Diurnal and nocturnal variations of PAHs in the Lhasa atmosphere, Tibetan Plateau: Implication for local sources and the impact of atmospheric degradation processing

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ABSTRACT

Due to the unique characteristics, such as intensive radiation, high altitude and low humidity, plateau climate importantly affects the airborne organic contaminants' behavior in the environment. In this study, USEPA priority polycyclic aromatic hydrocarbons (PAHs) and benzo[e]pyrene were detected in the air samples collected at two suburban sites in Lhasa city. The total concentrations of USEPA priority fifteen PAHs (except naphthalene) in the particulate phase ranged from 4.4 to 60 ng/m^3, while in the gas phase from 79 to 350 ng/m^3. Integrated results of the multiple diagnostic ratios indicated that the major potential sources of PAHs in Lhasa city were local incomplete combustion of wood and cow dung cake. Particulate and gaseous PAH levels in this study displayed two clear and different diurnal and nocturnal concentration patterns, however, no distinct diurnal and nocturnal variation was observed for the total suspended particles (TSP) concentrations. No significant correlation was found between TSP concentrations and particle-bound PAHs, meaning physicochemical processes play an important role in diurnal and nocturnal variations of PAHs in the atmosphere except emission sources in this study. Based on the diurnal and nocturnal changes of the percentage of particulate phase PAHs in total PAHs, it suggested that gas–particle partitioning driven by temperature makes a great contribution to the variations of PAHs concentrations. The most susceptible to transformation between gas and particle phase chemicals are PHE, ANT, FLA, PYR, BaA and CHR. In addition, our observation suggested that atmospheric reaction and photolytic degradation also exert an important impact on the variations of PAHs in both phases in the atmosphere of Lhasa city.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), a group of ubiquitous toxic organic pollutants, formed and emitted primarily from anthropogenic processes such as incomplete combustion of fossil fuel, solid biomass, and some of other organic materials, has received considerable attention for its potential risk to the environment and human's health (Bhargava et al., 2004; Lu et al., 2006). It is estimated that the total 16 U.S. Environmental Protection Agency priority PAH emissions from China was up to 116,000 tons in 2003 and the major contribution was from eastern China (Zhang et al., 2008). As persistent semi-volatile chemicals, PAHs can migrate from sources and then be deposited into the different environmental compartments of the remote areas via the grasshopper and cold trapping processes, for example, Polar Regions (Ding et al., 2007; Halsall et al., 1997, 2001), open ocean (Nizzetto et al.,

2008), and high altitude regions like Himalaya Mountains (Loewen et al., 2005; Wang et al., 2006).

Lhasa, located at the bottom of a small basin surrounded by the Himalaya Mountains and in the center of the Tibetan Plateau, is the capital of Tibet Autonomous Region, China. The Tibetan Plateau is the highest and biggest plateau on the earth, with an area of 2.5 million km^2 and an average elevation of over 4500 m, surrounded by massive mountain ranges. Traditional agriculture and animal husbandry are the main economic pillars for the Tibetan Plateau Region while industry only accounted for 8% of GDP of Tibetan Autonomous Region (http://www.tibet.stats.gov.cn/). Given its unique geographic position, low economic development level and limited human activities, the Tibetan Plateau Region was frequently of concern as a background site on the long range atmospheric transport (LRAT) study of persistent organic pollutants (POPs) at a global scale (Cheng et al., 2007; Wang et al., 2006). It has been reported that POPs can penetrate the barrier of Himalayan Mountains via LRAT and then further influence the atmosphere of hinterland of the Tibetan Plateau along with the invasion of Indian summer monsoon (Cheng et al., 2007; Wang et al., 2010). Numerous researchers considered that POPs in the environment of the Tibetan Plateau Region were predominantly originated from remote regions through LRAT and consequentially they believed that the measured POP concentrations obtained from environmental compartments in the Tibetan Plateau can be used as background values (Tao et al., 2010; Wang et al., 2007; Wu et al., 2011). These studies are mainly concerned with the role of long range transport of POPs, however, some evidences indicate that the local anthropogenic activity of Lhasa provided a significant contribution to atmospheric environment (Li et al., 2008; Xing et al., 2010). A recent study has found that air mass contaminated by PAHs in the urban environment of Lhasa had been primarily derived from local human activities, such as vehicle emissions and incense burning (Gong et al., 2011). In addition, Lu et al. (2006) reported that cow dung cake (CDC) burning in Tibetan region could result in serious PAH pollution in the indoor environment and hence affect human health.

However, the data for PAHs in air on the edge of Lhasa is very limited. The results are of great importance in evaluating the influence of urban airborne emissions on the regional background. The objectives of this study were (1) to measure the concentrations and describe the compound compositions of the atmospheric gaseous and particulate phase PAHs in urban fringe of Lhasa, (2) to identify the potential sources using isomer compounds, and (3) to illustrate the diurnal and nocturnal variations of PAHs and assess their potential controlling factors.

2. Methodology

2.1. Sampling sites and methods

This study was carried out in Lhasa city, Tibet Autonomous Region, China. The total area of the city is about 30,000 km^2 with a population of 400,000 at a height of 3600 m above sea level. The sampling site WS and ES are located at suburban area and about 6.5 km west and 6 km east of the Lhasa urban center, respectively. More information about these two sampling sites had been described by a previous study (Li et al., 2008).

Sampling was conducted simultaneously at the two sampling sites for a consecutive 12 hour period during daytime (7:30 a.m.–7:30 p.m.) and nighttime (7:30 p.m.–7:30 a.m.) from August 6 to August12, 2006. A total of twenty pairs of samples were collected at these two sampling sites. Air volumes of ~250 m^3 were drawn through a Quartz microfiber filter (QFF) (Grade GF/A, 20.3×25.4 cm, Whatman, Maidstone, England) using a high-volume sampler (of the Anderson type) at a flow rate of 0.350 m^3 min^{-1}, and subsequently through a 6.5 cm in diameter $\times$ 7.5 cm in thickness (a density of 0.030 g/cm^3) polyurethane foam (PUF) plugs. Prior to sampling, QFFs were baked at 450 °C for 12 h to remove any organic contaminants, and PUF plugs were Soxhlet extracted for 48 h with methanol and then acetone for 24 h, followed by two overnight extractions using dichloromethane (DCM). PUF plugs were dried overnight in a vacuum desiccator and stored in solvent-rinsed glass jars before use. During the sample collection, clean gloves were used and worn, and QFFs and PUFs were handled using acetone-rinsed stainless steel tongs. After sampling, QFFs were wrapped with prebaked aluminum foil and sealed with 2 layers of polyethylene bags. PUFs were placed in solvent rinsed glass jars with Teflon lined lids, and then transported to the laboratory and stored at −20 °C until extraction. Meteorological data, such as temperature, relative humidity, wind speed/direction, and precipitation were recorded during the sampling period. The correlations between relative humidity and PAHs were insignificant ($r = 0.363$, $p = 0.318$ for particulate PAHs and $r = -0.368$, $p = 0.296$ for gas PAHs), therefore relative humidity was not a factor affecting PAH concentration in this study, also the precipitation, the rain occurred only 3 times and they were very short, as a result, the influence of precipitation to the level of PAHs in the atmosphere was minimal.

2.2. Sample analysis

Before the extraction, filters and PUFs were spiked with 1000 ng of deuterated PAHs as surrogates and Soxhlet-extracted with DCM for 48 h. Extract was concentrated by a rotary evaporator and solvent-exchange was completed using hexane. Purification was accomplished by an 8 mm in diameter alumina/silica column in turn containing anhydrous sodium sulphate (1 cm), neutral silica gel (3 cm, 3% deactivated) and neutral alumina (3 cm, 3% deactivated). PAH fractions were eluted by 15 mL of a mixture of DCM and hexane (1:1 by volume). The eluent solvent was blown down to a final volume of 200 μL in hexane under a gentle stream of nitrogen. Prior to analysis, 1000 ng of hexamethylbenzene (Aldrich Chemical, Gillingham, Dorset, USA) was added as an internal standard.

PAHs were analyzed by an Agilent 7890 gas chromatograph equipped with a capillary column (DB-5MS, 30 m, 0.25 mm, 0.25 μm) and a mass spectrometric detector (MSD, Agilent 5975). Samples (1 μL) were injected under splitless mode with a 10 min solvent delay time. High purity helium was used as carrier gas with a flow velocity of 1.83 mL/min. The temperature of injector and transfer line was 290 °C and 300 °C, respectively. The initial oven temperature was set at 60 °C for 1 min and raised to 290 °C at a rate of 3 °C/min and held for 20 min. Sixteen PAHs were quantified: acenapthene (ACE), acenapthylene(ACY), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[e]

pyrene (BeP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP) and indeno[1,2,3-c,d]pyrene (IcdP).

Mixture and deuterated PAHs standards used in this study were obtained from Ultra Scientific Inc. (North Kingston, RI, USA), and all reagents were purchased from Honeywell Burdick & Jackson Company (Morristown, NJ, USA).

2.3. Quality control and quality assurance

The standards of PAHs were injected to the instrument for checking its stability daily and deviation of the instrument was less than ± 10%. Isotope-labeled PAHs were added into samples and field blanks to monitor the analytical procedure. The recoveries were 74% ± 13%, 89% ± 16%, 85% ± 14% and 87% ± 12% for acenapthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12, respectively. Six field blanks were taken at both sampling sites. The method detection limits (MDLs) were assigned as average values of blanks, with 3 times of standard deviations of obtained from the blanks. When the compounds were not detected in the blanks, 3 times of the instrumental detection limit (IDL) were used for calculating the MDLs. The IDL values were calculated from the lowest standards, extrapolating to the corresponding amount of analyte that would generate a signal-to-noise ratio of 3:1. All target compounds in the field and lab blanks were under the IDLs. The data reported in this study were not corrected by the percentage of recoveries.

A backup PUF was attached to the sampler in order to check the possible breakthrough of gaseous PAHs. Typically, the backup PUF contained <5% of the total vapor phase component, with greater penetration to the second plug observed for the lighter PAH compounds (PHE 3.3%, FLO 1.6%, ANT 0.9% and FLA 0.5%).

3. Results and discussion

3.1. Concentrations of PAHs

The total (gaseous + particulate) concentrations of 15 USEPA priority control PAHs (naphthalene was not quantified) varied between 87 and 240 ng/m³ at WS site and between 89 and 360 ng/m³ at ES site, with average concentrations of 160 ± 58 ng/m³ and 200 ± 92 ng/m³, respectively (Table 1). The total average gaseous and particulate PAH concentrations were 150 ± 60 ng/m³ and 10 ± 6.6 ng/m³ at WS site and 180 ± 95 ng/m³ and 20 ± 15 ng/m³ at ES site, respectively. Atmospheric PAH concentrations have been measured in many different sites throughout the world. After a year of continuous sampling, Li et al. founded that the total PAH concentration in air of Guangzhou, a coastal megacity in southern China, ranged from 200 to 474 ng/m³ (Li et al., 2006), much lower than Beijing in January (winter season) due to a great number of domestic coal combustion and emission from vehicles (Tao et al., 2007). The concentration of total PAH from Athens, Greece during June to November 2003 was reported, it was only an average of 28 ng/m³ (Vasilakos et al., 2007). Meijer et al. reported 15 years (1990–2005) of PAH concentrations in Europe, the results showed a decline trend of PAHs in the atmosphere and the concentration was relatively low compared to the PAHs reported from another part of the world (Meijer et al., 2008). In general, the observed PAH levels found in this study were much lower than many developed cities in China, however, they were higher than the urban atmosphere in Europe. Comparable and similar levels of total PAHs were reported at London, U.K., monitored from 1991 (166 ng/m³) to 1992 (122 ng/m³) (Halsall et al., 1994) and Taiwan (Chen et al., 2009).

BaP is widely known to be a highly carcinogenic and mutagenic substance and hence is seriously detrimental to human health. In this study, the average BaP concentration at ES site (1.4 ng/m³) was slightly higher than the results found at WS site (0.39 ng/m³). To compare with the four most developed cities in China, Guangzhou (2.3 ng/m³) (Li et al., 2006), Beijing (2.14-27.65 ng/m³) (Zhang et al., 2009), Shenzhen (2 ng/m³) (Liu et al., 2010) and Shanghai (1.42-32.98 ng/m³) (Guo et al., 2004), concentrations of BaP in Lhasa showed a relatively lower polluted level, however, they are much higher than those in some urban areas of developed countries and some regions (Harrison et al., 1996; Ohura et al., 2004; Panther et al., 1999).

The predominant PAHs in the gas phase were 2–3-ring compounds (ACY, ACE, FLO, and PHE were the most abundant) ranging from 87.8% to 98.8%, while the 5–6-ring chemicals, with low vapor pressure, dominated the particulate phase, only about 4% of these chemicals exist in the gaseous form. In contrast, 4-ring PAHs (PYR, BaA, CHR, BbF and BkF) were equally partitioned between the vapor and the particulate phases, which were consistent with other studies (Li et al., 2006; Liu et al., 2007). Significant positive correlations of PAH composition between WS and ES site in both particulate ($r = 0.696$, $p < 0.01$) and gas phases ($r = 0.995$, $p < 0.01$) were noticed, indicating that the presence of common or similar principal emission sources.

3.2. Source diagnostics

Parent PAH ratios are frequently used as diagnostic tool to identify the origin of PAHs such as unburned petroleum, liquid fossil fuel combustion and solid fuel combustion. In this paper, ANT/(ANT + PHE), BaA/(BaA + CHR), FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) of the particulate phase are selected as indicators and their values are compared with the results reported previously to investigate the emission sources of PAHs. The ratios of ANT/(ANT + PHE) and BaA/(BaA + CHR) at WS site were ranged from 0.08 to 0.14 (0.11 ± 0.02) and 0.21 to 0.37 (0.29 ± 0.05), respectively, and the corresponding values at ES site were in the range of 0.11 to 0.17 (0.15 ± 0.02) and 0.23 to 0.45(0.36 ± 0.08), respectively. It might be that a mixed petroleum spill/volatilization and combustion source potentially influenced the Lhasa air (Duan et al., 2007; Yunker et al., 2002). The ratio of FLA/(FLA + PYR), lower than 0.4 shows a characteristic of non-burned petroleum inputs and ratios between 0.4 and 0.5 for liquid fuel combustion while a value higher than 0.5 is a characteristic of solid biomass burning (Yunker et al., 2002). In this study, there was a significant difference of FLA/(FLA + PYR) values between the two sampling sites. At ES site, these values ranged from 0.15 to 0.46 (0.25 ± 0.11), suggesting that unburned petroleum sources dominantly influence this sampling site according to the study conducted by Yunker et al. (2002). However, it would be better to identify the sources of airborne PAHs if the diagnostic ratios of local emission sources were known, since the range for the values of diagnostic ratios could be too wide for the variations of sources. For example, the FLA/(FLA + PYR) for biomass burning were between 0.1 and 0.8 (Galarneau, 2008). The values of

Table 1
Average concentration in ng/m³ of the identified PAHs.

PAHs	W S			E S		
	Particulate	Gas	Total	Particulate	Gas	Total
ACY	0.08(0.00–0.11)	1.4(0.71–2.8)	1.5(0.78–2.9)	0.07(0.00–0.11)	1.4(0.72–2.7)	1.5(0.83–2.8)
ACE	0.44(0.32–0.63)	3.2(1.1–10)	3.6(1.6–11)	0.49(0.41–0.65)	5.4(1.0–18)	5.9(1.5–19)
FLO	1.1(0.84–1.5)	17(10–23)	18(11–24)	1.2(0.94–1.5)	17(9.2–25)	18(10–26)
PHE	1.3(0.96–1.9)	110(52–180)	110(53–180)	1.5(1.2–2.2)	130(50–280)	130(51–280)
ANT	0.17(0.10–0.29)	7.2(4.4–11)	7.4(4.6–11)	0.27(0.18–0.46)	11(5.4–17)	11(5.7–17)
FLA	0.89(0.57–1.2)	9.0(2.1–20)	9.9(3.3–21)	0.46(0.16–1.1)	0.84(0.12–2.4)	1.3(0.52–2.7)
PYR	0.19(0.06–0.54)	4.0(1.1–7.7)	4.2(1.2–7.8)	1.3(0.83–2.4)	11(3.0–26)	12(3.8–27)
BaA	0.21(0.04–0.69)	0.08(0.04–0.13)	0.29(0.12–0.76)	0.85(0.12–4.0)	0.17(0.05–0.25)	1.0(0.21–4.3)
CHR	0.46(0.13–1.2)	0.50(0.19–0.81)	0.95(0.54–1.8)	1.2(0.27–4.8)	0.80(0.18–1.6)	2.0(0.47–5.6)
BbF	1.2(0.36–3.9)	0.10(0.04–0.24)	1.3(0.41–4.0)	3.0(0.90–10)	0.21(0.02–0.69)	3.2(0.93–10)
BkF	1.1(0.31–3.5)	0.07(0.01–0.23)	1.2(0.36–3.6)	1.7(0.47–5.1)	0.18(0.01–0.60)	1.9(0.48–5.2)
BaP	0.37(0.09–1.3)	0.02(0.01–0.09)	0.39(0.09–1.3)	1.4(0.23–5.8)	0.05(0.01–0.15)	1.4(0.28–5.9)
DahA	0.38(0.09–1.3)	ND	0.34(0.00–1.3)	0.83(0.19–3.4)	0.01(0.00–0.02)	0.83(0.19–3.4)
IcdP	1.2(0.22–4.1)	0.01(0.00–0.03)	1.2(0.22–4.1)	3.4(1.0–11)	0.10(0.00–0.32)	3.4(1.1–12)
BghiP	1.0(0.26–3.6)	0.01(0.00–0.02)	1.0(0.26–3.6)	2.2(0.89–6.9)	0.07(0.00–0.23)	2.3(0.89–6.9)
$\sum$ PAHs	10(4.4–26)	150(79–230)	160(87–240)	20(8.3–60)	180(80–350)	200(89–360)

ND: not detected.

FLA/(FLA + PYR) at ES site were in good agreement with the results found by Lu et al., about 0.37 in a rural Tibetan residence severely contaminated by the burning of cow dung cake (CDC) (Lu et al., 2006), which indicates that ES site might be also impacted by PAHs derived from the burning of CDC due to ES site was located in the downwind position and the prevailing wind from the southwest frequently passed the site during the sampling campaign. Therefore, it is reasonable to consider that ES site was greatly impacted by CDC burning. The ratios at WS site were relative higher than ES site, from 0.68 to 0.93 (0.84 ± 0.08), indicating the predominance of solid fuel combustion such as wood and grass occurred at WS sampling site located in the vicinity of an agriculture land. IcdP/(IcdP + BghiP) ratio of 0.2–0.5 possibly indicates petroleum combustion, whereas solid fuel like coal, grass and wood combustion would provide a higher ratio >0.5 (Yunker et al., 2002). The corresponding ratio values for cars, diesel, and wood burning are 0.20, 0.37, and 0.62, respectively (Gogou et al., 1996; Ravindra et al., 2008). The IcdP/(IcdP + BghiP) ratios at WS and ES site were ranged from 0.46 to 0.57 (0.52 ± 0.03) and 0.53 to 0.63 (0.58 ± 0.03), respectively, implying that wood burning source was predominant. In addition, these IcdP/(IcdP + BghiP) ratios in this study were in line with the past results obtained from the Tibet indoor air samples contaminated by the combustion of cow dung cake (Lu et al., 2006). All these ratios suggested that incomplete combustion of solid biomass (wood and CDC) had a significant effect on the sampling sites, which is consistent with the conclusion made by a recent study using the measurements of ¹⁴C and results from the study suggested that carbon in particulates from the atmosphere of Lhasa between 2006 and 2007 were mainly derived from biogenic contribution (Huang et al., 2010). Additionally, The results were also corresponding with the energy consumption condition of Lhasa that biomass energy (wood and CDC) consumption was considered as the largest parts (about 40%) of total energy consumption, compared to coal and liquid fossil fuel, 5% and 16%, respectively (Hua, 2009).

Furthermore, the incense burning in the temples for religious activities might be another important emission source of PAH in Lhasa (Li and Ro, 2000). Lin et al. reported that PAH concentration measured inside the temple was up to 6258 ng/m³ and exceeded outdoor concentration by a factor of 27 (Lin et al., 2002). It seems clear that temples is a significant PAH emission source. In this study, the values of IcdP/(IcdP + BghiP) ratios were much higher than the concentration of PAH found at temples in Taiwan (Li and Ro, 2000; Lin et al., 2002). Incense burning was also found to be related to the high emission levels of BaP, FLA, PYR and BghiP (Huynh et al., 1991; Li and Ro, 2000). However, in this study the results were different, implied that incense burning had a small influence on the samples of this study seemingly. There were three possible reasons which could explain this phenomenon. Firstly, temples were far from the sampling sites; secondly, the composition of PAHs emitted from incense burning would be different due to the differences in the raw materials used in incense-making; thirdly, PAHs composition characteristics of incense burning in Tibet region were likely to vary from other low altitude palaces since very low oxygen content (60%–70% of normal condition) in the Tibetan atmosphere. However, the frequent religious practices in Lhasa and results confirming PAH generated from the incomplete combustion of incense sticks, with regards to

these hypothesizes that incense burning would be a potential PAH source to the Lhasa atmosphere. Further study is needed to investigate on the effect of incense burning on PAH emission.

The BaP/BeP ratio is affected by the strong reactivity in the atmosphere since BaP is susceptible to photolytic process due to its high reactivity (Butler and Crossley, 1981). Most of the fresh emissions show the similar ratios of BaP to BeP, thus the decline of the ratio can be regarded as an index of the aging of particles. Many studies usually calculated the ratio of BaP to BeP in order to discuss the atmospheric chemical processes (Ding et al., 2007; Li et al., 2006). However, there is no defined threshold for BaP/BeP value to distinguish the difference between local emission and aged particles. BaP/BeP ratios at remote sites were selected as aged aerosol type (Ding et al., 2007; Halsall et al., 1997), while the data from the polluted cities were chosen as emission sources (Duan et al., 2007; Ohura et al., 2004). Fig. 1 showed that the BaP/BeP ratios at the background sites were generally lower than 0.4, however, the values at emission source regions were generally higher than 0.4. Interestingly, the BaP/BeP values in the most samples of this study were higher than 0.4, which indicates that the air masses collected during sampling program in Lhasa city were relatively fresh. Therefore, local emission might play a significant role on PAH air contamination in Lhasa city.

3.3. Diurnal and nocturnal effects of PAHs

The variations of PAHs' concentrations in the gas and particulate phases are presented in Fig. 2 and the patterns showed a clear diurnal and nocturnal cycle of PAHs in Lhasa for both particulate and gas phases. The higher values of most gaseous PAHs occurred at daytime while most particulate PAHs exhibited their maxima values at nighttime at both sampling sites.

The Clausius–Clapeyron equation is used to describe the relationship between temperature and concentration of semi-volatile organic compounds (SVOCs) in gas and particulate phases for their volatilization from the surface (Hoff et al., 1992; Wania et al., 1998):

$$\ln P = -\triangle H/RT + C$$

where P is the partial pressure (atm) of SVOCs in the gas phase and calculated for each sample by the ideal gas law, $\triangle H$ is the enthalpy of vaporization (kJ/mol), R is the gas constant, T is an average temperature (K), and C is the constant. The regression between lnP and 1/T was statistically significant for PHE ($r = 0.733$, $p < 0.05$ at WS; $r = 0.855$, $p < 0.01$ at ES), ANT ($r = 0.701$, $p < 0.05$ at WS; $r = 0.764$, $p < 0.05$ at ES), FLA ($r = 0.684$, $p < 0.05$ at WS; $r = 0.662$, $p < 0.05$ at ES) and PYR ($r = 0.660$, $p < 0.05$ at WS; $r = 0.772$, $p < 0.01$ at ES) and their variability could be explained by temperature fluctuation at a level of 43%–73% (Fig. 3). With regard to these results, it could infer that these major gaseous PAH compounds in Lhasa atmosphere were mainly influenced by the volatilization from local sources or gas–particle portioning even though they were emitted continuously from pollution sources (Sitaras et al., 2004; Sofuoglu et al., 2001). In contrast, the correlations between most other gaseous PAHs (ACY, ACE, FLO, BaA, CHR, BbF, BkF) and temperature were not statistically significant ($p > 0.05$). In addition, low r values at both sampling sites suggested that

these compounds were mainly governed by primary emissions. Similar results were also found in Chicago, USA (Sofuoglu et al., 2001) and in Guangzhou, China (Li et al., 2006).

During the sampling, the concentrations of total suspended particles (TSP), WS (ES) site, were between 40.67(86.49) and 182.38(259.34) μg/m^3, with an average of 109.21 ± 46.44 (141.00 ± 62.56) μg/m^3. Some studies implied emission source as a predominant factor controlling the changes of PAHs with the evidence of positive correlation between PAH concentration and TSP contents (Chen et al., 2009; Hu et al., 2012). Interestingly, in this study TSP concentrations did not follow the regular diurnal and nocturnal fluctuation at both sampling sites (Fig. 4) and no significant correlations were observed among the total particulate PAH concentrations and TSP concentrations ($p = 0.2170$ at WS site, $p = 0.6379$ at ES site), which implied that not only emission sources, but also other processes control the variations of particle phase PAH concentrations, such as gas–particle partitioning. The concentration and fate of PAHs in atmosphere are strongly influenced by the gas–particle partitioning which is mainly ruled by the vapor pressures of chemicals, nature of particles and meteorological conditions, such as relative humidity and temperature (Sitaras et al., 2004; Vasilakos et al., 2007). Some studies have pointed out that seasonal change of atmospheric temperature could apparently boost the variation of concentrations of PAHs and the phenomenon of gas/particle partitioning shift (Duan et al., 2007; Li et al., 2006; Tan et al., 2006; Vasilakos et al., 2007). In this study, the diurnal and nocturnal variations of total particulate PAHs percentage in total PAHs for the sampling period at two sites and the relationship with temperature were investigated (Fig. 5). The results show that a clear diurnal and nocturnal variation occurred with the proportion of total particulate PAHs, lower values appear at daytime (1.90 to 6.88% at WS, 2.79 to 8.73% at ES) and higher percentages emerge at nighttime (6.44 to 19.18% at WS, 9.33 to 28.40% at ES). It could say that the contribution of gas–particle partitioning to the diurnal and nocturnal variation of PAHs concentrations is a strong evidence in the atmosphere in Lhasa. This could be explained by the temperature fluctuations, due to the unique geographic position and plateau causing dramatic daily temperature swings in Lhasa city. Temperature differences between day and night were found to be more than 10 °C during the sampling period. Significant correlations were observed between percentages of total particulate PAH and temperature at both sampling sites ($p < 0.01$), and the regression correlation coefficients (R^2) were 0.59 (WS) and 0.7351 (ES), respectively. The R^2 values were relative high for the moderate molecular weight chemicals, i.e., PHE(0.6514), ANT(0.6021), FLA(0.5051), PYR(0.5936), BaA(0.4554) and CHR(0.6488) at WS site, while very low R^2 were observed for lower (ACY, ACE, FLA) or higher molecular weight PAHs (BbF, BkF, BaP, DahA, IcdP, BghiP). It suggests that among the PAHs, moderate molecular weight PAHs play a much more important role in the transformation between gas and particle phases. Similar results occurred at the ES site. In general, the results of this study show that the redistribution of lower/higher molecular PAHs between gas and particle phases are difficult to be occurred as a result of their lower/higher vapor pressures. Nevertheless, the redistribution of moderate molecular PAHs between two phases are much easier to be conducted with the changes of temperature due to their appropriate vapor pressures, which execute a great impact on
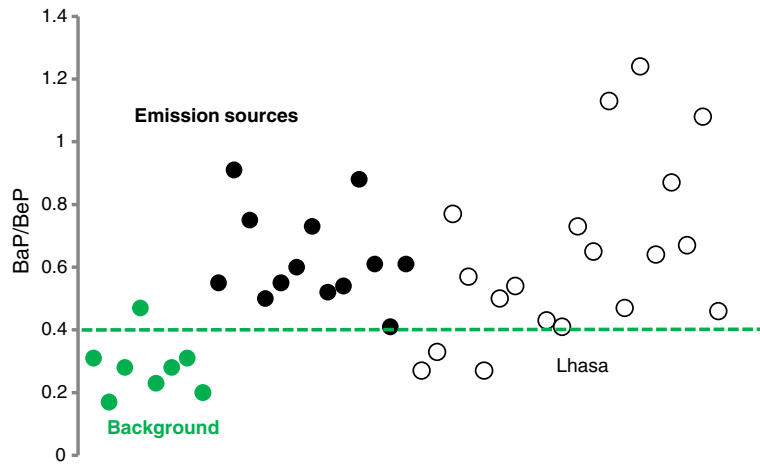
Fig. 1. BaP/BeP ratios at background (green filled dots), emission sources sites (black filled dots) and Lhasa city (circle points).
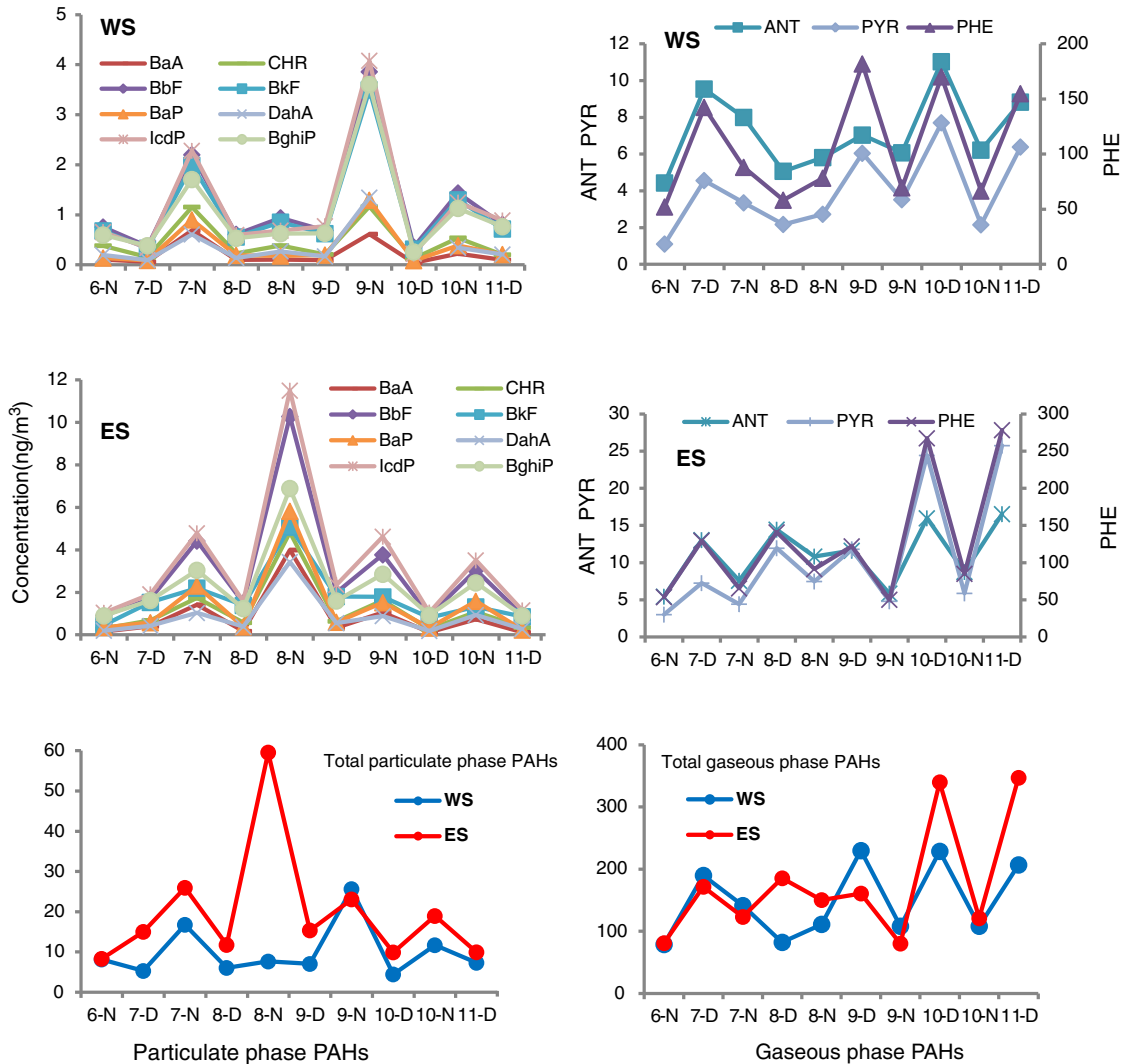

Fig. 2. Diurnal and nocturnal variations of PAHs at gas and particle phases in Lhasa city.
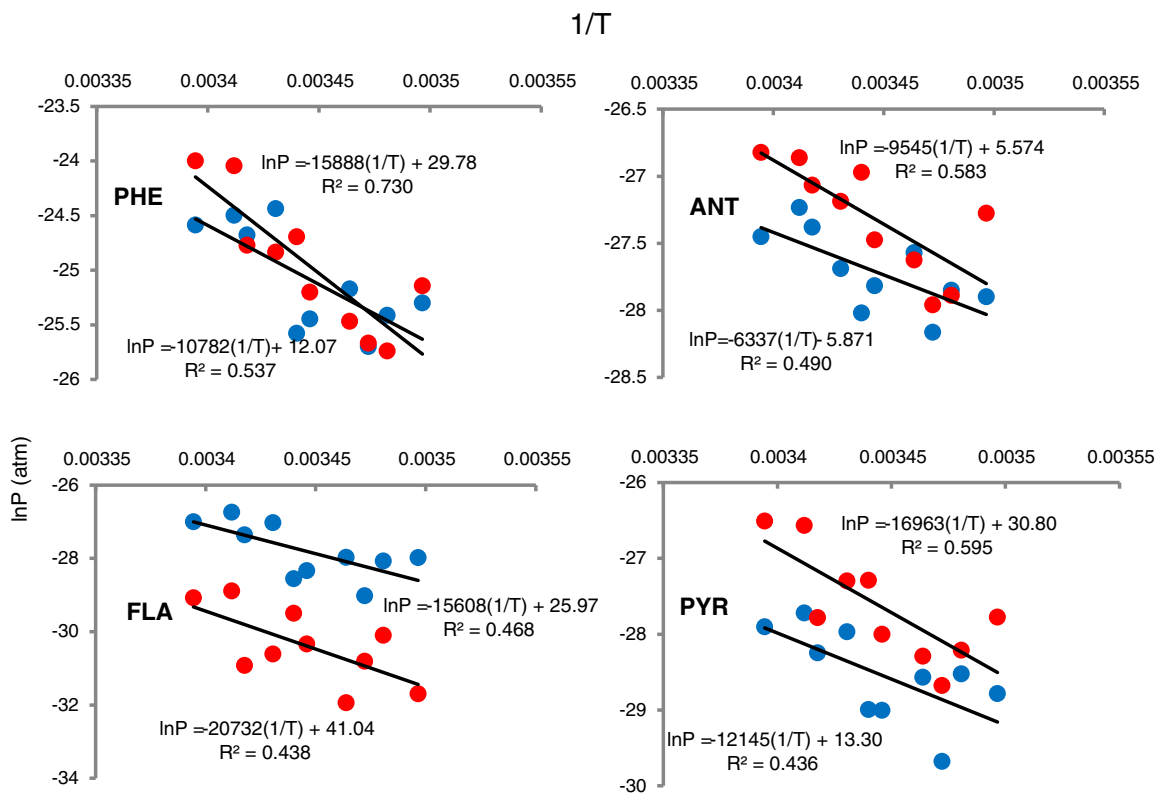
Fig. 3. Clausius–Clapeyron Plot for gaseous PAHs at WS (blue dots) and ES (red dots) in Lhasa.

the diurnal and nocturnal variation of PAHs concentrations in the air of Lhasa city.

As results of high altitude and intensive solar radiation of the Tibetan Plateau, it is expected that the levels of PAHs in the air of Lhasa city might be influenced by atmospheric degradation processing. ANT, BaA and BaP are expected to be degraded more quickly than their isomers because of their higher photolytic

reactivity (Butler and Crossley, 1981). Therefore, the ratios of ANT/PHE, BaA/CHR and BaP/BeP are usually used as indicators giving valuable information for the atmospheric degradation processes (Ding et al., 2007; Ohura et al., 2004). The higher ratio indicates a limitation of photochemical processes and the lower value illustrates that the degradation apparently occurred during sampling. The decomposition mechanism of
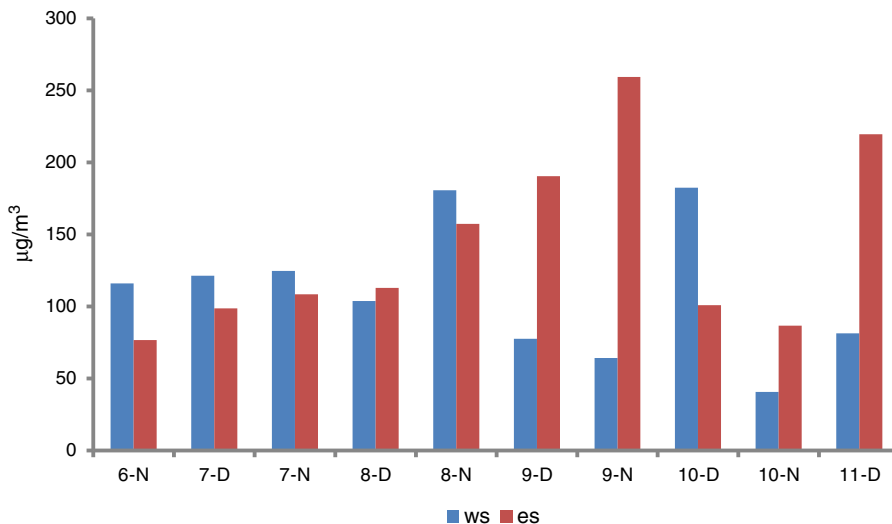

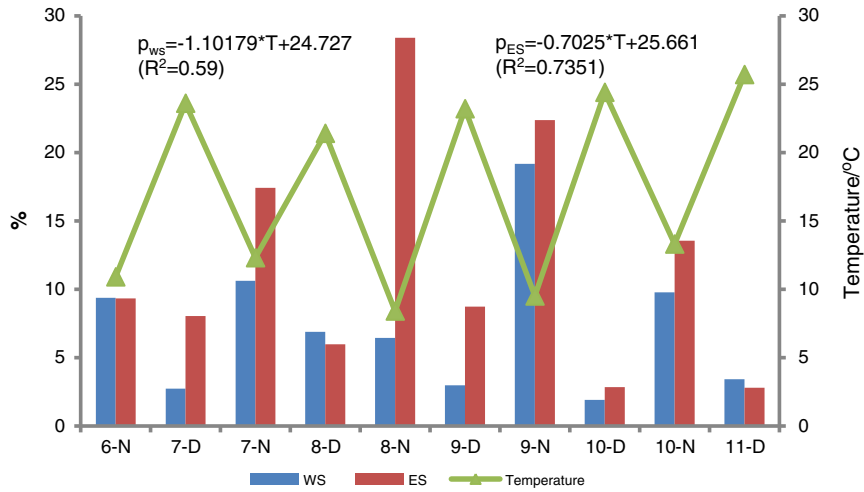**Fig. 4.** TSP concentrations in day and night during sampling campaign at both sites in Lhasa city.

Fig. 5. Diurnal and nocturnal variation of the percentage of total particulate PAH in total PAH and temperature fluctuation over sampling period. P_{WS}: percentage of total particulate PAH at WS site in total PAH. P_{ES}: percentage of total particulate PAH at ES site in total PAH. T: temperature.
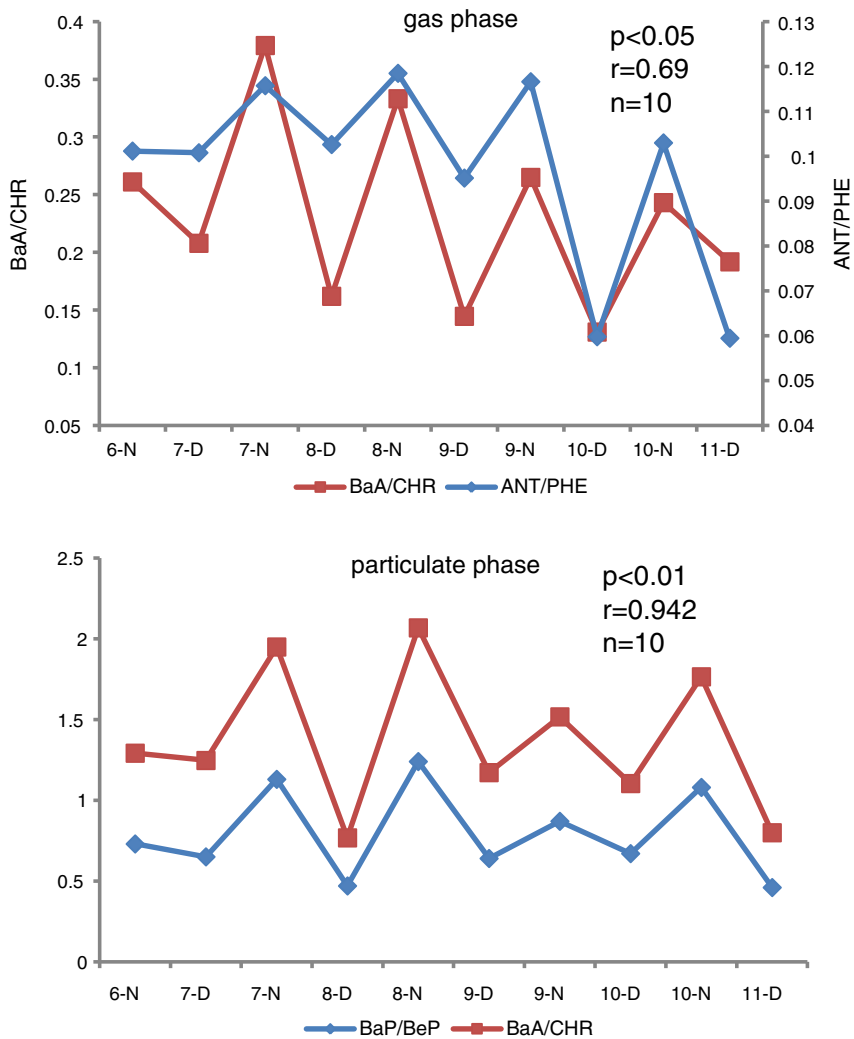

Fig. 6. Diurnal and nocturnal variations of reactive/stable PAHs in both phases during sampling periods at ES site.

gas and particulate phase PAHs in atmosphere are believed to behave differently. Gaseous PAHs are prone to react with the hydroxyl radical while particle-bound PAHs are susceptible to photodegradation (Tsapakis and Stephanou, 2007). Hence, in this paper gaseous ratios of ANT/PHE and BaA/CHR against time series were used to study gaseous PAHs' atmospheric fate, and particulate ratios of BaA/CHR and BaP/BeP ratios are used for particle-bound PAH. With the PHE and ANT mainly associated with the gas phase and the particulate phase is dominated by BaP and BeP, while BaA and CHR are important in both phases. These reactive/stable ratios of PAHs display distinct diurnal and nocturnal patterns at both phases in this study (Fig. 6), which seems to provide a great influence on the reduction in the degradation of gas and particulate PAHs in the atmosphere of Lhasa during daytime. These results are consistent with the fact that photolytic degradation and atmospheric reaction are relatively easy to occur at daytime due to the high temperature, intensive solar radiation and high OH radicals content. Significant correlations were observed between the ratios of BaA/CHR and ANT/PHE in the gas phase ($p < 0.05$, $r = 0.69$) and the ratios of BaA/CHR and BaP/BeP in the particulate phase ($p < 0.01$, $r = 0.942$), suggesting that these isomer pairs in gas or particles undergo similar removal mechanism. Results revealed that total particulate PAHs strongly correlated with BaA/CHR ($p < 0.05$, $r = 0.724$) and BaP/BeP ($p < 0.01$, $r = 0.775$). Significant correlations among total gaseous PAHs with ANT/PHE ($p < 0.01$, $r = -0.911$) and BaA/CHR ($p < 0.1$, $r = -0.572$) were found in this study as well. All these strong correlations demonstrate the important influence of degradation on the levels of PAHs in both phases. It should be noted that the Pearson coefficient (r) values between total particulate PAHs and reactive/stable PAH ratios were positive, meaning that photolytic degradation and temperature play a coordinating role in changing the diurnal and nocturnal pattern of particulate PAHs. However, negative r values were found between total gaseous PAHs and reactive/stable PAH ratios, suggesting that the atmospheric reaction was not only a vital removal pathway for gaseous PAHs but also an important factor influencing the diurnal and nocturnal variations of gas phase PAHs. On the other hand, from these results we can conclude that in this study the positive influence of temperature (volatilization, gas–particle partitioning) on the variations of gaseous PAHs concentrations is larger than the counter-effect of atmospheric reaction.

4. Conclusions

The concentrations of total PAHs in the atmosphere of Lhasa ranged from 87 to 360 ng/m^3. The predominant compounds were PHE, followed by FLO, ANT, PYR and FLA. Compared with other cities, PAH concentration in the atmosphere of Lhasa is potentially lower in pollution level. A BaP to BeP ratio of 0.4 was recommended as the boundary value that can serve to distinguish fresh local emissions from aged particulate. Results obtained from the diagnostic ratios suggested that incomplete combustion of wood and cow dung cake were the major sources of PAHs on the edge of Lhasa, implying that contaminated air has been transported from the urban area to the suburban area and potentially caused an impact on the regional background through contaminants diffusion and the convection currents of the atmosphere. The gaseous PAH concentrations at daytime were significantly higher than nighttime,

while the particular PAHs exhibited the opposite variation pattern. Volatilization, gas–particle partitioning, atmospheric reaction and photodegradation are suggested to influence on these two variations.

Economic development, fast growth of the tourism industry and unbalanced energy consumption structure have exerted negative influences on the air of Lhasa city. Therefore, it should be noted that government departments need to take some timely and effective measures to protect air quality and the fragile Tibetan Plateau ecosystem, such as by improving energy usage efficiency, adjusting the structure of energy consumption to give priority to the development of clean energy, and making more severe regulations on enterprises which pollute the atmosphere.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.atmosres.2012.12.016.

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