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Polycyclic aromatic hydrocarbon fingerprints in the Pichavaram mangrove-estuarine sediments, southeastern India

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Abstract

The sources and historical deposition of 16 polycyclic aromatic hydrocarbons (PAHs) were investigated in dated sediment cores from the Pichavaram mangrove-estuarine complex. The Σ PAH flux in mangrove and estuarine sediments are $0.064 \pm 0.031 \mu\text{g}/\text{cm}^2/\text{yr}$ and $0.043 \pm 0.020 \mu\text{g}/\text{cm}^2/\text{yr}$, respectively. The PAH flux in sediments increases up-core coinciding with rapid urbanization since the 1970s. The flux shows a decrease in recent years (since 1990) coinciding with less riverine discharge, and perhaps more effective implementation of environmental regulations. The sediments are dominated by low molecular weight PAHs suggesting anthropogenic input. Ratios of specific PAH isomer pairs suggest higher input of petrogenic over pyrogenic derived PAHs. Notably, the deposition of high molecular weight PAHs increase in mangrove surface sediments was due to lignite and firewood combustion. Because of their overall low concentrations in sediments it is unlikely these PAHs pose an immediate ecological hazard.

Key words: PAHs, sediment, mangrove, estuary, petrogenic, pyrogenic origin

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) have received much attention due to their carcinogenic and mutagenic potentials, and their ubiquitous presence in the environment (Flowers et al., 2002). PAHs enter the aquatic environment via industrial discharge, petroleum spills, combustion of fossil fuels, and various non-point source inputs such as agriculture, urban runoff, and atmospheric deposition (Yunker and McDonald, 2003; Ke et al., 2005; Cavalcante et al., 2009). Because of their low solubility and hydrophobic nature, PAHs adsorb to particulate matter and accumulate in sediments. Their stable molecular structure results in enhanced preservation and as a consequence, PAH analysis is a useful tool for paleoenvironmental reconstruction of anthropogenic processes in different environments such as lakes, rivers, estuaries, and marine sediments (Benlahcen et al., 1997; Yunker and McDonald, 2003; Christensen and Bzdusek, 2005; Cavalcante et al., 2009; Qiu et al., 2009; Choudhary and Routh, 2010).

Mangroves occur in the inter-tidal zones of tropical and sub-tropical regions that are very vulnerable to anthropogenic activities in coastal areas and upstream river sections. Therefore, it is not surprising that elevated concentrations of PAHs have been recorded in many estuarine and mangrove sites worldwide (Ke et al., 2005; Liu et al., 2009; Cavalcante et al., 2009). In this study, we investigated the ‘fingerprints’ of different PAHs in dated sediment cores from the Pichavaram mangrove-estuarine complex (Fig. 1) to trace their sources, and historical changes in depositional flux due to rapid urbanization in the catchment. We focused on 16 PAHs listed as priority pollutants by the US EPA (US EPA 1982) to trace their spatial and vertical distribution. The 16 PAHs were Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACP), Fluorene (FLR), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLT), Pyrene (PYR), Benz[*a*]anthracene (BaA), Chrysene (CHR), Benzo[*b*]fluoranthene (BbF), Benzo[*k*]fluoranthene (BkF),

Benzo[*a*]pyrene (BaP), Dibenz[*a,h*]anthracene (DhA), Indeno[1,2,3-*cd*]pyrene (IcP) and Benzo[*ghi*]perylene (BgP). Distribution of PAHs in Indian mangroves has rarely been investigated despite the fact these sensitive ecosystems are strongly affected by various anthropogenic activities. To the best of our knowledge, this is the first study providing temporal and spatial variation of PAH fluxes in an Indian mangrove. Our study should improve the understanding of PAH accumulation and historical changes in the Pichavaram mangroves that might be useful for knowledge of source apportionment, and tracing anthropogenic pollution in coastal areas.

2. Study area

The Pichavaram mangroves (latitude 11°23' - 11°30' and longitude 79°45' - 79°50'), are located between the Vellar and Coleroon River estuaries (Fig. 1). These tropical mangroves extend over 11 km² and consist of 51 islets, which are covered by forests (50%), waterways (40%), mud and sand flats (Kathiresan, 2000). The mangroves are dominated by tides, which are semi-diurnal in nature and the wave amplitude is up to 1 m. Alluvium is dominant in the western part, whereas fluvial, marine, and beach sands cover the eastern part of mangroves. Thirteen species of indigenous trees are present in the forests belonging to *Avicennia* and *Rhizophora* spp. (Kathiresan, 2000). The mangroves are influenced by anthropogenic pollutants from the Vellar and Coleroon estuaries as well as the Uppnaar River, and agricultural wastes from the Khan Saheb Canal. Various anthropogenic activities have resulted in a sharp decline (ca. 75%) of forest cover in the Pichavaram mangrove-estuarine complex (Kathiresan, 2000).

3. Methods

Five sediment cores were retrieved from the study area (Fig. 1). The locations were selected based on vegetation, land-use pattern, and pristine conditions vs. human-impacted sites. The first core near the Vellar estuary (core A) corresponded to a less vegetated and/or degraded

mangrove patch grazed by cattle, and had been logged for firewood. The second site (cores B, C, and D) corresponded to a dense undisturbed forested area in the mangroves. The third location (core E) was situated in the Coleroon estuary, and consisted of degraded mangrove vegetation. This area was heavily grazed by cattle, which had resulted in extensive soil compaction. Sampling was performed by forcing a hand-held auger and the cores varied in length from 25 to 80 cm. The cores were sectioned at 3 cm intervals and freeze-dried.

Core geochronologies were determined via ^{210}Pb dating (half-life 22.3 yr, Ranjan et al., 2011 for details). It was found that the ^{210}Pb activity was relatively low in all the sediment cores, and as a consequence, the sediment samples had to be sieved to $< 75\ \mu\text{m}$ before the radiogenic isotopes could be measured using alpha spectrometry. About 1-2 g of freeze-dried sediment was extracted with a mixture of CH_2Cl_2 and CH_3OH (9:1 v/v). A Dionex Accelerated Solvent Extractor 300 was used by programming it for three extraction cycles at 1000 psi and 100 °C. The extracts were injected in pulsed splitless mode into an Agilent 6890 gas chromatograph equipped with a DB5-MS column (30 m x 0.25 mm i.d. x 0.25 μm film), and run on selected ion mode. The GC oven was programmed from 70 °C (hold time 2 min) to 200 °C at 20 °C/min. The temperature was increased to 310 °C (hold time 15 min), and finally to 315 °C (hold time 2 min) at 5 °C/min. External standards (SRM 2260 from NIST and individual PAHs from Sigma-Aldrich) were used to identify the PAHs based on their mass spectra and retention times; deuterated chrysene (Cambridge Laboratory, USA) was used for quantifying the 16 PAHs. Recovery of internal spikes (deuterated pyrene and perylene) added prior to extraction ranged from 70-90%. In between the sample runs, blanks and external standards were run repeatedly. The detection limits of most PAHs were at ng/g, and sample reproducibility of duplicates was within $\pm 20\%$. PAH concentrations were expressed as $\mu\text{g/g}$ of dry weight of sediment and recalculated as fluxes.

4. Results and Discussion

The retention and preservation of PAHs in sediments depend on a number of factors including soil type (mineral and organic matter content), physico-chemical properties of individual PAHs, soil temperature and moisture, redox-potential, availability of nutrients, and microbial activity (Okere and Semple, 2012). In this study, we traced the distribution of organic carbon (OC) concentrations and total PAH (Σ PAH) fluxes between different sites on spatial and temporal scales (Figs. 2 and 5). PAH fluxes in mangrove sediments ($0.064 \pm 0.031 \mu\text{g}/\text{cm}^2/\text{yr}$) were higher than estuarine sediments ($0.043 \pm 0.020 \mu\text{g}/\text{cm}^2/\text{yr}$). Sediment properties such as OC and clay content influence the sorption and distribution of organic contaminants (Zhang et al., 2004). Consistent with this, the Pichavaram mangrove sediments with high silt+clay content and elevated %OC (Ranjan et al., 2010) correlated with high PAH concentrations ($r^2 = 0.53$). The Pichavaram mangrove sediments are anoxic (Ranjan et al., 2011), and they are protected from the direct impact of tidal waves compared to both estuarine sites (Fig. 1). Moreover, rapid circulation and low residence time in the water column resulted in washing out, which removed OC and PAHs from estuarine sediments. In contrast, mangrove sediments were fine-grained and had longer residence time in the water column, which favored PAH accumulation. These conditions contributed towards the overall accumulation (and perhaps enhanced preservation) of PAHs in mangrove sediments.

The low PAH concentration in core B despite the high silt+clay content and elevated %OC in mangrove sediments needs further clarification. Core B was located at the mouth of the creek draining into the estuary; this site was subjected to higher tidal flushing compared to cores C and D located further inland (Fig. 1). The more recent sediments (approximately above 15 cm) showed an increase in PAH flux at these sites (Fig. 2). PAHs are primarily derived from terrestrial sources, and hence, the low concentration of these compounds in core B was likely because it is dominated

by marine organic matter (Ranjan et al., 2010). In addition, the inland cores (particularly core C) were dominated by high molecular weight PAHs (see below), and these degrade less easily compared to low molecular weight PAHs, which were more abundant in core B.

The PAH sources in these sediments were assessed using the ratio of diagnostic PAH congeners (Fig. 3) and structural complexity i.e., number of PAH rings (Fig. 4). Phenanthrene (PHE) is thermodynamically a more stable isomer than anthracene (ANT). Hence, petroleum contains relatively more PHE than ANT, and it is characterized by the high PHE/ANT ratio (Benner et al., 1990). The plots between $ANT/(ANT+PHE)$ vs. $FLT/(FLT+PYR)$ and $BaA/(BaA+CHR)$ vs. $FLT/(FLT+PYR)$ in these sediments suggest that PAHs derived from a mixture of both petrogenic and pyrolytic sources (Fig. 3). However, petrogenic sources appeared to be the dominant source of PAHs in these sediments. This is consistent with the input of petroleum hydrocarbons which accumulated in the fine-grained sediments in Pichavaram mangroves (Venkatachalapathy et al., 2012). Recent studies indicate that the ratio of $FLT/(FLT+PYR) < 0.4$ is consistent with petroleum derived input; values between 0.4 and 0.5 indicate fossil fuel combustion, whereas ratios > 0.5 imply combustion of grass, wood or coal (Liu et al., 2009; Hu et al., 2010). In this study, $FLT/(FLT+PYR)$ ratios were > 0.5 (Fig. 3), and imply these pyrogenic PAHs derived from biomass combustion. The overall concentrations of various diagnostic PAHs (PHE, ANT, FLT, PYR, B(a)A and CHR) were low in core E, and hence it was difficult to assess the PAH sources in this core.

We indicated the low molecular weight (ΣLMW ; 2 and 3-ring compounds) and high molecular weight (ΣHMW ; 4 and 5-ring compounds) PAH deposition fluxes ($\mu g/cm^2/year$) to understand the historical changes in PAH input between the estuarine and mangrove sites (Fig. 5). While LMW PAHs were abundant in all these cores, HMW PAHs were more restricted to

mangrove sediments. The elevated flux of Σ HMW PAHs in mangrove sediments might be explained in two ways. Firstly, organic matter in mangrove sediments was mainly derived from higher terrestrial sources (mainly in situ mangrove vegetation) or riverine material (Ranjan et al., 2011). During sediment transport, LMW PAHs degraded easily due to solubilization and volatilization processes (Christensen and Arora, 2007; Tian et al., 2008a; Okere and Semple, 2012) raising the concentration of HMW PAHs. Secondly, biodegradation preferentially depleted the LMW PAHs over HMW PAHs (Cerniglia, 1992; Tian et al., 2008a; Lewis et al., 2009). Due to the higher organic content in mangrove sediments, there was elevated microbial activity compared to the estuarine sediments (Alongi et al., 2005), and it was likely that LMW PAHs in these sediments were preferably degraded (Christensen and Arora, 2007; Tian et al., 2008b).

HMW PAHs were more abundant in the up-core mangrove sediments (Fig. 5). Surveys in this area indicated that lignite and firewood were widely used for cooking, which could explain the increased input of HMW PAHs. HMW PAHs were mostly absent in the deeper (below 25 cm) and older sediments, which is consistent with the fact that there was lack of urban development in these areas before the 1970s (Kathiresan, 2000). Diagnostic of combustion derived 6-ring PAH as indeno (123-cd) pyrene occurred in some samples from mangrove cores B and C. The Nevyeli lignite mines, which are the largest open-pit mines in India, are located just 46 km away, and an electric power plant near Pichavaram with an estimated capacity for generating 2490 MW electricity, used the locally mined lignite. Moreover, several brick kilns located nearby have been operating for the past several years, where lignite and wood were used during combustion. It is likely the HMW PAHs were deposited by atmospheric input, and occurred near the surface (upper 10-15 cm) of this once pristine environment.

Previous studies indicate that LMW PAHs and their alkyl derivatives are mostly of petrogenic origin (Boehm et al., 1997; Christensen and Bzdusek, 2005). In contrast, HMW PAHs are produced due to pyrolytic activities (Fernandes et al., 1997). The abundance of LMW/HMW PAHs can therefore be used to distinguish the different PAH sources in sediments (Tam et al., 2001; Choudhary and Routh, 2010). In general, HMW PAHs are more abundant over LMW PAHs in river and marine sediments (Guo et al., 2007; Yan et al., 2009). However, in this study, the overall abundance of LMW PAHs in both estuarine and mangrove sediments indicated the distinct anthropogenic fingerprint of human activities. The input of LMW PAHs probably resulted from: 1) diesel powered motorized boats and trawlers, and 2) crude oil/gasoline spills that may have been transported from distal sources because small-size PAHs are more labile (Hu et al., 2010; Venkatachalapathya et al., 2012).

We used the Principal Component Analysis test to apportion the PAH sources in these sediments. The variance (66%) in these sediments was explained by 5 principal components; the low variance resulted from strong heterogeneity between the different sampling sites. We discussed the first three dominant components of which the first component responsible for 18% of the total variance in sediments weighed on FLT, BkF, BaP, DhA, and IcP. This group of PAHs is typically derived from combustion of diesel (Tavares et al., 2004; Bixiong et al., 2006). The second component responsible for 15% of the total variance included FLR and PYR, which are indicators of coal/lignite combustion (Zuo et al., 2007). The third component was responsible for 12% of total variance, and consisted of ACP, BaA, CHR, and BaP representing mixed sources from both diesel and coal/lignite combustion (Bixiong et al., 2006; Kulkarni et al., 2000). The three principal components attest to the anthropogenic fingerprint of these PAHs, which have increased in recent years (Figs. 2 and 4).

The typical absence of perylene in these cores was notable; perylene is produced naturally during sediment diagenesis by in situ sources (Silliman et al., 1999). The absence of perylene suggested an allochthonous origin of PAHs in the sediments, and implied these compounds must have derived from: 1) non-point sources that were subsequently transported as surface runoff and/ atmospheric deposition, and 2) anthropogenic activities in the catchment.

The impact of urban development in the region can be traced by relating the sediment age and sedimentation rate (Ranjan et al., 2011) with PAH fluxes. The PAH fluxes in these cores were low in the early nineteenth century and then, displayed a synchronous increase in the last four decades (i.e., after 1970; Figs. 2 and 5) irrespective of their location or variable sedimentation rates (Ranjan et al., 2011). This change was largely due to the socio-economic development in this region, which displayed dramatically increased agriculture and industrial activities in the upstream areas of the Cauvery River basin (Ramesh et al., 1990; Sarkar et al., 2005). There was extensive hydrocarbon exploration in the Cauvery River basin (ca. reserve of 700 million metric tons) since 1964 (MoPNG, 2011). The main industries along the Cauvery River are paper and sugar mills, chemical factories, cotton mills, steel and cement factories and oil refineries. The Tamil Nadu Pollution Control Board reported that annual pollution discharged by various industries in the Bhavni River (a tributary of the Cauvery River) contained 2.14 tons/year of oil and grease (Varunprasath and Daniel, 2010; Mukherjee and Nellyat, 2007). Likewise, in the coastal areas, increase in motorboats and fishing trawler traffic, logging, combustion, and aquaculture activities added to the pool of various inorganic and organic contaminants (Alongi et al., 2005; Venkatachalapathya et al., 2012). In particular, increase in use of fossil fuels, lignite/coal, and biomass combustion have added to the pool of various organic pollutants (including PAHs) and trace metals accumulating in these sediments (Mukherjee and Nellyat, 2007; Ranjan et al., 2011,

MoPNG, 2011). The impact of human activities on the accumulation of toxic contaminants in other mangroves has been well documented by several researchers (Tam et al., 2001; Zhang et al., 2004; Zuloaga et al., 2009). These studies reported accumulation of various combustion derived products in coastal sediments. Pollution at these sites correlated directly to anthropogenic activities, and was further worsened by their proximity to large urban centers (e.g., Tam et al., 2001).

Notably, the PAH flux in cores B and D decreased after 1990 (Fig. 2). The exact reason(s) for this trend was difficult to establish based on the available information. The government took initiatives to implement strict environmental regulations, particularly for discharging industrial waste and setting up of aquaculture ponds. Consistent with this, Takeoka et al. (1991) reported a decrease in transport of OM and input of contaminants e.g., hexachlorocyclohexane and DDT from upstream areas. Recently, an oil jetty was commissioned in 2003 in Nagapattanam for handling the transport of crude oil and petroleum products for the Cauvery River basin refinery (MoPNG, 2011). Perhaps this construction and diversion of the river course was related to the low annual discharge by the Cauvery River in downstream sections (Sandilyan et al., 2010). In addition, there was a large and sudden input of marine sediments deposited next to the tsunami in 2004. Because PAHs are derived from terrestrial sources, this observed decrease in PAH flux in the very recent sediments, might be attributed to that event (sediment dilution effect).

The overall PAH concentrations in the study area were low, and comparable to those from other mangroves and estuarine environments (Zhang et al., 2004; Zuloaga et al., 2009; Pietzsch et al., 2010). These concentrations were however, substantially lower than mangroves situated near large urban centers such as Hong Kong (Tam et al., 2001) or Sao Paulo, Brazil (Cavalcante et al., 2009; Medeiros and Bicego, 2004) indicating the importance of human activities in proliferation

and accumulation of these toxic compounds. Because most PAHs are very toxic and carcinogenic, we evaluated the Σ PAH concentrations for effect range low (ERL; 4 ng/mg) and effect range medium (ERM; 44 ng/mg) proposed by Long et al. (1995). Long et al. (1995) compiled the biological and chemical data from different laboratories, and performed toxicity tests on organisms in order to study the adverse biological effects of pollutants in marine and estuarine sediments. This criterion was frequently used to make a preliminary assessment of the sediment toxicity potential in different environments (Hui et al., 2009; Yan et al., 2009; Choudhary and Routh, 2010; Li et al., 2012). In both estuarine and mangrove sediments, the values remained far below the ERL and ERM limits for LMW and HMW PAHs. Thus, despite the fact that PAH concentrations increased, these compounds do not represent an immediate ecological hazard. A similar conclusion based on the presence of petroleum derived hydrocarbons in Pichavaram was recently reported by Venkatachalapathy et al. (2012).

Conclusions

The nature, distribution, and origin of 16 PAHs were analyzed for the first time in the Pichavaram mangrove-estuarine complex. The PAH distribution trends indicate higher concentrations of different PAHs in the mangrove sediments. Overall the LMW PAHs are more abundant at these sites suggesting an anthropogenic fingerprint. The vertical distribution shows that Σ PAH (particularly HMW PAHs) input markedly increased due to rapid urbanization and combustion processes over the last four decades. The low concentration of HMW PAHs in older sediments indicates the direct impact of increasing human activities in the area. Diagnostic PAH ratios show that most PAHs in these sediments are derived from petrogenic sources with limited inputs from pyrogenic processes involving combustion of firewood and lignite. It seems that PAH input decreased in the recent years due to the enforcement of strict environmental regulations.

Finally, the overall PAH concentrations in these sediments are below those of other polluted mangrove/estuarine sediments, and so do not constitute an immediate ecological threat.

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CAPTIONS:

Figure 1: Map of the Pichavaram mangrove estuarine system in southern India showing the sampling locations of cores A to E (Ranjan et al., 2010)

Figure 2: Down core variation of total PAH fluxes ($\mu\text{g}/\text{cm}^2/\text{yr}$; in white circle) and OC (%; in black circle) in sediments (ages are based on ^{210}Pb dating, Ranjan et al., 2011)

Figure 3: Ratio of different isomer pairs used to identify PAH sources

Figure 4: Distribution of PAHs with respect to $\% \Sigma$ (2+3)-rings, $\% \Sigma$ 4-rings, and $\% \Sigma$ (5+6)-rings PAHs in the Pichavaram mangrove estuarine sediments

Figure 5: Down core variations of LMW PAHs fluxes ($\mu\text{g}/\text{cm}^2/\text{yr}$; in white circle) and HMW PAHs fluxes ($\mu\text{g} / \text{cm}^2/\text{yr}$; in black circle) in sediments (ages are based on ^{210}Pb dating, Ranjan et al. 2011)

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Compounds	Abbreviation	No of Rings
Naphthalene	NAP	2
Acenaphthylene	ACY	3
Acenaphthene	ACP	3
Fluorene	FLR	3
Phenanthrene	PHE	3
Anthracene	ANT	3
Fluoranthene	FLT	4
Pyrene	PYR	4
Benz[a]anthracene	BaA	4
Chrysene	CHR	4
Benzo[b]fluoranthene	BbF	5
Benzo[k]fluoranthene	BkF	5
Benzo[a]pyrene	BaP	5
Dibenz[a,h]anthracene	DhA	5
Indeno[1,2,3-cd]pyrene	IcP	6
Benzo[ghi]perylene	BgP	6

Fig. 5.