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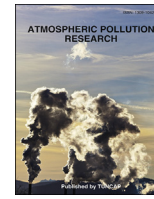

Original article

Characteristics and source apportionment of VOCs in the suburban area of Beijing, China

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A B S T R A C T

The measurement of volatile organic compounds (VOCs) was conducted during November 2014 in the suburban area of Beijing, China, covering the period of the Asia-Pacific Economic Cooperation (APEC) meeting period. The VOCs characteristics and source apportionment were analyzed. The average mass concentrations of VOCs were 27.6 ± 19.7 μg/m^3 during the sampling period, and aromatics and alkanes were the most abundant VOCs species in atmospheric environment in Beijing which were 12.2 ± 10.3 μg/m^3 and 11.3 ± 7.5 μg/m^3, respectively. The hourly variation of VOCs was found, with the highest concentration occurring at 8:00 to 9:30 and lowest at 12:30 to 14:00. The sampling period was divided into two periods: period I represent the period without emission-reduction measures, and period II represent the period with reduction measures. The VOCs concentrations during the period II was 31.0% lower than period I. The Maximum Incremental Reactivity (MIR) method was applied to analysis the ozone formation potential (OFP). The OFP of VOCs from period I was 1.6 times higher than period II, and the majority of VOCs species were alkenes and aromatics. Positive matrix factorization was applied to estimate contributions of potential VOCs sources. The vehicle exhaust emission was the major source of VOCs during the two periods, and the contribution to VOCs was 5.7% lower during period II than period I due to the emission-reduction of vehicle operation.

1. Introduction

Beijing, as the capital city, is the center of politics, culture and international communication of China, and has experienced considerable changes through rapid urbanization processes in the past decades. However, its growth has also been associated with a number of environmental concerns (i.e., increased industrial emissions, energy consumption, and vehicle population). The air pollution in Beijing has been changed from the early soot-type to the complicated pollution of soot-type and vehicle exhaust. The level of gaseous pollutants increased considerably in atmospheric environment and posed significant challenges to governments (Lee et al., 2006). According to the air quality report of 74 important cities published by Ministry of Environmental Protection of the People's Republic of China, only 47% days met the ambient air quality standard of China, which the Air Quality Index (AQI) is less than or equal to 100, in Beijing in 2014 (MEPPRC, 2015). Episodes of high ozone (O_3) concentrations also frequently occurred in Beijing, and the highest hourly concentration could reach 500.0 μg/m^3, which was 2.5 times higher than 200.0 μg/m^3 for 2nd-level air quality in China (GB 3095-2012). The volatile organic compounds (VOCs) are important precursors to the O_3 formation through the photochemical reactions in the presence of sun light (Louie et al., 2013). To reduce the O_3 effectively, VOCs should be given more attention (Suthawaree et al., 2012). For instance, the mainly reason of high O_3 concentration in Houston, United States was the highly reactive composition of VOCs emitted from petrochemical enterprise (Ryerson et al., 2003). Liao et al. (2014) indicated that the reduction of VOCs emission could decrease the peak O_3 concentration effectively in the northeastern U.S. The results proposed by other researchers (Song et al., 2007; Tang et al., 2009; Xu et al., 2008) also indicated that the level of O_3 concentration controlled by VOCs in recent years in Beijing. Additionally, VOCs are one of the

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most important precursors for secondary organic aerosols (SOA) formation. VOCs can form SOA by photochemical oxidation (Pachauri et al., 2013), which has significant adverse effects on human health (Hou et al., 2015; Zhang et al., 2008). Researches had examined the ability of their oxidation products to contribute to SOA formation. For instance, Li et al. (2015) conducted experiments on VOCs using an online system in China in 2014 and the secondary organic aerosols potential (SOAP) approach was used to estimate variations of precursor source contributions to SOA formation. Fractional aerosol coefficients (FAC) method was used to estimate the potential formation of SOA in Shanghai by Wang et al. (2013). The result indicated that aromatics are the most important SOA precursors.

In view of the negative effects of VOCs on the air quality, human health, and O_3 pollution, a variety of studies have been reported to investigate the characteristics and sources of VOCs. The seasonal variation of VOCs was measured in urban area of Dallas, USA from 1996 to 2004 (Qin et al., 2007). The time series for anthropogenic emission hydrocarbons showed an obvious seasonal cycle with relatively high concentration in winter and low concentration in summer which was connected with source emissions and meteorological conditions. The source apportionment of VOCs was also reported. Receptor-oriented source apportionment models were the main tools for the estimation of source contributions to pollutants. The widely used models are the principal component analysis (PCA) (Wang et al., 2015), positive matrix factorization (PMF) (Zhang et al., 2014), and chemical mass balance (CMB) (Olson et al., 2009). Zhang et al. (2014) indicated that gasoline-related emission and organic solvents were the main VOCs sources at Gongga Mountain in Sichuan, China, accounting for 35.1% and 21.8%, respectively. Guo et al. (2011) also indicated that organic solvents (46 ± 1%) and vehicular emissions (26 ± 1%) were the most significant contributors to ambient VOCs in Pearl River Delta. These previous studies could provide scientific support to further researches, such as global climate change, atmospheric chemical mechanism, and pollution control. However, for a comprehensive understanding of VOCs, there is still lack of temporal distribution, source apportionment, and environmental impact on O_3 in Beijing. The rapid growth of vehicle population and energy consumption had also greatly aggravated the levels of atmospheric pollutants in recent years (Lang et al., 2012). What is more, the Asia Pacific Economic Cooperation (APEC) was held in the suburban area in Beijing from 5th November to 11th November, 2014 in Huairou district, including the 22nd APEC Economic Leaders' Meeting. APEC is the most influential economic forum in our region and one of the most dynamic organizations for economic cooperation in the world. To achieve the goal of "blue APEC", emission-reduction measures had been carried out by Beijing and surrounding areas governments to guarantee the air pollution controlled and lessened. The measures had provided a golden opportunity for environmental protection workers to study the VOCs pollution characteristics.

In order to provide sound basis for the effective control of atmospheric VOCs, it is urgent and of great importance to examine the VOCs from the suburban area in Beijing during this period. Therefore, observations of ambient VOCs samples were conducted to discuss the characteristics from 1st November to 25th November, 2014 in Beijing, China. The objectives of this study mainly include: (1) analyzing the pollution levels of VOCs, comparing the VOCs concentrations before and after the emission-reduction measures, and evaluating the effective of the control measures; (2) investigating the ozone formation potential (OFP) of VOCs; (3) identifying the emission source contributions to VOCs. The discussions have significant theoretic values, and could provide a scientific technique support for improving Beijing's air quality.

2. Methods

2.1. Sample collection

Beijing (115.7°E–117.4°E, 39.4°N–41.6°N) is located in the northern part of the North China Plain, which is one of the most economically vibrant regions in China. Beijing belongs to the semi-humid continental monsoon climate, and prevailing northwest wind in winter, and southeast wind in summer. The annual average temperature is 10–12 °C, and annual average precipitation is about 600 mm. It possesses a population of over 21 million in 2015 and a land area of about 16,410 km^2. The University of Chinese Academy of Sciences (UCAS) site located in the Huairou district of Beijing was selected for collecting VOCs samples (Fig. 1). The sampling site was placed on the rooftop of an office building (20 m above the ground level) on the campus where the atmospheric mixing was even so as to reflect the condition of regional atmospheric pollution. The UCAS site was 2.2 km away from APEC meeting area. It is surrounded by mountains to the north and west, while buildings to its east and south. The road with moderate traffic is located 100 m away in the east side of the sampling site. Therefore, the UCAS site could represent a mixed educational activities, traffic and residential environment of suburban area.

In order to analyze the diurnal and hourly variation of VOCs, and to determine the effect of the emission-reduction measures, samples were collected on 25 days from 1st November to 25th November in 2014, and each day with three 1.5-hr sampling periods (8:00–9:30, 12:30–14:00, and 16:00–17:30) and one 4-hr sampling period (20:00–24:00). The four sampling periods could be well representative the VOCs concentrations during the early morning, noon, evening, and night. Samples were collected using electro-polished stainless steel canisters (3.2 L, Entech Instruments, Inc. California, USA) with a flow-controller (Entech, USA) (Li et al., 2014). In total, 100 VOCs samples were collected during the sampling period and sent to laboratory for analysis. Additionally, meteorological parameters (ambient temperature, relative humidity, wind speed, wind direction, atmospheric pressure and precipitation) were obtained from the Weather Underground website (www.wunderground.com). The concentrations of gaseous pollutants ($PM_{2.5}$, O_3, NO_2, SO_2, and CO) were obtained from Beijing municipal environmental monitoring center which were measured in Huairou town station. The Huairou town station was about 8.9 km away in the southwest side of the sampling site.

2.2. Chemical analysis

The VOCs samples collected in canisters were measured using Gas Chromatography − Mass Spectrometry (GC–MS, Model 7890A/5975C, Agilent Inc) according to the method recommended in Environmental Protection Agency (EPA) TO-15 (U.S. EPA, 1999). Samples were pumped into the pre-concentrator (Model7100, Entech Instruments Inc., California, US) which is equipped with 3-stage cryotraps (Module 1–3). Firstly, samples were entered into the first cryotrap (Module1) to remove H_2O, N_2, CO_2, CO and O_2 at −165 °C by liquid nitrogen, and they were then recovered by desorbing at 10 °C to leave most of the liquid H_2O behind in the first trap. Secondly, the cryotrap (Module2) was cooled to −50 °C, which was used to remove the Ar, CH_4, and CO_2 and trace water. The desorption temperature was then backflushed at 180 °C. Thirdly, VOCs samples were frozen to −160 °C in the Module3 trap which was constituted by the empty capillary (Liu et al., 2008b). The Module3 trap was then rapidly heated to 60–70 °C to make the VOCs samples vaporize rapidly. Helium was used as the purge gas for the cryogenic pre-concentrator and the carrier gas for GC

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