to 20 minutes.

The organic content was determined as per U.S. Geological Surveys (1987) procedure.

RESULTS AND DISCUSSION

Sixteen OC pesticides and PAHs selected to monitor the OC and PAH pollution in the sediments of Ganges river are tabulated in Table-l. Analysis was carried out using Gas Chromatography-Mass Spectrometry (GC-MS) technique.

A typical computerized reconstructed ion chromatogram of OCs and PAHs for which the sediment samples were analyzed are shown in Figures 2 and 3. The behavior in respect of peak shapes and separation of OCs and PAHs are very good.

From the results (Table l), it can be seen that out of sixteen samples analyzed, OCs and PAHs were not detected in three samples viz., Narora and Fatehgarh in December and Kannauj in October. The total OCs residues along the stretch under this study in different sediment samples ranged between 0.038 (Fatehgarh) and

Table 1. Organochlorine and polycyclic aromatic hydrocarbons in sediments of the Ganges River µg/g in 1988.

Organic Compounds	Sampling Stations															
	Narora				Kachala				Fatehgarh				Kannauj			
	Mar.	June	Oct.	Dec.	Mar.	June	Oct.	Dec.	Mar.	June	Oct.	Dec.	Mar.	June	Oct.	Dec.
α-BHC	0.002	ND	ND	ND	0.001	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
β-BHC	0.004	ND	ND	ND	0.002	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
γ-BHC	0.002	0.004	ND	ND	0.006	0.01	0.002	0.002	0.004	0.014	0.006	ND	ND	ND	ND	ND
Endosulfan-I	0.002	ND	ND	ND	0.002	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endosulfan-II	0.0004	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
p-p'-DDT	0.002	ND	ND	ND	0.016	ND	ND	0.004	ND	ND	ND	ND	ND	ND	ND	ND
p-p'-DDE	0.002	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
p-p'-DDD	0.0004	ND	ND	ND	0.002	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin	0.001	0.012	ND	ND	0.002	0.004	0.001	0.002	0.008	0.002	ND	ND	ND	0.006	ND	ND
Dieldrin	0.002	0.008	ND	ND	0.004	0.014	0.002	0.002	ND	ND	ND	ND	0.008	0.006	ND	ND
Endrin	0.001	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor	0.002	ND	0.002	ND	0.002	0.008	0.002	0.001	ND	ND	ND	ND	ND	ND	ND	0.006
Heptachlor epoxide	0.008	0.002	ND	ND	0.016	0.006	0.002	0.01	ND	0.002	ND	ND	0.018	0.002	ND	ND
Hexachlorobenzene	0.004	ND	ND	ND	0.001	0.001	0.002	ND	ND	0.002	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	0.008	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Phenanthrene	0.002	0.002	ND	ND	0.006	0.004	0.001	0.018	0.002	0.002	0.002	ND	ND	ND	ND	ND
Organic Matter (%)	0.453	0.186	0.482	0.105	0.111	0.091	0.478	0.103	0.075	0.226	0.259	0.388	0.045	0.123	0.116	0.123

ND = Not Detected

0.129 µg/g (Kachala). Of the various OCs detected, γ-BHC, aldrin, dieldrin, heptachlor and heptachlor epoxide were frequently detected, being identified in 56% (0.002-0.014), 56% (0.0012-0.12) 50% (0.002-0.014) 43% (0.0014-0.008) and 53% (0.002-0.018 µg/g), respectively, of the samples analyzed. Phenanthrene of PAH group was identified in 56% (0.0002-0.0176 µg/g) of the samples analyzed. PAHs were not detected at Kannauj. Benzo(a)pyrene was only detected at Narora in March. Generally low levels of organic contaminants were detected.

Since among the BHC, only the γ-isomer (lindane) was detected more frequently, it seems quit possible that α- and β- BHC were isomerized to the γ-isomer. This transformation could have been caused by bacterial activity and ultraviolet radiation in the water columns (Lenardon et al. 1984) and ultimately sink to the sediments. γ-BHC is more resistant to biological and chemical degradation under aerobic conditions (El Beit et al. 1981). It has been reported that γ- and β - isomers have very high mammalian toxicity (Tomizawa 1977). The α- and β- isomers were only detected at Narora and Kachala in March.

Heptachlor epoxide was detected more often and in higher concentration than its parent compound, Aldrin and dieldrin were detected throughout the stretch with maximum concentration at Kachala. The presence of aldrin which is known to undergo epioxidation to form dieldrin, it is possible to attribute the presence of these compounds to a local source of application (Lenardon et al. 1984). Apparently dieldrin is more resistant to degradation than aldrin (Tu and Miles 1976). Eldrin being highly degradable was only detected once.

DDT and its degraded residues were detected only in a few samples at Narora and Kachala. Under the National Malaria Eradication Programme (NMEP) of Government of India, DDT is now mainly used for vector control (Gupta, 1986). Nearly 85% of the DDT produced in India is used for mosquito control (Singh et al. 1988) therefore, the levels of ΣDDT observed could be attributed to municipal wastewater inflow from residential area into the river.

Low concentrations of endosulfan and hexachlorobenzene (HCB) were detected. As HCB is rarely used, its presence may be due to the use of pesticides containing HCB as an impurity (Umera et al., 1988). Serious fish kills due to endosulfan have occurred in Rhine river in Europe (Greve and Wit 1971).

It has been reported that one of the most important factors affecting the adsorption of OCs (Renate et al. 1986) and PAHs (Claude et al. 1986) by sediments is the organic matter content, The organic matter content (Table 1) observed in our study ranged between 0.045 and 0.482%. There seem to be no correlation between organic matter and the organic contaminants.

The population living along the bank of the river or around its vicinity are predominantly rural and agricultural. Although the OCs are the dominant group of

pesticides used for agriculture, but their consumption is very low and the frequency for vector control is also less, Narora is a recreational area. Narora and Kachala are densely populated along the bank of the river as compared to Fatehgarh and Kannauj where the residential area are quite far away. There is possibly very little contribution to pesticide levels as a result of agricultural runoff. It is very likely that these contaminants have been introduced into the river through municipal/sewage wastewaters from the residential settlements. Similar observations have been made (Wiersma et al. 1972) earlier, where city soil were found to be higher in pesticides than agricultural areas in monitoring the influence of local land use upon water bodies.

Kachala was comparatively the most polluted area, followed by Narora and least polluted were Fatehgarh and Kannauj. The consumption of the pesticides, particularly OCs for agriculture in the study belt is very low. Therefore,the contribution due to agricultural runoff is negligible. The major source of the contaminants is possibly the municipal/sewage wastewaters originating from residential areas.

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