POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN SEDIMENTS FROM THE ZIJIANG RIVER WATERSHED, HUNAN, CHINA

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Abstract: Zijiang River, a typical river in Hunan province, was studied for its sediment quality, by determining the levels of 16 polycyclic aromatic hydrocarbons (PAHs) in sediment samples. Total PAHs concentrations in surficial sediments varied from 760.10 ng g^{-1} to 7611.43 ng g^{-1}. The sources of PAH contamination were inferred from PAH composition, with petro-chemical product and petroleum combustion sources being the dominant source.
Key words: Distribution, PAHs, Zijiang River watershed, sediment

Introduction

Zijiang River watershed, covering an area of 28142 km^2, is located in the middle part of Hunan Province. Lengshuijiang City in the middle reaches of Zijiang River has long enjoyed the fame of "Antimony capital of the world". Due to its natural richness in mineral, Lengshuijiang City is a newly developed industrial city with large amount of medium and large scale state-owned enterprises. With continued rapid development and increased industrial growth in these areas, the ecological and environmental health of these estuarine systems face increasing pressure from contaminants associated with industrial development and manufacturing activities. Major organic contaminant sources in the surrounding area include oil spills and combustion generated PAHs from manufacturing plants. This paper aims to study the distribution, characteristic and their origin of selected parent PAHs in the sediments from the middle reaches of Zijiang River near the Lengshuijiang city, Hunan Province, China.

Materials and methods

Sampling and sample treatment

The locations of the sampling stations are shown in Figure 1. Sampling campaign was conducted at 12 sites in dry season of December 2008. Sites 3-12 were selected in the main stream, all of the sites are subject to several sources of contamination from anthropogenic activity. Sites 1-2 are from the tributaries near Lengshuijiang City. Top 5-cm surface sediments were taken using a stainless steel grab sampler and placed in precleaned glass jars. The sediment samples were cooled in a refrigerator (0 °C) during transport to the laboratory where they were stored at -20 °C until further analysis. Frozen aliquots of sediments were freeze dried by freeze drier (FD-1A, China), and were ground with a mortar and sieved through a 100-mesh sieve and then stored in pre-cleaned dark glass bottles before extraction.

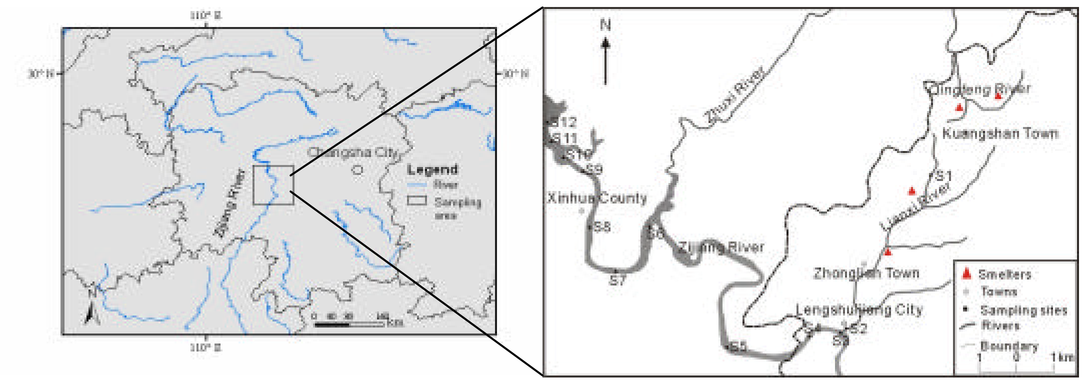

Fig.1 The study areas and sampling locations in the Zijiang River watershed

Sample Extraction

The extraction procedure for sediment samples followed the other authors[1]. Briefly, a freeze-dried sediment sample was spiked with surrogated standards (three perdeuterated PAH compounds: acenaphthene-d10, phenanthrene-d10 and chrysene-d12) and was Soxhlet extracted with 250 mL dichloro methane/hexane (1:1, v/v) for 24 h in a water bath maintained at 60 °C. Activated copper was added for desulfurization. The extract was concentrated and solvent-exchanged to hexane using a rotary evaporator. The hexane extract was subject to a 1:2 alumina/silica gel glass column for cleanup and fractionation. The column was eluted with 15mL of hexane, and the eluate was discarded. The second fraction containing PAHs was eluted with 70 mL of methylene chloride/hexane (30:70, v/v). Elutes were pre-concentrated with a gentle steam of purified nitrogen. Finally 10 μ l of the internal standards (hexamethylbenzene) was added and made up to1 ml in a volumetric flask with hexane. The purified extracts were transferred into a glass vial for analysis. Target analytes include 16 PAH compounds, i.e., naphthalene (Nap), acenaphthylene (Ace), acenaphthene (Ac), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Pyr), benzo[a]anthracene(BaA), chrysene, benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene(BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthrancene (DahA) and benzo[g,h,i]perylene (BghiP).

Instrument Analyses

Concentrations of PAHs were determined with a Varian 3800 Series II gas chromatograph (GC) equipped with a 1177 injector, a CP-8400 autosampler and an Varian-4000 mass selective detector (MSD) and an VF-5 capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness) from Varian (Walnut Creek, CA, USA). The chromatographic conditions of PAHs were the same as those detailed elsewhere[2].

Quality assurance

Spiked sediment samples were determined with good precision, and recoveries ranged from 64.1 to 103.10 % for PAHs. In addition, the errors involved in sampling were assessed by carrying out triplicate sampling of water at the same site and the analysis of sample extracts. Results showed good reproducibility of the sampling process.

Surrogate standards were added to all samples prior to extraction to quantify the procedural recoveries. The mean surrogate recoveries in the samples were 60.8 ± 16.8% for acenaphthene-*d*10, 102.3 ± 15.3% for phenanthrene-*d*10 and 88.9 ± 8.0% for chrysene-*d*12. Each extracts was analyzed in duplicate form and relative standard deviation were less than 20%.

Result and Discussion

Total PAH concentration

The total PAH concentrations in sediment of the Zijiang River watershed ranged from 760.10 ng g^{-1} to 7611.43 ng g^{-1}, with a mean concentration of 2792.75 ng g^{-1} (Table 1). The highest concentration was found at site 2 (7611.43 ng g^{-1}) and site 3 (5313.03 ng g^{-1}). Both the site 2 and 3 were located near Lengshuijiang City, reflecting that the input of PAH from Lengshuijiang town may be the main pollution maker. The high concentration was also found at site 8 (3643.06 ng g^{-1}), and the concentration gradually decreased along the river from site 8 due to the dilution of river water.

PAHs composition

In terms of individual PAH composition in sediment, all target compounds except DahA at site 1, IcdP at site S4 and S9 were detected at all the stations. In the 12 sites of the Zijiang River watershed, 4-ring PAHs including Flu, Pyr, BaA and Chr is most abundant, 3-ring PAHs takes second place (Fig.2). The average percentage of high-molecular weight PAHs (4–6 ring PAHs) to total PAHs ranged from 58% to 83%, with a mean percent 67% (Fig. 2). The importance of high molecular weight PAHs has been commonly observed in sediments from river, marine or lacustrine environments[3-6]. Doong and Lin[4] showed that 3-, 4-ring PAHs dominated PAH distributions in sediments from Gao-ping River in Taiwan. This result may reflect that low molecular mass PAH gradually decreased by degradation and adsorption, only those PAHs that have relative high molecular mass and more resistant to degradation can survive to reach the sediment leads to high-molecular weight PAHs higher in Daliao River Estuary. However, some study investigated the importance of low molecular weight PAHs[2,7].

Table 1 Concentration of 16 polycyclic aromatic hydrocarbons (ng g^{-1} dry wt) in surface sediments of 12 sampling stations.

Compounds	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
Nap	126.4	235.80	45.52	8.86	52.78	109.90	83.19	39.84	91.98	237.64	187.53	29.96
Ace	8.50	125.39	47.06	7.61	33.11	25.57	10.95	50.93	22.99	24.12	19.01	9.63
Ac	11.69	67.04	31.76	0.94	20.70	25.15	14.53	24.65	29.68	35.57	27.15	18.67
Flu	45.49	328.81	188.70	15.48	119.31	155.20	63.61	74.75	112.62	126.52	113.70	51.63
Phe	177.8	1356.4	814.28	157.47	716.50	601.92	243.43	474.26	466.57	487.32	448.09	198.7
Ant	21.69	372.69	246.43	40.01	171.61	129.30	42.17	127.18	70.60	74.63	66.55	29.80
Pyr	91.72	1366.9	881.98	246.07	643.08	404.41	159.55	542.80	362.06	321.56	271.62	132.1
Fl	71.35	1131.1	766.14	215.78	600.63	426.15	180.22	510.15	352.40	341.28	294.75	148.9
BaA	28.60	536.16	435.91	108.49	190.10	149.61	60.68	287.14	127.41	103.69	99.80	46.10
Chr	59.93	537.72	493.15	125.38	296.01	245.31	104.85	339.84	231.92	192.08	190.42	80.75
BbF	21.62	598.64	541.54	109.63	161.34	181.14	78.75	380.59	149.46	152.79	119.39	72.50
BkF	32.07	188.31	107.77	133.73	42.94	212.37	44.34	113.96	16.28	39.55	84.75	22.82
BaP	18.99	315.62	314.13	76.60	50.54	65.02	40.50	260.94	98.03	55.76	53.70	31.88
IcdP	21.45	168.06	98.16	nd	29.77	18.61	24.85	127.39	nd	35.86	21.70	30.98
BghiP	22.78	220.73	256.64	60.81	38.51	51.67	48.80	248.34	74.59	73.67	71.58	39.54
DahA	nd	61.96	43.83	18.06	22.05	15.90	23.10	40.31	30.58	28.02	27.48	22.21
ΣPAHs	760.1	7611.4	5313.0	1324.9	3188.9	2817.2	1223.5	3643.1	2237.2	2330.1	2097.2	966.2

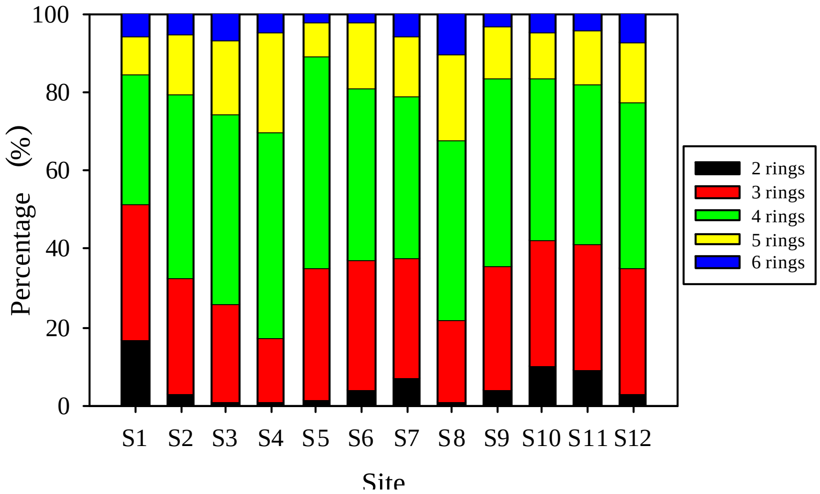

Fig.2 Percentage of individual PAHs values in sediment of the Zijiang River watershed

PAHs source

In order to survey the sources of PAHs in Zijiang River, Phen/Ant against Fl/Pyr and InP/(InP + BgP) against Fl/(Fl + Pyr) were plotted (Fig. 3). Based on the PAH isomer pair ratio measurements compiled by other authors[8-10]: Phen/Ant ratios lower than 10 indicates dominance of combustion processes, whereas values higher than 10 in petroleum input or diagenetic [8]; Fl/(Fl + Py) ratio < 0.40 petroleum, 0.40-0.50 petroleum combustion, and >0.50 combustion of coal, grasses and wood[4]; and IcdP/(IcdP + BghiP) < 0.20 petroleum, 0.20-0.50 petroleum combustion, and >0.50 combustion of coal, grasses and wood [9,10]. As is shown in Fig. 3a, mixed sources for all the samples were found. Fig. 3b also illustrated that petro-chemical product and petroleum combustion sources in the sediments.

Acknowledgments

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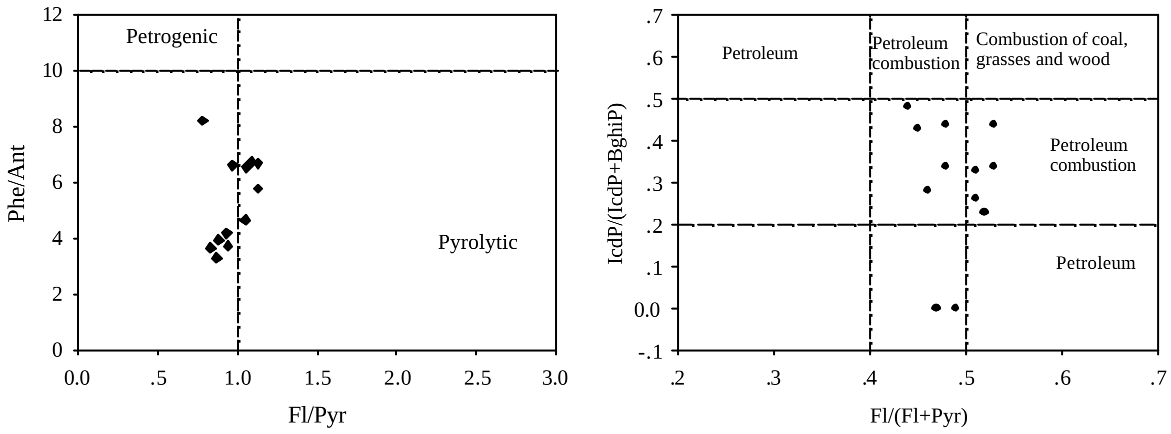

Fig.3 Plot of the isomeric ratios Phe/Ant vs Fl/Pyr, and Fl/(Fl+Pyr) vs IcdP/(IcdP+BghiP).

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