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Characterizing the level, photochemical reactivity, emission, and source contribution of the volatile organic compounds based on PTR-TOF-MS during winter haze period in Beijing, China

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ABSTRACT

The atmospheric volatile organic compounds (VOCs) are the key participators in the formation of secondary organic aerosol and other atmospheric photochemical processes. However, it is still far from clear understanding of the VOCs in Northern China. In this study, VOCs were measured using a proton transfer reaction-time of flight-mass spectrometer (PTR-TOF-MS) in the downtown area of Beijing during a winter haze period in December 2016. The average mixing ratios of VOCs on the haze days were (ppb): methanol (51.75), formaldehyde (41.65), acetaldehyde (15.81), acetone (7.92), C8-aromatics (7.35), toluene (6.11), benzene (4.30), MEK (2.53), acetonitrile (2.05), C9-aromatics (1.54), benzaldehyde (1.12), isoprene (1.00), styrene (0.62). These concentrations represented the largest values among the cities around the world. VOC concentrations varied dramatically, with the largest value mainly appeared on days having the weakest diffusion condition. Due to the different solar radiation in this period, the photochemical reactivity of the VOCs showed the minimum and maximum values on haze and clear days, respectively. The primary anthropogenic emissions contributed more than half of the mixing ratios of most VOCs. However, formaldehyde received 56.6% contribution from the secondary or biogenic sources, and this contribution mainly increased at the noon hours when sunlight was stronger.

1. Introduction

Volatile organic compounds (VOCs) are oxidized in the atmosphere mainly by reactions with the hydroxyl radical (OH) and produce a range of secondary pollutants such as ozone (O_3) and secondary organic aerosol (SOA) in the presence of solar radiation and NOx (de Gouw et al., 2005; Warneke et al., 2012; Han et al., 2018). VOCs cover a large variety of species including non-methane hydrocarbons (NMHCs) and oxygenated VOCs (OVOCs). The NMHCs are predominantly from the primary natural and anthropogenic emissions and the OVOCs originate from both direct emissions and photochemical oxidation of the NMHCs (Chen et al., 2014; Lü et al., 2009; Liu et al., 2017a, 2017b; Sahu et al., 2016a, 2016b).

The VOCs can remove OH radicals in the atmosphere. Therefore, the increasing emissions of VOCs can reduce the oxidation capacity of the troposphere (Sahu et al., 2016a). The carbonyls, a sub-group of OVOCs, also influence the photochemical cycles because they can release oxidants into the atmosphere after photochemical processes (Rao et al., 2016; Yuan et al., 2012). For instance, formaldehyde serves as an important source of HO radicals through photolysis (Parrish et al., 2012).

The Beijing area is suffering from severe O_3 pollution in summer and fine particles pollution all year round (Shao et al., 2009; Tie and Cao, 2009; Wang et al., 2017). Since the VOCs act as the crucial precursors in the chemistry of above pollution processes, study of VOCs in Beijing is booming, particularly in the last decade (Duan et al., 2012; Guo et al., 2017; Li et al., 2015; Pang and Mu, 2006; Wang et al., 2010; Wang et al., 2012; Wu et al., 2016; Xu et al., 2011; Zhang et al., 2014). The measurements of VOCs in Beijing were not only limited near the ground, but high tower and aircraft were also used as platforms to study the vertical distributions (Liu et al., 2013; Mao et al., 2008).

Based on previous studies in Beijing, the major sources of VOCs were identified with vehicular exhaust contributing almost more than

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half, followed by LPG (liquefied petroleum gas), painting operation, gasoline vapor as well as industrial processes (Duan et al., 2008; Song et al., 2007). In addition to the direct anthropogenic sources, levels of VOCs in Beijing were also affected by biogenic and secondary origins (Chen et al., 2014; Pang and Mu, 2006).

Some studies based on measurement (Shao et al., 2009) and air quality model (Xu et al., 2008) paid attention to the formation scheme of O_3 in Beijing and found that due to the relatively high levels of NO_x in the urban area the increase of O_3 was mainly VOCs-limited. The VOC reactivity and ozone formation potential were also evaluated for better understanding the role of the VOCs played in the atmospheric photochemistry over this area (Duan et al., 2008; Li et al., 2015; Zhang et al., 2014).

Most of the studies of VOCs in Beijing focused on the warmer seasons, primarily in summer (Duan et al., 2008; Li et al., 2015; Shao et al., 2009; Xu et al., 2011). In winter, heavy haze events with $PM_{2.5}$ (fine particulate matter with an aerodynamic equal to or < 2.5 μm) concentrations exceeding hundreds of $\mu g\,m^{-3}$ occurred frequently (Wu et al., 2016). And the fine particle compositions were characterized by high SOA fraction with 44–71% of the organic matter was SOA (Huang et al., 2014).

Till now, few studies concerned the VOCs in the cold season (wintertime) in Beijing (Pang and Mu, 2006; Sun et al., 2016; Wu et al., 2016; Zhang et al., 2014; Liu et al., 2017a). The concentration levels of primary emitted VOCs were observed higher in winter than in summer (Zhang et al., 2014). For the OVOCs, the levels showed an inverse seasonal pattern and OVOCs levels in winter were smaller than or comparable to the values found in summer (Chen et al., 2014; Pang and Mu, 2006; Zhang et al., 2014). Researchers also announced that the photochemical reactivity of VOCs in winter or winter-haze weather in Beijing could be different from that of summer season (Pang and Mu, 2006; Rao et al., 2016; Zhang et al., 2014). Sun et al. (2016) calculated the SOA formation potentials of VOCs in winter haze period of Beijing and found the SOA originated from VOC oxidation could extended from 2.1 to 13.2 $\mu g\,m^{-3}$.

In this paper we give the results of the PTR-TOF-MS measurements of 13 VOC species/classes (NMHCs and OVOCs) in the urban area of Beijing in the haze and clear weather in wintertime on December 12–22, 2016. The following issues were investigated: the time series, diurnal variations and concentration levels of ambient VOCs; the variation of VOC reactivity in different weather (severe haze, light haze and clear days); the emission ratios of VOCs; the percentages of anthropogenic/non-anthropogenic contribution to the VOC mixing ratios.

2. Experimental

2.1. Measurement site

This research was carried out in the capital city of China, Beijing, which has > 20 million residents and 5 million motor vehicles. The sampling site of VOCs was located in the Beijing Academy of Agriculture and Forestry (116.29° E, 39.93° N, this location is shown in Fig. 1), northwest of the city center between the 3rd and 4th Ring Road (the two main urban roads with ongoing traffic all day long). All sampling instruments were placed in a cabin with air inlet 2.5 m above ground. The surrounding of this cabin is mainly the residential and commercial district. The nearest road is about 150 m south. 50 km to the north and 20 km to the west of our sampling site, there are mountains with few habitants and human activities. However, to the east and south of the downtown of Beijing, they are Hebei province and Tianjin city with more industrial units and populous agricultural villages. In wintertime, residents in these areas used coal as the primary fuel for heating and cooking. Therefore, our sampling site was not only predominantly affected by local traffic exhaust but may also have some contributions of VOCs from coal burning (Liu et al., 2017a, 2017b) and industrial processes.

2.2. Sampling and analysis

2.2.1. Online measurement of VOCs using PTR-TOF-MS

The concentrations of VOCs in the previous studies conducted in Beijing were mostly analyzed by gas chromatography (GC) coupled with different mass detectors (Duan et al., 2008; Shao et al., 2009; Wu et al., 2016; Ho et al., 2018). Although PTR-Quad-MS (Quad, quadrupole) was used in recent years for monitoring VOCs online in more fine time resolution (Chen et al., 2014; Wang et al., 2014), it only determines the nominal mass-to-charge ratio of the protonated molecule and always does not allow a unique identification of the VOCs. The PTR-TOF-MS 8000 (Ionicon Analytik GmbH Innsbruck, Austria) used in this study could save more work of pre-treating air samples compared with the GC system and has a higher mass resolution compared with the Quad version PTR-MS.

Ambient air outside the cabin was drawn by a pump at a flow rate of about 15 $l\,min^{-1}$ through a 1.5 m long PFA Teflon tube. A substream of air was filtered by a Teflon membrane particle filter and drawn into the reaction drift tube of PTR-TOF-MS via 1/16 in. PEEK tubing inlet, which was heated at 60 °C. The flow rate of this inlet stream was 100 $ml\,min^{-1}$. The drift tube was operated at 60 °C, 2.2 mbar, and 600 V, which corresponded to an E/N ratio of 135 Td (E and N being the electric field strength and the number density of the gas, respectively; 1 Td = $10^{-17}\,V\,cm^2\,molecule^{-1}$). Our PTR-TOF-MS used H_3O^+ as the primary reaction ion, since it is suitable for analyzing air samples containing a wide variety of trace gases (Lindinger et al., 1998). The signal value of $H_3{}^{16}O^+$ (m/z = 19.0178) was calculated from $H_3{}^{18}O^+$ (m/z = 21.0226) based on the known natural isotopic ratio (499,1) of $^{16}O/^{18}O$. The average value of H_3O^+ was 3.0×10^6 counts per second (cps). In this study, all mass spectra were stored at a relatively low time resolution of 1 h, which may obtain a higher signal/noise ratio of the measured VOCs.

The zero air (background) generation and PTR-TOF-MS calibration were performed using a gas calibration unit (GCU-a: GCU-advanced v2.0) that also from the PTR-TOF-MS manufacturer, Ionicon. VOC-free zero air was produced by passing ambient air through a VOC scrubber catalyst (installed internally the GCU-a) heated at 350 °C. The PTR-TOF-MS was calibrated by GCU-a using a dynamic dilution of the multi-component gas standard (Apel Riemer Environmental Inc., USA), which contained 1 ppm ± 5% of the following compounds: formaldehyde, methanol, acetonitrile, acetaldehyde, acetone, isoprene, methyl ethyl ketone (MEK), benzene, toluene, styrene, benzaldehyde, ethylbenzene, and 1,3,5-trimethylbenzene.

The interference of alcohols (methanol and ethanol) on m/z 31 (formaldehyde) due to reacting with O_2^+ is known from the literature (Schripp et al., 2010). The count rate of O_2^+ was averaged for 5548 ± 1302 $counts\,s^{-1}$ (cps) during the sampling period in this study. It corresponded to the mean value of O_2^+/H_3O^+ of 0.21 ± 0.05%. It was comparable to the O_2^+/H_3O^+ (< 0.1%) value of the nitrogen-filled bag that were measured by Schripp et al. (2010) and it was significantly smaller than their O_2^+/H_3O^+ value (1%) of laboratory background. So the concentration of O_2^+ was low in our measurement. We considered that the interference of the O_2+ reaction with alcohols on the mixing ratio of formaldehyde would be negligible.

The protonated isoprene has an m/z of 69.07. However, this mass is also contributed by cycloalkanes (Erickson et al., 2014) and other C_5H_8 compounds such as 1,4-Pentadiene (Brilli et al., 2014). Therefore, the isoprene concentration measured by us in this study represented the total signals from all contributors.

Large changes in ambient humidity are known to affect the sensitivities of the VOCs when measuring using PTR system. This occurs due to a change in the ratio between the primary reagent ions (H_3O^+) and the cluster ions ($H_3O^+(H_2O)$, m/z = 37.0284) within the drift tube (de Gouw et al., 2003; Sarkar et al., 2016). To account for the humidity effect, the product ion signals were normalized to the standard reagent ion signals of 10^6 $counts\,s^{-1}$ (cps) using following equation introduced