

# Source Apportionment of Polycyclic Aromatic Hydrocarbons by Positive Matrix Factorization in Surface Sediments of Taihu Lake, China

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## Abstract

In order to identify 16 priority polycyclic aromatic hydrocarbons present in the surface sediments of Taihu Lake, 41 surface sediment samples were analyzed by GC-MS. The total concentrations of PAHs ranged from 262.06 ng/g to 1087.22 ng/g (dry weight). The source apportionment of PAHs by positive matrix factorization model indicated that the main source of PAHs in surface sediments of the lake were emissions from coal combustion, accounting for 53.40% of the total variance, followed by residential emissions, traffic emissions, and biomass combustion, accounting for 19.95%, 19.85, and 6.80%, respectively. The overall concentrations of PAHs were higher at nearshore places than in the middle of the lake, and the northeast region concentrations were higher than the southwest region concentrations.

**Keywords:** PAHs, surface sediments, Taihu Lake, source apportionment, PMF

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are known as a type of carcinogenic, mutagenic, and teratogenic pollutants. Combined with their persistence in the environment [1] and they have been of special concern for several decades. Source control is the best method to regulate such persistent organic pollutants in the environment, but the sources of PAHs are complex and include mainly the important anthropogenic sources of PAHs, including biomass burning, coal and petroleum combustion, and coking, as well as metal production [2]. Therefore, source apportionment is a core research subject in related studies.

Taihu Lake is the second largest freshwater lake in China and the largest lake in eastern China located in the Yangtze River delta, the economic center of China. The

population of this area is close to 36 million, representing about 3% of China's total population. It is one of the most densely populated areas in China and, consequently, its ecological environment could have significant impact on the production and life of residents [3].

Although many papers on PAHs in the surface sediments of Taihu Lake have already been published [4-6], the source apportionment in these studies was based only on the qualitative analysis of characteristic PAH diagnostic ratios or factor analysis methods such as principal component analysis (PCA). Furthermore, the number of samples was limited or the sampling was done only in certain parts of Taihu Lake [4-6]. Consequently, through the analysis of 41 surface sediment samples from Taihu Lake, this study used a positive matrix factorization (PMF) model to perform quantitative source apportionment for PAHs, aimed to provide a comprehensive and up-to-date understanding of PAHs in the surface sediments of Taihu and background information for ecological and environmental research of the lake.

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## Material and Methods

### Sampling

Taihu Lake is a shallow lake with an average depth of about 2 m located in eastern China between 30°55'40" N to 31°32'58" N and 119°52'32" E to 120°36'10" E. The length of the lake is about 68.5 km from north to south, averaging 34 km from west to east with the largest width at about 56 km, and its area is approximately 2,427.8 km<sup>2</sup>.

Forty-one surface sediment samples were collected using a grab sampler in May 2011, and the locations of sampling sites are shown in Fig. 1. The top 3 cm layer was carefully removed with a stainless steel spoon for subsequent analysis. All sediment samples were wrapped in aluminum foil and stored at -20°C up to the time of analysis.

### Analysis of PAHs

The procedures for the extraction and fractionation of PAHs followed those described by Mai [7]. Briefly, homogenized samples were freeze-dried and ground, and about 10 g of the sample was extracted by dichloromethane in a 250 mL Soxhlet extractor for 48 hr. Activated copper was added to remove the sulfur before extraction, after which the extracts were concentrated by rotary evaporation, solvent-exchanged to hexane, and submitted to a silica-alumina (2:1) column for clean-up and fractionation. The fraction was eluted with hexane/dichloromethane 1:1, v/v. Then the fractions were concentrated to 0.4 mL under a gentle N<sub>2</sub> stream. Hexamethylbenzene was added to the extract as an internal standard prior to instrumental analysis.

PAH concentrations were determined using an Agilent 5975C mass spectrometer interfaced to an Agilent 7890 gas chromatograph, and chromatographic separation was achieved by a DB-5MS capillary column (30 m, long × 0.25 mm inside diameter × 0.25 μm film thickness, Agilent) with a splitless injector and a mass spectrometer

detector. Helium was used as the carrier gas (1.0 mL/min). Samples were injected in the splitless mode with an injector temperature of 280°C. The oven temperature was programmed from 60°C to 180°C (1 min hold) at 8°C/min, and from 180°C to 300°C (2 min hold) at a 3°C/min rate. The mass spectrum was operated in the electron ionization (EI) mode (70 eV), and the mass scanning ranged between m/z 50 and 500 amu.

The concentrations of PAHs were determined by authentic standards of 16 U.S. EPA proposed priority PAHs (naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLUO), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (INP), dibenz[a,h]anthracene (DBA), and benzo[ghi]perylene (BghiP)).

All results for sediment samples were reported on a dry-weight basis. Moreover, the total PAH concentration was regarded as the sum of the concentrations of 16 U.S. EPA proposed priority PAH species for each collected sample.

Method blanks (solvent) and spiked blanks (standards spiked into solvent) were also conducted. In addition, surrogate standards were added to samples prior to extraction; the average surrogate recoveries were 92.2%±14.1% for phenanthrene-d10, 75.3%±11.9% for chrysene-d12, and 74.7%±9.5% for perylene-d12. Solvents were distilled twice, chemicals (e.g., alumina or silica) were solvent extracted, and glassware was cleaned by heating at 450°C for 6 hr. Blank procedures showed no noticeable interference in the analysis.

### PMF Modeling

The source apportionment of PAHs was done by means of PMF modeling. PMF was developed in the early 1990s and has often been applied to research on atmospheric and temporally distributed data sets [8-9]. Compared with PCA, PMF can assess the contribution from the specific source of an individual sample and utilize non-negativity

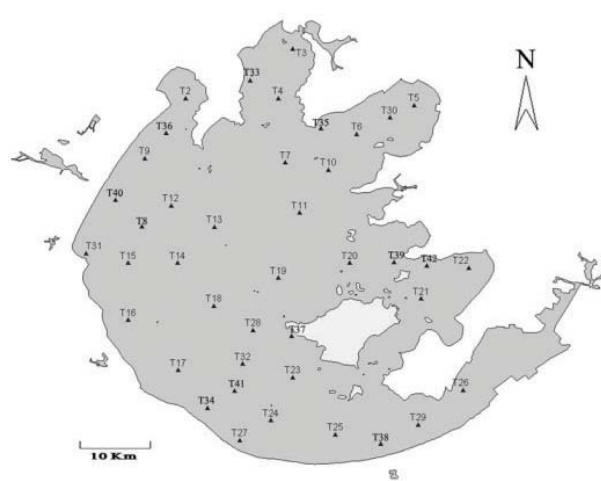
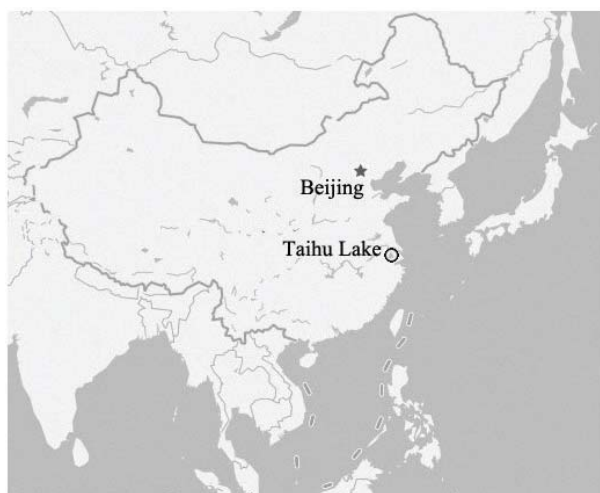


Fig. 1. Locations of sampling sites.

constraints for obtaining physically realistic meanings. In addition, the user does not need to provide source profiles of target compounds. These advantages make PMF highly suitable for research on source apportionment in sediments. In the past few years, PMF has been successfully applied to spatially distributed data sets to apportion the sources of PAHs in sediments [10]. The details of PMF were described by Paatero and Tapper [11]. In general, PMF defines that ambient element concentrations of an  $n \times m$  data matrix  $X$  can be factored into source contributions of an  $n \times p$  matrix  $G$  and source profiles of a  $p \times m$  matrix  $F$  with a residual  $n \times m$  matrix  $E$ :

$$X = GF + E \quad (1)$$

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (2)$$

...where  $x_{ij}$  is the measured concentration of the  $j$ th species in the  $i$ th sample,  $g_{ik}$  is the concentration from the  $k$ th source contributing to the  $i$ th sample,  $f_{kj}$  is the  $j$ th species fraction from the  $k$ th source,  $e_{ij}$  is the difference between the observations and the model.

Then, PMF minimizes an object function  $Q$  as

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left( \frac{e_{ij}}{s_{ij}} \right)^2 \quad (3)$$

...where  $e_{ij}$  is the difference between the observations and the model,  $s_{ij}$  is the uncertainty for each observation, and  $Q$  is the weighted sum of squares of differences between the PMF output and the original data set.

Before analysis, NAP was removed from the model because of the high uncertainties in its source fingerprints

and possible evaporative losses during the entire experiment [12]. In this study, an uncertainty of 20% was adopted based on the results from the regular analysis reported in standard reference material [7].

## Results and Discussion

### Spatial Distribution of Total PAHs

The total concentration of the 16 PAHs in the sediments ranged from 262.06 ng/g to 1087.22 ng/g with a mean concentration of 491.87 ng/g, and the overall concentration distribution indicated that nearshore places had higher concentrations than in the middle of the lake, with the concentrations in the northeast region being higher than those in the southwest region. The nearshore places were more strongly influenced by human activities, such as the combustion of coal, wood, and petroleum. The northeast region showed higher concentrations than the southwest region mainly because of the different degrees of economic development. Northeast areas included the Wuxi and Suzhou cities. Both these cities are developed areas, and rapid economic development in this area has resulted in high amounts of energy consumption and environmental pollution. This has made the PAH concentrations in the northeast region higher than in the southwest, which are under the administration of Huzhou. As shown in Fig. 2, the highest concentration of 16 PAHs was found at site T3 (1087.22 ng/g), and the next highest concentration was observed at T5 (901.30 ng/g). The lowest concentration of 16 PAHs was detected in the middle of Taihu Lake, at T37 (262.06 ng/g), close to Xishan Island. The high concentrations at T3 and T5 are due to the fact that they are close to the estuaries of the Liangxi River and the Wangyu River, respectively. The two rivers carry the discharge of vast amounts of pollutants from the factories and living

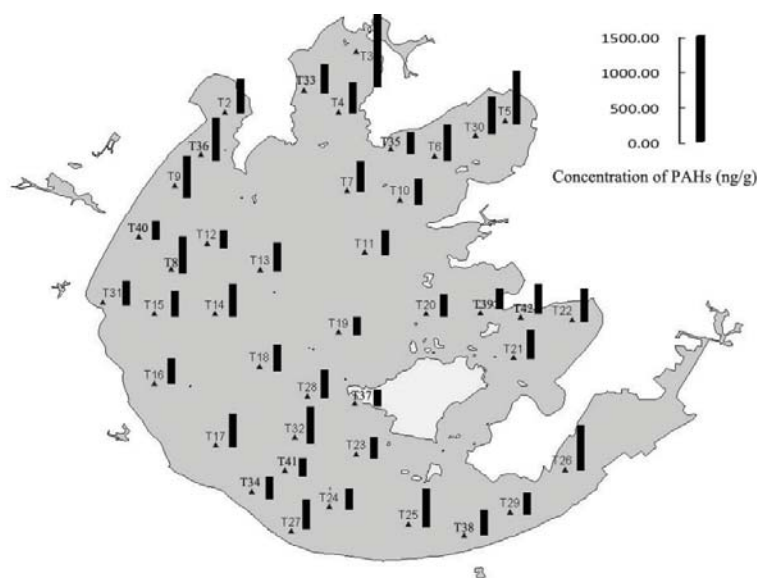


Fig. 2. Distribution map of total PAHs.

Table 1. The concentrations of individual PAH and total concentration.

PAHs	Maximum	Minimum	Mean	Standard Deviation
NAP	59.90	12.81	31.99	11.64
ACY	3.39	0.76	1.71	0.53
ACE	42.46	4.86	14.20	8.36
FLU	47.00	7.95	21.39	9.66
PHE	262.21	29.12	109.70	62.97
ANT	52.47	3.28	8.57	8.12
FLUO	139.02	32.10	63.02	24.74
PYR	107.21	23.85	43.28	16.75
BaA	101.42	9.85	20.87	17.24
CHR	79.19	11.04	20.56	11.13
BbF	149.02	27.47	52.15	21.15
BkF	47.97	1.36	16.18	8.32
BaP	93.21	10.45	21.42	13.88
INP	89.12	5.96	29.33	13.98
DBA	29.64	2.87	6.55	4.80
BghiP	95.54	17.17	30.96	14.85
$\Sigma 16\text{PAHs}$	1087.22	262.06	491.87	169.89

areas situated along the rivers; the pollutants enter the lake through the rivers and accumulate in the sediments. The low concentration at T37 is because of the good ecological environment of Xishan Island, which is a tourism island and designated as a National Forest Park.

Compared with other research on PAHs in the surface sediments in China, Taihu has a lower PAH concentration

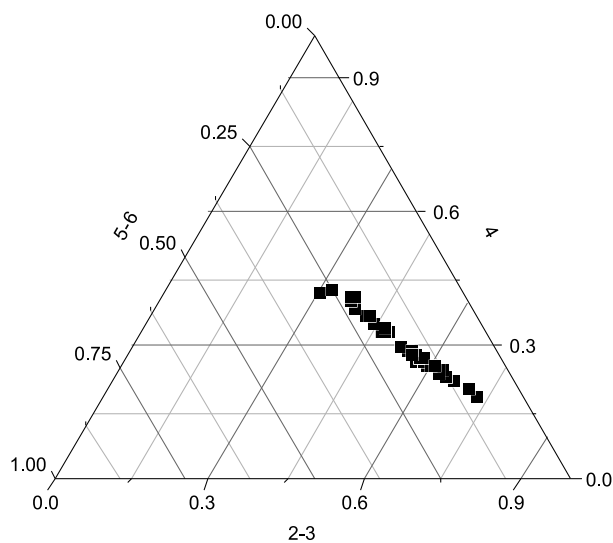


Fig. 3. Composition of PAHs by different rings.

than Baiyangdian Lake in north China (101.3 to 6360.5 ng/g) [13], close to Zhanjiang Bay in South China (41.96 to 933.90 ng/g) [14]. Compared with previous results reported for Taihu, the PAH concentrations determined in this study are higher than those reported in the research of Chen et al. in 2009 (63.1 to 885 ng/g) [15], and lower than those reported in the research of Zhang et al. in 2011 (209 to 3843 ng/g) [5].

### PAH Compositions

The concentrations of individual PAH and total concentrations were shown in Table 1, the 16 PAHs found in this study were PH > FLUO > BbF > PYR > NAP > BghiP > INP in decreasing order of concentration, and these compounds comprised 73% of total PAH concentration. The lowest was of ACY, then DBA and ANT. All 16 PAHs were detected in all samples.

The relative abundance of PAHs of different numbers of rings could reflect their sources [16], the 16 PAHs were categorized as 2-3-ring (NAP, ACY, ACE, FLU, PHE, ANT, FLUO), 4-ring (PYR, BaA, CHR, BbF, BkF), and 5-6 ring (BaP, DBA, INP, BghiP) PAHs. The distribution of these different PAHs in all the samples is shown in Fig. 3. The proportion of 2-3-ring PAHs and 4-ring PAHs was relatively high, whereas that of 5-6-ring PAHs was relatively low.

The composition of PAHs showed a predominance of PHE, FLUO, BbF, and 2-4-ring PAHs, which are all related with pyrogenic sources [17]. This may indicate that the release from energy consumption is a predominant contributor to the PAHs in Taihu.

### Source Apportionment of PAHs

The ratios of PAH congeners have been used for source apportionment, such as ANT/ANT+PHE, FLUO/FLUO+PYR, INP/INP+BghiP, BaA/BaA+CHR and so on. After analysis of several diagnostic ratios, Yunker et al. found that FLUO/FLUO+PYR and INP/INP+BghiP were more stable during the migration and transformation in the environment and the provenance information were more

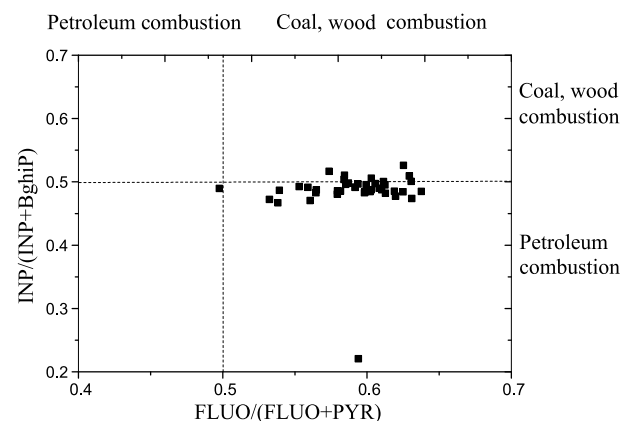


Fig. 4. Diagnostic ratios for source identification of PAHs.

dependable [18-19], they summarized that petrogenic sources have FLUO/FLUO+PYR < 0.4, between 0.4 and 0.5 reflects petroleum combustion, ratio > 0.5 suggests coal and wood combustion; INP/INP+BghiP < 0.2 suggests petrogenic sources, of 0.2 to 0.5 is possibly petroleum combustion, while coal and wood combustion would have a ratio > 0.5. The ratios of FLUO/FLUO+PYR and INP/INP+BghiP were in Fig. 4. Most samples were located at the area of coal, wood combustion and petroleum combustion, suggesting that the PAHs in surface sediment of Taihu Lake were mainly from pyrogenic sources.

In this study, concentrations of the 15 PAHs in the 41 samples were used as the input data to PMF 3.0. Factor numbers ranging from three to eight were applied in order to select the optimal solution. When the number of factors for the PMF was six, the Q(E) value was 113.24-113.26, which was almost the same as the theoretical Q(E) value of 113.26, indicating that the six factors were suitable for subsequent analysis. The values of the slope and r<sup>2</sup> were 0.84-1.06 and 0.93-0.99, respectively, indicating that the

modeled and actual concentrations fit well and that the six factors could fully explain the information in the data.

Factor profiles for the six-factor solution of the PMF model are shown in Fig. 5. The first factor, which accounted for 6.80% of total variance, found that ANT had a relatively high weightage. ANT can be used as a marker for wood combustion sources [20]. As ANT was present only in this factor, it indicated that factor 1 represented wood combustion. Factor 2 was loaded higher on BbF, INP, and BghiP, which are PAH compounds that are related to vehicular emissions [21]. Factor 2 explained 19.85% of the total variance. Factors 3 and 5 accounted for 43.21% of the total variance and were predominantly composed of PHE, which could be identified to be from a coal combustion source [21]. Factor 4 explained 19.95% of the total variance and mainly consisted of FLUO, PHE, BbF, and PYR, representative of residential emissions [12]. Residential emissions refer to combustion processes mainly occurring as a result of residential heating or cooking using coal, wood, and natural gas. Factor 6

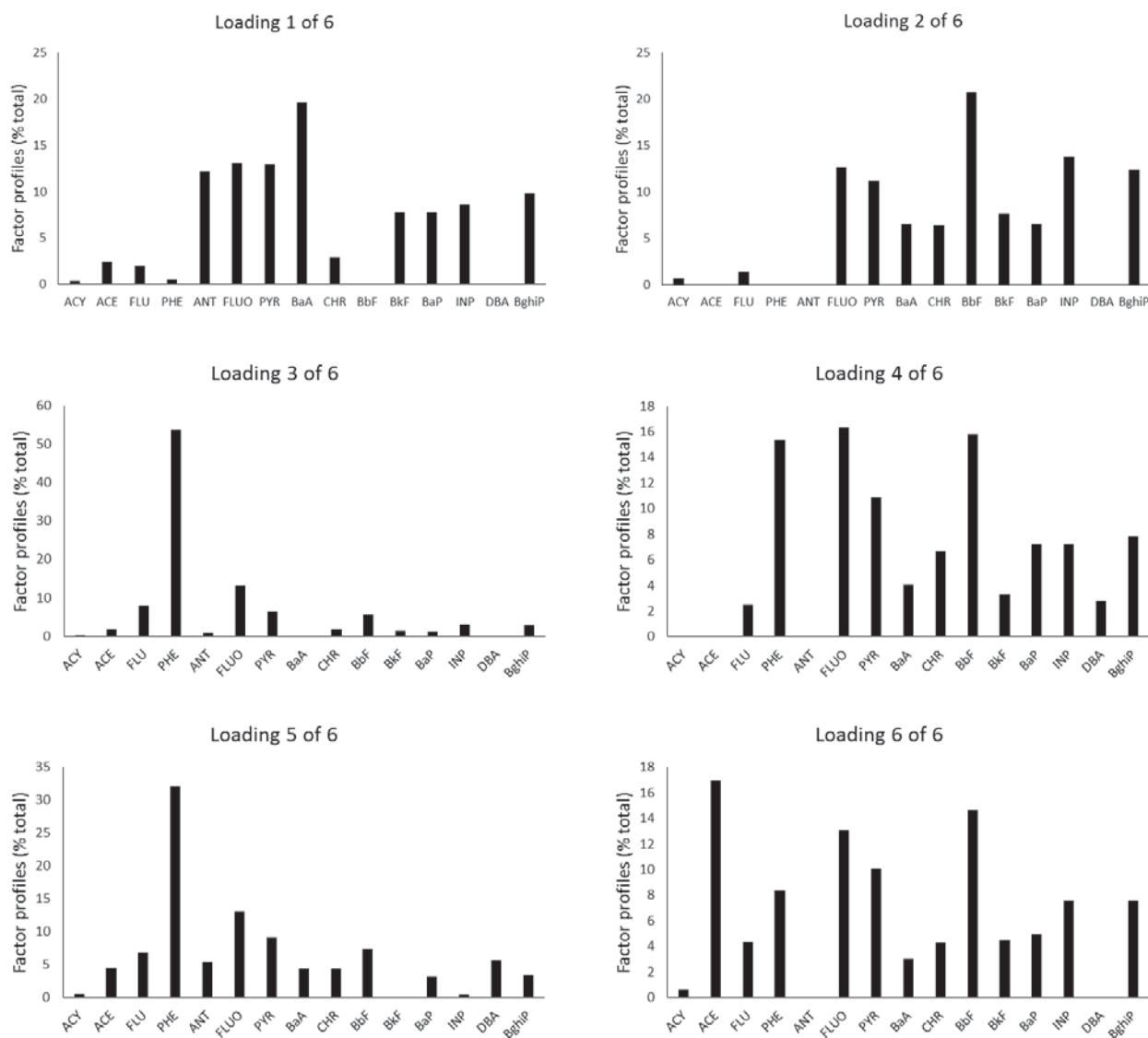


Fig. 5. Factor profiles obtained from PMF model.

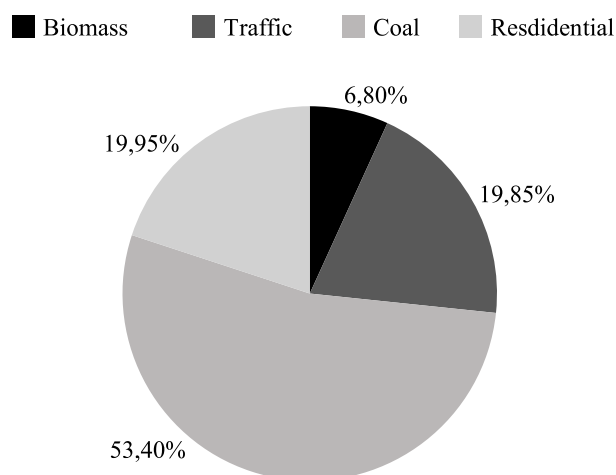


Fig. 6. Source average mass contributions of each factor to total PAHs.

explained 10.19% of the total variance, and was rich in ACE, FLUO, and BbF. ACE and FLUO are tracers of coke oven sources [22], and therefore factor 6 could represent a coke oven source. Because coke oven sources are related to coal combustion, factors 3, 5, and 6 were classified as coal combustion sources.

In summary, the main contributor of PAHs in Taihu Lake was coal combustion, accounting for 53.40% of the total variance. Other contributors were residential emissions, with a 19.95% contribution; traffic emissions, with a 19.85% contribution; and biomass combustion, with a 6.80% contribution (shown in Fig. 6). Most areas around Taihu are developed cities of Jiangsu Province, such as Suzhou, Wuxi, and Changzhou. Tremendous energy consumption is the outcome of rapid development, and coal is the predominant energy resource used for sustaining the energy structure in Jiangsu Province, accounting for about 70% of yearly energy consumption [23]. This energy structure results in coal combustion being the main contributor of PAHs. Further, the traffic emission is attributable to the hundreds of ships used for shipping and fishing in the lake, and as one of the densest areas in China, the energy consumption of inhabitants settled around Taihu Lake also leads to residential emissions that contribute to the PAHs in the sediments.

Zhang et al. used characteristic compound ratios to determine the source apportionment in 2011, only made a qualitative conclusion that the sediment PAHs in Taihu Lake originated from both pyrolytic and petrogenic sources [5]; Chen et al., did the source apportionment by factor analysis and multiple linear regression in 2009 and concluded that the conclusion was the combustion of coal or wood and the combustion of oil accounted for 45% and 50% of the total PAHs in the surface sediments of Taihu Lake, respectively [24]. Compared with previous studies, the source apportionment result of this study was more precise and the much more abundant sampling data made the result more reliable and representative.

## Conclusions

The analysis of the composition and distribution of PAHs in the surface sediments of Taihu was used to perform quantitative source apportionment of PAHs by the PMF model. The model results indicated that the main contributor of PAHs in Taihu Lake was coal combustion, accounting for 53.40% of the total variance, the next was 19.95% for residential emissions, followed by 19.85% for traffic emissions, and 6.80% for biomass combustion. Compared with previous studies, the result of this study was more precise and the much more abundant sampling data made the result more reliable and representative. In addition, the overall distribution of PAHs showed higher concentrations at nearshore places than in the middle of the lake, with the northeast region showing a higher concentration than the southwest region.

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