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Polycyclic Aromatic Hydrocarbons in Sediments from Kolleru Wetland in India

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Polycyclic aromatic hydrocarbons (PAHs) form a large group of organic compounds, characterised by the presence of two or more condensed aromatic rings. A number of PAHs are considered hazardous to human health (Samiullah1985; IARC 1983; WHO 1984) and effects on birds and aquatic organisms (Connell and Miller 1981a; 1981b; Miller and Connell 1980; Miller 1982). The main sources of PAHs are domestic, industrial and agricultural wastes, atmospheric inputs (Hoffman et al. 1984; Takada et al. 1990; Wild et al. 1990a; 1990b) combustion of fossil fuels (NAS 1972), traffic, domestic heaters, electricity production and coke production from coal, and natural sources (Eadie et al. 1982; Wakeham et al. 1980; Laflamme and Hites 1978; Christensen and Zhang 1993). There is a slow accumulation of fossil hydrocarbons by organisms living in polluted waters (Spacie and Hamelink 1995). Because of their high stability, hydrocarbons tend to be preserved in the fish and enter into humans consuming the contaminated fish. Thus the high toxicity of aromatic hydrocarbons can be a potential public health risk (Grimmer 1983). Most studies show that atmospheric input is one of the sources of PAHs to sediments and soils, especially for remote sites (Takada et al. 1990).

Kolleru Lake, a valuable wetland, is situated in India between latitude $16^0 32^1$ and $16^0 47^1$N and longitude $81^0 05^1$ and $81^0 27^1$ E (Figure-1). The lake produces fish and is an important sanctuary for indigenous and migrating birds, particularly in winter seasons. Kolleru Lake fish is the staple food for the people living in the lake region. The lake is solely connected to the Bay of Bengal through Upputeru river at a distance of 60 km. The catchment area of the lake is 4763 km^2. The wetland is subjected to environmental pollution by sewage, industrial and aquaculture waste, agricultural run-off and other human activities. The lake receives water through drains, channels and rivers carrying silt and organic matter. Industrial effluents from chemical, distilleries, tanneries, sugar, paper and oil industries are discharged into the lake by such systems. In addition, domestic waste from surrounding towns and villages, agricultural runoff from fields, and waste from aquaculture ponds in the lake region directly enter the lake. The lake water is used for drinking and agriculture and aquaculture purposes. Since sediment acts as the main potential source for persistent chemical pollution, its analysis has been used to detect polycyclic aromatic hydrocarbons (PAHs) and assess ecological effects. There

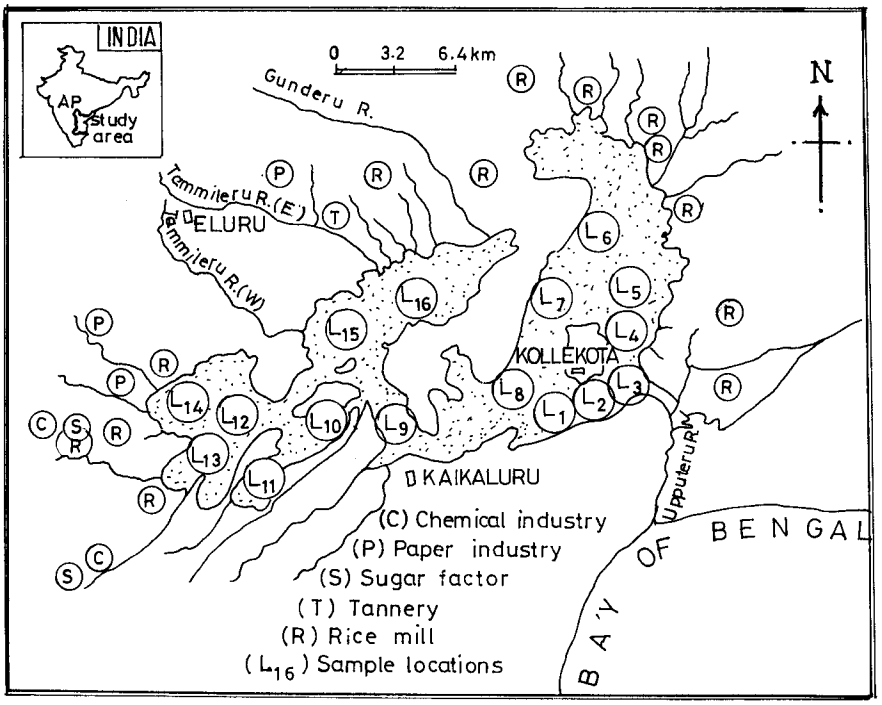

Figure 1. Sampling locations in Kolleru Lake

have been many qualitative studies of PAHs in sediments from world lakes (Christensen and Zhang 1993; Wakeham et al..1980; Eadie 1984). Such studies on PAHs levels in lake sediments have not been carried out in India. Therefore the main objective of the present study was to establish the baseline levels of polycyclic aromatic hydrocarbons in sediments.

MATERIALS AND METHODS

Analytical grade benzene was used for the extraction of polycyclic aromatic hydrocarbons (PAHs). Florisil and glass wool were pre-extracted with benzene. The florisil was heated at 300^{0}C overnight while glass wool was heated at 100^{0}C. PAH standards and florisil (60-80 mesh) were procured from Aldrich Chemical Co., Ltd. USA. All glassware was benzene rinsed.

Surface sediment samples (0-5cm) were collected using a stainless steel grab sampler in wide mouthed glass jars at sixteen locations for three seasons a year over three years. The locations are shown in the Fig-1. Samples were stored on ice and then processed immediately upon return to the laboratory. Before analysis, the sediment samples were freed from granules and shells. The samples were well mixed in a pre-cleaned aluminum plate and air-dried at ambient temperature for 48 hours, oven-dried at 45^{0}C and powdered.

After mixing thoroughly, 0.5 kg of dried sediment was soxhlet extracted for 12 hr with analytical grade benzene. The extract was concentrated to 10 ml using a rotary flash evaporator and transferred to a prewashed glass vial. The extract was concentrated to about 1 ml and was cleaned by passing through a florisil column (15 g-deactivated Florisil with water 2% v/w) to remove the co-extracted matter from the extract, which interferes with the chromatographic determination. The florisil column was eluted with 100 ml benzene. All extracts were filtered prior to analysis using a 0.5 μm filter.

Extracts were analyzed by high-pressure liquid chromatography (Schimadzu LC.6A Model). 2μl injections of the extract were separated on Shippack CLC-ODS reverse phase stainless steel column of 6mm ID x 150 mm length with a mixture of acetonitrile and water (80:20) running over 30 min at a flow rate of 2.0 ml/min. PAHs were detected using a UV detector. Data were quantified using a Microprocessor LR-4A. PAH identification was based on retention times with those of standard samples. The eleven PAHs compounds quantified were anthracene, fluroanthene, pyrene, crysene, benzo (a) pyrene, dibenzo (ac) anthracene, dibenzo (ah) anthracene, benzo (ghi) perylene and corenene. Total values of perylene and benzo (e) pyrene are reported, as they were not resolved. Organic matter in sediments was determined according to the chromic acid digestion method (Hayward 1953).

Fortified solutions were made up in HPLC grade benzene and at concentrations between 0.1 and 5 μg/μl of selected PAHs. 1kg of dried sediment sample was fortified with different concentrations of selected PAHs. The control sediment sample and fortified sediment samples were extracted with benzene to establish the minimum detectable limit (MDL) and percentage recovery. Recovery of PAHs was in the 80 to 95% range. The minimum detectable limit (MDL) for PAHs is 43 ng/g, but for benzo (ghi) perylene, dibenzo (ac) anthracene and dibenzo (ah) anthracene minimum detectable limit is 226 ng/g. None of the data reported were corrected for recovery. The control sample analysis was carried out to check for solvent impurities and no peak was identified.

RESULTS AND DISCUSSION

The sediment samples collected from Kolleru Lake can be divided into eastern zone (L_1 - L_8) and western zone (L_9-L_{16}) samples. The mean and range of polycyclic aromatic hydrocarbons (PAHs) in sediments from these zones are presented in Table 1 and 2. The concentrations of PAHs in sediments are compared with sediment quality guidelines (CEQG 1999; MacDonald et al. 2000). PAH sediment quality guidelines for the protection of aquatic life on a dry weight basis are anthracene (5.87μg/kg), fluoranthene (111 μg/kg), pyrene (53.0 μg/kg), chrysene (57.1 μg/kg), benzo (a) pyrene (31.9 μg/kg) and isomers of dibenz(ah)anthracene (6.22 μg/kg). The percentage of organic matter content in Lake Sediments from eastern zone and western zone on an average ranged between 4.0 to 6.7 and 3.4 to 6.2, respectively.

Sediment of the lake were found to be contaminated with various PAHs and they were higher than the standards (CEQG 1999; MacDonald et al. 2000). High concentrations of PAHs were detected in sediments of the eastern zone in comparison to those of western zone. This can be attributed to the fact that most of the rivers, drains and channel waters carry large quantities of sewage and industrial waste, agricultural runoff, silt and organic matter into the western zone. However, the eastern zone is downstream, while the western zone has the chance of getting washed off by the continuous flow of water. Due to the high turbulence of rivers, drains and channels in the western zone, suspended particles settled at the eastern zone of the lake. Hence there is a greater chance for the accumulation of PAHs in the sediments of eastern zone. No important seasonal variation was observed in the concentrations of PAHs from Kolleru Lake.

Polycyclic aromatic hydrocarbons and excess nutrients can have profound environmental impacts (Grimmer 1983). Polycyclic aromatic hydrocarbons, pesticides, nutrients and heavy metals in water, sediments and fish from Kolleru Lake degraded the quality of Kolleru Lake water (Sreenivasa Rao 1997; Sreenivasa Rao and Ramamohana Rao 2000; 2001a; 2001b; Sreenivasa Rao et al. 1999). The values of total organic matter in sediments have shown variation between sampling points of eastern and western zones of the lake. The organic matter content in eastern zone sediments is higher than the western zone. The high content of organic matter of eastern zone sediments is primarily attributed to the relatively higher supply of organic matter from abundant vegetation, agricultural runoff, domestic waste and industrial effluents. The sediments of the western zone of the lake contain less organic matter, which is mainly due to dilution by the addition from rivers, drains, and channels. The higher PAH flux for sediment sample (L_2) may in part be related to the higher organic matter in lake sediments.

The increase in the concentrations of PAHs in lake sediments can be attributed to municipal and industrial effluents, watershed and agricultural runoff and atmospheric deposition. A significant proportion is applied to agricultural land adding nutrients and organic matter. Sewage waste contains PAHs and may be transferred from sediments to the human food chain after uptake by aquatic organisms like fish. Bioaccumulation of organic pollutants from sediments has been reported (Neff 1984). Bottom sediments, algae, higher water plants, zooplankton and fish accumulate benzo(a)pyrene to concentrations about 10^3-10^4 times that in water (Jones et al. 1989). PAHs have been found in sewage waste and agricultural soil (Wild et al. 1990a, 1990b).

In summary, the study indicates that polycyclic aromatic hydrocarbons (PAHs) and organic matter were highest in sediments from the eastern zone of Kolleru Lake and they were higher than the sediment quality guidelines for the protection of aquatic life. PAH content in Kolleru Lake wetland sediments may be accumulated by lake fish and enter humans and birds consuming the contaminated fish. The concentrations of PAHs in Kolleru wetland sediments noted here provide a baseline for future research into environmental contamination of the wetland.

Table 1. Mean and range of polycyclic aromatic hydrocarbons (PAHs) in sediments from eastern zone of Kolleru lake wetland (μg/kg, dry weight)

PAH	L_1	L_2	L_3	L_4	L_5	L_6	L_7	L_8
1	5.8 4.9 - 6.2	6.7 5.6 – 7.1	4.2 2.8 – 5.6	6.1 4.2 – 6.7	6.6 5.1 – 6.9	6.2 4.8 – 6.8	5.4 3.9 – 6	4.0 2.8 – 5.6
2	5.7 4.1 – 6.8	47.7 29.4 – 59	10.5 7.6 – 18	3.4 2.1 – 4.5	0.7 0.4 – 1.0	0.4 0.2 – 0.6	BDL	2.0 0.9 – 2.9
3	6.3 3.5 – 7.4	66 48 - 82	12.4 6.5 – 22	1.5 0.8 – 2.4	1.8 0.7 – 2.9	BDL	BDL	2.6 1.2 – 3.6
4	23.0 15 – 30	229 185 - 286	36 25 - 44	10.5 6.8 - 22	BDL	BDL	BDL	BDL
5	11.4 7.5 – 16	77 55 - 99	18 11 - 28	12.3 7.2 - 20	2.2 0.9 – 3.1	BDL	BDL	4.3 2.4 – 5.2
6	9 4.1 – 12	38 26 - 52	17 8.5 - 20	11 5.4 – 23	BDL	BDL	BDL	BDL
7	BDL	332 252 - 398	24 16 - 36	BDL	BDL	BDL	BDL	BDL
8	BDL	2.7 1.8 – 3.7	1.9 1.0 – 3.0	7 4.5 - 12	2.1 1.2 – 3.8	BDL	BDL	BDL
9	BDL	104 86 - 135	16 13 - 26	BDL	BDL	BDL	BDL	BDL
10	10.6 5.8 – 17	27.3 18 - 43	11 7.6 – 19	23.8 14.8 – 31	7.5 5.2 – 12	20.9 11.5 – 36	13.9 8.2 – 20	11.5 6.5 – 24
11	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Note: 1). Organic Matter, 2). Anthracene, 3). Fluroanthene, 4). Pyrene, 5). Crysene, 6). Total of Benzo (e) Pyrene and Perylene, 7). 1,2,3,4 Dibenzanthracene, 8). Benzo (a) Pyrene, 9). 1,2,5,6 Dibenzan-thracene, 10). Bnzo(ghi) perylene, 11). Coronene, $L_1 - L_{16}$: Sampling Locations, BDL : Below Detectable Limit

Table 2. Mean and range of polycyclic aromatic hydrocarbons (PAHs) in sediments from western zone of Kolleru lake wetland (μg/kg, dry weight)

PAH	L_9	L_{10}	L_{11}	L_{12}	L_{13}	L_{14}	L_{15}	L_{16}
1	5.6 3.8 – 5.9	5.1 3.4 – 6	5.4 4.1 – 6.8	3.4 2.6 – 4.6	6.2 4.5 – 6.9	5.8 3.8 – 6.5	4.8 2.4 – 7	5.2 3.6 – 6.2
2	0.2 0.1 – 0.3	BDL	0.4 0.2 – 0.5	0.9 0.3 – 1.6	BDL	BDL	1.2 0.8 – 2.6	1.6 0.6 – 2.4
3	BDL	BDL	BDL	BDL	BDL	BDL	11.2 6.8 – 20	36.5 19.5 - 48
4	2.3 1.8 – 3.4	BDL	BDL	BDL	BDL	0.36 0.2 – 0.5	33.0 21 - 47	BDL
5	2.1 1.2 – 2.8	BDL	BDL	2.6 1.2 – 4.5	0.8 0.3 – 1.2	0.9 0.3 – 1.9	3.4 2.5 – 5.6	4.4 3.2 – 6.4
6	BDL	BDL	BDL	BDL	BDL	BDL	5.2 3.9 – 6.5	0.3 0.1 – 0.5
7	BDL	BDL	BDL	BDL	BDL	BDL	2.8 1.4 – 3.8	BDL
8	BDL	BDL	BDL	BDL	BDL	BDL	BDL	21.5 9.4 – 39
9	BDL	BDL	BDL	BDL	BDL	BDL	BDL	41.3 29 – 62
10	BDL	BDL	BDL	20.5 9.8 – 36.4	65 42 – 82	12.8 6.5 – 18	29 15 - 44	102 85 – 137
11	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Note: 1). Organic Matter, 2). Anthracene, 3). Fluroanthene, 4). Pyrene, 5). Crysene, 6). Total of Benzo (e) Pyrene and Perylene, 7). 1,2,3,4 Dibenzanthracene, 8). Benzo (a) Pyrene, 9). 1,2,5,6 Dibenzan-thracene, 10).B nzo(ghi) perylene, 11). Coronene, $L_1 – L_{16}$: Sampling Locations, BDL : Below Detectable Limit

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