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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.

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.,

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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×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]