Seasonal variation, phase distribution, and source identification of atmospheric polycyclic aromatic hydrocarbons at a semi-rural site in Ulsan, South Korea☆

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) in gaseous and particulate phases (n = 188) were collected in Ulsan, South Korea, over a period of one year (June 2013–May 2014) to understand the seasonal variation and phase distribution of PAHs as well as to identify the seasonal PAH emission sources. The target compounds were the 16 US-EPA priority PAHs, with the exception of naphthalene, acenaphthylene, and acenaphthene. Winter and spring had the highest and lowest PAH concentrations, respectively. The mean of the Σ_{13} PAHs in the gaseous phase (4.11 ng/m^3) was higher than that in the particulate phase (2.55 ng/m^3). Fractions of the gaseous or 3- and 4-ring PAHs (i.e., Flu, Phe, and Ant) were high in summer, and those of the particulate or 5- and 6-ring PAHs (i.e., BkF, BaP, Ind, DahA, and BghiP) increased in winter. Gas/particle partitioning models also demonstrated the increased contributions of the particulate PAHs in spring and winter. Source identification of PAHs was undertaken using diagnostic ratios, principal component analysis, and positive matrix factorization. The results indicated that pyrogenic sources (e.g., coal combustion) were dominant in winter. Other types of pyrogenic (e.g., industrial fuel combustion) and petrogenic sources were the main PAH sources in summer and autumn. The influence of both sources, especially in summer, might be due to seasonal winds transporting PAHs from the industrial areas. Two types of pyrogenic sources, diesel and coal combustion, were identified as the main PAH sources in spring. This study clearly demonstrates a source–receptor relation of PAHs at a semi-rural site in a heavily industrialized city.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are compounds having at least two aromatic rings in their chemical structures. PAHs can be separated into two classes, namely low-molecular-weight (LMW) and high-molecular-weight (HMW) compounds. The former have two or three aromatic rings and exist predominantly in the vapor phase, whereas the latter have more than four aromatic rings and tend to adsorb onto airborne particles (Baek et al., 1991b). The United States Environmental Protection Agency (US-EPA) selected 16 specific species on the basis of their representative harmful effects, available information, and higher levels compared to other PAHs (Ravindra et al., 2008). Levels and the phase distribution of

PAHs have been reported to differ seasonally (Albuquerque et al., 2016). In particular, winter tends to show the highest PAH concentration among the four seasons due to a decline in atmospheric vertical dispersion and an increase in domestic burning for heating. Fractions of the gaseous PAHs are higher in summer, while the particulate PAHs contribute more in winter since lower temperatures can generate condensation of PAHs on atmospheric suspended particles (Gustafson and Dickhut, 1997).

PAHs are emitted from natural sources such as forest fires and volcanic eruptions (Ravindra et al., 2008). However, the most noticeable sources are related to human activities such as combustion processes and vehicle exhaust (Choi et al., 2012b). The emission sources of PAHs can be identified through several methods, including diagnostic ratios (DRs), principal component analysis (PCA), chemical mass balance (CMB), and positive matrix factorization (PMF). The DR method determines the possible sources of PAHs by comparing the observed ratios to those from previous studies. This method assumes that the PAH isomers are

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regarded to have the same physicochemical properties and that they are transformed or decomposed at the same rate (Biache et al., 2014). Hence, it is inferred that DR values are preserved when PAHs are transported from emission sources to receptors. However, the fact is that isomeric PAHs have different chemical properties, leading to a change in the ratios when PAHs are transported in the atmosphere. As a result, the emission sources of PAHs can be misinterpreted, and the applicability of DRs should be considered carefully.

Statistical tools such as PCA are also applied for PAH source identification. PCA converts a data set into a few important explanatory factors, or principal components (PCs), accounting for most of the variance and highlighting the most important information of the original data set. Emission sources of PAHs can, therefore, be interpreted based on the PC values. However, a drawback of PCA is that it might not entirely separate the emission sources (Cesari et al., 2016; Jain et al., 2017). In other words, more than two emission sources might overlap in one PC, resulting in a deficiency of emission sources when interpreting the PCA results. Apart from PCA, PMF, a model developed by the US-EPA, can also be used to determine the PAH emission sources. In the PMF, the initial data sets are structured into two new data matrices or factors, including factor contributions and factor profiles (US-EPA, 2014). The emission sources of PAHs can be determined by comparing PAH profiles from the PMF results with those from previous studies. The number of factors or sources can be set in the PMF, and the stability of a selected solution can be checked (Brown et al., 2015; US-EPA, 2014). Thus, an under- or overestimation of emission sources can be controlled.

This study investigated the atmospheric PAHs at a semi-rural site of Ulsan, one of the largest industrial cities of South Korea. The predominant industrial activities of Ulsan comprise petrochemical, chemical, non-ferrous, automobile, and shipbuilding production. Among them, petrochemical and non-ferrous industrial activities, especially aluminum production, are noticeable sources of PAHs because of the operational combustion processes used in their production (Kwon and Choi, 2014; Nikolaou et al., 1984; Ravindra et al., 2008). Previous studies reported that oil, diesel, and gasoline combustion (Kwon and Choi, 2014; Van-Tuan et al., 2010), coal/biomass burning, and coke ovens (Kwon and Choi, 2014) were the main sources of PAHs in Ulsan. Additionally, the atmospheric PAHs in Ulsan were mostly investigated in one phase, such as the gaseous (Choi et al., 2012b) or the particulate (Dong and Lee, 2009; Van-Tuan et al., 2010) phase, and over a short period of time, such as one (Choi et al., 2012b) or two (Lee and Lee, 2004) seasons or for a month (Dong and Lee, 2009). Moreover, it is known that prevailing seasonal winds play an important role in contamination characteristics of PAHs in Ulsan (Choi et al., 2012b; Lee and Lee, 2004). Therefore, seasonal variations of both gaseous and particulate PAHs in Ulsan need to be investigated.

In this study, both gaseous and particulate PAHs were collected from a semi-rural site in Ulsan over four seasons (June 2013–May 2014) to understand the seasonal variation and phase distribution of PAHs. In addition, the seasonal emission sources of PAHs were identified. Data on meteorological conditions and criteria air pollutants around the study area were also collected to examine their relations with atmospheric PAHs. This is the first study to observe the gas/particle partitioning of PAHs at a relatively high temporal resolution in Ulsan.

2. Materials and methods

2.1. High volume air sampling

Air samples were collected at 5 m above the ground level at the Ulsan National Institute of Science and Technology (UNIST), Ulsan, South Korea. UNIST (35° 34N, 129° 11E; 47 m above sea level) is at a semi-rural area, located west side of the urban and industrial areas of Ulsan (Fig. 1). Two high volume air samplers (Sibata HV-700F, Japan) were used to collect duplicate PAH samples in the gaseous and particulate phases (n = 188) over four seasons (June 2013–May 2014). Samples from the November and December 2013 sampling efforts were lost [n = 16: 8 glass fiber filters (GFFs) and 8 polyurethane foam disks (PUFs)]. The air sampling was conducted once a week for 24 h (from 11:00 a.m. to 11:00 a.m. of the next day). The total air volume of each sample was 1007.9 m^3, and the operational flow was set at 700 L/min. Samples in the particulate and gaseous phases were collected using a GFF (20.3 cm × 25.4 cm, Advantec, Japan) and a PUF disk (4.5 cm radius × 5.0 cm height, Ziemer Chromatographie, Germany), respectively.

Prior to sampling, the GFFs and PUFs were pre-treated by baking at 400 °C for 4 h followed by 30 min of sonication cleaning with both acetone and n-hexane, respectively. The GFFs and PUF disks were kept in aluminum foil and transported to the sampling site without exposure to ambient air. After sampling, they were put in aluminum foil and polyethylene double zippered bags and stored at −9 °C until analysis.

2.2. Meteorological conditions and criteria air pollutant data

Meteorological conditions are one of the most important factors governing the levels and behavior of atmospheric PAHs (Tham et al., 2008). Hence, meteorological data were collected from two of the Korean meteorological administration (http://kma.go.kr) automatic weather stations located near the sampling site, namely Sangbuk (35° 34N, 129° 05E) and Bukjung (35° 33N, 129° 19E). In addition, the Hysplit model (http://ready.arl.noaa.gov/HYSPLIT_traj.php) was used to evaluate the possibility of long-range transport of PAHs to the sampling site.

Criteria air pollutant data (SO_2, CO, O_3, NO_2, and PM_{10}), measured at air pollution monitoring stations in Ulsan, were also obtained via the website of the Ulsan Institute of Health and Environment (http://air.ulsan.go.kr). The Samnam (35° 29N, 129° 18E) and Mugeo (35° 33N, 129° 15E) stations were selected for data collection because they are in the vicinity of the sampling site.

2.3. Chemical analysis and QA/QC

PAHs were separately extracted from the GFFs and PUFs using Soxhlet extractors with 350 mL of n-hexane/acetone (9:1) (Choi et al., 2012b). Prior to the extraction, the samples were spiked with surrogate standards (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}). The extracted samples were then concentrated to 10 mL using a Turbo Vap (Caliper, USA). Subsequently, 1 mL of the extract underwent silica gel cleanup on a column comprising 2 g of sodium sulfate, 5 g of silica gel (activated at 600 °C for 2 h), and 2 g of anhydrous sodium sulfate. An elution solvent composed of 70 mL of n-hexane/dichloromethane (9:1) was used. The sample was then concentrated to 0.5 mL using a nitrogen evaporator (Eyela, Japan), transferred to gas chromatography (GC) vials, and finally spiked with an internal standard (p-terphenyl-d_{14}).

The final samples were analyzed using gas chromatograph coupled to a mass spectrometer (GC/MS, 5975C, Agilent, USA). The analyte separation process was performed on a DB-5MS column (30 m × 0.25 mm × 0.25 μm). An amount of 1 μL of the final sample was injected into the GC at 300 °C under splitless mode. The initial temperature of the GC was 70 °C and was increased to 240 °C at 10 °C/min increments; finally, it was increased to a final temperature of 300 °C at 5 °C/min increments. Helium was used as the