Potential health risks of polycyclic aromatic hydrocarbons associated with sediment and seafood from a Ramsar site

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Abstract: Sixteen polycyclic aromatic hydrocarbons were determined in sediments and edible biota from Chilika, the largest brackish water lagoon in Asia. Mean PAH level in sediments was 13,674 ng/g dry weight, higher than reported studies from the region. High molecular weight species dominated total PAH profile indicating pyrolytic origin. Assessment of sediment associated individual PAHs effect on aquatic organisms of the lagoon revealed all the compounds, except naphthalene and anthracene, to be present above the lower range of concentrations related to toxicity. Risk quotient of PAHs revealed that Acenaphthene, Fluorene and Dibenz[a,h]anthracene require priority management concerns. PAH levels in crabs and prawns were 394.4 and 153.0 ng/g d.w., higher than reported studies. BaP_{eq} concentrations were 42.9 and 15.2 ng/g d.w. in crabs and prawns respectively. Carcinogenic PAHs accounted for 33.5% to the total PAHs in edible biota but consumption can be considered safe with respect to lifetime excess cancer risk guidelines.

Keywords: Chilika lagoon; sediments; polycyclic aromatic hydrocarbons; PAHs; mud crab; prawn; health risk assessment.

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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of persistent organic pollutants. PAHs are by-products of incomplete combustion of organic material and are released into the aquatic environment through wastewater discharge, effluents from coke and petroleum industries, atmospheric deposition of traffic and industrial emissions, urban runoff and oil spills. PAHs are ubiquitous in the environment and human exposure to these species are known to lead to elevated levels of DNA adducts, mutations, reproductive effects, and cancers of lung, respiratory tract and urinary bladder (Bosetti et al., 2007). Intake of contaminated food has been identified as the main pathway for PAH exposure in humans (Martorell et al., 2010). Sediments are important sources of information for impacts of anthropogenic activities on coastal environments and are the ultimate sinks of PAHs emitted from anthropogenic processes on land and water surfaces. PAHs bio accumulates in edible biota and upon prolonged exposure through consumption, can cause human health hazards (Llobet et al., 2006). Regardless of the uptake route, the concentration of PAHs in marine/freshwater biota is dependent on the concentration of the same in sediments. Profiles of PAH distribution in sediments can help to ascertain the sources and to assess the potential health hazards associated with the consumption of edible marine biota.

Coastal ecosystems are posed both with terrestrial influences, which are mostly anthropogenic and marine influences, mostly natural. These ecosystems are complex, fragile and vulnerable. Chilika is one such ecologically sensitive lagoon. It lies in the east coast of India and is the largest lagoon in Asia. Chilika lagoon is a wetland of international importance according to the Ramsar convention (group A – sites containing representative, rare or unique wetland types and group B – sites of international importance for conserving biological diversity). It is the largest site for migratory birds in the Indian subcontinent. The site is an important area for breeding, wintering and staging for 33 species of water birds. The lagoon was included on the Montreux Record in 1993 due to problems caused by siltation and sedimentation which was choking the mouth of the lagoon. Montreux Record is a list of wetlands of international importance where changes in ecological character have occurred, or are likely to occur as a result of technological developments, pollution or other human interference. It was removed from the Record in 2002 following rehabilitation efforts. However, according to the recent Ramsar update for Chilika, the lagoon continues to be threatened from domestic sewage pollution and overexploitation of fishery resources (RSIS, 2012). The lake is endemic to numerous threatened plants and animals. It supports a rich aquatic biodiversity including

268 species of fish, 28 species of prawn and 34 species of crab (Bhatta and Panda, 2008). Fishery resources and other edible organisms such as prawn and crabs among others from the lagoon are commercially important items with high export value. India mainly exports crustaceans and molluscs in the international market and its leading trade partners are the USA, Japan, Spain, China and the UK (NPC, 2010). India was among the top three countries in terms of crustacean production in 2008 (FAO, 2011). Prawn and crabs from the lagoon accounted for ~40% of the total catch from the Indian state of Odisha in 2008–2009. These sea food items are a popular delicacy and the source of livelihood of more than 0.2 million local fishermen around the lagoon (Mohapatra et al., 2007). Thus, Chilika has both ecological and socioeconomic significance.

However, the lagoon is faced with a general increase in pollution from several rivers in the drainage basin. Studies have referred to several types of inputs, viz., urban, domestic, industrial and agricultural wastes, which results in significant alteration in the water quality of Chilika (Pal and Mohanty, 2002). The amount of untreated sewage discharged to the Chilika lagoon from Bhubaneswar, the capital city of Odisha is estimated to be ≈550 million litres day^{-1}. Apart from that, huge amount of untreated domestic wastewater from 141 village communities in and around the lagoon find its way to the lagoon (Panigrahi et al., 2009).

The objectives of the present study were to carry out, for the first time, a preliminary investigation of the PAH load of the sediments and the contamination levels of PAHs in mud crabs and prawns from this lagoon along with health risk assessment upon consumption of same.

2 Materials and methods

2.1 Study area and sampling

Sediment samples along with mud crab and prawn samples were collected from Balugaon village site, Chilika as shown in Figure 1. Chilika (19º28'–19º54' N; 85º06'–85º35' E) is a shallow water body and is about 65 km in length, spreading from northeast to southwest parallel to the coastline with a variable breadth reaching a maximum of 20.1 km. The lagoon is spread over an area of 950 km^2 during summer, which swells up to 1,165 km^2 during monsoon (Siddiqui and Rao, 1995). Panigrahi et al. (2007) stated that the lagoon has several hydrological influences such as

1 drainage from unregulated degraded catchment basin lying on the western and southern boundaries

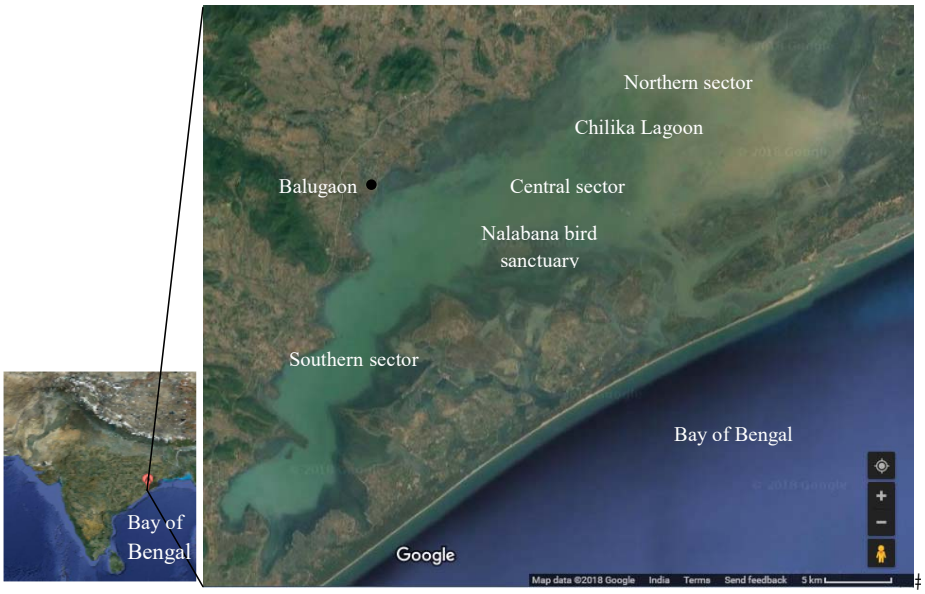
2 silt borne fresh water discharges from the distributaries of Mahanadi River (Daya, Bhargavi, Kusumi, Salia, Nuna, Malaguni, etc. discharge approximately 375,000 cusecs of fresh water carrying about 13 million metric tonnes of silt annually to the lagoon) along with a series of other small 52 channels

3 exchange of lagoon water with Bay of Bengal.

The study was preliminary in nature, five surface (1–5 cm deep) sediment samples were collected by a clean augur from five important stretches along the coast with respect to mud crab harvest. The sampling spots were chosen at a distance of 500 metres from each and sampling was carried out in the pre monsoon period (June, 2010). Samples were then

sealed in zipped polythene bags and transported to the laboratory in ice packs. They were preserved at 4ºC until further processing. Similarly, mud crab (*Scylla spp*.) and prawn (*Penaeus monodon*) samples were collected, packed in ice packs and transported to laboratory and then stored at –20°C.

Figure 1 Map showing the study area (denoted by a solid black dot) (see online version for colours)



● Study area

Source: Google Earth

2.1.1 Chemicals and reagents

Standard mixture containing 16 PAHs (16 compounds specified in EPA Method 610) and deuterated PAHs internal standard mixture (Naphthalene-d8; Acenaphthene-d10; Phenanthrene-d10; Chrysene-d12 and Perylene-d12) were procured from Supelco (Bellefonte, PA, USA). All solvents (toluene, n-hexane and acetonitrile) were purchased from Merck (India) Ltd. and were of HPLC grade. Water used in the analyses was high-purity deionised water (18.2 MΩ cm^{-1}) taken from the Milli-Q system (Millipore, USA).

2.2 PAHs analysis

PAHs were extracted from dried, homogenised and sieved (< 63 µm size) sediment samples (≈5 g). Cleaned, lyophilised, powdered and homogenised prawn and mud crab tissue samples (≈3 g) were used for PAHs extraction. Ultrasonication (Sonicator 3000, Misonix Inc., USA) with toluene (15 min in the pulse mode twice) was used for the extraction. Samples were subsequently concentrated to 0.5–2 ml by rotary evaporation (Büchi rotavapor, Switzerland) and cleaned up using silica gel (Silica gel 60, particle size

0.0630–0.200 mm, 70–230 mesh ASTM, purchased from Merck KGaA, Darmstadt, Germany) column (4 mm i.d.). The fraction containing PAHs was again concentrated to 0.5–2.0 ml by rotary evaporation and solvent was exchanged with acetonitrile for further chromatographic analysis. PAHs were analysed on a high performance liquid chromatography (HPLC) system (Waters, USA) equipped with a tunable absorbance UV detector (254 nm) and a waters PAH C18 column (4.6 mm × 250 mm, particle size 5 μm). The mobile phase was a gradient of acetonitrile and degassed water (50% acetonitrile held for five min; linear gradient to 100% acetonitrile in 5–20 min; 100% acetonitrile held till 28 min and linear gradient to 50% acetonitrile from 28 min to 32 min; flow rate: 1.5 ml min^{-1}). Quantification of PAHs was done by internal calibration method and their identification was carried out by comparing their retention times with those of authentic standards. Samples were spiked with internal standard solution prior to extraction in order to monitor procedural performance and matrix effects. Surrogate compounds were represented for the analyses as follows: Naphthalene-d8 for Naphthalene (Naph); Acenaphthene-d10 for Acenaphthylene (Acy), Acenaphthene (Acen) and Fluorene (Flu); Phenanthrene-d10 for Phenanthrene (Phen), Anthracene (Anth), Fluoranthene (Flan) and Pyrene (Pyr); Chrysene-d12 for Benz[a]anthracene (B[a]A) and Chrysene (Chry); Perylene-d12 for Benz[b]fluoranthene (B[b]F), Benz[k]fluoranthene (B[k]F), Benz[a]pyrene (B[a]P), Dibenz[a,h]anthracene (DB[ah]A), Benz[ghi]perylene (B[ghi]P) and Indeno[1,2,3-cd]pyrene (IP).

2.3 Analytical quality control

Quality assurance and control measures were adopted at each step to ensure reliability of results. The HPLC instrument was calibrated using sets of at least five standards covering the range of concentrations encountered in the literature. The calibration curve was linear in the concentration range with linear regression coefficients (R^2) > 0.99 for linear least-squares fit of data. Sample contamination was avoided by use of cleaned glass wares, analytical grade chemicals and high-purity deionised water. Reagent blanks were analysed to remove analytical bias. The data were subsequently blank-corrected as required. Sediment samples were analysed in triplicates to ensure precision. Relative standard deviations (RSDs) of replicate measurements were < 10% for PAHs. Overall recoveries of PAHs ranged from 76% for Acen to 91% for B[k]F.

2.4 Calculation of lifetime cancer risk assessment from the consumption of crab and prawn

Dietary intake for PAHs and lifetime cancer risk assessment from the consumption of crab and prawn were calculated as carried out by Moon et al. (2010). Briefly, the general equation for estimating exposure through ingestion of food items was used as follows:

$$\text{Excess cancer risk} = (\text{EI} \times \text{ED} \times \text{CSF}) / (\text{BW} \times \text{AT})$$

where EI is estimated intake (mg/kg/d), ED is exposure duration (30 years for adults), CSF is the oral cancer slope factor ($(mg/kg/d)^{-1}$), BW is the body weight of humans and AT is the averaging time for carcinogens (70 years for adults). CSF values for individual PAHs were obtained from the integrated risk information system reported by the USEPA (2004). Estimated intake was calculated by multiplying the concentration of the

compound by the consumption rate. Average consumption rate was taken as 1.8 and 1.6 g/day for crab and prawn respectively.

3 Results and discussion

3.1 Results of the study

The concentration of PAHs in sediment samples are provided in Table 1. The total PAH (Σ_{16} PAHs) concentrations ranged from 11,734 to 15,080 ng/g d.w. with a mean concentration of 13,674 ± 1,368 ng/g d.w. 5–6 ring PAHs dominated at three sites (≈42% of the Σ_{16} PAHs), whereas, 2–3 ring PAHs dominated (≈57%) at two remaining sites. High concentration of PAHs in the sediments can be attributed to various sources in the catchment area. Large inflow of fresh water through various rivers and rivulets at the northern end of the lagoon could also be a potential source of PAHs into the lagoon environment. Previous studies have concluded that there is a general increase in the pollution load from agricultural, aquaculture and domestic sources from the huge drainage basin of Chilika lagoon (Ghosh and Pattnaik, 2006). Mean concentrations of total PAHs in crab and prawn samples are shown in Table 2. The carcinogenic Σ_7 PAHs accounted for ≈31% and 36% to the Σ_{16} PAHs concentrations in crabs and prawns respectively. Low molecular weight PAHs recorded ≈42% and 39% of the Σ_{16} PAHs for crabs and prawns respectively whereas the high molecular weight PAHs dominated by contributing ≈57% and 60% of the Σ_{16} PAHs in crabs and prawn respectively. This might be due to the feeding habits and lower metabolic rate of crabs and prawns as compared to fish. Fish species have been shown to accumulate higher amounts of LMW PAHs against filter feeding bivalves, which accumulate HMW PAHs from ingestion of particles having higher amounts of adsorbed HMW PAHs as compared to LMW PAHs (Moon et al., 2010). Mean B[a]P_{eq} concentration were recorded to be 42.9 and 15.2 ng/g for crabs and prawns respectively.

3.2 Discussion of the study results

3.2.1 Comparison of the results with other studies

The total concentration of 16 PAHs in the present study was higher than that from surface sediments of Sunderban wetland mangrove, north eastern coast of Bay of Bengal, India [Σ_{16} PAHs ranged from 241 to 1,376 ng/g d.w. (Domínguez et al., 2010)]. Further, a study by Saha et al. (2009) reported that surface sediment samples collected from canals, rivers, a lake, and coastal environments in India registered the highest PAHs concentration (mean: 11,300 ng/g d.w.) among eight tropical Asian countries. Several studies have reported high concentration of PAHs from lagoon sediments. For example, Fabbri et al. (2006) reported total PAHs concentrations of 2,500–120,000 ng/g d.w. from Pialiassa Baiona lagoon, Italy. Similarly, Affian et al. (2009) reported concentrations of 1,050–770,000 ng/g d.w. from Ebrie lagoon, West Africa. Also, Culotta et al. (2006) from Stagnone lagoon, Italy reported TPAHs concentration of 72–18,381 ng/g d.w.

The measured concentration of PAHs in crabs and prawns are found to be higher than those found in South Korea by Moon et al. (2010), Adriatic Sea by Perugini et al. (2007), Egypt by Loufty et al. (2007) and Kuwait by Saeed et al. (1995).

Table 1 Mean concentrations of PAHs (ng/g d.w.), diagnostic ratios and risk quotient (RQ) values in sediment samples

PAHs	*Sed 1*	*Sed 2*	*Sed 3*	*Sed 4*	*Sed 5*	*Average*	*TEF*[1]	*BaPeq*	*ERL*[2]	*ERM*$_b$	*RQ*$_{bcs}$	*RQ*$_{wcs}$
Naph	143.5	133.4	122.5	110.3	121.7	126.3 ± 12.6	0.001	0.13	160	2,100	0.05	0.90
Acy	275.2	44.0	322.0	353.6	51.8	209.3 ± 150.0	0.001	0.21	44	640	0.07	8.04
Acen	1,643.6	5,609.5	1,923.0	2,112.1	6,607.9	3,579.2 ± 2341	0.001	3.58	35	1,040	2.46	225.04
Flu	919.2	1,076.9	1,075.4	1,181.1	1,268.6	1,104.2 ± 131.1	0.001	1.10				
Phen	389.0	463.5	480.0	499.8	529.0	472.3 ± 52.5	0.001	0.47	240	1,500	0.26	2.20
Anth	126.3	129.9	147.7	140.0	153.0	139.4 ± 11.3	0.01	1.39	853	1,100	0.11	0.18
Flan	1,579.1	1,431.3	1,790.0	2,029.2	1,340.0	941.1 ± 278.8	0.001	0.94	600	5,100	0.26	3.38
Pyr	898.1	756.0	1,050.7	1,110.0	890.6	1,633.9 ± 140.7	0.001	1.63	665	2,600	0.29	1.67
B[a]A	847.8	479.8	900.0	1,089.4	565.2	776.4 ± 250.4	0.1	77.64	645	4,400	0.31	2.62
Chry	518.6	342.9	606.8	600.0	420.0	497.6 ± 114.9	0.01	4.98				
B[b]F	588.3	476.8	688.4	756.0	561.7	614.2 ± 109.4	0.1	61.42	NA	NA	NA	NA
B(k)F	693.3	311.0	811.2	890.9	366.4	614.6 ± 262.1	0.1	61.46	NA	NA	NA	NA
B[a]P	781.6	604.7	914.5	1,004.4	712.4	803.5 ± 158.8	1	803.53	430	1,600	0.38	2.34
D[ah]A	980.2	278.2	1,146.8	1,259.5	327.7	798.5 ± 463.4	1	798.49	63.4	260	1.07	19.87
B[ghi]P	747.7	480.3	874.8	960.7	565.8	725.9 ± 202.3	0.01	7.26	NA	NA	NA	NA
IP	602.2	507.7	704.6	773.9	598.0	637.3 ± 103.3	0.001	0.64				
Σ_{16} PAH	11,734	13,126	13,558	14,871	15,080	13,674 ± 1,368		1,825	4,000	44,792	0.26	3.77
Σ_7 CPAH	5,012	3,001	5,772	6,374	3,551	4,742						
2–3 ring	3,497	7,457	4,071	4,397	8,732	5,631						
4 ring	3,325	2,667	3,741	4,229	2,796	3,351						
5–6 ring	4,912	3,002	5,747	6,245	3,552	4,692						
Phen/Anth	3.1	3.6	3.2	3.6	3.5	3.4		(< 10 pyrolytic) (Gschwend and Hites, 1981)				
Flan/Pyr	1.8	1.9	1.7	1.8	1.5	1.7		(> 1 pyrolytic) (Gschwend and Hites, 1981)				
B[a]A/Chry	1.6	1.4	1.5	1.8	1.3	1.5		(> 1 pyrolytic) (Colombo et al., 1989)				
LMW/HMW	0.4	0.8	2.3	2.4	0.7	1.3						

Note: [1]TEF adopted from Nisbet and LaGoy (1992)
[2]ERL and ERM values adopted from NOAA.

Table 2 Mean concentrations of 16 PAHs (ng/g d.w.) in mud crab and prawn samples along with dietary intake and excess cancer risk estimation

PAHs	*Crab*	*Prawn*	*TEF*	BaP_{eq}		*Daily intake (ng/day)*		*Excess cancer risk*	
				Crab	*Prawn*	*Crab*	*Prawn*	*Crab*	*Prawn*
Naph	6.02 ± 0.7	3.33 ± 0.3	0.001	0.01	0.003	10.83	5.33	NA	NA
Acy	13.22 ± 1.6	4.04 ± 0.4	0.001	0.01	0.004	23.79	6.47	NA	NA
Acen	78.94 ± 9.8	18.08 ± 1.9	0.001	0.08	0.02	142.10	28.92	NA	NA
Flu	44.15 ± 5.5	14.13 ± 1.5	0.001	0.04	0.01	79.46	22.60	NA	NA
Phen	19.70 ± 2.4	16.75 ± 1.7	0.001	0.02	0.02	35.47	26.80	NA	NA
Anth	6.06 ± 0.7	4.54 ± 0.4	0.01	0.06	0.05	10.92	7.27	NA	NA
Flan	33.84 ± 4.2	22.54 ± 2.4	0.001	0.03	0.02	60.92	36.06	NA	NA
Pyr	33.78 ± 4.2	18.58 ± 1.9	0.001	0.03	0.02	60.80	29.73	NA	NA
B[a]A	22.32 ± 2.7	6.21 ± 0.6	0.1	2.23	0.62	40.18	9.93	2.1E-07	5.2E-08
Chry	24.91 ± 3.1	7.97 ± 0.8	0.01	0.25	0.08	44.84	12.75	2.3E-07	6.6E-08
B[b]F	22.76 ± 2.8	8.91 ± 0.9	0.100	2.28	0.89	40.97	14.26	2.1E-07	7.4E-08
B[k]F	16.93 ± 2.1	6.93 ± 0.7	0.1	1.69	0.69	30.48	11.08	1.6E-07	5.8E-08
B[a]P	22.98 ± 2.8	6.78 ± 0.7	1.0	22.98	6.78	41.36	10.85	2.2E-07	5.7E-08
D[ah]A	12.97 ± 1.6	5.98 ± 0.6	1.0	12.97	5.98	23.35	9.57	1.2E-07	5.0E-08
B[ghi]P	17.05 ± 2.1	3.24 ± 0.3	0.01	0.17	0.03	30.68	5.18	NA	NA
IP	18.75 ± 2.3	4.99 ± 0.5	0.001	0.02	0.005	33.75	7.98	1.8E-07	4.2E-08
Σ_{16} PAH	394.38 ± 49.2	152.98 ± 16.2		42.88	15.22	709.88	244.78	1.3E-06	4.0E-07
Σ_7 CPAH	141.62	47.75							

Table 3 Diagnostic ratios of PAHs observed at the sites along with corresponding source signatures obtained from existing literature

	Sed 1	*Sed 2*	*Sed 3*	*Sed 4*	*Sed 5*	*Mean*	*Literature values*
Phen/Anth	3.1	3.6	3.2	3.6	3.5	3.4	(< 10 pyrolytic)[a]
Flan/Pyr	1.8	1.9	1.7	1.8	1.5	1.7	(> 1 pyrolytic)[a]
B[a]A/Chry	1.6	1.4	1.5	1.8	1.3	1.5	(> 1 pyrolytic)[b]
Anth/Anth+Phen	0.25	0.22	0.24	0.22	0.22	0.23	Combustion (> 0.1) Petroleum (< 0.1)[c]
B[a]A/B[a]A+Chry	0.62	0.58	0.6	0.64	0.57	0.6	Petroleum (< 0.2), Combustion (> 0.35)[d]
Flan/Flan+Pyr	0.64	0.65	0.63	0.65	0.6	0.63	Petroleum (< 0.4), Gasoline (0.4), Coal/wood (> 0.5)[d, e]
IP/IP+B[ghi]P	0.45	0.51	0.45	0.45	0.51	0.47	Gasoline (0.22), Diesel (0.5), Petroleum (1.3)[f]
B[a]A/Chry	1.63	1.4	1.48	1.82	1.35	1.54	Vehicles (0.53), Smelters (0.6), Wood (0.79), Coal/coke (1.11)[g]
IP/B[ghi]P	0.81	1.06	0.81	0.81	1.06	0.91	Wood (0.29), Gasoline (0.4), Diesel (1), Coal/coke (1.09)[g, h]
B[b]F/B[k]F	0.85	1.53	0.85	0.85	1.53	1.12	Wood (0.92), Vehicles (1.26), Smelters (2.69), Coal/coke (3.7)[g]
B[a]P/B[ghi]P	1.05	1.26	1.05	1.05	1.26	1.13	Vehicles (0.3–0.78), Coal (0.9–6.6)[e]

Notes: [a](Gschwend and Hites, 1981)
[b](Colombo et al., 1989)
[c](Budzinski et al., 1997)
[d](Yunker et al., 2002)
[e](Simcik et al., 1999)
[f](Yassaa et al., 2001)
[g](Dickhut et al., 2000)
[h](Caricchia et al., 1999).

3.2.2 Diagnostic ratios

Diagnostic ratios were used to find the possible sources of PAHs in the lagoon sediments. The calculated values are presented in Table 3. It is evident from the various ratios that the origin of PAHs in the sediments of Chilika lagoon is generally pyrolytic. Sarkar et al. (2012), Domínguez et al. (2010) and Saha et al. (2009) also reported pyrolytic sources of PAHs from Sunderban wetland and other coastal sediments. The ratio of LMW/HMW PAHs ranged from 0.4–2.3. Three out of the five sites exhibited low ratios (< 1), indicating pyrolytic sources whereas the others exhibited relatively higher ratios, indicating the presence of petrogenic sources. Thus the presence of both, petrogenic and pyrolytic sources can be inferred. This might also suggest the modification of the PAHs source signatures during the interplay of various physical, chemical and biological mechanisms in transport and post depositional phases of sediments (Bícego et al., 2006).

Ratios such as Anth/(Anth+Phen) and B[a]A/(B[a]A+Chry) indicated towards combustion as the predominant source of PAHs in the lagoon sediments. Ratio of B[k]F/B[b]F indicated towards vehicular sources of PAHs in the sediments. IP/(IP+B[ghi]P) ratio revealed diesel combustion as the chief source of PAHs. Diesel sources could be either from vehicular sources or from the local diesel generators sets used for electricity generation and diesel powered trawlers for fishing, extensive shrimp and prawn farming in the study site. Isomer pair ratios of Flan/(Flan+Pyr), B[a]A/Chry, B[a]P/B[ghi]P indicated towards coal and wood combustion as the source of PAHs in sediments. Coal and wood combustion is common in the catchments area of the lagoon. Apart from the deposited sediments, contamination in the lagoon sediments can also be through inputs from 0.2 million fisher-folk inhabitants around the lagoon. These local communities depend on wood combustion for cooking.

3.2.3 Principal component analysis (PCA)

PCA by SPSS 14.0 was used to apportion and confirm the sources indicated by PAHs isomer pair ratios. Factors were identified by varimax rotation along with Kaiser Normalisation. Eigen value of > 1 was the criterion for selecting factors and a factor score of 0.5 was selected as the lowest level of significance within a factor. The results of the PCA are presented in Table 4. 96% of data variance was explained by two factors (PC1 and PC2). PC1 was represented by high loadings of Acy, Flan, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[a]P, D[ah]A, B[ghi]P and IP. Loadings of Flan, B[a]A, Chry, B[b]F, B[k]F, B[a]P, DB[ah]A, B[ghi]P, and IP pointed towards mixed sources of gasoline and diesel emissions. Loadings of Acy, B[k]F and B[a]P suggested towards wood/biomass combustion. PC2 was represented by coal tracers such as Flu, Phen and Anth (Khalili et al., 1995). Overall, PCA indicated towards gasoline, diesel, coal and wood/biomass combustion sources of PAHs in the lagoon sediments. Also, the results confirmed the sources diagnosed by PAHs isomer pair ratios.

3.2.4 Risk assessment

The potential toxicity of sediments was evaluated using the benzo[a]pyrene equivalent ($B[a]P_{eq}$) concentration. The $B[a]P_{eq}$ for the PAH mixture was calculated using the following equation: $B[a]P_{eq} = (C_i \text{ X TEF})$, where C_i is the concentration of the PAH and TEF is the toxic equivalence factor adopted from Nisbet and LaGoy (1992). The mean B[a]Peq concentration was 1,824.8 ng/g d.w.. These values are higher than those reported from sediments of Sunderban wetland by Domínguez et al. (2010) and Sarkar et al. (2012).

The effects range low (ERL) and the effects range median (ERM) given by US National Oceanic and Atmospheric Administration (NOAA) have been used to assess the lagoon sediment quality by comparing the obtained values with the environmental quality thresholds (Long et al., 1995). ERL and ERM are relevant for assessing the potential effects of sediment-associated contaminants on aquatic organisms. In the present study, individual ERL values were violated for all compounds except Naph and Anth at all the sites. The individual ERM values were exceeded by only (Acen + Flu) and DB[ah]A at all sites. Overall, the ERL value of 4,000 ng/g was exceeded at all the sites but the threshold ERM value (44,792 ng/g) was not violated at any site.

Table 4 Results of PCA

	Rotated component matrix	
	Component	
	1	*2*
Naph		
Acy	0.982	
Acen		
Flu		0.976
Phen		0.992
Anth		0.882
Flan	0.941	
Pyr	0.935	
B[a]A	0.99	
Chry	0.977	
B[b]F	0.956	
B[k]F	0.996	
B[a]P	0.974	
D[ah]A	0.988	
B[ghi]P	0.998	
IP	0.931	

Note: Extraction method: PCA.
Rotation method: varimax with Kaiser Normalisation.

Levels of risk posed by PAHs in sediments were determined by the calculation of RQ as carried out by Domínguez et al. (2010). Risk quotient under best-case scenario (RQbcs) and worst-case scenario (RQwcs) were determined as sediment quality values are generally given in limits (upper and lower). The values are represented in Table 1. RQbcs values obtained showed that only (Acen + Flu) and DB[ah]A exceeded the threshold value (RQbcs > 1), thus indicating the need for attention and control measures for the above said chemicals. Based on RQwcs values, Naph and Anth, recorded values < 1, thus indicating that the said chemicals require lower priority in terms of management concerns. It is important to mention here that in cases where RQbcs < 1 or RQwcs > 1, a refined methodology of risk assessment should be involved (Domínguez et al., 2010).

Daily intake of PAHs for Indian adult population was found to be 709.8 and 244.7 ng/day for crab and prawn respectively. Calculated excess cancer risk due to consumption of the food items are shown in Table 2. The risk values through consumption of crabs and prawns for the Indian adult population for a lifetime exposure exceeded the cancer risk guideline value (1×10^{-6}) (USEPA, 1989). These results are close to the guideline value for cancer risk, especially for crab samples. The prawn samples however, have shown safe values for cancer risk through the lifetime consumption of the analysed food items at the concentration determined in the present study. It should be emphasised that the calculated risk is inclusive of uncertainty. Uncertainty can be due to error in reporting estimated consumption by the local villagers. Volatility of PAHs, especially LMW PAHs can yield in uncertainty in the measured

PAHs level. This might underestimate the risk. PAHs bioavailability was also assessed by the calculations of biota sediment accumulation factors (BSAF). These factors are site specific and one of the best ways to evaluate the bioavailability of sediment-bound PAH. It is carried out by comparing PAH concentrations in sediment and a sediment-dwelling organism as follows:

$$BSAF = (C_B / f_L) / (Cs / f_{OC})$$

where C_B is the concentration (ng/g d.w.) of PAHs in biota, f_L is the lipid fraction [4.05% in crab (Manivannan et al., 2010) and 4.3 % prawn (Dinakaran et al., 2009)], CS is the concentration (ng/g d.w.) of PAHs in sediments, f_{OC} is the organic carbon content (2.28%, Sundararajan and Srinivasalu, 2010) of coastal sediments.]

A BSAF value of unity indicates equilibrium between the sediment and organism, assuming the PAH have equal affinity to organism lipid and sediment organic carbon. BSAF values less than unity indicate a reduction in availability of PAHs (Neff, 2002). In this study, BSAF values were found to range between 0.009–0.03 in crab and between 0.002–0.02 in prawns from the lagoon (Table 5). It can thus be concluded that all the USEPA priority PAHs had very low bioavailability, as indicated by the low BSAF values. It is noteworthy, that LMW PAHs (2–3 rings) have higher BSAF in comparison to HMW PAHs (4, 5 and 6 rings). Molecular structure and size of PAHs are known to influence the bioavailability of PAHs. LMW PAHs are bio-available by virtue of their physico-chemical properties such as higher solubility and volatility in comparison to the HMW PAHs (Alexander, 1999). The crab BSAF values were higher than prawn BSAF values. Surface to volume ratios and size dependent feeding behaviour of mud crab might play a role in higher BSAF than prawns (Newman and Mitz, 1988).

Table 5 BSAF values in crab and prawn samples

	BSAF	
PAHs	*Crab*	*Prawn*
Naph	0.027	0.014
Acy	0.036	0.010
Acen	0.012	0.003
Flu	0.023	0.007
Phen	0.023	0.019
Anth	0.024	0.017
Flan	0.020	0.013
Pyr	0.012	0.006
B(a)A	0.016	0.004
Chry	0.028	0.008
B(b)F	0.021	0.008
B(k)F	0.016	0.006
B(a)P	0.016	0.004
D(ah)A	0.009	0.004
B(ghi)P	0.013	0.002
IP	0.017	0.004

4 Conclusions

Mean total PAH level in the sediments of Chilika lagoon, a wetland of international importance and a Ramsar site, was 13,673 ng/g dry weight, higher than previous studies from South-east Asia. 5–6 ring PAHs dominated at three sites (≈42% of the Σ_{16} PAHs), whereas, 2–3 ring PAHs dominated (≈ 57%) at two remaining sites of the study. Low molecular weight PAHs recorded ≈42% and 39% of the Σ_{16} PAHs for crabs and prawns respectively whereas the high molecular weight PAHs dominated by contributing ≈57% and 60% of the Σ_{16} PAHs in crabs and prawn respectively. Carcinogenic PAHs accounted for ≈31% and 36% to the Σ_{16} PAHs concentrations in crabs and prawns respectively. Diagnostic ratios and PCA indicated pyrolytic sources, particularly diesel and coal/wood combustion as sources of PAHs in the lagoon sediments. Lower range of sediment quality thresholds was exceeded at all the sites. RQ of PAHs revealed that Acenaphthene, Fluorene and Dibenz[a,h]anthracene require priority management concerns. PAH levels in crabs and prawns from Chilika lagoon, the largest brackish water lake in Asia, were higher than recent studies but consumption can be considered safe with respect to lifetime excess cancer risk guidelines. Moreover, low BSAF in prawns and crabs samples from the lagoon suggest that the studied PAHs have low bioavailability.

References

Affian, K., Robin, M., Maanan, M., Digbehi, B., Djagoua, E.V. and Kouamé, F. (2009) 'Heavy metal and polycyclic aromatic hydrocarbons in Ebrié lagoon sediments, Côte d'Ivoire', *Environ. Monit. Assess.*, Vol. 159, Nos. 1–4, pp.531–541.

Alexander, M. (1999) *Biodegradation and Bioremediation*, Academic Press Inc., San Diego, CA.

Bhatta, K.S. and Panda, S. (2008) 'Post hydrological changes in landings of fishery resources in Chilika lagoon', *Proceedings of Taal 2007: The 12th World Lake Conference: 1894–1902*.

Bícego, M.C., Taniguchi, S., Yogui, G.T., Montone, R.C., Silva, D.A.M., Lourenço, R.A., Martins, C.C., Sasaki, S.T., Pellizari, V.H. and Weber, R.R. (2006) 'Assessment of contamination by polychlorinated biphenyls and aliphatic and aromatic hydrocarbons in sediments of the Santos and São Vicente Estuary System, São Paulo, Brazil', *Mar. Pollut. Bull.*, Vol. 52, No. 12, pp.1784–1832.

Bosetti, C., Boffetta, P. and La Vecchia, C. (2007) 'Occupational exposures to polycyclic aromatic hydrocarbons, and respiratory and urinary tract cancers: a quantitative review to 2005', *Ann. Oncol.*, Vol. 18, No. 3, pp.431–446.

Budzinski, H., Jones, I., Bellocq, J., Piérrad, C. and Garrigues, P. (1997) 'Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary', *Mar. Chem.*, Vol. 58, Nos. 1–2, pp.85–97.

Caricchia, A.M., Chiavarini, S. and Pezza, M. (1999) 'Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy)', *Atmos. Environ.*, Vol. 33, No. 23, pp.3731–3738.

Colombo, J.C., Pelletier, E., Brochu, C., Khalil, M. and Catoggio, J.A. (1989) 'Determination of hydrocarbon sources using n-alkanes and polyaromatic hydrocarbon distribution indexes. Case study: Rio de la Plata Estuary, Argentina', *Environ. Sci. Technol.*, Vol. 23, No. 7, pp.888–894.

Culotta, L., De Stefano, C., Gianguzza, A., Mannino, M.R. and Orecchio, S. (2006) 'The PAH composition of surface sediments from Stagnone coastal lagoon, Marsala (Italy)', *Mar. Chem.*, Vol. 99, Nos. 1–4, pp.117–127.

Dickhut, R.M., Canuel, E.A., Gustafson, K.E., Liu, K., Arzayus, K.M., Walker, S.E., Edgecombe, G., Gaylor, M.O. and MacDonald, E.H. (2000) 'Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in Chesapeake Bay region', *Environ. Sci. Technol*., Vol. 34, No. 21, pp.4635–4640.

Dinakaran, G.K. and Soundarapandian, P. (2009) 'Biochemical status of edible palaemonid prawn Macrobrachium idella idella (Hilgendorf, 1898)', *Adv. J. Food Sci. Technol*., Vol. 1, No. 1, pp.19–26.

Domínguez, C., Sarkar, S.K., Bhattacharya, A., Chatterjee, M., Bhattacharya, B.D., Jover, E., Albaiges, J., Bayona, J.M., Alam, M.A. and Satpathy, K.K. (2010) 'Quantification and source identification of polycyclic aromatic hydrocarbons in core sediments from sundarban mangrove wetland, India', *Arch. Environ. Contam. Toxicol.*, Vol. 59, No. 1, pp.49–61.

Fabbri, D., Baravelli, V., Giannotti, K., Donnini, F. and Fabbri, E. (2006) 'Bioaccumulation of cyclopenta[cd]pyrene and benzo[ghi]fluoranthene by mussels transplanted in a coastal lagoon', *Chemosphere*, Vol. 64, No. 7, pp.1083–1092.

FAO (2011) *Demand and Supply of Feed Ingredients for Farmed Fish and crustaceans – Trends and Prospects*, FAO Fisheries and Aquaculture Technical Paper 564, Food and Agriculture Organization of the United Nations, Rome.

Ghosh, A.K. and Pattnaik, A.K. (2006) 'Chilika Lagoon', in *Lake Basin Management Initiative*, International Lake Environment Committee [online] http://www.ilec.or.jp/eg/lbm (accessed 1 August 2012).

Gschwend, P. and Hites, R. (1981) 'Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the north-eastern United States', *Geochim. Cosmochim. Ac.*, Vol. 45, No. 12, pp.2359–2367.

Khalili, N.R., Scheff, P.A. and Holsen, T.M. (1995) 'PAH source fingerprints for coke ovens, diesel and gasoline engine highway tunnels and wood combustion emissions', *Atmos. Environ.*, Vol. 29, No. 4, pp.533–542.

Llobet, J.M., Falcó, G., Bocio, A. and Domingo, J.L. (2006) 'Exposure to polycyclic aromatic hydrocarbons through consumption of edible marine species in Catalonia', *Spain. J. Food Prot.*, Vol. 69, No. 10, pp.2493–2499.

Long, E.R., MacDonald, D.D., Smith, S.L. and Calder, F.D. (1995) 'Incidence of adverse biological effects within range of chemical concentrations in marine and estuary sediment', *Environ. Manage.*, Vol. 19, No. 1, pp.81–97.

Loufty, N., Fuerhacker, M., Tundo, P., Raccanelli, S. and Ahmed, M.T. (2007) 'Monitoring of polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like PCBs and polycyclic aromatic hydrocarbons in food and feed samples from Ismailia city, Egypt', *Chemosphere*, Vol. 66, No. 10, pp.1962–1970.

Manivannan, K., Sudhakar, M., Murugesan, R. and Soundarapandian, P. (2010) 'Effect of feed on the biochemical composition of commercially important mud crab Scylla tranquebarica (Fabricius 1798)', *Int. J. Anim. Veter. Adv*., Vol. 2, No. 1, pp.16–20.

Martorell, I., Perelló, G., Martí-Cid, R., Castell, V., Llobet, J.M. and Domingo, J.L. (2010) 'Polycyclic aromatic hydrocarbons (PAH) in foods and estimated PAH intake by the population of Catalonia, Spain: temporal trend', *Environ. Int.*, Vol. 36, No. 5, pp.424–432.

Mohapatra, A., Mohanty, R.K., Mohanty, S.K., Bhatta, K.S. and Das, N.R. (2007) 'Fisheries enhancement and biodiversity assessment of fish, prawn and mud crab in Chilika lagoon through hydrological intervention', *Wetl. Ecol. Manag.*, Vol. 15, No. 3, pp.229–251.

Moon, H-B., Kim, H-S., Choi, M. and Choi, H-G. (2010) 'Intake and potential health risk of polycyclic aromatic hydrocarbons associated with seafood consumption in Korea from 2005 to 2007', *Arch. Environ. Contam. Toxicol.*, Vol. 58, No. 1, pp.214–221.

Neff, J.M. (2002) *Bioaccumulation in Marine Organisms. Effects of Contaminants from Oil Well Produced Water*, Elsevier Science Publishers, Amsterdam, The Netherlands.

Newman, M.C. and Mitz, S.V. (1988) 'Size dependence of zinc elimination and uptake from water by mosquitofish Gumbusia affinis (Baird and Girard)', *Aqua. Toxicol.*, Vol. 12, No. 1, pp.17–32.

Nisbet, I.C.T. and LaGoy, P.K. (1992) 'Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAH)', *Regul. Toxicol. Pharm.*, Vol. 16, No. 3, pp.290–300.

NPC (2010) *Productivity and Competitiveness of Indian Manufacturing: Food Processing Sector. Economic Services Group*, National productivity council, New Delhi.

Pal, S.R. and Mohanty, P.K. (2002) 'Use of IRS-1B data for change detection in water quality and vegetation of Chilika lagoon, east coast of India', *Int. J. Remote Sens.*, Vol. 23, No. 6, pp.1027–1042.

Panigrahi, S., Wikner, J., Panigrahy, R.C., Satapathy, K.K. and Acharya, B.C. (2009) 'Variability of nutrients and phytoplankton biomass in a shallow brackish water ecosystem (Chilika Lagoon, India)', *Limnology*, Vol. 10, No. 2, pp.73–85.

Panigrahi, S.N., Acharya, B.C., Panigrahy, R.C., Nayak, B.K., Banarjee, K. and Sarkar, S.K. (2007) 'Anthropogenic impact on water quality of Chilika lagoon RAMSAR site: a statistical approach', *Wetl. Ecol. Manag.*, Vol. 15, No. 2, pp.113–126.

Perugini, M., Visciano, P., Giammarino, A., Manera, M., Di Nardo, W. and Amorena, M. (2007) 'Polycyclic aromatic hydrocarbons in marine organisms from the Adriatic Sea, Italy', *Chemosphere*, Vol. 66, No. 10, pp.1904–1910.

RSIS (2012) 'Ramsar sites information service', *Ramsar Report for Chilika Lake* [online] http://ramsar.wetlands.org/Database/Searchforsites/tabid/765/Default.aspx (accessed 21 December 2012).

Saeed, T., Al-Yakoob, S., Al-Hashash, H., Al-Bahloul, M. (1995) 'Preliminary exposure assessment for Kuwaiti consumers to polycyclic aromatic hydrocarbons in sea food', *Environ. Int.*, Vol. 21, No. 3, pp.255–263.

Saha, M., Togo, A., Mizukawa, K., Murakami, M., Takada, H., Zakaria, M.P., Chiem, N.H., Tuyen, B.C., Prudente, M., Boonyatumanond, M., Sarkar, S.K., Bhattacharya, B., Mishra, P. and Tana, T.S. (2009) 'Sources of sedimentary PAHs in tropical Asian waters: differentiation between pyrogenic and petrogenic sources by alkyl homolog abundance', *Mar. Pollut. Bull.*, Vol. 58, No. 2, pp.189–200.

Sarkar, S.K., Binelli, A., Chatterjee, M., Bhattacharya, B.D., Parolini, M., Riva, C. and Jonathan, M.P. (2012) 'Distribution and ecosystem risk assessment of polycyclic aromatic hydrocarbons (PAHs) in core sediments of Sundarban Mangrove Wetland, India', *Polycyclic Aromat. Compd.*, Vol. 32, No. 1, pp.1–26.

Siddiqui, S.Z. and Rama Rao, K.V. (1995) 'Limnology of Chilika Lake', in Director (Ed): *Fauna of Chilika Lake*, Wetland Ecosystem Series-I, pp.11–136, Zoologica Survey of India (Calcutta).

Simcik, M.F., Eisenreich, S.J. and Lioy, P.J. (1999) 'Source apportionment and source/sink relationship of PAHs in the coastal atmosphere of Chicago and Lake Michigan', *Atmos. Environ*., Vol. 33, No. 30, pp.5071–5079.

Sundararajan, M. and Srinivasalu, S. (2010) 'Geochemistry of core sediments from Gulf of Mannar, India', *Int. J. Environ. Res*., Vol. 4, No. 4, pp.861–876.

United States Environmental Protection Agency (USEPA) (1989) 'Risk assessment guidance for Superfund', *Human Health Evaluation Manual (Part A)*, Interim final EPA/540/1-89/002, Vol. 1, Office of Emergency and Remedial Response, USEPA Washington, DC.

United States Environmental Protection Agency (USEPA) (2004) 'Risk-based concentration table', *Integrated Risk Information System (IRIS)*, USEPA, Philadelphia, RA.

Yassaa, N., Meklati, B.Y., Cecinato, A. and Marino, F. (2001) 'Particulate n-alkanes, n-alkanoic acids and polycyclic aromatic hydrocarbons in the atmosphere of Algiers City Area', *Atmos. Environ*., Vol. 35, No. 10, pp.843–851.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, H., Goyette, D. and Sylvestre, S. (2002) 'PAHs in the Fraser River basin: a critical appraisal of PAHs ratios as indicators of PAH source and composition', *Org. Geochem*., Vol. 33, No. 4, pp.489–515.