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Vertical characteristics of VOCs in the lower troposphere over the North China Plain during pollution periods☆

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ABSTRACT

In recent years, photochemical smog and gray haze-fog have frequently appeared over northern China. To determine the spatial distribution of volatile organic compounds (VOC) during a pollution period, tethered balloon flights were conducted over a suburban site on the North China Plain. Statistical analysis showed that the VOCs concentrations peaked at the surface, and decreased with altitude. A rapid decrease appeared from the surface to 400 m, with concnetrations of alkanes, alkenes, aromatics and halocarbons decreasing by 48.0%, 53.3%, 43.3% and 51.1%, respectively. At heights in the range of 500 −1000 m, alkenes concnetrations decline by 40.2%; alkanes and halocarbons concnetrations only decreased by 24.8% and 6.4%, respectively; and aromatics increased slightly by 5.5%. High concentrations VOCs covered a higher range of height (400 m) on heavy pollution days due to lacking of diffusion power. The VOCs concentrations decreased by 50% at 200 m on light pollution days. The transport of air mass affected the composition and concentration of high-altitude VOCs, especially on lightly polluted days. These air masses originated in areas with abundant traffic and combustion sources. Reactive aromatics (k_{OH}>20,000 ppm^{-1} min^{-1} and k_{OH}<20,000 ppm^{-1} min^{-1}) were the main contributor to the ozone formation, accounting for 37%, on the surface on light pollution days. The contribution increased to 52% with pollution aggravated, and increased to 64% with height. The contributions of reactive aromatics were influenced by the degree of air mass aging. Under the umbrella of aging air mass, the contribution of reactive aromatics increased with height.

1. Introduction

Volatile organic compounds (VOCs) are a very important class of atmospheric pollutants. Their reaction with OH, O_3, and nitrogen oxides (NOx) generates and aggravates ground-level ozone pollution in the presence of sunlight, thus directly affecting regional air quality (Atkinson, 2000; Kroll and Seinfeld, 2008). In recent years, China's air quality has deteriorated, and extreme air pollution events are frequent. Although the implementation of environmental protection measures effectively reduced the annual average concentrations of SO_2 and NO_2, the level of ozone has remained high and exhibited an increasing trend (Gao et al., 2017; Tang et al., 2009).

The photochemical formation during daytime had been proved to be an important source of surface ozone (Lin et al., 2004) and contributed about 50% of the Near-surface ozone (Fast et al., 2002; Morris et al., 2010) especially in urban areas. Therefore, the study of urban area VOCs is of significance to solving the problem of ozone (Liu et al., 2016; Yan et al., 2017). At present, the study of ozone has been expanded from two-dimensional to three-dimensional spectrum. Large number of models and experimental observations have focusing on the vertical profile and formation mechanism of ozone (Isabelle et al., 2001; Langmann, 2000; Ma et al., 2012; Wang et al., 2001). However, due to the lag in the development of VOCs vertical observations, the formation and evolution of atmospheric ozone remain unclear.

Despite the implication of the vertical distribution of VOCs, few researches have been published due to the associated experimental difficulties. Vertical sample collection has usually been performed on aircraft (Reeves et al., 2010), tethered balloons(Sangiorgi et al.,

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2011; Wöhrnschimmel et al., 2006), or high towers(Deng et al., 2015; Mao et al., 2008a). Large number of samples can be collected from high towers, but the observational heights are less than 300 m. The aircraft can ascend from several decades kilometer to the stratosphere and cover large range, but the aircraft survey is difficult to monitor the height below 1000 m. Tethered balloons are more flexible relative to the high towers and aircraft for the vertical observation of the lower atmosphere, and can free to design sampling gradients and duration. Some studies have qualitatively and quantitatively described the vertical distribution of VOCs using tethered balloons, such as Wöhrnschimmel et al. (2006) and Mao et al. (2008b), who reported that the concentrations of VOCs decreased with height. Some quantitative results have shown an exponential concentration profile with altitude, as reported by Koβmann et al. (1996), and a pronounced decrease by 74–95% below the mixing layer, as reported by (Sangiorgi et al., 2011). However, these studies have limitation of less samples and scarce species. Moreover, the vertical variations in the composition of VOCs, especially, the composition of reactive species, have not been reported, which determines the atmospheric oxidation capacity.

At the beginning of this century, haze has been occurring more frequently in several cities of northern China, including Beijing (the capital of China), Tianjin, and Shijiazhuang (Wang et al., 2013), with haze covering parts of the North China Plain during pollution episodes (Tao et al., 2012). The southern Hebei area of the North China Plain, including Shijiazhuang, Xingtai, is one of the regions with both the highest number of haze days and the most rapid growth in haze frequency. Numerous observational and modeling studies have focused on the spatial and temporal characteristics of aerosols in the North China Plain (Wang et al., 2012; Zhao et al., 2013, 2015). However, few studies have quantified the relationship between meteorological factors and the concentrations of coarse particulate matter (Hao et al., 2011; Wang and Hao, 2010), we still lack a sufficient understanding of the spatial and temporal characteristics of VOCs under pollution conditions in this area.

This manuscript analytical data obtained from near-ground and tethered balloon measurements in a suburban site located in Hebei during a large-scale pollution event on the North China Plain from December 22nd to 31st, 2015. Measurements included vertical distributions of VOCs and meteorological parameters up to 1000 m above ground level. The objectives of this study were threefold, i.e. 1) to quantify the vertical variation in the VOCs concentrations and composition at the Hebei plant, 2) to analyze the vertical development of VOCs under different pollution conditions, and 3) to investigate the vertical evolution of the ozone generation capacity of VOCs.

2. Experimental methods

2.1. Monitoring site

Shijiazhuang (38.03 N, 114.26 E) is the capital of Hebei Province, located in the southern part of the North China Plain, approximately 264 km southwest of Beijing. Shijiazhuang have high population density reaching to 5073.5/square kilometers, and adjacent to the Taihang Mountains, that forms part the Piedmont region, this region is relatively heavy polluted (Fig. 1). The fieldwork was conducted at the Meteorological Administration of Luancheng, which is located in the southeast of Shijiazhuang and is a suburban area approximately 12 km from the center of Shijiazhuang. No direct industrial sources of atmospheric pollutants are located near the site.

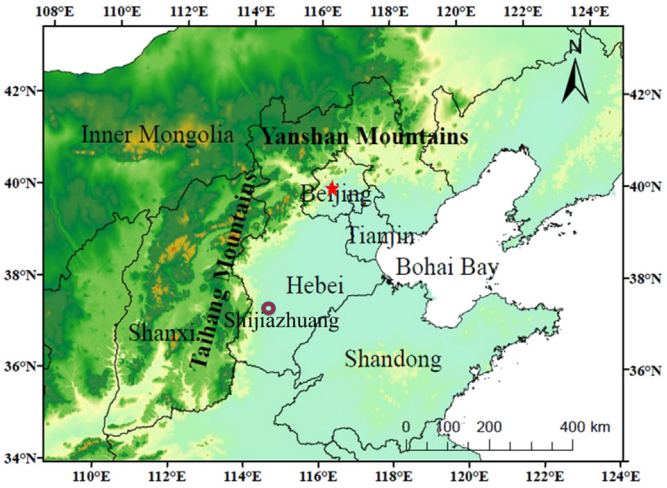

Fig. 1. Map of location of the sampling site.

2.2. Instrumental method

2.2.1. VOCs data (GC-MS/FID)

Sampling at different levels above the ground was achieved by a spherical helium-filled tethered balloon, which was equipped with a meteorological station and VOCs sampling system on a sample platform attached bellow the balloon. The VOCs sampling device composed of a battery, a relay, a small air pump and 3 L Tedlar bags (Supelco, St. Louis, MO, USA). To minimize the interference of particulate matter, a quartz filter was equipped on the front of the air pump. The collection of air samples at different heights was accomplished using a remote-control device, which switched the pump on and off by a remote handheld controller. Tedlar bags were baked for 40 min in a 50 °C oven and cleaned under vacuum before being used. Air was pulled down into the bags through a 1/16 diameter Teflon tube by air pump that provides a flow rate of 1 L/min calibrated with float flowmeter. Two bags filled with pure N_2 were randomly selected and used as background blanks.

VOCs vertical profile samples were obtained from November 22nd to 31st, 2015. Air samples were collected into bags at 100 m, 200 m, 300 m, 400 m, 500 m, 600 m, 800 m and 1000 m (all the heights were determine by air pressure). The sampling flow rate was 1 L/min and the sampling time is 3–5min. 16 vertical profiles were carried out and a total of 88 VOCs samples were collected, of which 53 samples were collected on heavy pollution days, 30 samples on light heavy pollution days and only 5 near-surface samples on clear days. Clear days often accompanied by strong winds during the observation period, the surface wind speed was generally more than 3 m/s, which led to the tethered balloon drifted and difficult to launch. All of the VOCs samples were sent to the laboratory in Beijing for analysis using a three-stage preconcentration system (7200 concentrator, Entech Inc., USA), followed by gas chromatography (GC) (Shimadzu 2012SE) analysis. In this analytical setup, dual columns are coupled to a mass spectrometer (MS) for C_4-C_{12} compounds and flame ionization detector (FID) for C_2-C_3 compounds were configured. The detailed analysis method was described in Sun et al. (2016).

2.2.2. Other data

For each vertical VOCs profile, the meteorological parameters (wind speed, wind direction, temperature and humidity) were recorded by an automatic meteorological observation instrument (Milos520, Vaisala, Finland). The atmospheric mixing layer heights (MLHs) were measured with a single-lens lidar ceilometer (CL51,

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