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Atmospheric isoprene and monoterpenes in a typical urban area of Beijing: Pollution characterization, chemical reactivity and source identification

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ABSTRACT

Continuous observation of isoprene, α-pinene and β-pinene was carried out in a typical urban area of Beijing from March 2014 to February 2015, using an AirmoVOC online analyzer. Based on the analysis of the ambient level and variation characteristics of isoprene, α-pinene and β-pinene, the chemical reactivity was studied, and their sources were identified. Results showed that the concentrations of isoprene, α-pinene and β-pinene in the urban area of Beijing were lower than those in richly vegetated areas; the concentrations of isoprene were at a moderate level compared with those of previous studies of Beijing. Concentrations of isoprene, α-pinene and β-pinene showed different seasonal, monthly, daily and diurnal variations, and all of the three species showed higher level at night than those in the daytime as a whole, the variations of isoprene, α-pinene and β-pinene mainly influenced by emission of sources, photochemical reaction, and meteorological parameters. Isoprene was the largest contributor to the total OFP values than α-pinene and β-pinene. α-Pinene was the largest contributor to the total SOAFP values than isoprene and β-pinene in autumn, while isoprene was the largest one in other seasons. Isoprene, α-pinene and β-pinene were derived mainly from biological sources; and α-pinene level were also affected by industrial sources. To reduce the concentrations of isoprene, α-pinene and β-pinene, it is necessary to scientifically select urban green plant species, and more strict control measures should be taken to reduce the emission of α-pinene from industrial sources, such as artificial flavors and resins synthesis processes.

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Introduction

Volatile organic compounds (VOCs) are important precursors of secondary pollutants, such as near-ground-ozone, peroxyacetyl nitrate (PAN) and secondary organic aerosols (SOAs) (Wang et al., 2016; R.R. Wu et al., 2016; F.K. Wu et al., 2016). Isoprenoids are compounds including isoprene, monoterpenes and sesquiterpenes, which use isoprene as their basic unit. Their structures are complex and diverse, ranging from linear hydrocarbon chains to ring structures (Chen et al., 2000; Li et al., 2008; Winters et al., 2009). Levels of anthropogenic VOCs are generally higher in the morning and evening, while isoprenoids generally reach their maximum concentrations at noon or in the afternoon under high temperature and high solar radiation (SR) (Lee and Wang, 2006). Isoprenoids having high reactivity are involved in regional photochemical reactions, which affect the concentration of the OH radical (Hantson et al., 2017), as well as the formation of ozone and SOA (Riva et al., 2016). High concentration of isoprenoid is known to have negative impact on human health. Under the condition of relative higher concentrations, isoprene will causes headache, nausea and dyspnea, and α-pinene and β-pinene will cause irritation to the eyes, skin, respiratory system, and kidney damage. (Zhou, 1997). The concentration of isoprenoids in ambient air is low, they will not have the direct poisoning effect on human, but their secondary products, like aldehydes, would have direct poisoning effect on human health. Because of their high emissions, high reactivity, and impact on human health, they have been extensively studied.

In recent years, the rapid development of China's economy, involving industrialization and urbanization, has triggered many pollution problems. In 2016, among 338 prefecture-level-and-above cities, only 84 cities (24.9%) met the China Air Quality Standard (MEP of China, 2016). Beijing, as China's political and cultural center, developed rapidly in recent decades, making it one of the most heavily polluted areas in China. In 2016, its average $PM_{2.5}$ concentration and maximum 8-h average 90th percentile concentration of ozone reached 73 and 199 μg/m^3, respectively. These values are 1.09 times and 0.24 times above their corresponding secondary standard limits, specified in the Ambient Air Quality Standard (GB3095-2012) (MEP of China, 2016). Earlier studies documented that the annual emission of biological VOCs (BVOCs) was 1.6×10^{10} gC in Beijing in 1998, of which 7.9×10^9 gC was isoprene and 3.5×10^9 gC was monoterpenes (Wang et al., 2003). Emissions in the Chaoyang district were highest of the eight districts of Beijing (Zhang et al., 2014). As precursors to SOA and ozone, isoprene, α-pinene and β-pinene have an important impact on the air quality of Beijing; therefore, research to characterize them is imperative in Beijing.

Nowadays, research of isoprenoids has mainly focused on the pollution characterization, sources, and reaction mechanisms of isoprenoids in ambient air. A large number of studies have shown that isoprene, α-pinene and β-pinene generally reach their maximum concentrations at night, except during summer, when isoprene reaches its maximum concentration during the daytime (Li et al., 2013; Riba et al., 1987). Considering the effect of meteorological factors on isoprenoids, the concentration of isoprene is mainly affected by light and temperature (Chang et al., 2014; Lee and Wang, 2006), while the concentrations of α-pinene and β-pinene are mainly affected by temperature and relative humidity (RH) (Chen et al., 2016; Wang et al., 2011). In cities, isoprene, α-pinene and β-pinene are derived from both anthropogenic emissions and biogenic emissions. Anthropogenic emissions of isoprene are related to mobile sources (Li et al., 2013; Zou et al., 2015; Schürmann et al., 2007). α-Pinenes are related to mobile sources (Dai et al., 2010), household heating (Rouvière et al., 2006), and the process of spices and resin synthesis (He and Wang, 2008). Guenther et al. (1995) studied different isoprene products under different model conditions; and Zhao (2008) studied the SOA formation by oxidation of α-pinene, using smog chamber experiments. In the past, studies of isoprenoid in ambient air in Beijing mainly focused on pollution characterization, sources and the contribution of isoprenoid to the formation of ozone. Specifically, the emission of isoprene is mainly related to biological sources in summer, automobile exhaust in winter, and a combination of both sources in spring and autumn (Li et al., 2013). The initial isoprene and ambient measured isoprene contributed 22% and 10%, respectively, to the OFP values for total measured VOCs (Xie et al., 2008). Clearly, the seasonal variation and sources of isoprene, α-pinene and β-pinene and their contribution to the formation of SOAs is yet to be studied in depth. Most previous studies of isoprenoids in Beijing have operated offline, and have no continuous observation over long periods. Such studies cannot compare with the high temporal resolution acquired through continuous long-term monitoring.

In this study, VOCs in ambient air were continuously measured from 1 March 2014 to 28 February 2015, yielding information on pollution levels, temporal variation, and the impacts of various meteorological factors on isoprene, α-pinene and β-pinene in ambient air. In addition, their photochemical reactivities and contribution to the formation of ozone and SOA were studied and their sources were also identified. Based on these analyses, suggestions for measures of control for isoprene, α-pinene and β-pinene in ambient air in urban Beijing were proposed.

1. Material and methods

1.1. Monitoring site and period

The monitoring site is located in the Chinese Research Academy of Environmental Sciences (CRAES) (40.04°N, 116.42°E) in the Chaoyang District of Beijing. The site is 2 km from the North Fifth Ring Road, and west of Beijing Subway Line 5. It is surrounded by residential areas and shopping malls, with no obvious signs of local pollution (Xia et al., 2014).

Since June 2013, VOCs in ambient air have been continuously monitored using AirmoVOC online analyzer (GC-866, Chromatotec Group, France), yielding a valuable long-term data set. This equipment is located in the Atmospheric Photochemical Smog Simulation Laboratory on the second floor of the atmospheric environment observation station, the sampling port is 8 m above-ground. Simultaneously, on the same rooftop, concentrations of $PM_{2.5}$ were monitored. The meteorological variables and concentrations of O_3 were monitored on another rooftop, 10 m from the online VOCs

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