



Concentrations, seasonal variations, and outflow of atmospheric polycyclic aromatic hydrocarbons (PAHs) at Ningbo site, Eastern China

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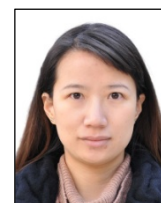
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ABSTRACT

Thirty six pairs of gas and particle (PM_{2.5}) atmospheric samples were collected by high-volume samplers from July 2009 to March 2010 at an eastern background site in Ningbo and analyzed for polycyclic aromatic hydrocarbons (PAHs). The total (gas+particle) air concentrations of 16 PAHs ranged from 11.0 to 103 ng m⁻³, with an average of 46.0±23.4 ng m⁻³. Seasonal trends of PAH concentrations were observed with high concentrations in winter and low in summer, mainly due to regional sources and meteorological conditions. The association with other airborne pollutants and diagnostic ratio analysis indicated that PAHs in Eastern China background were predominantly from coal/biomass combustion. Coal combustion controlled atmospheric PAHs in winter, whilst biomass burning became important in summer and autumn. Located at eastern coastal areas, Ningbo site was chosen to estimate the atmospheric outflow of PAHs. Transport fluxes were characterized by elevated values in spring and winter. Southward transport fluxes dominated during the sampling period, presenting the transport from northern to southern China.

Keywords: PAHs, rural site, biomass combustion, atmospheric outflow



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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) of natural and anthropogenic origin are major carcinogenic constituents in the atmosphere. Many studies have focused on PAHs due to their ubiquity in the environment and adverse effects on human beings. Generally, the contribution of anthropogenic activities exceeds that of natural processes, and thus densely populated and industrialized areas were seriously polluted by PAHs (Marr et al., 2004; Sharma et al., 2007; Mohanraj et al., 2011). However, atmospheric movement may transport PAHs from sources to remote areas. Reports at Arctic and oceans have proved that some pristine areas far away from anthropogenic activities can be influenced by PAHs pollution through air mass movement (Ding et al., 2007).

China is the world's largest emitter of PAHs (Zhang et al., 2011). High concentrations of PAHs were extensively detected around this country (Bi et al., 2003; Guo et al., 2003; Feng et al., 2006a; Feng et al., 2006b; Li et al., 2006; Luo et al., 2010), inducing elevated lung cancer risk to Chinese population via inhalation exposure (Zhang et al., 2009). PAHs released in China could also be dispersed rapidly through air, and many recent studies have shown that the elevated PAH concentrations are monitored in surrounding countries and continents located downwind of China, including Korea, Japan, and North America, which can be

attributed to the outflow of PAHs from China under certain meteorological conditions (Killin et al., 2004; Lee et al., 2006; Tamamura et al., 2007; Lang et al., 2008).

As one of the most prosperous economic regions in China, the Yangzi River Delta (YRD), which is situated in the eastern part of China and composed of many mega cities, has suffered majorities of industries and agricultural development. Although this area is not a region with high PAH emission density, the outflow plume of PAHs from Northern China delivered by stronger westerly winds always introduced elevated PAH concentrations in Eastern China (Zhang et al., 2011). The measurement of ambient concentrations is integral to understanding the relationship between emissions of pollutants and their environmental impacts. Atmospheric concentrations are used to benchmark levels of pollution, document trends in concentration, reconcile emission inventories, elucidate atmospheric processes and constrain chemical transport models. A previous study have suggested the best sampling locations for capturing the outflow plume of PAHs from China were at 27–40°N (Zhang et al., 2011). In this paper, a regional background site, Ningbo Atmospheric Environment Observatory (NAEO, 29°40.8'N, 121°37'E, 550 m ASL), in Eastern China was selected. PAHs in air samples were analyzed. The aims are to investigate the concentration levels and seasonal characteristics of atmospheric PAHs at the regional background site, to identify potential sources, and address atmospheric outflow of PAHs.

2. Methodology

2.1. Site description and regional emission sources

Ningbo Atmospheric Environment Observatory (NAEO) is located in a rural mountaintop (29°40.8'N and 121°37'E with 550 m ASL) in East China (Figure 1). It is a rural site surrounded by hills and forests. The nearest city Ningbo (20 km) is the second largest city of Zhejiang Province. Besides, there are a number of smaller pollution sources in rural locations, such as villages, small industrial plants, and agriculture fields with biomass burning. Local weather is subjected to the subtropical monsoon climate. It is hot and humid in the summer, when maritime air masses reached the sampling site passing through the south part of China under the influence of the Pacific anticyclone. On the contrary, winter is relatively cool and dry, when westerly or monsoon northwesterly winds caused by the Siberian anticyclone dominate, transporting air masses from North and central China to NAEO.

2.2. Sampling procedure

In total, 36 paired 24-hr gaseous and aerosol PM_{2.5} samples were collected once every week from July 2009 to March 2010 on the roof of a building at NAEO using high volume samplers (Graseby–Anderson) operating at 0.3 m³ min⁻¹. Particulate phase PAHs were captured on pre-combusted (450 °C, 12 hr) PALL quartz microfibre filters and then gaseous PAHs were adsorbed on pre-cleaned polyurethane foam (PUF, 6.5 cm diameter, 7.5 cm length), respectively. Field blanks were exposed to the atmosphere only for a few seconds. After sampling, all the samples were wrapped with clean aluminum foil, sealed in clean jars, and kept at -18 °C until analysis.

2.3. Analytical procedure

The gaseous and aerosol samples were spiked with a mixture of surrogate standards containing deuterium labeled PAHs and Soxhlet-extracted with dichloromethane (DCM) for 24 hours, separately. Activated copper granules were added in excess to the collection flask to remove elemental sulfur. Half of each sample extract was concentrated with a rotary evaporator and solvent-exchanged into hexane with a volume of 0.5 mL. Purification was carried out with an 8 mm i.d. alumina/silica column containing anhydrous sodium sulfate (1 cm), neutral silica gel (3 cm, 3% deactivated) and neutral alumina (3 cm, 3% deactivated). The PAH fractions were eluted with 15 mL of a mixture of dichloromethane

and hexane (1:1, V/V). The eluent solvent was blown down to a final volume of 0.2 mL under a gentle stream of nitrogen. Before analysis, hexamethylbenzene was added to each concentrated sample solution as an internal standard.

The PAHs were analyzed on an Agilent 7890 gas chromatograph equipped with a capillary column (DB-5MS, 30 m, 0.25 mm, 0.25 μm) and a mass spectrometer (MSD, Agilent 5975). Each extract (1 μL) was injected in splitless mode with a 10 min solvent delay time. High purity helium was used as the carrier gas, with a flow rate of 1.83 mL min⁻¹. The temperature of the injector and transfer lines was 290 °C and 300 °C, respectively. The initial oven temperature was set at 60 °C for 1 min, raised to 290 °C at a rate of 3 °C min⁻¹ and then held for 20 min. Sixteen individual PAHs were quantified: naphthalene (Nap), acenaphthene (Acp), acenaphthylene (Acpy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenzo[*a,h*]anthracene (Dib), benzo[*g,h,i*]perylene (BghiP) and indeno[1,2,3-*c,d*]pyrene (Ind).

2.4. Quality control

The instrumental stability was checked daily using PAH standards, and the deviation was less than 10%. Isotope-labeled PAHs were added to samples and field blanks to monitor the analytical and sampling procedure. The recoveries were 36±11%, 67±14%, 106±19%, 119±13% and 101±12% for naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12, respectively. All the target compounds in the laboratory blanks were not detected. Six field blanks were taken during the whole sampling procedure. The method detection limits (MDLs) were defined as the average concentrations of target compounds in procedural blanks plus three times the standard deviation, and MDLs were as follows: 3.7 pg m⁻³ for Nap, 0.02 pg m⁻³ for Flu, 2.1 pg m⁻³ for Phe, 0.1 pg m⁻³ for Ant, 0.02 pg m⁻³ for Flua, 0.01 pg m⁻³ for Pyr, 0.32 pg m⁻³ for BaA and 0.02 pg m⁻³ for BaP. Levels of BbF, BkF, BaP, Ind, DahA and BghiP in PUF samples were below the MDLs, therefore only Acp, Acpy, Flu, Phe, Ant, Flua, Pyr, BaA and Chr in the gas phase are discussed throughout the text. A backup PUF was attached to the sampler to check the possible breakthrough of gaseous PAHs, which indicates the PUF plugs caught more than 95% of target compounds in the atmosphere. All the data were corrected for recovery in this study.

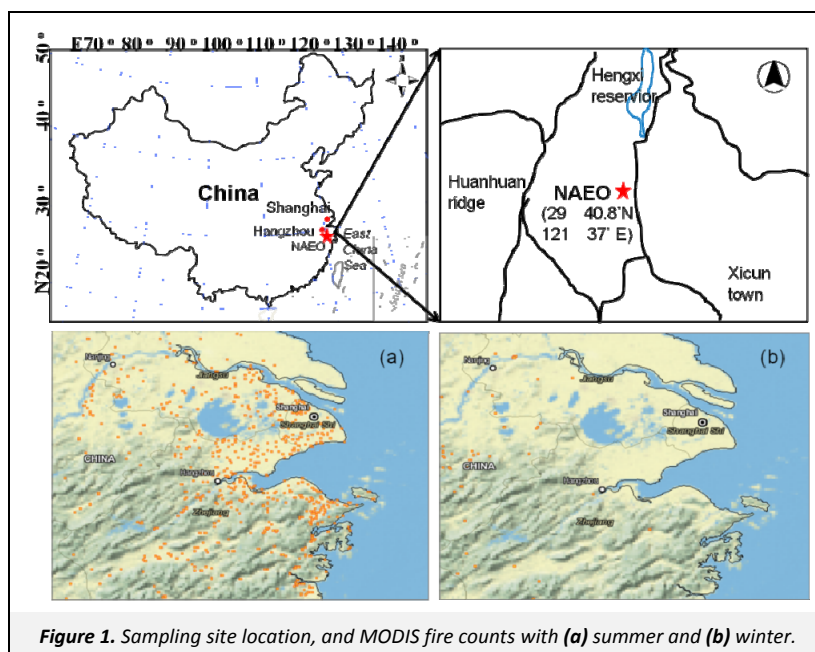


Figure 1. Sampling site location, and MODIS fire counts with (a) summer and (b) winter.

3. Results and Discussion

3.1. Concentrations of PAHs

In this study, sixteen PAHs were quantified (Table 1). The total (gas+particle) PAH concentrations ranged from 11.0 to 103 ng m⁻³, with an average of 46.0±23.4 ng m⁻³. The total gaseous and particulate PAH concentrations ranged from 4.01 to 102 ng m⁻³ and from 0.35 to 52.8 ng m⁻³ with mean values of 32.4±18.1 ng m⁻³ and 12.9±14.8 ng m⁻³, respectively. The average BaP concentration was 1.01 ng m⁻³, which exceeds the European target value of 1.0 ng m⁻³ (European Commission), even though NAEO is a rural site. As illustrated in Table 2, the average total PAH concentration at NAEO was similar to the background site Mountain (MT). Waliguan (the Global Climate Observing System of the World Meteorological Organization in tropical zone) (Cheng, 2006) and rural site in Italy (Perrone et al., 2012), and also higher than the high mountain regions in Europe (Fernandez et al., 2002), MT Taishan (Li et al., 2010), while lower than those found in other urban or suburban sites such as Guangzhou (Li et al., 2006), Shanghai (Chen et al., 2011), Beijing (Zhou et al., 2005), Hong Kong (Lee et al., 2001), Seoul in Korea (Park et al., 2002). Eastern China is a significant source of atmospheric PAHs (Zhang et al., 2011). The concentration

levels indicate that NAEO site is still influenced by regional sources, such as biomass burning in adjacent rural areas, although local pollution is limited.

3.2. Distribution of PAHs in the gas and particle phases

The vapor phase PAH concentrations were approximately two to three times higher than those of particle PAHs. Phe was the most abundant PAH compound in the vapor phase, accounting for 52% of the total PAH mass, followed by Flu (15%), Flua (14%) and Pyr (7%), whereas the particulate PAHs were predominantly low-volatile five- to six-ring compounds (Molecular Weight 250–300), including BbF (17%), Ind (15%) and BghiP (12%), BaP (7%), BkF (6%). Four-ring compound BaA had similar concentrations in both gaseous (0.68 ng m⁻³) and particulate phase (0.76 ng m⁻³). The gas-particle partitioning of different PAH compounds indicates a strong relationship with aromatic ring numbers (Figure 2), which was consistent with other studies (Odabasi et al., 1999; Bi et al., 2003). For example, two- and three-ring PAHs (Nap, Acpy, Acp, Flu, Phe) were dominantly present in the gas phase (>96%), while five- to six-ring PAHs (BkF, BaP, Ind, Dib, BghiP) were associated with particle phase.

Table 1. Average concentrations and ranges (ng m⁻³) of gas and particulate PAHs at the NAEO background station during the sampling period

PAHs	Gas	Particulate	Total
Nap	2.29±1.88 (nd-6.70)	0.03±0.05 (nd-0.26)	2.32±1.88 (nd-6.70)
Acp	0.32±0.76 (nd-3.45)	0.01±0.02 (nd-0.07)	0.33±0.76 (nd-3.45)
Acpy	1.24±3.62 (0.01-14.4)	nd (nd-0.01)	1.24±3.62 (0.01-14.4)
Flu	4.84±2.78 (nd-10.8)	0.02±0.03 (nd-0.13)	4.85±2.78 (nd-10.8)
Phe	16.8±12.5 (2.00-71.9)	0.40±0.76 (nd-3.38)	17.2±12.4 (2.06-71.9)
Ant	0.42±0.91 (nd-4.23)	0.18±0.63 (nd-3.68)	0.60±1.07 (0.04-4.24)
Flua	4.71±2.56 (nd-12.5)	1.11±1.72 (0.01-5.94)	5.82±3.40 (0.01-12.5)
Pyr	0.52±1.44 (nd-7.56)	0.92±1.44 (0.01-4.88)	1.44±1.93 (0.01-7.56)
BaA	0.68±0.45 (nd-1.54)	0.76±0.94 (nd-3.72)	1.44±1.03 (0.03-3.72)
Chr	0.51±0.42 (nd-2.09)	1.28±1.62 (0.01-6.13)	1.79±1.63 (0.04-6.13)
BbF	nd	2.24±2.10 (nd-7.66)	2.58±2.13 (0.34-7.66)
BkF	nd	0.82±0.94 (nd-3.49)	0.87±0.96 (nd-3.49)
BaP	nd	0.95±1.19 (nd-4.28)	1.01±1.24 (nd-4.28)
Dib	nd	0.64±0.66 (nd-6.58)	0.67±0.66 (0.24-6.58)
BghiP	nd	1.55±1.79 (nd-2.43)	1.67±1.89 (nd-2.43)
Ind	nd	1.98±1.71 (nd-6.13)	2.11±1.73 (nd-6.13)
∑ ₁₆ PAHs	32.4±18.1 (4.01-102)	12.9±14.8 (0.35-52.8)	46.0±23.4 (11.0-103)

nd: not detected

Table 2. Comparison of mean PAH (gas and/or particle) concentrations between Ningbo and other background and/or urban, coastal sites

Sampling site	Mean concentration (ng m ⁻³)	Literature
Ningbo	46.0 (gas+particle)	This study
MT. Waliguan	18.20 (gas+particle)	Cheng (2006)
MT. Taishan	6.88 (particle)	Li et al. (2010)
Italy	33.4 (particle)	Perrone et al. (2012)
Redo	1.3-2.6 (gas+particle)	Fernandez et al. (2002)
Gossenkolle and ØvreNeadalsvatn	2.0-3.7 (gas+particle)	Fernandez et al. (2002)
Guangzhou	313 (gas+particle)	Li et al. (2006)
Shanghai	216 (gas+particle)	Chen et al. (2011)
Beijing	116 (particle)	Zhou et al. (2005)
Hong Kong	91 (particle)	Lee et al. (2001)
Seoul, Korea	89.3 (gas+particle)	Park et al. (2002)

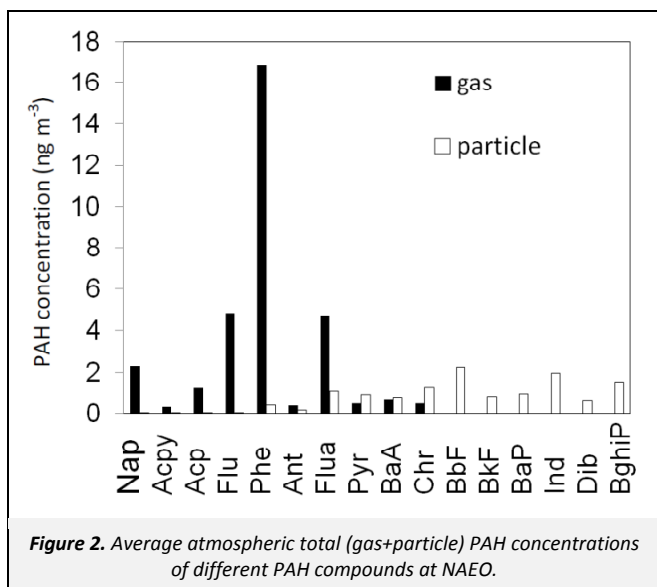


Figure 2. Average atmospheric total (gas+particle) PAH concentrations of different PAH compounds at NAEO.

The gas–particle partition status can be described by Equation (1) (Simcik et al., 1999):

$$\log K_{pi} = m \log p_{Li}^0 + b \tag{1}$$

where K_{pi} ($m^3 \mu g^{-1}$) is the partition coefficient, m and b are the slope and intercept of the regression line, respectively. K_{pi} is defined as $K_{pi} = C_{pi} / (C_{gi} \times TSP)$, where TSP is the concentration of total suspended particulate matter, C_{pi} and C_{gi} ($\mu g m^{-3}$) are the concentrations of compounds in the particle and gas phases, respectively. The relationship between K_{pi} and the temperature dependent sub-cooled liquid vapor pressure p_{Li}^0 (Torr) of a specific compound was estimated to explore equilibrium conditions of PAHs. PAHs size distribution is unimodal with

maximum for the small size particles (Gupta et al., 2011). If PAHs in $PM_{2.5}$ substitute those in TSP, significant correlation coefficients ($p < 0.01$) can be observed at NAEO for Flua ($r^2 = 0.5804$), BaA ($r^2 = 0.3531$) and Chr ($r^2 = 0.6604$). Their slopes varied in the range of -1.255 to -1.045 , which were steeper than -1 and different from other previous studies carried in rural and/or remote atmospheres area (Gustafson and Dickhut, 1996; Fernandez et al., 2002). This could be attributed to non-equilibrium conditions and/or sampling artifacts.

3.3. Seasonal variation

Figure 3 shows the total gas and particulate PAH concentrations during different seasons along with the meteorological parameters. A clear seasonal variation was observed in total (gas+particulate) PAHs, with elevated levels in the winter, followed by the autumn and lowest in the summer. This result was in agreement with other studies (Gigliotti et al., 2000; Park et al., 2002; Terzi and Samara, 2004; Vardar et al., 2008; Morville et al., 2011). The seasonal difference could be explained by the increased fossil fuel consumption in the cold season. In addition, meteorological conditions like lower atmospheric mixing height, decreased sunlight intensity as well as frequent temperature inversions would deteriorate PAHs pollution in winter.

Seasonal trend was apparent for PAHs concentration in the gaseous phase, the PAHs concentration levels was highest in autumn (39.6 ng m^{-3}) and gradually decreased in winter (31.0 ng m^{-3}) and then in summer (23.9 ng m^{-3}). For particulate PAHs, the variation trend was observed different to that of in gaseous phase, with highest in winter (24.3 ng m^{-3}) and then in autumn (8.21 ng m^{-3}) and in summer (1.63 ng m^{-3}). During the wintertime, PAHs, except Nap, tended to partition onto the particle phase. This may be attributed to lower temperatures, allowing condensation of volatile and semi-volatile PAHs onto atmospheric particles.

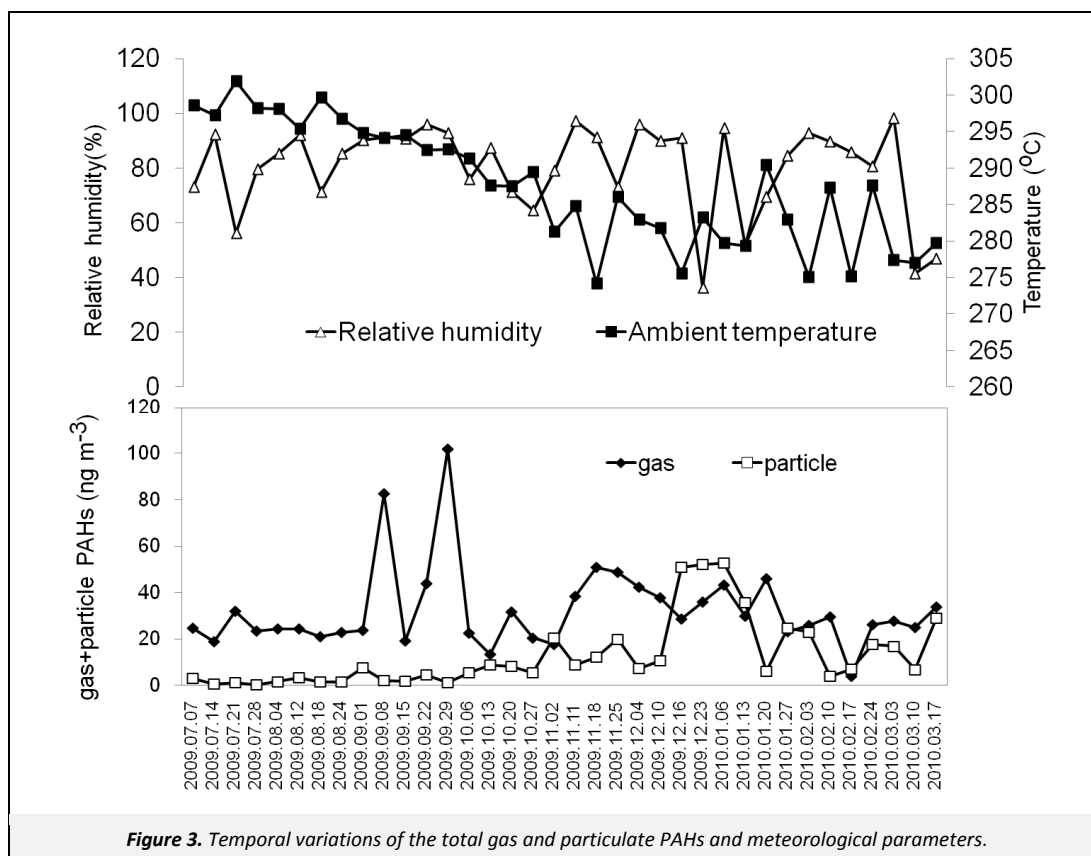


Figure 3. Temporal variations of the total gas and particulate PAHs and meteorological parameters.

3.4. Impact of meteorological factors

There was no statistically significant relationship between PAH concentrations and wind speed or humidity. The Clausius–Clapeyron equation has been applied to investigate the relationship between temperature and semi-volatile organic compound (SOC) behaviors and their possible sources (Wania et al., 1998):

$$\ln P = m \left(\frac{1}{T} \right) + b \quad (2)$$

where, the term $\ln P$ is the natural logarithm of partial pressure of SOC gas phase (atm), T is the ambient temperature in Kelvin, m is the slope ($m = -\Delta H/R$, where H is the characteristic environmental phase-transition energy of the compound (kJ mol^{-1}) and R is the gas constant), and b is the intercept of the line. Generally, a shallow slope or low temperature dependence indicates that long-range transport controls atmospheric levels at a sampling site. Steeper slopes indicate high surface concentrations in the vicinity of the site (Wania et al., 1998). In present study, the relationships were not statistically significant or yielded low r values, indicating that those compounds were controlled by primary emissions or phase transfer processes were of minor importance at NAEO.

3.5. Source apportionment of PAHs

In this study, concentration of particulate PAHs were significantly correlated with measured organic carbon (OC) ($r=0.897$, $p<0.01$), elemental carbon (EC) ($r=0.900$, $p<0.01$) and $\text{PM}_{2.5}$ ($r=0.899$, $p<0.01$). Thus, PAHs could have similar sources with OC, EC and $\text{PM}_{2.5}$. High total PAH concentrations observed in winter ranged from 11.0 to 96.0 ng m^{-3} , with an average of $55.4 \pm 23.7 \text{ ng m}^{-3}$. The proportion of Flu in the gas phase commonly increased in this period. Flu can be considered as an indicator of coal combustion in China (Xu et al., 2012). The increase indicates that PAH enhancement in winter was possibly due to cold season at Central and Northern China from November to March. Thus, the high PAHs at NAEO could be resulted from increased fossil fuel combustion such as coal combustion for heating in Northern and/or Central China, from where air masses were being passed. This assumption was supported by a ^{14}C study at this site, with the highest EC concentration, lower $f_{\text{C}(\text{EC})}$ values and levoglucosan levels (Liu et al., 2013). Besides, plenty of coal combustion at local industry also may contribute to high PAHs levels at NAEO. In summer, lowest concentration was observed with average of $25.6 \pm 4.18 \text{ ng m}^{-3}$ (ranged from 19.2 to 33.2 ng m^{-3}). ^{14}C value of EC, OC/EC ratio and levoglucosan concentration in the atmosphere was found to be also higher at NAEO (Liu et al., 2013). It proves that biomass burning from upwind Shanghai region and surrounding area (fire counts seen from Figure 1) was one of the major sources for ambient PAHs in East China, which also can be supported by PAH diagnostic ratios. Although there are limitations of source apportionment by PAH isomeric ratios (Katsoyiannis et al., 2011; Katsoyiannis and Breivik, 2014), a plot of $\text{Flua}/(\text{Flua}+\text{Pyr})$ against $\text{Ind}/(\text{Ind}+\text{BghiP})$ for the particle $\text{PM}_{2.5}$ samples also suggests that most of data points lie within where an indicative of the influence of grass, wood and coal combustion source (Figure 4). Only fewer points mainly from the summer and autumn period derived from the petroleum and/or petroleum combustion. In addition, southern or eastern monsoon air masses brought clean oceanic air from Pacific Ocean along with precipitation, which made PAHs levels lower than other seasons (Figure 3). Furthermore, photochemical reactions may decrease PAH levels during summer season.

3.6. Atmospheric outflow

Previous modeling work suggested that the PAH outflow from China concentrates near 30°N (Zhang et al., 2011). Given the geographical location, observation at NAEO can be applied for

comparison. Based on atmospheric concentrations and meteorological data, the atmospheric fluxes of PAHs were estimated. The outflow of PAHs in this study was calculated by multiplying the PAH concentrations (ng m^{-3}) with wind velocity (m s^{-1}). Figure 5 illustrates the seasonal transport and outflow patterns of PAHs estimated at NAEO. An arrow in the picture points to the direction to where the wind is blowing over NAEO. The outflow is conveyed through the size of vector. The longer the arrows, the larger the outflow fluxes. Seasonally, the outflow fluxes transported from China were much larger in winter than summer and autumn. This was in agreement with a recent modeling study for outflow of PAHs emitted from China indicating that elevated transport flux occurred in spring and winter (Zhang et al., 2011).

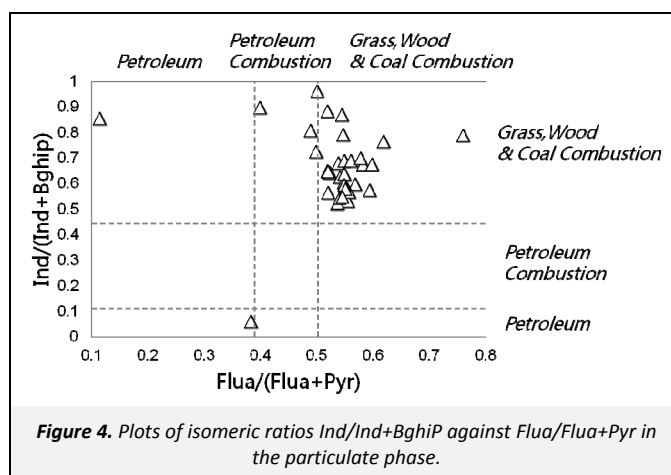


Figure 4. Plots of isomeric ratios $\text{Ind}/(\text{Ind}+\text{BghiP})$ against $\text{Flua}/(\text{Flua}+\text{Pyr})$ in the particulate phase.

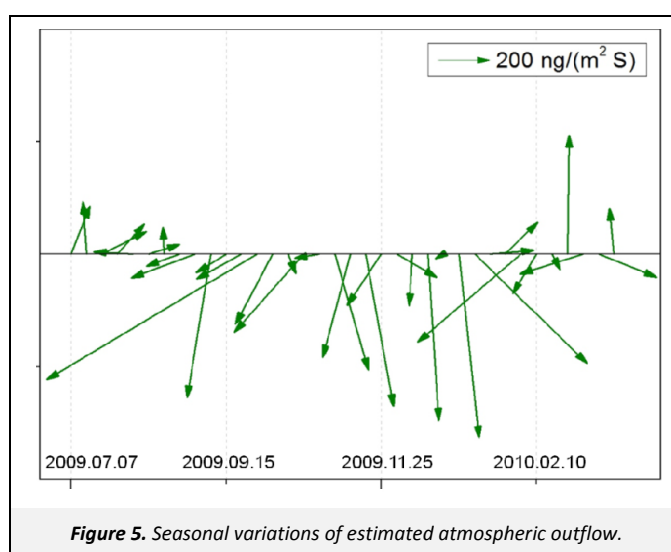


Figure 5. Seasonal variations of estimated atmospheric outflow.

The northwestward transport was of minor importance during the whole sampling period (Figure 5). Outflow fluxes from China to Korea and/or Japan (northeastward) were also considerably low, although a high value occurred in spring. On the contrary, the wind directions blowing to southern China dominated the whole sampling period, and contributed high outflow fluxes of PAHs with the maximum of $817 \text{ ng m}^{-2} \text{ s}^{-1}$ reached on 6th January, 2010. The transported flux proportion of northward, southward, eastward and westward was about 1:7:1:2. Zhang et al. (2011) suggested that about 80% atmospheric PAHs were transported out of China transported through the eastern boundary of the country. However, this study showed that a southward transport was dominant. The difference between monitored and modeled results can be attributed to two factors. First, wind field and PAH concentrations exhibited inter annual variations. Second, the present observation did not include samples from April to June,

when PAHs were transported toward the northeast according to the previous work.

4. Conclusions

Samples collected at the NAO station in Ningbo from July 2009 to March 2010 and PAHs were quantified. Seasonal variations and potential sources were characterized in this study. The results showed that the total (gas+particle) air concentrations of 16 PAHs ranged from 11.0 to 103 ng m⁻³, with an average of 46.0 ± 23.4 ng m⁻³. The average gaseous and particulate PAHs levels ranged from 4.01 to 102 ng m⁻³ and 0.35 to 52.8 ng m⁻³, respectively. Phe was the predominant PAH compound in vapor phase, followed by Flu, Flua and Pyr. While the particulate PAHs were dominantly five- to six-ring compounds such as BbF, Ind and BghiP, BaP, and BkF. Seasonal trends of PAH concentrations were observed with higher in winter and lower in summer. Evaporation from the surfaces was minor and possible ongoing sources or atmospheric transport from the intensive agricultural areas around the sampling station may result in high PAH concentrations. Combined with ¹⁴C value, diagnostic ratios, correlation analysis and concentration variations, we concluded that the high PAH levels in winter may be attributable to the energy consumption like increased fossil fuel usage in the cold season and atmospheric PAHs transported from northern or mainland China. Meteorological factors such as regional climatic conditions, lower atmospheric mixing height, decreased sunlight intensity as well as frequent temperature inversion may also intensify the PAH pollution in winter. During the summer, the contribution of biomass burning became significant. Atmospheric outflow was estimated based on the present observations. Elevated transport fluxes were found during the spring and winter seasons and southward transport dominated.

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