SOURCE APPORTIONMENT OF ATMOSPHERIC AND SEDIMENTARY PAHS FROM KOLKATA, INDIA USING COMPOUND-CLASS-SPECIFIC RADIOCARBON ANALYSIS (CCSRA)

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ABSTRACT. Polycyclic aromatic hydrocarbons (PAHs) are major air pollutants that are ubiquitously produced by the combustion of organic materials, and it is extremely important to identify their pollution sources. In this study, molecular fingerprinting and compound class-specific radiocarbon dating (CCSRA) were performed on PAHs from canal sediments and air samples collected in Kolkata, India's third largest city (population approximately 16 million), where PAHs pollution has been a serious problem. Average PAH (Σ12-parent PAHs) concentrations in air samples were 65.1 ng m^{-3} in summer and 70.9 ng m^{-3} in winter and in canal sediments were 32.7 μg g^{-1}, which are classified as "very high-level" pollution. Molecular fingerprinting using methyl-PAH/PAH (MPAHs/PAHs) ratios and isomer pair ratios with molecular weights of 178, 202, 228, and 276 suggested that wood and coal combustion were the dominant sources of PAHs in the sediment, and that atmospheric PAHs were influenced by oil combustion in addition to them. The fraction of contemporary carbon (fC) of sedimentary PAHs (0.056–0.100), together with the extremely low MPAHs/PAHs ratio results, lead to the conclusion that the major source of the high concentration of PAHs in the canals is from coal combustion. On the other hand, the fC of atmospheric PAHs (0.272–0.369) was close to the share of biomass fuels in India's domestic fuel consumption in 2011 (about 35%). Furthermore, the observed fC-discrepancy between atmospheric and sedimentary PAHs in the same urban environment was interpreted to give an insight into the loading pathway of PAHs to canal sediments in Kolkata.

KEYWORDS: compound specific radiocarbon analysis, micro-scale AMS, polycyclic aromatic hydrocarbons, source apportioning.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) form one of the most important classes of persistent pollutants (Blumer 1976). Some PAHs are carcinogenic and mutagenic. Due to their adverse effects on human/ecological health and widespread distribution around in the environment, identification of sources of PAHs is of particular concern (Pedersen et al. 2004). PAHs are generally produced through the incomplete combustion of organic matter (e.g., fossil fuels, biomass, or detrital organic matter) and emitted into the atmosphere. Because of their hydrophobic nature, once these semi-volatile organic compounds enter the aquatic environment through atmospheric deposition, PAHs accumulate in the underlying sediment and are stored for long periods of time. Surface sediments provide an ideally homogenized natural archive of particle-borne pollution, integrating the input over the past several years as a result of the combined processes of deposition, runoff, water mixing, and sedimentation.

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Accordingly, many researchers have investigated the levels of PAHs in riverine, lacustrine and marine sediments to understand their environmental distribution and have focused on identifying their sources (Okuda et al. 2002; Zakaria et al. 2002; Saha et al. 2009).

Our previous studies analyzed 174 surface sediments from various Asian countries (Laos, Malaysia, Cambodia, the Philippines, Thailand, Indonesia, Vietnam, Japan and India) for PAHs (Saha et al. 2009). The results depicted the very unique nature of Indian sediments: They exhibit high levels of PAHs and a strong pyrogenic signature with very low ratios of methylated- to parent PAHs, in contrast to other tropical Asian countries where PAHs are mainly generated from petrogenic sources (Saha et al. 2009). Fingerprinting of sedimentary PAHs with source materials suggested that the PAHs may have originated from the combustion of fossil fuels (primarily coal) and biomass (grass and wood). This uniqueness of Indian sediments may be due to massive use of fossil fuels (coal, coal products) and biomass (wood) as major energy sources by most industries in India, whereas petroleum and its products are major energy sources in other tropical Asian countries. This motivated us to apply microscale compound specific or compound class specific radiocarbon analysis (CSRA or CCSRA) to PAHs in Indian sediments (Kumata et al. 2006; Uchida et al. 2005). The 5730-year half-life of radiocarbon (^{14}C) makes it an ideal tracer for distinguishing combustion products derived from fossil fuels (^{14}C-free) from those from modern biomass fuels (contemporary ^{14}C) (Currie et al. 1997; Kumata et al. 2006; Uchida et al. 2023b).

In addition to sedimentary PAHs, we also intended to perform CCSRA for atmospheric PAHs to better understand the exact origin of pyrogenic PAH emissions (between coal and biomass) to the Indian environment. India's energy consumption has changed dynamically in recent decades, increasing from 9.00×10^6 TJ in 1990 to 2.29×10^7 TJ in 2015 (IEA World Energy Balances, https://www.iea.org/countries/india, last accessed on Jan 10, 2023). This increase is mainly attributed to the increased consumption of coal and oil (by factors of 2.5 and 3.6, respectively), while the increase of biomass-based fuels consumption remains relatively small, namely by a factor of 1.5. Such an energy shift would affect the relative importance of combustion sources. Therefore, a comparison of ^{14}C-based source apportionment between atmospheric and sediment samples from the same environmental setting was also attempted in this study. The objectives of the present study were as follows: (1) to elucidate the ^{14}C content of atmospheric and sedimentary PAHs by using CCSRA, and (2) to discuss the likely measures to reduce PAH pollution in the Kolkata environment based on the comparison between the obtained CCSRA results (receptor data) with statistics (source data).

MATERIALS AND METHODS

Sample Collection

Sediment samples: Kolkata is the main commercial and financial center of eastern India, with a population of 15.55 million (2016). In 2006, two surface sediment samples were collected from canals of Kolkata (Figure 1). Out of two canal sediment samples, one sample was taken from Northern canal (KKNC) and one from Southern canal (KKSC) of Kolkata. These two locations were chosen because the preliminary survey showed it has extremely high-level contamination (Saha et al. 2009). The North canal, named as "Keshtopur Canal", stretches over a distance of 43 km and flows into Bidyadhari River, a tributary of Hugli River. Earlier this canal was used for passenger and cargo movement but later due to extensive encroachment on the canal banks, it became a stagnant body of filthy water and a pollution hazard. The south canal, named as "Tolly's Nullah (previous name Adi Ganga)", used to be a branch of Hugli
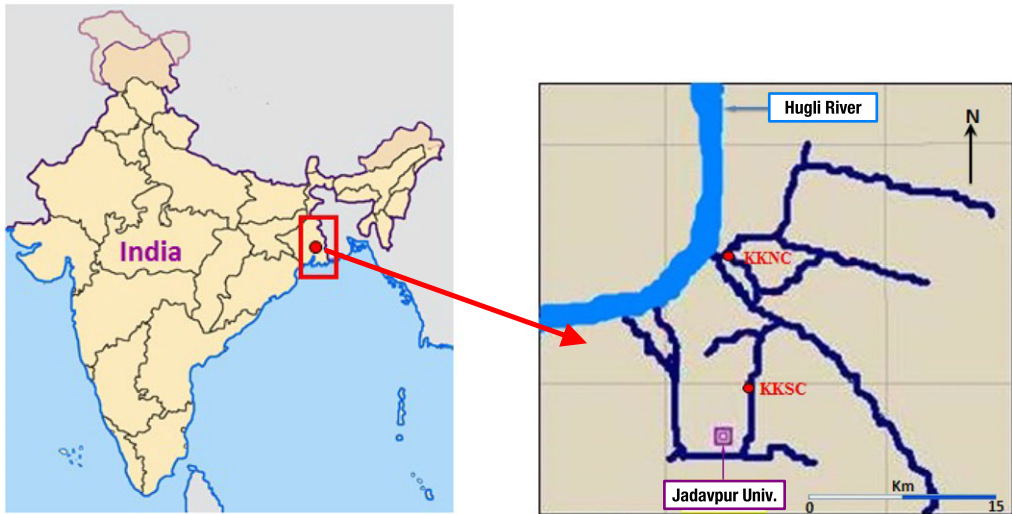
Figure 1   Map of the sampling locations of surface sediments in north and south canals (KKNC and KKSC) and air samples (Jadavpur University) around the city of Kolkata, India.

River previously. It originates from Hugli at hastings near Dholaghat bridge and passes through the Kidderpore area which is known for an active port in this area. The south canal was a main stream towards the Bay of Bengal. But during last few decades, it turned into a sewer channel for the southwestern part of Kolkata due to disposal of waste of all kinds by small factories, eateries and residences along the bank of the canal and huge siltation caused by increasing population of Kolkata.

The sediment samples were collected by using the Ekman dredge and top 0–5 cm of sediments was taken using precleaned stainless steel scoop. Based on both active input of terrestrial materials to the canals and strong flushing of the bottom sediment caused by frequent and strong rain in the tropical area, the top 5 cm layers of the sediments are assumed to represent relatively recent input for the last one to two decades. The samples were placed in tightly sealed solvent-rinsed stainless-steel containers and transported on ice to laboratory. The samples were stored at -30°C and freeze dried before analysis.

Air samples: Five 24-hr air samples were collected monthly during May to October 2011 (summer sample) and three were collected during January to February 2011 and in November 2011 (winter sample) on the roof of a 4-story building in Jadavpur University, Kolkata, India (22.4991N, 88.3714E). Air sampling was performed using a high-volume air sampler (Sibata HV-1000F) consisting of a quartz fiber filter (Pallflex 2500QAT-UP, 200×250 mm) and three polyurethane foam plugs (PUF; Sibata 8013-0941A polyurethane for dioxin, $\phi 90$ mm $\times$ 50 mm) arranged in series to collect both particulate and gaseous PAHs. The flow rate of air sampler was 800 L min^{-1}. The collected filters and PUFs were separately wrapped in aluminum foil and stored in press-seal bags at –30°C. Preceding sampling the filters were heated at 450°C for 5 hr. Also prior to use polyurethane foam plugs were rinsed in water and then with acetone, and Soxhlet extracted twice for 24 hr with acetone. Finally, they were dried in a vacuum desiccator and sealed in glass jars until sampling.

Extraction and Cleanup Procedures for PAHs Determination

Details of the extraction and purification procedures for determination of PAHs concentrations in sediment and aerosol samples were described previously (Saha et al. 2017). In brief, PAHs were extracted from dry samples using pressurized solvent extractor (Dionex ASE 200 or ASE 300) with a mixture of dichloromethane (DCM) and methanol (95:5, v/v). To determine gaseous PAHs, PUF samples were extracted in Soxhlet apparatus for ~12 hr with DCM. One sixth (sediment) to one third portion (air sample) of each extract was roto-evaporated, spiked with recovery surrogates (anthracene-d_{10}, *p*-terphenyl-d_{12}, benzo[a]anthracene-d_{12}, and perylene-d_{12}), and then applied to 2-step silica gel column chromatography as detailed elsewhere. Silica gel (5% water deactivated) column chromatography was used to eliminate polar components. Aliphatic and aromatic hydrocarbons were fractionated through a fully activated silica gel column following activated copper treatment for elemental sulfur removal. PAHs fractions were analyzed by a gas chromatograph coupled to a quadrupole mass-selective detector (GC-MS; Agilent 5973N) as described (Boonyatumanond et al. 2006). Separation of analytes were conducted by using a 30 m fused silica capillary column (HP-5MS) programmed as follows: initial temperature 70°C for 2 min, ramp to 150°C at 30°C min^{-1} then to 310°C at 4°C min^{-1}, and hold for 10 min.

Identification and quantification were performed in selected ion monitoring (SIM) mode as described in Saha et al. (2009). In the present study 14 parent PAH species and 12 methylated PAH species were quantified. The parent PAHs and their abbreviation in bracket are as follows: phenanthrene (Phe), anthracene (Anth), fluoranthene (Fluo), pyrene (Pyr), benz[a] anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene + benzo[k]fluoranthene (BFs), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Pery), indeno[1,2,3-cd]pyrene (InP), benzo[ghi]perylene (BgP), and coronene (Cor). On GC-MS, they were monitored at *m/z* 178 (Phe, Anth), *m/z* 202 (Fluo, Pyr), *m/z* 228 (BaA, Chr), *m/z* 252 (BbF, BFs, BeP, BaP, Pery), *m/z* 276 (InP, BgP), and *m/z* 300 (Cor).

Four isomers of methylphenanthrenes were monitored at *m/z* 192, which were identified as 3-, 2-, 9- and 1-methylphenanthrene (3-, 2-, 9-, and 1-MP) in the order of elution. The identification was based on the comparison of retention time with an authentic standard (1-MP) and of retention indices (Lee et al. 1979; Takada et al. 1990). Three peaks of methylpyrenes (MPy) and/or methylfluoranthenes were observed at *m/z* 216 and five peaks of methylchrysenes (MC) and/or methylbenz[a]anthracenes were monitored at *m/z* 242. The details of peak identification were given in a previous report (Saha et al. 2009). To make a comparison of our values with literature data, sum of major 12 parent PAHs, i.e., Phe, Anth, Fluo, Pyr, BaA, Chry, BbF, BkF(BjF), BaP, InP, BgP, DBA was calculated as Σ12 PAHs. Concentrations were recovery corrected with spiked surrogates (consistently > 80%). Reproducibility in four replicate analyses was 1% to 19% relative standard deviation. Procedural blanks were run in each batch, and analytical values ≥ 5× the blank were considered as significant.

Preparation of Purified PAHs Fraction

CCSRA samples were prepared from the leftover extract basically the same manner as in the previous study (Kumata et al. 2006). In brief, the extracts of each sample were saponified with 0.5 M KOH/methanol for 2 hr under reflux. Neutral organic compounds were separated from acidic compounds by two-phase partitioning. The organic phase containing neutral compounds was applied to silica gel column chromatography (deactivated with 2% water) to separate aliphatic and aromatic hydrocarbons into N1 and N2 fractions. PAHs in the N2

fraction were further purified by DMF-hexane cleanup. PAH fractions from the aerosol filters and corresponding PUF samples were combined prior to this DMF-hexane cleanup. Treatment of the sediment extracts by, alkaline/methanol saponification, silica gel column chromatography and DMF provided a sufficiently clean PAHs fraction for successful isolation of PAHs by PCGC. Therefore, PAHs with 3 aromatic rings (i.e. phenanthrene and anthracene), those with 4 rings (i.e. fluoranthene and pyrene) and those with 5–6 rings were pooled separately and analyzed for ^{14}C as "Phe+Anth", "Fluo+Pyr" and "HMW" PAHs, respectively (Table 2).

PAH fractions from air samples contained large amounts of unresolved complex mixture (UCM) even after the above procedures. To reduce adverse effect of UCM on PCGC peak isolation, ring class separation was performed using a cyano/amino bonded normal phase high performance liquid chromatography (HPLC) technique. The PAHs purified from air samples were injected into an HP 1200 HPLC with a photodiode array detector (monitoring 210–350 nm) and fractionated into ring-size classes on a 25 cm × 4.6 mm i.d. Partisil 5 PAC column (Whatmann; 1:2 cyano/amino bonded phase column) connected in series with a precolumn (2 cm × 4.6 mm i.d.; packed with Partisil 5 PAC). HPLC conditions as reported elsewhere (Kanke et al. 2004; Takada et al. 1990) were modified and used in this study. A binary solvent (*n*-hexane and 2-propanol) was used as the mobile phase. HPLC run in the gradient mode (2 ml min^{-1}). The linear gradient was programmed to go from 100% n-hexane until 1 min, then declined to 98.25% by 15 min, 89.9% by 17 min and then held for 3 min. Four fractions were collected at 5.0–6.3, 6.3–9.2, 9.2–14.0 and 14.0–16.2, containing PAHs with 3 rings, 4 rings with MW ≤216, 4 rings with MW ≥228 and 5–7 rings, respectively and separately analyzed by GC-FID to check if background UCM level is sufficiently reduced. Then, the resulting 3- and 4-ring aromatic fractions were then injected onto the PCGC system and the peaks of 9 compounds (i.e., Phe, Anth, 3-, 2-, 9-, and 1-MPs, 4H-cyclopenta[def]phenanthrene, Fluo and Pyr) were pooled together and analyzed for ^{14}C (Table 2).

Preparation of Graphite Targets and Microscale AMS-^{14}C Analyses

The PAH extracts were repeatedly injected onto a PCGC until sufficient amount (>10 μg-C) of compounds was obtained in each trap. The PCGC system used consists of an Agilent Technology 7890A gas chromatograph, equipped with a flame ionization detector (FID), a 7693A Autoinjector and a Multimode Inlet (MMI), and integrated with zero-dead volume effluent splitter and a Gerstel preparative fraction collector (PFC) unit. The PCGC system was operated under conditions optimized for PAHs (Mandalakis and Gustafsson 2003). The harvested compounds were recovered from the glass traps with dichloromethane (Cica, dioxin analysis grade, Kanto Chemical Co., Inc.). An aliquot (2%) was used to determine the purity and yield of the compound by GC-FID. Any residual column bleed was eliminated by eluting through a silica gel column, and the isolates were transferred to precombusted quartz tubes, where the solvent was evaporated under N$_2$ stream and CuO was added to each tube. The tubes were evacuated (10^{-6} Torr), flame sealed, and combusted at 500°C for 1 hr (Uchida et al. 2010, 2023a; Bao et al. 2018). The CO$_2$ was then reduced to graphite. The use of a specially designed ultra-low background graphite reactor vessel and automated vacuum line (Uchida et al. 2004, 2023a, 2023b) enabled successful graphitization for the small amount samples (i.e., 16–29 μg-C) treated in this study. Prepared graphite targets were analyzed for ^{14}C/^{12}C by NEC 5 MV tandem Pelletron AMS System (15SDH-2) at NIES-TERRA, the National Institute for Environmental Studies. All ^{14}C measurements are expressed as percent modern carbon (pMC), defined as the percentage of modern carbon, with reference to HoxII, the international ^{14}C

dating standard, SRM4990C, with a $\delta^{13}C$ correction for the ^{14}C activity of the sample using the following equation (Stuiver and Polach 1977).

$$\text{pMC} = \left[\left(^{14}C/^{12}C \right)_{\text{sample}} / \left(0.749 \times \left(^{14}C/^{12}C \right)_{\text{HoxII}} \right) \right] \times 100$$

The fraction of contemporary carbon (fC) expression was introduced to compensate for the temporal variation of the biosphere ^{14}C value using the pMC of the atmosphere ($\text{pMC}_{\text{(atm)}}$) at the time of sampling, as below.

$$f\text{C}_{\text{(sample)}} = \text{pMC}_{\text{(sample)}} / \text{pMC}_{\text{(atm)}}$$

RESULTS AND DISCUSSION

Concentrations and Molecular Compositions of PAHs in Sediments and Air Samples

The concentrations of Σ12-parent-PAHs in KKNC and KKSC sediments were 26.3 and 37.9 μg g^{-1} respectively. As shown in Figure 2, PAHs from surface sediments were depleted in alkylated-species, which is characteristic of high-temperature combustion sources as discussed later. The sum of gaseous and particulate Σ12-parent-PAHs in air ranged from 23.7–151.0 (average: 65.1) ng m^{-3} for summer and 65.3–81.5 (average: 70.9) ng m^{-3} for winter samples. As shown in Figure 3, the air concentrations of PAHs were mostly in gaseous form. These sedimentary and atmospheric concentrations are categorized "very high-level" pollution even within Asian megacities (Saha et al. 2009, 2017).

Source Diagnosis by MPAHs/PAHs Ratios

To evaluate the relative contributions of petroleum combustion and coal and wood combustion, the three ratios of alkylated PAHs to their respective parent PAHs: methylphenanthrenes to phenanthrene (MP/P), methylpyrenes + methylfluoranthenes to pyrene + fluoranthene (MPy/Py) and methylchrysenes + methylbenz[a]anthracenes to chrysene + benz[a]anthracene (MC/C) and the ratio of all alkyl PAHs to respective parent PAHs (MPAHs/PAHs) were examined according to Saha et al. (2017) and references therein. This diagnosis is based on the thermodynamically stable nature of the parent PAHs compared to their alkylated species (Blumer 1976). High-temperature combustion, such as that of coal and wood, depletes alkylated PAHs, whereas they remain abundant in petroleum formed diagenetically in the crust at low temperatures. The mixing of residual petroleum components with combustion products results in higher ratios of methyl PAHs to parent PAHs in vehicle exhaust compared to those from coal and wood combustion. Indeed, analyses of PAHs in various source materials collected in tropical Asian countries (crude oil, automobile exhaust, and coal-combustion-derived soot from cooking and brick yards and wood-combustion-derived soot) in our previous studies (Saha et al. 2009, 2012) revealed that vehicle exhaust have high values of these four PAHs ratios (i.e., MP/P > 3.5, MPy/Py > 1.5, MC/C > 2.0, MPAHs/PAHs > 2.2) while combustion products from coal and wood combustions exhibit low ratios (i.e., MP/P < 0.5, MPy/Py < 0.15, MC/C < 0.2, MPAHs/PAHs < 0.3).

Table 1 summarizes these diagnostic methylated/parent PAH ratios for sediment and aerosol samples from the Kolkata environment. Comparing the observed values with the above mentioned criteria, the methylated/parent PAH ratios for both KKNC and KKSC were mostly categorized as "influenced by high temperature sources burning wood and/or coal fuels". On the other hand, aerosol PAHs show more contributions from petroleum combustion. This is
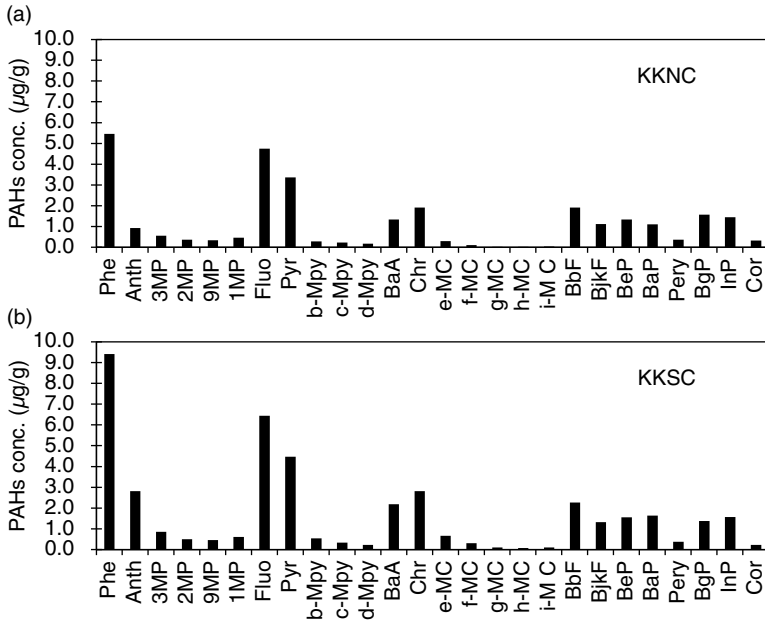
Figure 2 Concentrations of individual PAHs quantified in surface sediments from (a) Nothern canal (KKNC) and (b) Southern canal (KKSC) in Kolkata, India.

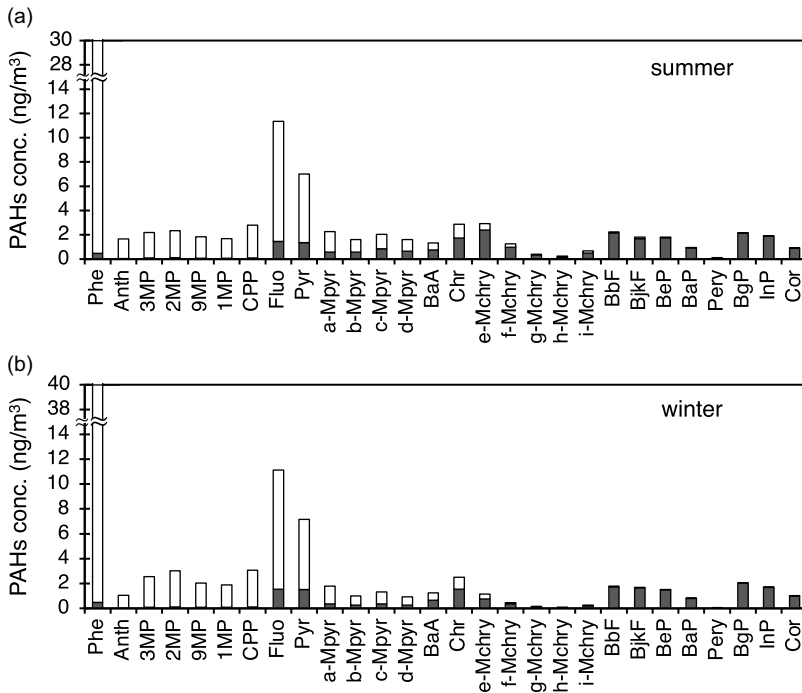
Figure 3 Concentrations of individual PAHs in gaseous (open bar) and particulate forms (solid bar) in air samples from Kokata, India.

Table 1 The source diagnostic ratios of methylated/parent PAHs and isomer pairs in surface sediments and atmospheric aerosols from Kolkata, India.

| | Air (particulate only) | | | | Surface sediment | |
	Winter		Summer		KKNC	KKSC
Methylated/parent PAHs ratio						
MP/P	0.87	±0.40	0.98	±0.26	0.32	0.26
MPy/Py	0.10	±0.02	0.15	±0.01	0.09	0.10
MC/C	0.21	±0.03	0.33	±0.05	0.16	0.25
MPAHs/PAHs	0.22	±0.07	0.33	±0.07	0.16	0.17
Isomer pair ratio						
Anth/Anth+Phe	0.07	±0.00	0.08	±0.01	0.15	0.23
Fluo/Fluo+Pyr	0.50	±0.01	0.52	±0.01	0.58	0.59
BaA/BaA+Chr	0.31	±0.02	0.31	±0.01	0.41	0.44
InP/InP+BgP	0.46	±0.02	0.46	±0.03	0.52	0.47

partly due to higher contributions from vehicle exhaust to PAHs in air samples than in canal sediments.

To comprehend the above source diagnosis, other isomer pair ratios i.e., Fluo/Fluo+Pyr, Anth/Anth+ Phe, BaA/BaA+Chr, InP/InP+BgP were also examined (Table 1). The isomer pair ratios in canal sediments corresponded to Anth/Anth+Phe > 0.1, BaA/BaA+Chr > 0.35, Fluo/Fluo+Pyr > 0.5 and InP/InP+BgP > 0.5, which predicts that the sediments from KKSC and KKNC are strongly influenced by combustion derived PAHs and/or those from grass, wood and coal burning (Yunker et al. 2002). Two isomer pair ratios with low susceptibility to photolytic alteration, corresponded to Fluo/Fluo+Pyr ≥ 0.5 and InP/InP+BgP between 0.2 and 0.5, suggesting mixed contributions from petroleum combustion and grass, wood and coal burning.

[14]C-PAHs in the Atmosphere and Surface Sediments

Table 2 lists the CCSRA results of atmospheric and sedimentary PAHs. The values of fC for sedimentary PAHs ranged from 0.056 to 0.100 and those for atmospheric PAHs were 0.369 in summer and 0.272 in winter, indicating that fossil carbon is the dominant source for both sedimentary PAHs (90–95% fossil) and atmospheric PAHs (63–73% fossil). The ^{14}C data for canal sediments are comparable to those reported for urban reservoir sediments from the United States (Reddy et al. 2002), Stockholm, Sweden (Mandalakis et al. 2004) and in Tokyo, Japan (Kanke et al. 2004). Although the extremely low ^{14}C abundances of sediementary PAHs in these studies were roughly interpreted as originating from coal and/or petroleum combustions, the very low fC values for PAHs in the canal sediments observed in this study, together with the very low MPAHs/PAHs ratios (Table 1), clearly indicate that coal combustion is the predominant source of high levels of PAHs in the canals of Kolkata.

As for the ^{14}C data for atmospheric PAHs, they were comparable to those, e.g., from Tuzla, Bosnia-Herzegovina (Zencak et al. 2007) and Tokyo, Japan (Kumata et al. 2006). Even higher values have been reported for a background site around Stockholm, Sweden (Mandalakis et al. 2005) and rural and urban sites in the Balkans (Zencak et al. 2007). Notably, the fC values of 27–37% for atmospheric PAHs are in good agreement with statistics on energy consumption in

Table 2   [14]C content (pMC) for atmospheric and sedimentary PAHs from Kolkata (numbers in parentheses are fC).

	Surface sediment		Air (aerosol + gaseous)[a]	
	KKNC	KKSC	Summer	Winter
Phe + Anth	10.6	8.4	35.8	26.4
	(0.100)	(0.079)	(0.369)	(0.272)
MPs[b]	—	—		
Fluo + Pyr	5.9	8.3		
	(0.056)	(0.078)		
HMW[c]	7.6	8.5	—	—
	(0.072)	(0.08)		

[a]Include Phe+Anth, MPs, and Fluo+Pyr

[b]Include 3-, 2-, 9- and 1-methylphenanthrenes, 4H-cyclopenta[def]phenanthrene and 2-methylanthracene.

[c]Include benz[a]anthracene + chrysene/triphenylene + benzo[b+j+k]fluoranthenes + benzo[e+a]pyrenes + indeno[123-cd]pyrene + dibenz[ah]anthracene + benzo[ghi]perylene.
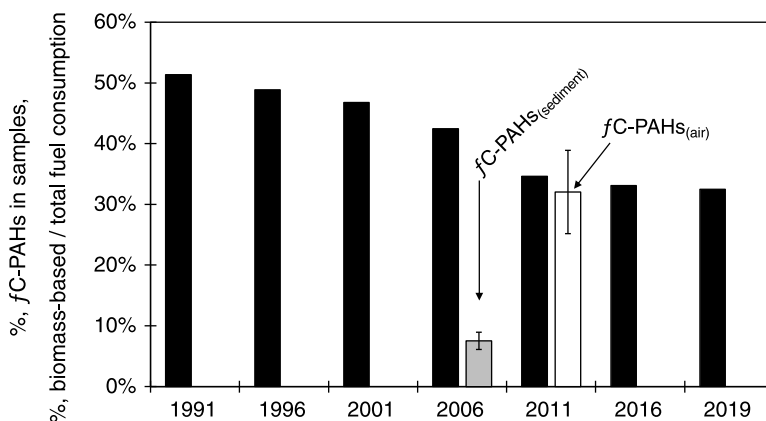

Figure 4   Comparison of the fraction of contemporary carbon (fC) values obtained by CCSRA for atmospheric (open bar) and sedimentary PAHs (gray bar) with the relative contribution of biomass-based fuels to the fuel based energy consumption. Biomass-based fuel refers to "Renewables and waste" and fuel based refers to the sum of *"Coal, peat and oil shale"*, *"Crude, NGL and feedstocks"*, *"Oil products"*, *"Natural gas"*, and *"Renewables and waste"* defined in IEA, *World Energy Balances (database)* (2021).

India (IEA World Energy Balances) (Figure 4). According to the statistics for 2011, the consumption of biomass-based fuels in India was about 5.81×10^6 TJ, which corresponds to about 35% of the fuel-based energy supply (i.e., sum of coal, natural gas and oils, biomass-based fuels). The agreement between the fC values of atmospheric PAHs and energy consumption statistics is in contrast to the interpretation of atmospheric ^{14}C-PAHs described in previous literature (Mandalakis et al. 2005; Kumata et al. 2006), where observation of the modern carbon contribution to atmospheric PAHs higher than would be expected from energy supply statistics has been interpreted as being due to differences in emission factors for PAHs from biomass burning and fossil fuel burning. Furthermore, the fC values of 27–37% are consistent with the inference made in our previous study that biomass, coal, and petroleum

combustion contribute equally (Saha et al. 2017), but the contribution of coal and petroleum combustion cannot be discussed from this result.

Next, the fC-discrepancy between the 2011 atmospheric samples and canal sediments collected in 2006 will be discussed. In this study, there is a five-year difference in the timing of the collection of atmospheric samples and canal sediments. If it can be assumed that the emission status of PAHs to the atmosphere in Kolkata has not changed dramatically during this 2006–2011 period, then the fC values for atmospheric PAHs in 2006 would be similar or slightly higher than in 2011. Therefore, the difference in timing of sampling does not explain the observed fC-discrepancy between the atmosphere and the sediments. The fC-discrepancy between atmospheric and sedimentary PAHs, normally with higher ^{14}C value in the former, has been previously reported in Tokyo, Japan and in Europe (Uchida and Kumata 2014 and references therein). These observations have been interpreted as due to differences in the length on the time axis reflected by the samples. That is, air samples reflect only the pollution of the sampling period, whereas surface sediments reflect the accumulated pollution load over the past several years to decades.

The vertical distribution of ^{14}C-PAHs in sediments was reported in only one case, in the core sediments of metropolitan Tokyo, Japan (Kanke et al. 2004). They reported increasing trend in the ^{14}C abundance of phenanthrene and methylphenanthrenes towards the surface of the core sediment, while their concentrations decreased. If the surface layer of such sediments is measured as an accumulation of time-series changes, the ^{14}C abundance of the latest atmospherically deposited particles would be apparently attenuated by the incorporation of PAH-bound particles deposited during a period when the impact of fossil fuel combustion was stronger. However, this scenario may not be the case for the Kolkata environment. According to 1990 statistics, the oldest data for India in the IEA dataset (IEA World Energy Balances), the relative contribution of biomass-based fuels (4.28×10^6 TJ) to the fuel based energy consumption (8.24×10^6 TJ) was 52%, which decreased gradually to 35% in 2011. This suggests that contamination of old PAH-bound particles would result in fC-discrepancy, where the sediments show higher ^{14}C abundance than the atmosphere, but the measured results were the opposite.

Based on the above considerations, the likely explanation for the observed fC discrepancy between atmospheric and sedimentary PAHs is the incorporation of highly contaminated, large diameter PAH-bound particles from coal combustion via runoff events and/or short-range wind-induced suspension/deposition. To reduce such particulate PAH load in the aquatic environment of Kolkata, regulation of particulate emission from stationary and domestic sources for coal combustion and installation of particle settling pond in the runoff-discharge system will be an effective measure.

SUMMARY

In order to determine the source of PAHs pollution in Kolkata, India, where intense pollution has been reported, molecular composition analysis and CCSRA of PAHs in air and canal sediments were conducted. As for PAHs in the canal sediments, observation of very low fC values as well as the MPAHs/PAHs ratio indicated that coal combustion was the major source of contamination. For PAHs in the air, about one-third of the pollution was estimated to be from biomass combustion, consistent with pollution rates estimated from energy consumption statistics. The results indicate the necessity of reducing emissions from combustion sources of

biomass, coal, and petroleum, respectively, in order to reduce air pollution. In this study, the discrepancy between fC values of PAHs in air and sediments in the same urban environment was found. This indicates that particulate matter entering canal sediments through surface runoff is more important than atmospheric deposition as a pollution loading pathway, and thus its control is essential for the reduction of pollution.

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