Screening Level of PAHs in Sediment Core from Lake Hongfeng, Southwest China

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Abstract Using data from a 25-year retrospective of polycyclic aromatic hydrocarbons (PAHs) in sediment core from Lake Hongfeng, Southwest China, their possible sources and potential toxicologic significance were investigated. The total PAH concentrations (16 priority PAHs as proposed by the United States Environmental Protection Agency) in sediments ranged from 2936.1 to 5282.3 ng/g and gradually increased from the analyzed deeper sediments to surface sediments. PAHs were dominated by low molecular-weight components, especially phenanthrene (PHEN) and fluorene (FLU). However, a significantly increased number of high molecular-weight (HMW) PAHs was found in upper segments. The temporal trends of individual PAH species suggest that there may have been a change in energy use from low- to high-temperature combustion, especially after approximately 2001. PAH input to Lake Hongfeng originated mainly from domestic coal combustion and biomass burning, whereas fuel combustion characteristics have also been found in recent years. Sediment-quality assessment implied that potential adverse biologic impact could be a probability for most low-ring PAHs (including naphthalene, acenaphthylene, acenaphthylene, FLU, PHEN, and anthracene). Nevertheless, more concern should be paid to HMW PAHs in the future due to their rapidly increasing trends in upper sediments. Because only one core was analyzed in this study, more work is needed to confirm the sources and toxicity of PAHs in Lake Hongfeng.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in various environmental compartments. They can be released into the environment by way of various anthropogenic and natural processes. Potential source candidates include incomplete combustion of fossil fuels, burning of biomass or municipal wastes, accidental oil spillage, and digenesis of organic matter (Liu et al. 2005; Guo et al. 2006, 2007). Due to their high hydrophobicity and strong particulate-oriented behaviors, PAHs are partitioned preferentially to sediments in aquatic ecosystems (Kannan et al. 2005; Colombo et al. 2006). Therefore, sediment is the most important sink for PAHs in the aquatic environment. Because of their potential (or, in some cases, proven) carcinogenicity, immunotoxicity, genotoxicity, and reproductive toxicity, PAHs in contaminated sediments can directly affect sediment-dwelling organisms (Sverdrup et al. 2002; Gu et al. 2003). Moreover, contaminants in sediment can re-enter the aquatic environment by way of resuspension, resulting in secondary contamination (Zeng and Venkatesan 1999). Thus, contaminated sediments represent a continuing source of toxic substances in aquatic environments that could be harmful to wildlife and humans.
by way of the food chain (Kannan et al. 2005). Therefore, both the potential toxicology and the fate of PAHs in sediments have provoked considerable concern.

Lake Hongfeng (106°20′E to approximately 106°27′E and 26°36′N to approximately 26°36′N) is a reservoir, established in 1960, that lies 33 km west to Guiyang City, the capital city of Guizhou Province in Southwest China (Fig. 1). It has surface and catchment areas of 57.2 and 1596 km², respectively, with an average depth of 10.5 m and a volume of 6.01 × 10⁸ m³ (Li et al. 2008). It is the most important drinking-water source for Guiyang City. There are nearly two dozen factories (including a firepower plant and several chemical plants, etc.) in its catchment area, and a large volume of improperly treated wastewater has been discharged to this reservoir (He et al. 2008). These factors, together with contaminants discharged by a great number of yachts that are shuttled across the lake, have caused water quality to greatly deteriorate and thus seriously threaten the drinking-water supply. To keep up with the rapid urbanization and industrialization in the catchment area and to provide more quality water, the local government has undertaken great efforts to improve drinking-water sources (http://www.law-lib.com). The degrees of eutrophication and mercury pollution have been reported elsewhere (He et al. 2008), but no part of that report investigated persistent organic pollutants.

The main objectives of the present work were (1) to determine the temporal trend of PAH contamination in Lake Hongfeng, (2) to identify possible sources of contamination, and (3) to assess potential toxicologic impacts.

Materials and Methods

Chemicals and Reagents

A standard solution of 16 United States Environmental Protection Agency (USEPA) priority PAHs (including naphthalene [NAP], acenaphthylene [ACE], acenaphthene [AC], fluorene [FLU], phenanthrene [PHEN], anthracene [ANT], fluoranthene [FLUO], pyrene [PYR], benzo[a]anthracene [BaA], chrysene [CHR], benzo[b]fluoranthene [BbF], benzo[k]fluoranthene [BkF], benz[a]pyrene [BaP], indeno[1,2,3-cd]pyrene [INP], dibenz[a,h]anthracene [DBA], and benzo[ghi]perylene [BghiP]) and internal standards (2-fluorobiphenyl and terphenyl-d₁₄) were purchased from Accustandards (New Haven, CT). A mixture solution of 5 perdeuterated PAHs (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂) were obtained from Ultra Scientific (North Kingstown, RI). All solvents and reagents used in the extraction and cleanup procedures were analytic-reagent grade, and all organic solvents were redistilled. Neutral silica gel (100–200 mesh) and alumina (80–100 mesh) were extracted with a mixture of dichloromethane and methanol (1:1) for 72 h and baked at 180°C and 250°C, respectively, for 12 h. Sodium sulfate was baked at 450°C and stored in sealed containers.

Sampling

Sediment core was taken from the center of Lake Hongfeng in May 2006 (Fig. 1). A 37 cm-long sediment core, mainly composed of silt with a little gravel in the deeper segments, was collected by a gravity corer and sectioned in situ at 1-cm intervals. The cored sediments were undisturbed, as indicated by clear water, sediment interface, and preservation of fine-sediment laminations, and therefore had little influence on radiodating and chemistry results. The sediments were wrapped in baked (450°C) aluminum foil and
transported on ice to the laboratory, where they were stored at −20°C until further treatment.

Extraction and Instrumental Analyses

The sample extraction procedures have been described in detail elsewhere (Mai et al. 2002). In brief, an aliquot of approximately 5 g freeze-dried sample, spiked with a mixture of five perdeuterated PAHs as recovery surrogates and 2 g activated copper added for desulfurization, was Soxhlet-extracted with 200 ml mixture hexane and acetone (1:1, v:v) for 48 h. The extracts were concentrated and solvent-exchanged to hexane. Cleanup and fractionation of the concentrated extract was performed using an alumina/silica gel chromatographic technique. The aliphatic and aromatic fractions were successively eluted with 15 ml hexane and 70 ml dichloromethane/hexane (3:7, v:v), respectively. The second fraction was concentrated under a gentle flow of high-purity nitrogen to 200 μl. The internal standards 2-fluorobiphenyl and terphenyl-d14 were added before instrumental analysis.

Analyses of PAHs were performed on an Agilent 6890 gas chromatograph (GC) system equipped with an Agilent 5975B mass selective detector operating in selective ion monitoring mode using a DB-5 capillary column (60 m length × 0.25 mm i.d. × 0.25 μm film thickness). Splitless injection of 1.0 μl sample was conducted with an auto-sampler. The GC oven temperatures were programmed from 90°C to 180°C at a rate of 10°C/min, to 220°C at a rate of 2°C/min, and then to 290°C at a rate of 8°C/min (hold for 30 min).

Dating of the Sediment Core

Dating of sediment core was performed using 137Cs activity. The method for the determination of 137Cs activity has been described elsewhere (Wan et al. 2005). In brief, 137Cs activity was determined using gamma-spectrometry on a Canberra S-100 multichannel spectrometer mated to a GCW3022 H-P Ge coaxial detector (efficiency 50%). The gamma peak at 661.6 keV peak of 137Cs was used to determine the 137Cs activity of these standards. Liquid standards were supplied by the Institute of Atomic Energy, Chinese Academy of Sciences (catalog no. 7137 and source no. 586-26-2). Based on the pronounced peak at the 33- to 34-cm interval (Supplemental Fig. 1), an average sedimentation rate of 0.81 cm y−1 was obtained.

Quality Control and Quality Assurance

The surrogate recoveries in all samples were 56.2% ± 8.8% for naphthalene-d8, 73.0% ± 10.9% foracenaphthene-d10, 69.8% ± 17.8% for phenanthrene-d10, 89.1% ± 7.4% for chrysene-d12, and 95.9% ± 15.9% for perylene-d12. A procedural blank, triplicate spiked blank, and triplicate spiked matrices were analyzed for each batch of samples. The mean recoveries of 16 PAHs ranged from 75.8% ± 4.9% to 114.3% ± 8.2% in triplicate spiked blanks and from 60.8% ± 1.1% to 120.9% ± 9.1% in triplicate spiked matrices. Only trace levels of targets were detected in blanks and were subtracted from those in sediments samples. Detection limits were 0.03–0.05 ng/g dry weight for PAHs (defined as a signal-to-noise ratio [S/N] > 10). The results were expressed on a dry-weight basis, and surrogate recoveries corrected.

Results and Discussion

Temporal Trends of PAHs in the Sediment Core

PAHs were analyzed only in the upper portion of the sediment core (0 to 20 cm). The temporal trend of 16 USEPA-proposed priority PAHs (designated as ΣPAH16), as assessed against depth and depositional year, are showed in Fig. 2. ΣPAH16 concentrations in sediments ranged from 2936.1 to 5282.3 ng/g (all concentrations are normalized to dry weights except where specified), and the fluxes ranged from 985.2 to 1772.4 ng m−2 y−1. The flux was calculated using the following equation (Eq. 1):

\[
F = C_i \rho_i \gamma_i
\]

where \( C_i \) (ng/g), \( \rho_i \) (g/cm³), and \( \gamma_i \) (cm/y) refer to the concentration, the dry mass density, and the sedimentary
rate of the segment i, respectively. Generally, the $\Sigma PAH_{16}$ concentrations gradually increased from the analyzed deeper segments to surface sediments. Among the 16 USEPA-priority PAHs, PHEN was the predominant PAH, followed by NAP and ANT, accounting for 35.7% ± 7.0%, 16.2% ± 4.3%, and 13.9% ± 2.6% of total PAHs, respectively (Supplemental Fig. 2). PHEN and FLU mainly originated from low- and moderate-temperature combustion processes, such as biomass and domestic coal burning (Harrison et al. 1996; Mai et al. 2003). The predominance of PHEN and ANT in the sediments suggests that PAHs in sediments were mainly from biomass and domestic coal burning. On the contrary, high molecular-weight (HMW) PAHs (including BbF, BkF, BaP, DBA, INP, and BghiP) accounted for only 11.5% ± 4.5% of total PAHs. Nevertheless, the contribution of HMW PAHs to total PAHs significantly increased (an increase from 10.1% to 23.6%) from the 4- to 6-cm sediment layer to the top sediment layer. The opposite (a decrease from 75.9% to 55.7%) was true for low molecular-weight (LMW) PAHs, including NAP, AC, ACE, FLU, PHEN, and ANT.

The vertical profiles of 16 PAHs in sediment core are shown schematically in Fig. 3. The temporal trends of PHEN and FLU basically followed that of total PAHs before 1995 but was different thereafter, especially in surficial sediments, where the concentrations of PHEN and FLU decreased significantly. This suggests that there may have been a change in energy use from low- to high-temperature combustion, especially after approximately 2001. BaA and CHR are dominant in the emissions produced by petroleum combustion (Sicre et al. 1987). The temporal trends of BaA and CHR in the sediment core were roughly similar. Different from those of PHEN and FLU, the concentrations and fluxes of CHR gradually increased from deep to surficial sediments, with a rapid increase after approximately 1998. This provided more source evidence for BaA, indicating that more liquid fossil fuel may have been used in the past decade. HMW PAHs are products of high-temperature combustion processes, mostly involving industrial coal combustion, vehicular emission, and gas-fired cooking (Miguel and Pereira 1989; Harrison et al. 1996; Mai et al. 2003). The temporal trends of HMW PAHs were quite similar to each other and resembled that of BaA, which was characterized by a rapid increase after approximately 1998. This confirms that there was probably a change in energy use from low- to high-temperature combustion after approximately 1998.

Potential Toxicologic Significance

Assessing Sediment Quality Using Biologic Thresholds

One method for assessing potential toxicologic impacts is to use biologic thresholds. The effects-range low (ERL) and the effects-range median (ERM) values formulated by Long et al. (1995) have been widely used for assessing sediment quality (McCready et al. 2000; Qiao et al. 2006; Xu et al. 2007). ERL and ERM values are intended to define chemical concentration ranges that are rarely, occasionally, or frequently associated with adverse biologic effects. In the present work, the measured concentrations of PAHs in surficial sediment was used for comparison with ERL and ERM values to derive hazard ratios (HR_ERL and HR_ERM) representing the ratio of measured concentration of individual PAHs species to ERL and ERM values, respectively. If HR_ERL was <1, adverse biologic effects were rarely associated with the PAH contamination. If HR_ERL was >1 or HR_ERM was >1, adverse biologic effects were occasionally or
frequently associated with PAH contamination. The assessment results are listed in Supplemental Table 1 and are schematically shown in Fig. 4. Although none of the HR_ERM values were >1, HR_E RL of most low-ring PAHs (including NAP, AC, ACE, FLU, PHEN, and ANT) and DBA were >1, suggesting that potential adverse
biologic impact is probable and that further examination is required.

**Assessing Sediment Quality Based on Toxic Equivalency Factors**

Another assessment method is based on toxic equivalency factors (TEFs). This assessment method focuses on seven carcinogenic PAHs components (including BaA, CHR, BbF, BkF, BaP, DBA, and INP). Among the seven carcinogenic PAHs components, BaP is the only one having sufficiently toxicologic data for derivation of a carcinogenic factor (Peters et al. 1999). For other carcinogenic PAH components, TEFs were used for quantification (Nadal et al. 2004). According to the USEPA, the TEFs for BaP, BaA, CHR, BbF, BkF, INP and DBA are 1, 0.1, 0.001, 0.1, 0.01, 0.1, and 1, respectively (Law et al. 2002). The total BaP equivalent (TEQ) for seven carcinogenic PAH components can be calculated by the following equation (Eq. 2):

\[
TEQ = \sum Ci \times TEF_i,
\]

where \( Ci \) is the concentration of individual PAH and \( TEF_i \) is the corresponding TEF. The TEQ value for the surface sediment from Lake Hongfeng was 334.3 ng/g. Regarding individual carcinogenic PAH components, the contribution to the TEQ of each PAH component decreased in the following order: DBA (44.0%) > BaP (37.0%) > BbF (7.4%) > INP (6.5%) > BaA (4.7%) > CHR (0.1%). This indicates that more concern should be paid to DBA and BaP. A considerably high TEF has been reported for oil-polluted intertidal sediments collected from Yeosu Bay, South Korea (Lee and Yi 1999). The TEQ, which ranged from 94 to 856 ng/g (average 407) for seven carcinogenic PAH components, has been estimated for surface sediments from Meiliang Bay in the northern part of Taihu Lake in Eastern China (Qiao et al. 2006). The TEQ in this study was lower than those of surface sediments from Meiliang Bay but higher than other reported data, such as the bottom sediments from Guba Pechenga, Barents Sea, in Russia (Savinov et al. 2003).

**Conclusion**

PAHs in the sediment core from Lake Hongfeng, Southwest China, and their possible sources and potential toxicologic significance, have been identified. The ΣPAH<sub>16</sub> concentrations in sediments ranged from 2936.1 to 5282.3 ng/g and gradually increased from deep to surface sediments. PAHs were dominated by LMW components, especially for PHEN and FLU. However, a significantly increased level of HMW PAHs was found in upper layers of sediment. The temporal trends of individual PAHs suggest that there may have been change in energy use from low- to high-temperature combustion, especially after approximately 2001.

Source identification indicates that PAH input mainly originated from domestic coal combustion and biomass burning. Increasing fuel combustion source has also been found in recent years. Potential adverse biologic impact is probable for DBA and most low-ring PAHs, and more concern should be paid to HMW PAHs, taking into account

### Table 1  Characteristic PAH molecular diagnostic ratios

| PAHs Petrogenic | Pyrogenic | Results from the present work |
|-----------------|----------|-----------------------------|
| ANT/(ANT + PHEN) | <0.1 | >0.1 | 0.12 ± 0.02 (0.11–0.16) |
| BaA/(BaA + CHR)  | <0.2 | >0.35 | 0.40 ± 0.03 (0.38–0.48) |
| FLUO/(FLUO + PYR) | <0.4 | >0.4 | 0.52 ± 0.02 (0.49–0.55) |
| INP/(INP + BghiP) | <0.2 | >0.2 | 0.53 ± 0.06 (0.47–0.64) |

where Fuel combustion indicates that TEF fuel combustion > Grass/coal/wood combustion.
their rapid increasing trends in upper sediments. Because only one core was analyzed, more work is needed to confirm the sources and toxicity of PAHs in Lake Hongfeng.

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