

Occurrence and Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Bolgoda and Beira Lakes, Sri Lanka

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Abstract The pollution of polycyclic aromatic hydrocarbons (PAHs) has been widely used to assess the potential impact of anthropogenic activities on aquatic environments because their occurrence in water is closely tied to urban activities. Many PAHs possess mutagenic and carcinogenic properties (Menzie et al. 1992). PAH distribution and toxic potentials have therefore been the focus of numerous studies in waterways including the Great Lakes (USEPA Report 1994), Yanisei Bay (Dahle et al., 2003), and the Fraser River basin (Yunker et al., 2002). Sri Lanka, a small island nation with a dense population of about 20 million people, faces a multitude of environmental stresses ranging from deforestation to traffic congestion and the deterioration of water quality. This study was undertaken to understand the occurrence, sources, and potential impacts of PAHs in the waterways of Sri Lanka. Two lakes, Beira and Bolgoda, were selected for the study due to their economic value and high level of pollution. Beira Lake, situated in downtown Colombo, the capital city of Sri Lanka, is highly polluted. Sources of pollution are multifarious. For instance, clusters of communities have sprung up along the edges of the lake in recent times and many shacks have been built. These communities are generally not connected to municipal sewer systems and substantial quantities of domestic sewage and untreated wastewaters are discharged directly into the lake. Small industries have also grown rapidly around the lakes, most of which are not

believed to have adequate facilities to treat industrial wastewater, especially organic wastes. In addition, Sri Lanka has experienced an upsurge of motor vehicles, including millions of three-wheelers and minivans that are powered by leaded gasoline and diesel fuels. Traffic congestion and severe air pollution due to vehicle emissions are now common daily occurrences and are considered a major potential source of PAHs in the lakes. Although Bolgoda Lake is situated some distance from Colombo, it is heavily polluted due to the growing number of towns with an attendant increase in small businesses and various industries along its shores. These new developments have undoubtedly impacted the lake through the discharge of PAHs and other anthropogenic chemicals present in industrial wastewater and from street runoffs. The lake, additionally, receives a large quantity of pollutants from the industrial zone in the north.

The pollution caused by PAHs has led to various studies on the distribution and origin of PAHs in the environment (Yunker et al., 1996; Budzinski et al., 1997). Based on the proportions of different PAHs, most studies aim to distinguish PAHs of petrogenic sources from those of pyrolytic origins. The PAHs of petrogenic origin, prevalent in coals and fossil fuels, are formed from diagenesis of sedimentary organic material under low to moderate temperature and tend to consist of low-molecular-weight PAHs with two to three aromatic rings (Potter et al., 1998). The pyrolytic PAHs, on the other hand, are formed at much higher temperatures (greater than 500°C for example) and consist mainly of four or more aromatic rings (Commings, 1969). Thus, an increase in the proportion of higher-molecular-weight PAHs is taken to be indicative of contaminations of mainly pyrolytic origin. The prevalence of high-molecular-weight PAHs in the urban dusts (Wise et al., 1988) and in atmospheric particles (Sicre et al., 1987) illustrates the

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chemistry of their formation at high temperature. The purpose of this study was to determine the PAH concentrations and distribution with respect to sampling location, origin and sources in two polluted lakes.

Materials and Methods

Figure 1 shows a map of Beira and Bolgoda Lakes, indicating the various sampling sites. In comparison to most lakes around the world, both lakes are characterized by extreme shallowness with an average depth of 2–3 m. Being in a tropical region near the equator, they experience little seasonal variation of water temperature (26–28°C) and receive frequent rainstorms, ranging from local thunderstorms that can occur almost daily to the southwest monsoons from May to September. In the catchment area where the lakes are located, rainfall ranges from about 4 in. in January to nearly 14 in. in October.

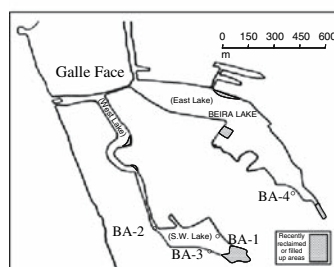
Surface sediment samples (0–3 cm) were collected using a scoop in the shallow point of selected sites during 2003–2004. Samples were collected in glass jars and were stored frozen at –20°C until analysis. Moist sediments were subjected to Soxhlet extraction. The methodology for the extraction and fractionation is similar to that described by O'Malley (O'Malley et al., 1994). Briefly, 10 g of sediment was extracted with 50 mL of dichloromethane at three cycles per hour for 24 hours. After cooling to ambient temperature, residual water was removed by adding 2–3 g of sodium sulfate. The contents were then evaporated at 35°C to near dryness (1–2 mL) and then to dryness under a gentle stream of nitrogen. The PAH fraction was then enriched using silica-gel chromatography as follows. A slurry of activated silica gel in dichloromethane was transferred to a small glass column (10.0 cm x 1.0 cm internal diameter [I.D.]). The gel was equilibrated with 30 mL of pentane, 2 mL of the extract was loaded, 25 mL of pentane was passed through, and the PAH fraction was eluted with 25

mL of dichloromethane:pentane (4:6, v/v) and taken to dryness under a gentle stream of nitrogen. For analysis by high-performance liquid chromatography (HPLC), the extract was exchanged into acetonitrile. PAH recoveries were determined by adding known quantities of PAH mixtures to the sediments (5–10 grams) and subjected to the same extraction procedures. The extraction recoveries are summarized in Table 1.

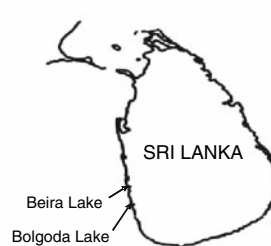
Water samples were also collected from the surface in 1-L amber glass bottles with screw caps. The water samples containing both dissolved and colloid-adsorbed PAHs were extracted using a separatory funnel. Into a 1-L separatory funnel, 500 mL of water sample and 50 mL of dichloromethane were added and extracted three times. PAH recoveries were checked by adding known quantities of PAH mixtures to distilled water. These spiked waters were then extracted using the same procedures (Table 1).

PAHs were analyzed by HPLC and gas chromatography coupled to mass spectrometry (GC/MS). To identify the individual PAHs, the HPLC procedure based on U.S. Environmental Protection Agency (U.S. EPA) Method 8310 was used. Quantitation was performed by the external standard method with individual PAH standards. The GC/MS methodology was based on U.S. EPA 625 Method. Samples were quantified by gas GC/MS on a Thermo Electron GCQ Plus ion trap mass spectrometer. Spiked samples containing a mixture of 11 PAHs and two reference compounds were analyzed every ten samples. Perfluoro-*n*-butylamine was used as the calibration compound to ensure instrument performance. Samples were separated and analyzed on an Altech DB-5MS capillary column (0.32 mm I.D. x 0.1 mm film thickness x 30 m). A Thermo Electron HS 2000 autosampler was used for all sample injections. Helium was used as carrier gas at a constant flow rate of 1.4 mL/min. The gas chromatograph oven temperature was programmed as follows. The initial temperature was maintained at 100°C and held for 1.0 min following injection. The temperature was then ramped at 20°C/min to 200°C and held there for 10 min. Finally the temperature was ramped at a rate of 10°C/min to 300°C.

Fig. 1 Sampling sites in Beira Lake (a) and Bolgoda Lake (b) in Sri Lanka



(A) BEIRA LAKE



(B) BOLGODA LAKE

The injection volume was 5 μL and the injector was maintained at 250°C. A splitless injection was used with septum purge operative throughout the analysis. The mass spectrometer was operated in electron impact mode for all analysis with an electron energy of 70 eV. A five point calibration routine was used for every analysis of each PAH, with at least one calibration point of higher or lower concentration than the concentration of the unknown

compound under consideration. The estimated minimum detection limits were 2.0 $\mu\text{g L}^{-1}$ for water samples and 5 $\mu\text{g kg}^{-1}$ for sediment samples.

Results and Discussion

As shown in the map (Fig. 1a) sampling in Beira Lake was conducted at four sites over a period of 18 months. Composite sediment and overlying water samples were collected from the sites and were analyzed for eleven parent PAHs. The overall concentration range for the sediments was found to be between 152 and 569 $\mu\text{g/kg}$ with an average of 329 $\mu\text{g/kg}$ dry sediment (Table 2). When the individual sites were compared, the total PAH concentrations from the BA-2 site were substantially below those obtained from the other sites (BA-1, BA-3, and BA-4). These sites are adjacent to an area of high traffic density, with numerous shops and small industries of various kinds in close proximity, thus direct local input of PAHs from the street runoff into the lake is probably most significant. Parts of the region around these sampling sites had recently undergone sediment dredging (hatched area) and are speculated to be heavily contaminated by metals and other contaminants.

Table 1 Extraction recoveries (%) determined in reference samples^a

PAH	Sediment	Water
Naphthalene	65	9
Acetnaphthene	84	11
Phenanthrene	99	41
Anthracene	60	35
Fluoranthene	92	51
Pyrene	95	42
Chrysene	101	30
Benzo[a]pyrene	75	8
Benzo[k]fluoranthene	92	33
Dibenz[ah]anthracene	74	21
1-nitropyrene	49	17

^a Mean recovery ($n = 3$)

Table 2 Average PAH^a and ratio of two-three ring^b to four-five ring^c PAHs from Beira and Bolgoda Lakes^d

a. Beira Lake	BA-1		BA-2		BA-3		BA-4					
<i>Water</i> (ng/L)												
Average PAH	78 ± 5.0		46 ± 3.0		112 ± 4.7		85 ± 5.6					
2–3 ring PAH	38 ± 2.0		38 ± 2.0		62 ± 4.0 ^c		56 ± 3.4					
4–5 ring PAH	112 ± 7.3		52 ± 3.5		154 ± 5.2		108 ± 7.3					
<i>Sediment</i> (µg/kg)												
Average PAH	569 ± 33.0		152 ± 8.1		465 ± 25.0		371 ± 21.0					
2–3 ring PAH	84 ± 4.3		82 ± 4.8		262 ± 12.5		100 ± 5.5					
4–5 ring PAH	973 ± 56.9		210 ± 10.9		635 ± 35.5		597 ± 33.8					
b. Bolgoda Lake	WG-1		WG-2		BNL-1		BNL-2		BSL		BG	
<i>Water</i> (ng/L)												
Average PAH	40 ± 2.2		127 ± 6.3		70 ± 3.7		67 ± 2.5		71 ± 2.6		71 ± 3.1	
2–3 ring PAH	34 ± 2.3		74 ± 3.5		61 ± 3.2		51 ± 2.3		60 ± 2.9		53 ± 2.6	
4–5 ring PAH	45 ± 2.1		171 ± 8.6		78 ± 4.2		81 ± 2.7		80 ± 2.4		86 ± 3.5	
<i>Sediment</i> (µg/kg)												
Average PAH	406 ± 24.1		865 ± 50.1		115 ± 6.2		934 ± 24.0		121 ± 6.8		249 ± 13.0	
2–3 ring PAH	83 ± 4.4		377 ± 22.8		65 ± 3.4		360 ± 18.5		88 ± 4.7		67 ± 3.8	
4–5 ring PAH	674 ± 40.6		1273 ± 72.9		156 ± 8.5		1413 ± 28.5		149 ± 8.5		400 ± 20.6	

^a Average of 11 PAH species: naphthalene, acetnaphthene, phenanthrene, anthracene, fluoranthene, benzo[k]fluoranthene, pyrene, chrysene, 1-Nitropyrene, benzo[o]pyrene, dibenz[a,h]anthracene

^b Average of 5 PAH species: naphthalene, acetnaphthene, phenanthrene, anthracene, fluoranthene

^c Average of 6 PAH species: benzo[k]fluoranthene, pyrene, chrysene, 1-Nitropyrene, benzo[o]pyrene, dibenz [a,h] anthracene

^d The mean \pm SEM ($n = 3$ –5)

The region around the B-2 site by comparison is less populated and the traffic not as congested.

The results from the analysis of overlying water samples in Beira Lake (Table 2a) show that PAH concentrations in the water column at the BA-2 site were also lower (46 ± 3.0 ng/L) than those of the other three sites, which ranged from 78 to 85 ng/L. On the other hand, a comparison of individual PAH concentrations in the sediment did not correlate well to those of water column at all sites (Fig. 2: BA-3 and BA-4 sites not shown), probably due to rapid mixing and transport of the PAH-adsorbed colloidal particles in the shallow water column. The majority of PAHs in the water column are expected to be associated with colloidal particles since PAHs have low aqueous solubility as indicated by their high $\log K_{ow}$ values (3.36 for naphthalene to 6.90 for coronene [Neff, 1979]). The reduced site-to-site variability of the PAH concentrations in the water column could also be explained by the rapid equilibration of the colloidal particles. Various external factors such as wind velocity over the evaporating surface, the frequency and intensity of rain storming events around the lakes, the effects of intense sunlight on PAH degradation, and the year-round warm water temperature probably influence the loading of PAHs in the lake.

Bolgoda Lake (Fig. 1b), like Beira Lake, is also located in the catchment area but some distance away from the city of Colombo. However, it is expected to experience a substantial PAH loading since the lake is surrounded by a fair number of small industries, such as incinerators and electricity power plants that are situated close to the lake, many of which produce gaseous emissions and generate wastewaters that are expected to contain high concentrations of PAHs. The PAH levels for the sediments in this lake ranged from 121 ± 6.8 $\mu\text{g/kg}$ at the BNL-1 site to 934 ± 24 $\mu\text{g/kg}$ sediment at the BNL-2 site with a mean of 448 $\mu\text{g/kg}$ sediment. Overall PAH levels in sediment samples in the Bolgoda Lake were thus somewhat higher than those of Beira Lake. The concentrations at the WG-2 site were also

high at 865 $\mu\text{g/kg}$. The potential sources of PAHs around the site are 16 small industries, including a number of gas stations and a chemical industry, most of which have the potential to discharge significant quantities of PAHs through wastewaters as well as gaseous emissions. In addition, Bolgoda Lake receives massive amounts of industrial effluents via the Ganga river, a major tributary flowing out of the Lady Catherine industrial zone in the north (Dehiwala area). The region around site WG-2 was probably impacted by the effluents from the industrial zone more than the other sites because of its location and other geologic characteristics. On the other hand, heavy contamination of the sediments in BNL-2 site in the west is probably attributable to the Panadura estuary where the exchange of lake water with the polluted sea coast occurs and possibly reflects localized geographic variation of some unknown origin. The extent of the contribution to the PAHs present in the industrial effluents from the industrial zone in Dehiwala area is unlikely to be important at this site because of the low levels of PAHs observed around the BNL-1 site, which is closer to the WG-2 site. Located in the general vicinity of the BNL-1 site are a number of small industries such as a garment factory, several gas stations, and a large farm. Also, the general area is not as congested and the population is somewhat smaller than the areas in the vicinity of other sites. These conditions perhaps explain the low levels of PAHs observed around the site. The PAH levels of the remaining sites (WG-1, BSL, and BG) were also low, ranging between 115 and 247 $\mu\text{g/Kg}$. BG and BSL sites have one to two gasoline stations each. None of the small industries in the area (for instance, hotels and shops) support activities expected to be directly associated with generation of PAHs. The total PAH concentrations for the six aqueous samples ranged from 40 to 127 ng/L with an average of 79 ng/L (Table 2b). The PAH distribution in the water column was thus similar to that of Beira Lake in that the PAH concentrations in the water column showed less variability for similar reasons (data not shown).

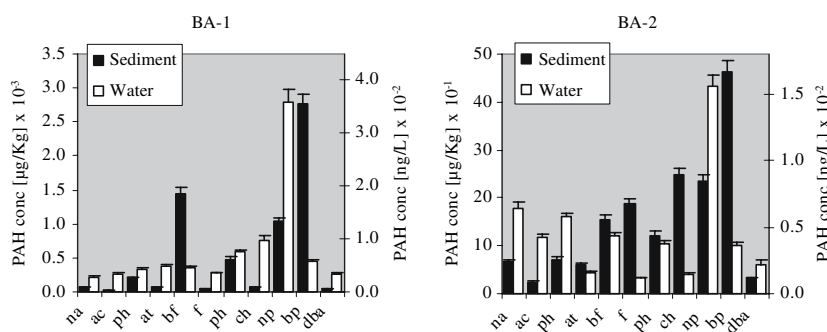


Fig. 2 PAH levels in water and sediments collected from two sites in Beira Lake. Values are mean \pm standard error of mean. np = naphthalene, ac = acetnaphthene, ph = phenanthracene, at = anthracene,

bf = benzo(k)fluoranthene, f = fluoranthene, p = pyrene, ch = chrysene, np = 1-Nitropyrene, bp = benzo(a)pyrene, dba = dibenzo(a,h)anthracene.

Another objective of this study was to determine potential sources of PAHs at each site. Total concentrations of four- to five-ring PAHs were compared to those of two- to three-ring PAHs. Of the eleven major parent PAHs analyzed, five had 4–5 aromatic rings (benzo[*k*]fluoranthene, pyrene, chrysene, benzo[*a*]pyrene, and dibenz[*a,h*]anthracene) and the remaining four PAHs had 2–3 rings (naphthalene, acenaphthene, phenanthrene, and anthracene). In Beira Lake inputs of PAH with 4–5 rings ranged from 58 to 66% of total concentrations for the water samples and 71 to 92% for the sediments (Table 2). A similar profile existed for Bolgoda Lake, where the PAHs with 4–5 rings comprised 57–62% for the water samples and 62–86% in the sediments. Thus, the distribution patterns of PAH in both lakes are indicative of dominant contributions from pyrolytic sources at all sites, although significant site-to-site variation existed. Alternatively, the concentration ratios of phenanthrene/anthracene (P/A) and fluoranthene/pyrene (F/P) have been applied to distinguish between PAHs of pyrogenic and petrogenic sources (Benner et al., 1990; Lake et al., 1979; Gschwend et al., 1981). This approach is based on the rationale that for parent PAHs, combustion processes under the conditions of limited oxygen availability tend to produce proportionately more PAH isomers with greater thermodynamic stability (Albert et al., 1988). For example, for the three ring PAHs, the more stable phenanthrene is expected to be produced in higher proportion than its isomer, anthracene, during the combustion processes. A report presented by Budzinski (Budzinski et al., 1997) showed that PAHs of pyrolytic origin generally have P/A ratios of 1–10. The study further showed that F/P ratios fall between 1 and 2 for the pyrolytic PAHs. The calculated values in Beira and Bolgoda lakes generally indicated dominance of pyrogenic sources, although there were exceptions (data not shown). For instance, the water samples collected from the BA-4 site had a P/A ratio of 14.5 and F/P ratio of 0.2, which suggested a strong input of petrogenic PAHs. The calculated values from this application are therefore in general agreement with the method based on the 4–5 ring/2–3 ring PAH ratios. In addition, the concentration of 1-nitropyrene was examined as PAHs are known to react with certain functional groups such as nitro groups ($-\text{NO}_2$) under high temperature conditions, forming nitrated PAHs (Paputa-Peck et al. 1988). For instance, emissions from combustion of fossil fuels, diesel fuels in particular, produce 1-nitropyrene and other related products. 1-Nitropyrene is potentially mutagenic and carcinogenic in humans (IARC 1998). As shown in Table 2, its levels were twice that of the average PAHs both in the sediment and water samples from Beira Lake, particularly in samples from the BA-1, BA-3, and BA-4 sites where the traffic flows are generally

heavy and the percentage of the vehicles powered by diesel fuels is high. Thus the results appear to reflect high local inputs of 1-nitropyrene generated by motor vehicles.

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