Science of the Total Environment 560–561 (2016) 62–72

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Evolution process and sources of ambient volatile organic compounds during a severe haze event in Beijing, China

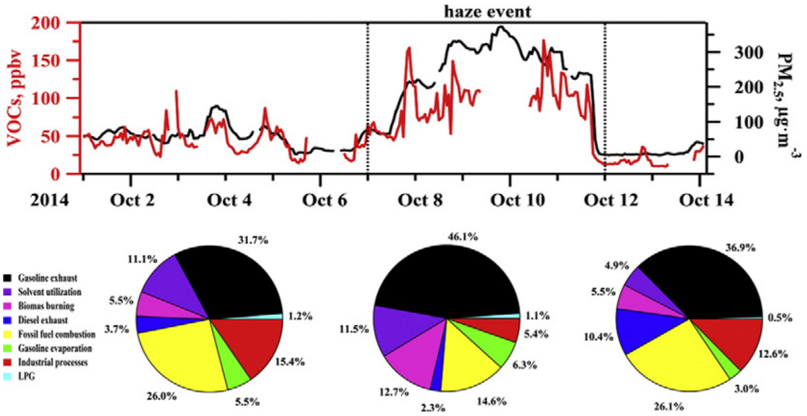
Rongrong Wu, Jing Li, Yufang Hao, Yaqi Li, Limin Zeng, Shaodong Xie *

College of Environmental Sciences and Engineering, State Key Joint Laboratory of Environmental Simulation and Pollution Control, Peking University, Beijing 100871, China

HIGHLIGHTS

- Ambient VOCs were measured by an on-line GC-FID/MS in October 2014, Beijing.
- Formation process and sources of VOCs during a severe haze event were investigated.
- Mixing ratios of VOCs during the event were 2 to 5 times as that in non-haze days.
- The extremely high levels of VOCs were largely driven by vehicular emissions.
- Biomass burning, as well as stationary synoptic condition aggravated the pollution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 January 2016
Received in revised form 26 February 2016
Accepted 6 April 2016
Available online 17 April 2016

Editor: D. Barcelo

Keywords:
VOCs
Source apportionment
Vehicular emissions
Biomass burning
Evolution process

ABSTRACT

108 ambient volatile organic compounds (VOCs) were measured continuously at a time resolution of an hour using an online gas chromatography–frame ionization detector/mass spectrometry (GC–FID/MS) in October 2014 in Beijing, and positive matrix factorization (PMF) was performed with online data. The evolution process and causes for high levels of VOCs during a haze event were investigated through comprehensive analysis. Results show that mixing ratios of VOCs during the haze event (89.29 ppbv) were 2 to 5 times as that in non-haze days, There was a distinct accumulation process of VOCs at the beginning of the haze event, and the mixing ratios of VOCs maintained at the high levels until to the end of pollution when the mixing ratios of ambient VOCs recovered to the normal concentration levels in a few hours. Some reactive and toxic species increased remarkably as well, which indicates a potential health risk to the public in terms of VOCs. Eight sources were resolved by PMF, and results revealed gasoline exhaust was the largest contributor (32–46%) to the ambient VOCs in Beijing. Emissions of gasoline exhaust surged from 13.46 to 40.36 ppbv, with a similar variation pattern to total VOCs, indicating that high levels of VOCs were largely driven to by expanded vehicular emissions. Emissions of biomass burning also increased noticeably (from 2.32 to 11.12 ppbv), and backward trajectories analysis indicated regional transport of biomass burning emissions. Our findings suggested that extremely high levels of VOCs during the haze event was primarily attributed to vehicular emissions, biomass burning and regional transport, as well as stationary synoptic conditions.

1. Introduction

Haze pollution, characterized by high levels of $PM_{2.5}$ (fine particulate matter with an aerodynamic diameter equal to or < 2.5 μm), low visibility,

---

* Corresponding author.
E-mail address: sdxie@pku.edu.cn (S. Xie).

http://dx.doi.org/10.1016/j.scitotenv.2016.04.030
0048-9697/

poor air quality, and accompanied by increase in respiratory symptoms and deceases (Chen et al., 2013; Huang et al., 2014a; Ouyang, 2013), has been a serious environmental problem in China. In the year of 2013, several severe and persistent haze event engulfed China (Wang et al., 2015a; Yang et al., 2015; Zheng et al., 2015), with record-breaking hourly $PM_{2.5}$ concentration of ~900 μg m^{-3}, which badly affect regional air quality and human health (Peplow, 2014; Sun et al., 2014; Wuebbles et al., 2007). According to monitoring results, the annual average haze days in China reached a historical high value of 35.9 in 2013. In some regions, such as the Beijing-Tianjin-Hebei district and the Yangtze River Delta region, it even exceeded 100 days (MEP, 2015). Measurements at 161 major cities showed that the annual average $PM_{2.5}$ concentration was 62 μg m^{-3} in 2014, about twice that of China's Ambient Air Quality Standard of 35 μg m^{-3} (MEP, 2014). To alleviate the severe particulate pollution, the Chinese State Council promulgated the "Air Pollution Prevention and Control Action Plan", devoting to reducing $PM_{2.5}$ by 25% on the concentration level of 2012 up to 2017 (State Council, 2013). To achieve this goal, many emission control measures were put forward, such as upgrading low-efficiency coal-fired industrial boilers and furnaces, and desulphurization of flue gas emitted by coal-fired power plants, which effectively reduce SO_2 emissions, a primary precursor of secondary inorganic aerosols (Wang et al., 2013).

Acute particulate pollution has also attracted great scientific interest. Extensive studies have been conducted to investigate the characteristics and formation mechanisms of haze pollution in China (Huang et al., 2014a; Liu et al., 2013; Wang et al., 2015a; Zhao et al., 2013). However, the formation mechanism of a haze is complicated, which not only involved physical evolutions, but also chemical reactions (Sun et al., 2014; Yang et al., 2015), and has not been clearly understood. According to recent studies, serious haze events are greatly driven by intensive secondary formation of aerosols, and aggravated by unfavorable meteorological conditions (Huang et al., 2014a; Yang et al., 2015; Zhao et al., 2013). In addition, large anthropogenic emissions and regional transport are also responsible for haze pollution (Liu et al., 2013; Yang et al., 2015; Zhao et al., 2013).

Volatile organic compounds (VOCs) are crucial precursors for secondary organic aerosol (SOA) and tropospheric ozone (Johnson et al., 2006; Ran et al., 2011; Robinson et al., 2007; Zhang et al., 2014). Photochemical oxidation as well as multiphase reactions of VOCs can form semi-volatile and intermediate species, leading to formation of SOA (Ait-Helal et al., 2014; Aumont et al., 2012; Volkamer et al., 2006). Recent study found that the severe haze pollution in China was largely driven to by secondary aerosol formation, responsible for 30–77% and 44–71% of $PM_{2.5}$ and organic aerosol, respectively, of which VOCs account for ~25–30% of the $PM_{2.5}$ mass and 44–71% of OM mass via SOA production (Huang et al., 2014a). Guo et al. (2014) also identified the haze episodes in Beijing were also governed by aerosol formation, while emissions of VOCs are responsible for large secondary PM formation. Consequently, VOCs are critical for the severe urban and regional haze pollution in China. Moreover, VOCs are detrimental to human health (Bunch et al., 2014; Huang et al., 2014b; Taioli et al., 2007). Therefore, knowledge of characterization and sources of VOCs, especially in pollution days, are vital to remediation of haze pollution from the policy perspective. However, VOCs are currently less constrained in China because of inadequate technologies and lack of trained staff, and previous studies about the haze events mostly focused on particulate matter, scarcely on VOCs. Therefore, studies on characteristics and evolution processes of VOCs during haze events are urgently needed and would be beneficial to provide scientific support for the government to make effective air pollution control measures in China.

There were four severe haze events in the North China Plain in October 2014, of which the pollution on October 7–11 was the most serious, with daily average concentration of $PM_{2.5}$ in Beijing approaching 250 μg m^{-3} (see Fig. S1). The large-scale and persistent haze pollution affected ~0.3 million km^2 and 400 million people. Few studies have reported this haze event, particularly the characteristics and evolution processes of VOCs during this period. In this study, field observations were conducted from October 1–16 in Beijing. 108 VOC compounds were measured by an online gas chromatography–frame ionization detector/mass spectrometry (GC–FID/MS) system. The concentrations and chemical compositions of VOCs before, during and after the event were compared, and positive matrix factorization (PMF) analysis was conducted using hour values of VOC data to investigate the source characterization. Meanwhile, meteorological data and backward trajectories were analyzed to help understand the formation and evolution processes of the VOC pollution.

2. Methods

2.1. Site description

The sampling site of VOCs was located in the technology and physics building of Peking University (PKU) (39.99°N, 116.33° E), northwest of Beijing city (see Fig. 1). The surrounding area of this site is mainly commercial and residential district, without large industrial sources. Transportation may be the major contributor of VOCs at this site because it is directly between Chengfu Road and the 4th Ring-Road, one of main traffic lines in Beijing. Besides, cooking is another potential source, due to booming catering service in the vicinity. The sampling site was outside of the window of a five-story building, with a height of approximately 20 m above the ground and a distance of 50 m away from the nearby main road. All the instruments were installed in an air-conditioned room that kept at 20 °C. Mass concentrations of $PM_{2.5}$ and other gaseous pollutants (including CO, O_3, NO_2, and SO_2) were measured by Beijing Municipal Environmental Monitoring Center at the Wanliu site (39.97°N, 116.31° E), which is the nearest automatic monitoring site to PKU.

2.2. Sampling and analysis

The sampling and analysis of VOCs was achieved automatically by a custom-built GC–FID/MS system (TH-017, made by Wuhan Tianhong Instrument Co., Ltd., Hubei, China) at a time resolution of 1 h. The availability of this system for VOCs measurement are well verified and it has been used in several large field campaign (Chen et al., 2014; Li et al., 2014; Yuan et al., 2013). Ambient air was sampled and pumped into a cryogenic preconcentration unit at a flow rate of 60 mL min^{-1} with sampling time of 5 min at the beginning of each hour. A teflon filter was placed in the inlet to prevent particulate matters from entering the instrument, and a water trap and an asbestos tube were used to remove H_2O and CO_2 from the air samples. The cryofocus unit was cooled down to −150 °C by liquid nitrogen to trap VOCs in the air samples. Thereafter, the trapped VOCs were released from the trapping tubes by rapidly heating to 100 °C and then injected into GC with dual capillary columns that were connected to different detectors, in which the C2–C5 non-methane hydrocarbons(NMHCs) were separated on a PLOT(Al_2O_3/KCl) column and quantified by FID, while the C5–C12 compounds (including hydrocarbons, oxygenated volatile organic compounds (OVOCs), halocarbons, and other species) were separated on a nonpolar DB-624 column and detected by quadrupole mass spectrometry detector. Detailed instrumental and operational parameters are described and shown in Table S1 in the Supplementary Materials.

Quantification of C2–C5 and C5–C12 compounds was achieved by external and internal standard methods, respectively, and linearity (R^2) of the calibration curves for all VOC compounds reached above 0.99. To assure the quality of analysis data, routine calibration was operated every day, by using a calibration gas with a mixing ratio of 1 ppbv and consisting of 56 kinds of VOC components, which was provided by the Environmental Technology Center in Canada, to check the stability of the instrument. Deviations between measured and nominal concentrations of the daily calibration were within 10%. The precision for hydrocarbons and other VOCs was below 6% and 15%, respectively (Li et al., 2014). Minimum detection limit is species-specific, varying from 0.003 ppbv for 2,2,4-