Comparative study of volatile organic compounds in ambient air using observed mixing ratios and initial mixing ratios taking chemical loss into account – A case study in a typical urban area in Beijing

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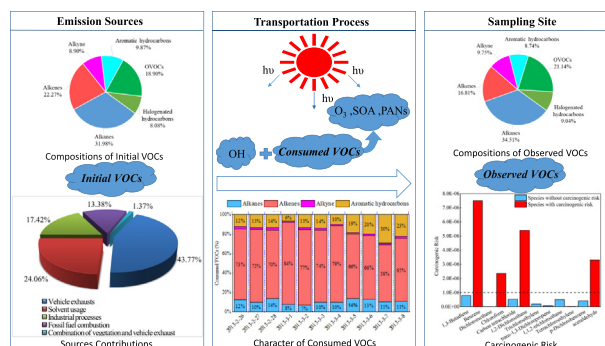[h] Environmental Research Institute, Shandong University, Jinan 250100, China
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HIGHLIGHTS

- The more accurate VOC pollution characteristics was obtained through a comparative study of observed and initial mixing ratio.
- The characteristics of consumed VOCs during the transportation was determined.
- The OFP of Ini-D was underestimated 23.41% compared with the OFP of Obs-D.
- VOCs species with carcinogenic risk or noncarcinogenic risk were identified in ambient air.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Volatile organic compounds (VOCs) can react with atmospheric radicals while being transported after being emitted, resulting in substantial losses. Using only observed VOC mixing ratios to assess VOC pollution, is therefore problematic. The observed mixing ratios and initial mixing ratios taking chemical loss into consideration were performed using data for 90 VOCs in the atmosphere in a typical urban area in Beijing in winter 2013 to gain a more accurate view of VOC pollution. The VOC sources, ambient VOC mixing ratios and compositions, variability and influencing factors, contributions to near-ground-ozone and health risks posed were assessed. Source apportionment should be conducted using initial mixing ratios, but health risks should be assessed using observed mixing ratios. The daytime daily mean initial mixing ratio (72.62 ppbv) was 7.72 ppbv higher than the daytime daily mean observed mixing ratio (64.90 ppbv). Alkenes contributed >70% of the consumed VOCs. The nighttime daily mean observed mixing ratio was 71.66 ppbv, 6.76 ppbv higher than the daytime mixing ratio. The observed mixing ratio for 66 VOCs was 40.31% higher in Beijing than New York. The OFPs of Ini-D (266.54 ppbv) was underestimated 23.41% compared to the OFP of Obs-D (204.14 ppbv), improving emission

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control of ethylene and propene would be an effective way of controlling O_3. Health risk assessments performed for 28 hazardous VOCs show that benzene, chloroform, 1,2-dichloroethane, and acetaldehyde pose carcinogenic risk and acrolein poses non-carcinogenic risks. Source apportionment results indicated that vehicle exhausts, solvent usage and industrial processes were the main VOC source during the study.

1. Introduction

The World Health Organization (WHO) defines volatile organic compounds (VOCs) as organic compounds with boiling points of 50–260 °C and saturated vapor pressures >133.32 Pa at 20 °C (WHO, 1987). Most VOCs are very reactive and can react with oxidants such as OH radicals in ambient air to produce highly oxidized secondary pollutants such as near-ground-ozone, aldehydes, ketones, highly active radicals (RO, RO_2, and HO_2), and peroxyacyl nitrates (Koppmann, 2010). These secondary pollutants can undergo photochemical reactions to form photochemical smog and secondary organic aerosols (SOAs). VOCs can be inhaled by humans and cause carcinogenic and non-carcinogenic effects. According to the International Agency for Research on Cancer, benzene is a human carcinogen (Group 1) and trichloroethylene, tetrachloroethylene, and 1,2-dibromoethane are probably carcinogens (Group 2A) (Ramirez et al., 2012). It is therefore urgent that research of VOCs in ambient air is performed.

Many studies have been performed on the characteristics, sources, effects on human health of VOCs in the atmosphere, on measures to control VOCs in the atmosphere, and on the relationships between VOCs and near-ground-ozone and SOAs (Guo et al., 2017; Wu et al., 2016; Zhang et al., 2017b). However, the conventional method using only observed VOC mixing ratios is problematic because many VOC species are very reactive, large amounts will react with radicals while being transported from their sources to the sampling site. These losses are important because they are related to the photochemical reactions (Wang et al., 2013). The amounts of VOCs consumed by reactions should therefore be taken into account when studying VOCs in the atmosphere.

Several methods are currently used to calculate VOC losses. One is the ratio method, in which two primary hydrocarbons emitted from the same source and with obvious evidence of photochemical aging are used to calculate the photochemical age of an air mass and to estimate the loss of chemicals (Mckeen et al., 1996).

A comparative study of the observed mixing ratios and initial mixing ratios considering chemical losses was performed using data for 90 atmospheric VOC species in a typical urban area in Beijing in winter 2013 to allow a more accurate view of atmospheric VOC pollution to be gained and to determine the scope of the observed and initial mixing ratios. The results were used to assess the VOC mixing ratios, compositions, variability, the factors influencing VOC mixing ratios, the health risks posed by VOCs, the ozone formation potentials (OFPs) and the sources of VOCs.

2. Materials and methods

2.1. Sampling site and study period

The sampling site was on the roof of the Chinese Research Academy of Environmental Sciences Atmospheric Environment Observation Station (40° 02′ N, 116° 25′ E) in the Chaoyang District in Beijing. The site was 15 m above ground level, and the samples were collected 1.5 m above the roof. The site was 0.3 km from Beiyuan Road and 2.1 km from North Fifth Ring Road. There are large residential areas, office areas, schools, hospitals, and shopping malls near the site. The site is adjacent to major roads and a subway station, and the area has a high traffic load and is densely populated (Fig. 1). The air at the site will reflect the air most residents of the area will be exposed to.

Samples were collected at 08:30–9:00, 13:30–14:00, 18:00–18:30, and 22:00–22:30 on each day between 26 February and 7 March 2013. No sample was collected at 22:00–22:30 on 28 February because of strong wind and a high dust concentration. Samples were also collected at 08:30–9:00 and 13:30–14:00 on 8 March 2013. In total, 41 samples were collected during the study period.

2.2. Sampling and analysis

TO-15 method, the standard method for analyzing toxic organic chemicals in ambient air recommended by the US Environmental Protection Agency (US EPA), was used. Fused silica-lined stainless steel canisters (3.2 L, Entech Instrument, Inc., Simi Valley, CA, USA) were used, and the compressed gas in each canister had a maximum pressure of 2.76×10^5 Pa. The canisters were evacuated <50 mTorr and then pressurized to 20 psi with high-purity nitrogen using a 3100A canister cleaner (Entech Instruments Inc., Simi Valley, CA, USA). After three cycles of evacuation and refilling, the canisters were evacuated to <20 mTorr for use. The sampling rate, controlled by a flow-limiting valve, was 101.5 ml/min, and the sampling time was 30 min. A sampling canister was placed away from any air outlets on the roof. Meteorological data for the sampling site (wind direction, wind speed, temperature, and ultraviolet radiation) were recorded every minute during each sampling period using a weather station (MAWS301, Vaisala, Netherlands). Criteria air pollutant data from the National Olympic Sports Center City Environmental Observation Station in Chaoyang District in Beijing (39° 59′ N, 116° 24′ E), the closest environmental observation station to the sampling site, were used.

As described in Wang et al. (2010), VOC samples were quantified using a system including a cryogenic pre-concentrator (Model 7100, Entech Instruments, Inc., Simi Valley, CA, USA) and a gas chromatograph (GC, HP-7890A, Hewlett Packard Co., Palo Alto, CA, USA) equipped with a quadrupole mass spectrometer (MSD, HP-5975C, Hewlett Packard), and a flame ionization detector (FID). The flow rate of the carrier gas which was high-purity helium (He) was 1.2 ml/min. Each aliquot of 300 ml from a canister was drawn into the cryogenic trap and cooled to −180 °C for preconcentration. The trap was resistively heated to 60 °C within seconds, and a stream of high purity He flushed the trapped VOCs onto the columns. Most of the target compounds were separated on a DB-624 column (60 m × 0.25 mm × 1.8 μm, J&W Scientific) and detected with MSD, C_2–C_3 components were separated on a PLOT (AL/KCL) column (30 m × 0.25 mm × 3.0 μm, J&W Scientific, Folsom, CA, USA) and detected with FID. The GC oven was initially held at 30 °C for 7 min and was raised to 120 °C at 5 °C/min; after 5 min the temperature was raised to 180 °C at 6 °C/min and held for 7 min.

The multi-component standard gas containing 56 VOCs (PAMS, Spectra Gases, Inc., Newark, New Jersey, USA) and multi-component standard gas which was recommended in the TO-15 method (TO-15, Spectra Gases, Inc., Newark, New Jersey, USA) were used as a calibration standard for the GC-MSD/FID system. Bromochloromethane, 1,4-difluorobenzene, and 1-bromo-3-flurobenzene were used as internal standards for GC/MSD quantification. Daily calibrations were done before analyzing canister samples. The deviations between analytical results of daily calibration and theoretical concentrations were within 10%. The VOC species analyzed, method detection limits, and linear correlation coefficients of the calibration curves (r^2) are shown in Table 3.