Science of the Total Environment 557–558 (2016) 531–541

Contents lists available at ScienceDirect

Science of the Total Environment

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

Effects of rigorous emission controls on reducing ambient volatile organic compounds in Beijing, China

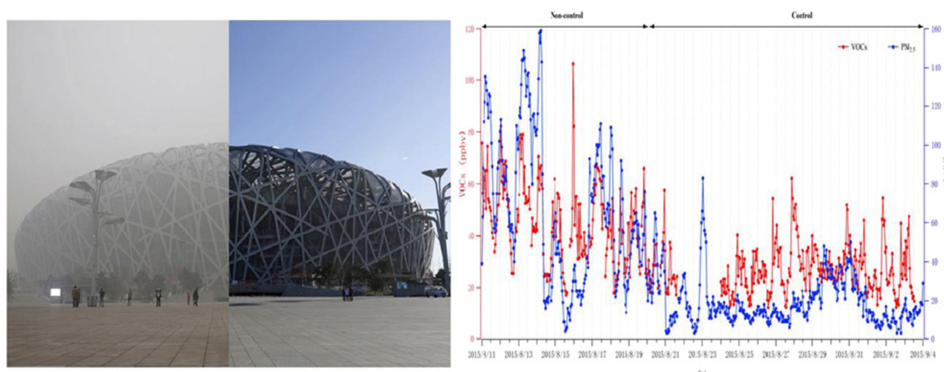
Jing Li, Rongrong Wu, Yaqi Li, Yufang Hao, Shaodong Xie *, Liming Zeng

College of Environmental Science and Engineering, State Key Joint Laboratory of Environmental Simulation and Pollution Control, Peking University, Beijing, People's Republic of China

HIGHLIGHTS

- 102 VOCs species were measured in August to September 2015, Beijing, China.
- Effects of rigorous emission controls on ambient VOCs were analyzed.
- The mixing ratios of ambient VOC were reduced by 40%.
- Contributions of vehicle-related sources were most reduced.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 January 2016
Received in revised form 23 February 2016
Accepted 19 March 2016
Available online 31 March 2016

Editor: D. Barcelo

Keywords:
VOCs
Source apportionment
Pollution control
Megacity

ABSTRACT

102 volatile organic compound (VOC) species were measured online using a gas chromatography–mass spectrometry/flame ionization detector (GC–MS/FID) at an urban site in Beijing in 11 August to 3 September 2015, when a series of rigorous air quality control measures were implemented in Beijing city and neighbouring provinces. Positive matrix factorization (PMF) was applied to identify emission sources from 1 h averaged values of VOC data. Based on the online VOC data and the PMF analysis results, the effectiveness of different control measures were investigated. The PMF results were compared with an emission inventory data. Results show that the rigorous air quality restrictions implemented were successful. The averaged ambient VOC mixing ratios during the emission control period and non-control period were 27.53 and 45.42 ppbv, respectively. The mixing ratios of total VOC during the control period were reduced by 40%. Alkanes were the most abundant chemical group in the two periods, followed by oxygenated volatile organic compounds (OVOCs). Almost all quantified VOC species decreased during the control period. Tracers of industrial sources and vehicle exhaust reduced most, including some halocarbons, esters and aromatics. Eight sources were resolved by online PMF analysis for ambient VOCs in Beijing. Contributions of those sources varied significantly during the control and non-control period. Compared with the values before control, contributions of vehicle-related sources were most reduced, followed by solvent utilization. Reductions of vehicle-related sources, solvent utilization, secondary formation, fuel combustion, and biogenic were responsible for 65%, 19%, 10%, 5%, and 1% of the reductions in ambient VOCs. Both PMF results and emission inventory data indicated that the control measure on traffic was very effective in reducing ambient VOCs in Beijing, with the emission reductions of about 50%.

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

http://dx.doi.org/10.1016/j.scitotenv.2016.03.140
0048-9697/

1. Introduction

Rapid industrialization and urbanization in developing countries has led to an increase in air pollution (Huang et al., 2014). In China, fine particles ($PM_{2.5}$) pollution is a serious environmental problem (Guo et al., 2012). Moreover, tropospheric ozone (O_3) levels in China have been rapidly increased during recent years (Wang et al., 2009; Zhang et al., 2014). It is reported that the severe haze pollution in China was driven to a large extent by secondary aerosol formation and O_3 chemistry in many regions that are volatile organic compound (VOC)-sensitive (Tang et al., 2012; Xue et al., 2014). VOCs are important precursors of secondary organic aerosol (SOA) and photochemically produced O_3·Thus, reducing VOC emissions are quite vital to air pollution control in China. Moreover, many VOCs adversely affect public health. Therefore, it is very necessary to formulate a cost-effective policy for reducing VOC emissions in China.

To alleviate the severe air pollution, the Chinese State Council has issued the “Air Pollution Prevention and Control Action Plan” in September 2013. The Action Plan defines ten measures to prevent and control air pollution, devoting to reducing $PM_{2.5}$ by 25% by 2017 (State council, 2013). Moreover, over the past two years, a series of VOCs control plans at provincial level and industrial VOCs emission standards have been promulgated. Although prevention and control measures have been proposed for many years, it is difficult to obtain evidence and quantify the effect of those measures.

The 2015 China Victory Day parade emission controls provide an opportunity to study the impacts of emission controls on VOCs. Beijing, the economic, political and cultural center of China, is one of the megacities in the world. It is suffering from heavy air pollution from both local and region emissions. In August to September 2015, the 2015 China Victory Day parade and the World Athletics Championships were held along in Beijing. To guarantee good air quality during the parade and the championships, the city government has set rigorous plans to reduce emissions of air pollutants in Beijing from August to September. Other neighbouring provinces (including Tianjin, Hebei, Shandong, Shanxi and Inner Mongolia provinces) cooperated with Beijing to ensure good air quality during the anniversary. A detailed description of the main regulations is shown in Table 1.

To quantitatively assess the effect of control measures on ambient VOCs, receptor models and monitoring data can be combined (Li et al., 2015a). Frequently-used receptor models include principal component analysis (PCA) method, chemical mass balance (CMB) method, and positive matrix factorization (PMF) technique (Paatero and Tapper, 1994; Watson et al., 2001). PMF is the most widely used model to study VOC source contributions in urban which would not be affected by uncertainties in emission profiles (Bon et al., 2011; McCarthy et al., 2013).

In this study, 102 C_2-C_{12} VOC species were measured by an online system, gas chromatography–mass spectrometry/flame ionization detector (GC–MS/FID), with a time resolution of 1 h at Peking University (PKU) in 2015, from 11 August to 3 September. The VOC species mixing ratios, and diurnal variations before and during control were investigated and compared in detail. To evaluate the effect of air quality control measures on VOCs, PMF model was used to extract the VOC sources in this campaign, the source contributions before and during the control period were contrasted. In addition, a comprehensive analysis was performed with another air pollutant control event. In order to evaluate the effectiveness of each control measure comprehensively, the PMF results were compared with an emission inventory data.

Table 1
Air-quality regulations taken by the Chinese government from 20 August to 3 September 2015.[a]

Target sources	Description of control measures
Vehicles	Odd-even license plate number rule applied for all vehicles in Beijing expect public transport; Non-Beijing vehicles were not allowed to drive inside the sixth ring road of Beijing during the morning and evening peak time; 80% of Government cars were forced out of service; Cargo trucks: not allowed to drive inside the 6th Ring Road.
Industry	Typical industries, including petrochemical industry, building materials industry, coating industry, printing industry, furniture industry were required to reduce production, or totally halted from operating in Beijing and surrounding provinces.
Fuel combustion	Coal-fired boilers in urban Beijing were required to complete clean energy transformation before 20 August 2015; Coal-fired units of two large thermal power plants were required to closed and natural gas generator units were required to put into use before 20 August 2015; Small boilers were required to be shut down; Coal-fired power plants were required to cut emissions by 30%; Coal-fired equipment of factories was required to cut emissions by 30%.
Dust	Construction sites were halted from operating in Beijing.
Others	Declared a holiday for public-sector employees in China.

[a] http://www.zhb.gov.cn/.

2. Methodology

2.1. Sampling site description

The measurements in this study were conducted from 11 August to 3 September at an urban site on the top of a fifth-story building on the Peking University campus in Beijing, with a height of approximately 15 m above the ground (the PKU site: 39.99°N, 116.33°E). The building is surrounded by several two-story buildings and one side road at its north. The site is located in northwestern Beijing city, about 500 m north of the 4th ring road (a main traffic line), and 10 km from the center of Beijing (Fig. 1). The surrounding area of this site is mainly commercial and residential, and the major nearby emission source of sampling site was vehicular traffic. This site is considered to be representative of a typical urban environment in Beijing (Song et al., 2007; Zhang et al., 2014; Li et al., 2015b; Wang et al., 2015). To evaluate the effect of the control measures, the whole study was divided into two parts: non-control period (11–19 August 2015) and control period (20 August–3 September 2015). Mass concentrations of $PM_{2.5}$ 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 (http://www.aqistudy.cn/). Meteorological data used in this study were collected from National Climate Data Center (NCDC, http://www7.ncdc.noaa.gov/CDO/cdo), which provided the meteorological data at Beijing Capital International Airport (40.06°N, 116.62°E).

2.2. Sampling and analysis

The continuous sampling and analysis of ambient VOCs were achieved automatically by a custom-built online GC–MS/FID system (TH-PKU 300B, Wuhan Tianhong Instrument Co. Ltd., China), with a time resolution of 1 h. The ambient VOCs was sampled and plumed into an electronic refrigeration and pre-concentration system. In order to prevent particulate matters entering into the sampling system, a teflon filter was placed in the sample inlet. A soda asbestos tube and a water removal trap were used to remove CO_2 and moisture before VOC analysis. Ambient C_2-C_{12} VOC species were analyzed by dual detectors, of which C_2-C_5 hydrocarbons were separated on a PLOT-Al_2O_3 column (15 m × 0.32 mm ID × 3 μm, J&W Scientific, USA), and measured by the FID channel, while other compounds were separated on a semi-polar column (DB-624, 60 m × 0.25 mm ID × 1.4 μm, J&W Scientific, USA) and quantified using a quadrupole MS detector.

We performed calibrations at five concentrations from 0.4 to 8 ppbv for each compound before sample analysis. The GC-FID system was calibrated by external standards and the GC–MS system was calibrated by internal standards. Rigorous QA (quality assurance) and QC (quality