PATTERN AND SOURCES OF PAHS POLLUTION IN SEDIMENT OF HANGZHOU, CHINA

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Introduction **Polycyclic aromatic hydrocarbons (PAHs), a class of compounds that consist of two or more fused aromatic rings, are ubiquitous in the aquatic environment. Concern over PAHs results from their known carcinogenic behavior [1]. Because of their hydrophobic nature PAHs may accumulate to high concentrations in sediments. At the same time, PAHs in sediments can arise from many sources and sources identification is of great importance to control PAHs pollution effectively. Certainly, analytical method and pretreatment are the bases and controlled steps for research. Consequently, the paper is aimed to fulfill PAHs pollution data in China on the basis of an effective analytical method. Sources analysis method was also introduced to further investigation of PAHs in the study. Meanwhile, potential toxicological significance is evaluated by comparison with effect-based sediment quality guidelines.**

Materials and methods **Reference PAHs (17 compounds, each at 200 µg/mL) were obtained from Suplco Company. All solvents used for sample preparation and analysiswere HPLC grade from TEDIA Company, USA. Ottawa sand (dispersion agent, Fish Scientific) and hydromatrix (drying agent, Varian Associations Inc) were taken from Dionex Corporation along with Accelerated Solvent Extraction (ASE 100). Deionised water came from a PALL system (PALL, USA). Chromatography silica gel (200-300 mesh) used for sample purifying was purchased from Huadong medical corporation .**

11 surface sediment (about 0-5 cm) samples were collected with a grab sampler, among which two were from Hangzhou section of Qiantang River, three from the West Lake, four from Hangzhou section of Jinghang Canal (also called Hangzhou canal), two from city inland river. After transported to the laboratory, the sediment samples of the above surveys were air dried at room temperature, grounded to 2 mesh and stored at –67 ^{o}C until analysis. Samples were extracted with ASE , purified then analyzed with HPLC/UV.

Results and discussion

PAHs spacial distribution **17 PAHs were detectable in sediments at 8 locations. The total PAHs in the sediments ranged from 308.4 to 3037 ng/g dry weight, with the highest found in sample 6 (from Jinghang Canal), the lowest found in sample 2 (from Qiantang River)□Table 1□. Generally speaking, PAHs pollution in sediments of Jinghang Canal was the heaviest and almost 1 order of magnitude higher than those of Qiantang River. Jinghang Canal was built in Ming Dynasty by hand to connect Beijing and Hangzhou passing through many cities and had served as an important shipping route for centuries. In Hangzhou, it was an industrial area where the canal was running, thus the canal was took as a receptor water body for industrial discharges. At the same time, thousands of ships were driven on the canal, which led to heavy oil pollution. Present studies about PAHs pollution in sediments obtained from literature [2-10] was shown in Fig. 1. Global rivers, lakes, estuaries, harbors and canals showed different levels of PAHs ranging from ppb to hundreds of ppm. Fig. 1 showed that, PAHs pollution in Hangzhou sediments could be categorized as low to moderate compared to the global PAHs concentrations. However, they were high in those of Chinese sediments.**

Table 1 Concentrations of PAHs in sediment samples (ng/g)

	1	2	3	4	5	6	7	8	9	10	11
NA	98.66	87.25	197.7	130.1	276.0	191	130.9	83.17	139.40	210.4	191.6
2AC	13.35	29.60	8.026	15.79	21.05	15.79	21.05	19.08	32.24	28.95	31.58
AC	2.410	5.556	10.62	24.10	19.61	68.63	1.838	3.717	5.801	8.987	7.761
FLUOR	12.12	23.61	38.76	16.03	37.53	116.3	14.62	9.866	24.49	30.66	21.49
PHEN	47.14	51.43	195.0	192.9	344.3	322.1	48.57	60.71	67.86	174.3	122.9
AN	5.000	2.961	29.13	39.81	44.66	68.45	5.194	6.845	7.670	11.65	16.50
FLUR	Global	This study	Chinese			7	13.53	12.50	9.145	13.06	8.772
PY	24.39	17.03	178.9	191.1	284.6	298.8	35.57	32.52	27.44	32.52	34.55
BaA	5.233	1.292	94.32	80.75	147.9	164.1	5.103	5.491	7.235	25.84	16.80
CHRY	6.128	1.776	96.80	49.73	94.14	119.9	7.060	7.060	9.325	23.98	17.76
BeP	8.238	--	190.1	193.3	354.9	405.6	9.823	11.41	14.58	82.38	48.80
BbF	4.036	--	100.9	102.9	217.9	211.9	4.843	4.641	4.036	16.55	9.282
BkF	2.205	--	33.07	37.48	52.91	103.6	2.205	2.072	3.307	10.36	3.086
BaP	4.188	--	104.7	96.31	173.1	182.9	5.304	5.165	5.863	33.50	15.08
DA	0.000	--	9.226	9.127	16.37	23.81	--	--	0.893	4.365	2.183
BP	53.05	75.29	90.69	131.8	188.2	241.3	47.91	70.16	75.29	133.5	112.9
IN	7.079	5.148	77.22	79.37	140.5	157.7	6.113	7.615	12.23	34.32	19.31
total PAHs	317.8	308.4	1659	1589	2750	3037	360.1	342.9	449.5	881.2	693.2

--: not detected

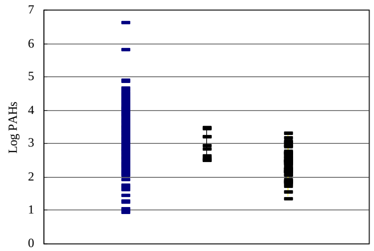

Figure 1 PAHs concentrations in this study and reported in literatures

Risk assessment **Concern over PAHs resulted from their known carcinogenic behavior. Because of their hydrophobic nature, PAHs may accumulate to high concentrations in sediments. Recently, such countries as Australia, New Zealand, USA had published sediment quality guidelines, which were not available in China. Thus Freshwater Sediment Screening Guidelines[11-12] was used to estimate the potential of adverse effects resulting from PAHs pollution in Hangzhou. In this approach, lowest effects level (LEL) and severe effects level (SEL) sediment quality guidelines were derived from biological effect data. LEL indicate concentrations at which adverse benthic impact may begin to occur (level tolerated by most benthic organisms). Water column species and wildlife are potential risk via biomagnification (food chain toxicity) if site-related sediment concentrations of pollutants are at or above the LEL. Contamination at SEL level indicates severe impacts to the benthic community in most cases. The SEL is calculated from a site-specific TOC level. To calculate a site-specific SEL, TOC is multiplied by the table SEL. LEL and SEL are derived for 12 PAHs and do not exist for some light molecular weight compounds. Thus in this paper, risk assessment were performed based on the 12 PAHs. For each site, mean LEL quotients were calculated for PAHs by dividing the concentrations of the individual PAH compounds by their respective LEL guidelines, summing these quotients and dividing by the total number of PAHs (12). Mean SEL quotients for PAH were also calculated in the same manner. The mean quotients accounted for the presence of mixtures of toxic chemicals and degree to which individual chemicals exceeded their guidelines. This method assumed additivity of toxic effect (no synergistic or antagonistic effects) and a mean LEL quotient≥1 implied that, at least one compound exceeded the LEL and therefore adverse impact might occur. A mean SEL quotient ≥1 showed severe impact began to imposed on benthic organisms.**

All sediments samples had a mean PAH SEL quotient≤1.0 (Table 2) and at most sites, the concentrations of individual PAH compounds did not exceed their LEL guidelines, consequently, only sediment 6 had a mean LEL quotient for 12 PAHs ≥1 indicating potential to have adverse effect in sensitive species. Thus it was believed that most aquatic sediment in the study had PAH levels that would not expected to cause adverse impact in benthic biota.

Table 2 Mean LEL and SEL quotients for different samples

	1	2	3	4	5	6	7	8	9	10	11
Mean LEL quotients	0.011	0.011	0.006	0.006	0.006	0.005	0.007	0.004	0.002	0.002	0.001
Mean SEL quotients	0.102	0.156	0.436	0.347	0.611	1.039	0.112	0.104	0.176	0.281	0.205

Sources analysis **A lot of molecular ratios of specific hydrocarbons had been developed (Table 3). Those ratios were calculated for this study in Table 4, among which, (BaP/BP) only provided a range for coal-burning. Results may differ by use of different ratios. Here, if an inconsistent answer was not reached, a factor (PP) was produced to quantify the possibility of the pyrolytic by using the following equation:**

PP= (FLUR/PYsample−1) / 1+(IN/BPsample−1) / 1+ (10−PHEN/ANsample) / 10

If PP>0----major source was pyrolytic origin

PP<0---- major source was petroleum origin

Table 3 Some significant ratios for sources analysis

Ratio	Pattern
FLUR/PY [13]	**>1: pyrolytic origin; <1: petroleum origin**
IN/BP [14]	**>1: combustion source; <1: petrogenic source**
PHEN/AN [15]	**<10: combustion source; >10: petrogenic source**
BaP/BP [16]	**1.2-5: wood burning, and coal burning**

Table 4 Ratios in this study

	1	2	3	4	5	6	7	8	9	10	11
FLUR/PY	0.99	0.42	1.13	1.03	1.17	1.13	0.38	0.38	0.33	0.40	0.25
IN/BP	0.13	0.07	0.85	0.60	0.75	0.65	0.13	0.11	0.16	0.26	0.17
PHEN/AN	9.43	17.4	6.69	4.84	7.71	4.71	9.35	8.87	8.85	14.96	7.44
BaP/BP	0.08	0.00	1.15	0.73	0.92	0.76	0.11	0.07	0.08	0.25	0.13
PP	-0.81	-2.25	**0.31**	**0.15**	**0.14**	**0.32**	-1.43	-1.39	-1.39	-1.84	-1.32

PP: possibility of PAHs from the pyrolytic

In this way, sources analysis were achieved with a quantity method coupled with some significant ratios with the results showing petroleum origin was the chief source to PAHs pollution in all sediments with the exception of sediments from Jinghang Canal where combustion sources had a larger contribution. The peculiar PAHs source in sediment of Jinghang Canal were probably due to the discharges of point sources like steel-melting plant, oil-refining factory, coke plant, gas manufacture plant located around the canal, and residential coal combustion on the ships.

Acknowledgement

We thank Dionex Corporation for providing Accelerated solvent extractor. This project is supported by 973 program of Ministry of Science and Technology of China(2003CB415004).

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