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Research article

Airborne volatile aromatic hydrocarbons at an urban monitoring station in Korea from 2013 to 2015

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ABSTRACT

The concentrations of C_6-C_{10} volatile aromatic hydrocarbons (AHCs) in air were measured at an urban air quality monitoring station in Jong-Ro, Seoul, Korea, between 2013 and 2015. Their temporal patterns (e.g., diurnal, intraweek, daily) were assessed individually and collectively as groups of benzene, toluene, ethylbenzene, styrene, and xylene (BTESX); total aliphatic hydrocarbon (TALHC: C_2-C_{12}); total aromatic hydrocarbon (TARHC: C_6-C_{10}); and total hydrocarbon (THC: C_2-C_{12}). The highest mean AHC concentrations over the 3-year study (in ppb (v/v)) were observed for toluene (6.0 ± 4.3), followed by the xylenes (1.5 ± 1.3), ethylbenzene (0.85 ± 0.93), benzene (0.73 ± 0.77), and styrene (0.16 ± 0.30) nL/L. The mean ppbC ((v/v), nL•atm•C/nL•atm) values for BTESX, TALHC, TARHC, and THC were 65.8, 113, 77.7, and 191 ppbC, respectively. For most AHC species (e.g., toluene, styrene, and BTESX), only weak seasonal trends were observed in contrast to temporally varying species like nitric oxide (NO) (e.g., 26.3 ppb (January–February) vs. 8.5 ppb (July–August) during weekdays in 2013). Furthermore, toluene and NO concentrations were much higher (up to a factor 3) on weekdays than on Sunday for most weeks. This might reflect reduced anthropogenic activities on Sunday.

1. Introduction

Urban populations have increased rapidly in recent decades, particularly in the developing world. As such, the fraction of the world's population in urban areas has also increased to ~54.5% in 2016, and is projected to approach 60% in 2030 (UN, 2016). Furthermore, the total population of the world is expected to increase from 7.0 billion in 2011 to 9.3 billion in 2050, and such growth is likely to be absorbed mostly by urban areas in developing countries. In 2015, the world's population growth was 1.1%/year and global growth in real gross domestic product (GPD) was 3.3%/year (CIA-World-Factbook, 2017). The Republic of Korea (RoK) is a good example of such industrialization and urbanization, with 83.2% of its total population living in urban areas (UN, 2011). Due to rapid urbanization, densely populated megacities face enormous pressure on basic infrastructure, civic facilities, the environment, and public health (Gurjar et al., 2010). Consequently, urban ecologies and residents can be exposed to highly polluted air masses from industrial and vehicular sources (Panepinto et al., 2014).

Volatile organic compounds (VOCs) are one of the major indicators of urban air quality and associated anthropogenic activities including both mobile (e.g., vehicular tailpipe emissions) and stationary sources (e.g., industrial emissions, fuel combustion, and power plants) (De Abrantes et al., 2004). In urban areas, both mobile and stationary emissions are significant sources of VOCs: hydrocarbons make up a major fraction of total VOCs, while aromatic hydrocarbons (AHCs: including benzene, toluene, ethylbenzene, and xylene, which are commonly known as BTEX) constitute ~60% of non-methane hydrocarbons (NMHC) in urban areas (Lee et al., 2002). Note that AHCs account for 20–40% of the total ambient VOCs in modern urban ambient environments (Derwent et al., 2000). In an urban area of Japan (Saitama, 15–20 km north of the Tokyo urban center), the sources of VOC emissions were apportioned as follows: vehicle exhaust (14–25%), gasoline vapor (9–16%), liquefied natural gas (LNG) and liquefied petroleum gas (LPG) (7–10%), and other evaporative sources (49–71%) (Morino et al., 2011).

Airborne AHCs have a negative impact on human health as well as on the environment (e.g., photochemical ozone formation, acid rain, increased global greenhouse gas effect, and reduced visibility) (Dewulf and Van Langenhove, 1999; Hung-Lung et al., 2007; Lin

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et al., 2004). The degradation of air quality, as reflected by high AHC emissions (e.g., at certain sites in the USA), is suspected to contribute to various human diseases such as cancer, birth defects, and many other serious illnesses (Mukund et al., 1996). At the local scale, the presence of certain AHCs (like toluene) was also considered a meaningful indicator of olfactory nuisances (e.g., at or near landfill sites) (Termonia and Termonia, 1999).

In this research, the Jong-Ro study site was chosen as an air quality monitoring station operating as part of a Photochemical Assessment Monitoring Station (PAMS: protocol type III (US-EPA, 1994). The PAMS program was initially developed by the United States Environmental Protection Agency (US-EPA) based on the report “Rethinking the Ozone Problem in Urban and Regional Air Pollution” released by the National Academy of Science (NAS) in 1991. The PAMS network site location (four types: Type I, Type II, Type III, and Type IV) was selected based on careful consideration of meteorology, topography, and proximity to emission sources of ozone precursors (VOC and nitrogen oxides) (US-EPA, 1998). The JR site is located near a major east-west road (Jong-Ro) within an urbanized area near a business district; the predominant wind direction is from the west, and the maximum [O_3] occurs in the early afternoon (Fig. 1Sa) (Chambers et al., 2017). Historically, a PAMS type III site was operated in the Sung-Su district, Seoul (Nguyen et al., 2009).

The purpose of this study was mainly to investigate the environmental behavior of AHCs with an emphasis on BTESX (BTEX plus styrene) in the urban area of Seoul with comparisons with other urban areas in the world and to update the knowledge base. To this end, we measured the concentrations of these airborne compounds (a total of 56 hydrocarbons including BTESX) at a single urban site (Jong-Ro), Seoul, South Korea for the period 2013 to 2015. A background site like the Tae-Ahn Peninsula (Kim et al., 2015) was not studied due to limitations in data access. The BTESX data were analyzed in relation to other relevant pollutants that were measured concurrently (such as $PM_{2.5}$, PM_{10}, NO, NO_2, NO_x, CO, O_3, and SO_2) along with meteorological data. These data were investigated by grouping the data on various temporal scales (e.g., diurnally, weekly, seasonally, and annually). The results obtained from this study will allow us to explore the general and fundamental characteristics of an individual ambient hydrocarbon level. These data can also be used to assess various inter-correlations (e.g., in pairs or groups, with inorganic pollutant species (e.g., NO, O_3), and meteorological parameters) within an urban area in Seoul, Korea. Furthermore, the AHC temporal profiles of AHCs can give insight into their relationship with other pollutants as well as temporal factors controlling their distribution (e.g., fossil fuel usage).

2. Methodology

2.1. Site characteristics

Our study site (JR PAMS type III, 37.57094 N and 26.99653 E) was located in the Jongno-gu urban area of Seoul and is part of the Seoul PAMS system. Fig. 1Sb shows the wind direction at the JR site, which is from the west (270 ± 20°) and is downwind of local industrial areas. The general positioning of the JR PAMS type III stations is shown in Fig. 1Sc. A roadside air quality monitoring (AQM) station (Fig. 1Sd) is located near the type III PAMS monitoring station at Jong-Ro; this station is positioned near a busy E-W main road (34,900 ± 3340 vehicle movements in each direction per day in January 2015 (http://topis.seoul.go.kr/refRoom/openRefRoom_2_2.do, accessed September 2017). The AQM station monitors NO, NO_2, O_3, wind speed, solar radiation, PM_{10}, and a number of other pollutants.

The densely populated capital city of South Korea (Seoul) has 10 million residents and ~3 million registered vehicles (mostly consuming fossil fuel), leading to substantial pollutant emissions (Kim et al., 2013). Seoul is located in the east-west Han River valley and is flanked by low mountains to the north and south (Kim et al., 2015), potentially leading to air stagnation (Lee et al., 2008; Park et al., 2004). Seoul has predominant east-west winds (Fig. 1Sc). The densely populated Jongno-gu urban area (155,575 residents: 6500 persons/km^2) is famous for being the traditional heart of Seoul and is of economic importance. The main offices of many major national companies like Kumho Asiana Group, Kyobo Life, Lotte Group, SK Group, Hyundai Engineering & Construction, Daewoo E&C, Daelim Group, and East Asia Daily are located in Jongno-gu district (Fig. 1). The Jongno-gu district also accommodates major government headquarters, e.g., the Ministry of Security and Public Administration, the Ministry of Unification, the Ministry of Foreign Affairs, the Ministry of Education, the Ministry of Culture, Sports and Tourism, and the Ministry of Health and Welfare (Jong-Ro, 2017).

2.2. Instrumentation

The monitoring station used an automated gas-chromatograph (Auto-GC). The concentrations of various hydrocarbons ($n = 56$) were measured routinely and included AHCs (e.g., benzene, toluene, ethylbenzene, styrene, and xylene). All 56 hydrocarbons were measured using a combination of an online thermal desorption system (Unity/Air Server, Markes International) and a GC/Deans (Gas Chromatography) switch/Dual FID (Flame Ionization Detector) system (Varian 3800GC, USA). Detailed information related to the instrumentation and methods for both air pollutants and meteorological parameters is given in Table 1. Additionally, the uncertainties of the pollutant measurements were estimated as: <0.005 ppm (O_3, NO_2, and SO_2), 0.5 ppm (CO), >2% for PM_{10}, and ±20% (VOC) as reported by the National Law Information Center, South Korea (NLIC, 2016). The average concentrations of the AHCs and criteria airborne pollutant species were monitored on an hourly basis together with meteorological data at the Jong-Ro (JR) site, Seoul, South Korea, from Jan 01, 2013 to Dec 31, 2015.

2.3. Data management and data sorting

The meteorological parameters and concentrations of AHC, non-aromatic hydrocarbons, and pollutant species were measured concurrently at the JR monitoring station and were reported as hourly averaged values following the basic KMOE (Korean Ministry of Environment) protocols. For the subsequent analysis at varying temporal scales, the initial raw data were analyzed on various times scales, i.e., daily, weekly, monthly, and annually, by following the procedures of our previous study (Kim and Shon, 2011). The data for all components or meteorological parameters were either examined individually or as groups (e.g., BTESX, TALHC, TARHC, and THC).

The details of the target hydrocarbons are shown in Table 2. The raw concentrations were initially reported in parts per billion (ppb: volume basis, nL/L). The various hydrocarbons were assigned to specific groups (e.g., BTESX, TALHC, TARHC, and THC), and the total parts per billion carbon (ppbC, or nmolC/mol) were calculated for each group. This group concept was used to assess the quantitative importance (as ppb C) of a given hydrocarbon in a mixture of hydrocarbon (Arriaga-Colina et al., 2004). Here, the total ppbC for a group was defined as $\Sigma_{i=1}^{n} ppb_i.CN_i$ where ppb_i is the concentration of the ith component, CN_i is its carbon number, and n is the number of components in the selected group. Pair-wise statistical analysis (like Pearson correlation) as well as calculation of basic statistical