



Characterization and source apportionment of volatile organic compounds based on 1-year of observational data in Tianjin, China[☆]



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ABSTRACT

From November 2014 to October 2015, the concentrations of volatile organic compounds (VOCs), O₃ and NO_x were simultaneously monitored by using online instruments at the air monitoring station belonged to Tianjin Environmental Protection Bureau (TEPB). The results indicated that VOCs concentrations were higher in autumn and lower in spring, while O₃ concentrations were higher in summer, and lower in winter. The diurnal variations of VOCs and NO_x (NO₂ plus NO) showed opposite tendency comparing to that of O₃. The concentrations of alkanes were higher (the average of 18.2 ppbv) than that of aromatics (5.3 ppbv) and alkenes (5.2 ppbv), however, the alkenes and aromatics made larger contributions to ozone because of their high reactivity. Tianjin belonged to the VOC-limited region during most of seasons (except summer) according to the VOC/NO_x ratios (the 8:1 threshold). The automobile exhaust, industrial emission, liquefied petroleum gas/natural gas (LPG/NG), combustion, gasoline evaporation, internal combustion engine emission and solvent usage were identified as major sources of VOCs by Positive Matrix Factorization (PMF) model in Tianjin, and the contributions to VOCs for the entire year were 23.1%, 19.9%, 18.6%, 10.6%, 8.7%, 5.4% and 4.7%, respectively. The conditional probability function (CPF) analysis indicated that the contributing directions of automobile exhaust and industrial emission were mainly affected by source distributions, and that of other sources might be mainly affected by wind direction. The backward trajectory analysis indicated that the trajectory of air mass originated from Mongolia, which reflected the features of large-scale and long-distance air transport, and that of beginning in Jiangsu, Shandong and Tianjin, which showed the features of small-scale and short-distance. Tianjin, Beijing, Hebei and Northwest of Shandong were identified as major potential source-areas of VOCs by using potential source contribution function (PSCF) and concentration-weighted trajectory (CWT) models.

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1. Introduction

Along with its economic development and urbanization, the concentrations of atmospheric pollutants in urban area are rapidly increasing (An et al., 2014; Barletta et al., 2005; Liu et al., 2008b). Volatile organic compounds (VOCs) are important atmospheric pollutants due to their detrimental effects. The photochemical reaction of VOCs and NO_x could produce O₃ in the troposphere

(Carter, 1994; Sillman, 1995), which increased the atmospheric oxidizing ability and adversely influenced the atmospheric quality and human health (Jobson et al., 2004; Wei et al., 2014). Therefore, more attentions have been paid for VOCs and related gaseous pollutants (NO_x and O₃) from the anthropogenic sources (Bo et al., 2008; Li et al., 2014; Wei et al., 2008; Zou et al., 2015). Seinfeld (1989) have reported that a transition from VOC-limited to NO_x-limited region at a VOC/NO_x ratio of approximately 8:1 in Los Angeles in the 1980s. The gas-phase photochemical transformations of NO_x and VOCs, as well as their roles in the O₃ formation, are also widely studied in recent years (Geng et al., 2008; Zou et al., 2015). Additionally, some reports have established the national or regional emission inventories of VOCs, or have

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conducted source apportionment of VOCs, which indicated automobile exhaust, fuel evaporation, combustion, solvent usage and petroleum/chemical industry, etc., were major emission sources (Bo et al., 2008; Bari et al., 2015; Liao et al., 2015; Wei et al., 2008).

As well known that the Beijing-Tianjin-Hebei (BTH), the Yangtze River Delta (YRD) and the Pearl River Delta (PRD) regions have been experiencing severely atmospheric pollutions. However, previous studies on pollution characteristics or the VOCs sources in China have mainly concentrated in the PRD and YRD regions or Beijing city (An et al., 2014; Geng et al., 2008; Li et al., 2015; Shao et al., 2016; Wang et al., 2009a; Zhang et al., 2008; Zheng et al., 2013; Zou et al., 2015), while that of Tianjin city is relatively less and limited (Han et al., 2015). Tianjin is the third largest megacity in China, which has a population of more than 14 million until 2013 (Tianjin Statistical Yearbook, 2014). The rapid increasing of industrial activity-levels and automobile number, results in massive emissions of VOCs and NO_x, which are O₃ precursors in the air, so that the secondary pollution-events could always occur in Tianjin. The number of automobiles has been more than 2.7 million until 2013 at Tianjin (Tianjin Statistical Yearbook, 2014). The petrochemical industry is one of eight critical industries of Tianjin and is mainly situated in the Tianjin Binhai New Area (TBNA) (Han et al., 2015), which is a national level development area. Moreover, the electronics, metallurgy, biomedical, new energy, etc., are also important industries at Tianjin (Chen et al., 2010). The high formation potential for ozone or secondary pollution existed in terms of massive emissions of VOCs and NO_x from automobiles, petrochemical industry and other industries such as electronic, metallurgy, etc. Additionally, Carter (1994) had reported that the O₃ levels would be lower without VOCs. Therefore, VOCs played a critical role in ozone production in the air. However, the knowledge of variation characteristics of VOCs, NO_x and O₃, as well as VOCs emission sources in the air at Tianjin, are still limited. While these information is very important for development of efficient VOCs or O₃ control strategies to reduce atmospheric secondary pollutions (Tie et al., 2007; Saeaw and Thepanondh, 2015).

Therefore, the main objectives of this study are to: (1) understand variation characteristics of VOCs, NO_x and O₃; (2) identify source categories of VOCs and estimate their contributions by using PMF model; (3) analyze the local source impacts from varying wind directions by CPF analysis; and (4) analyze the transport pathway of air mass and potential source-areas of VOCs by using the backward trajectory, PSCF and CWT models, respectively.

2. Materials and methods

2.1. Site description

From November 2014 to October 2015, the monitoring campaign was carried out at the air monitoring station (39°5'49.30" N, 117°9'4.47" E) belonged to TEPB, which was located on the rooftop of a five-story building. The location of the monitoring station was described in Fig. 1. It is located in the center of Tianjin city, where pollution-events of high-concentration O₃ usually occur according to the monitoring data. The meteorological conditions during the monitoring period were shown in Fig. S3 of supplementary material and Table 1. As Fig. S3 shown, northeasterly and northwesterly winds prevailed in spring and winter, northeasterly, northwesterly and southwesterly winds prevailed in summer and autumn. The mean wind speeds (WS) were 1.8–2.2 m/s and temperature averaged 1.9–27.1 °C, and the mean relative humidity (RH) was up to 38.7–54.5%, during each season.

2.2. Instruments

The ozone was measured by Thermo Scientific™ Model 49i Ozone Analyzer based on UV Photometric technology, which was a dual cell photometer, the concept adopted by the NIST for the national ozone standard. The Thermo Scientific™ Model 42i NO-NO₂-NO_x Analyzer utilized chemiluminescence technology to measure the amount of nitrogen oxides in the air, which was a single chamber, single photomultiplier tube design that cycled between the NO and NO_x modes.

The GC5000 analysis system (AMA Instruments GmbH, Ulm, Germany) was used to monitor VOC species in the air. VOCs (C₂-C₁₂) were continuously measured at a 1 h sampling interval by this analysis systems coupled with Gas Chromatography-Flame Ionization Detector (GC-FID) system, which was comprised of GC5000VOC for C₂-C₆ species and GC5000BTX for C₆-C₁₂ species. For GC5000VOC, the sample was pre-concentrated on the dual-stage enrichment module, and diverted to the focusing module through a 6-port VALCO valve after desorption. Then, the components with lower boiling points were desorbed from the focusing module and injected through another 6-port VALCO valve into a fused silica capillary column (50 m × 0.32 mm inner diameter × 5 μm thickness) for separating light VOCs (C₂-C₆), with the remaining heavier components with higher boiling points being back-flushed out. For GC5000BTX, the sample was pre-concentrated on the single-stage enrichment module for organic components. Ozone precursor standard photochemical gases approved by the US EPA were used for the equipment calibration before monitoring. The standard gases were provided from the Photochemical Assessment Monitoring Stations (PAMS) and included 56 standard gases with concentrations of 1 ppbv. Standard gases were used for the calibration and verification of equipment by the 5-point method for every two weeks, and the correlation coefficient usually varied from 0.995 to 0.999.

The meteorological data including temperature, RH and WS were measured by a VAISALA WST520 automatic weather station with a time resolution of 5 s.

2.3. PMF model

PMF is an advanced receptor model that decomposes a matrix of sample data (X) into two matrices: source profile matrix (F) and source contribution matrix (G), based on observations at the sampling site (Paatero and Tapper, 1994; Paatero, 1997). Briefly, PMF model can be expressed as follows:

$$X_{ij} = \sum_{k=1}^p g_{ik}f_{kj} + e_{ij} \quad (1)$$

Where, X_{ij} is the j th species concentration of the i th sample, g_{ik} is the contribution of the k th source to the i th sample, f_{kj} is the source profile of j th species from the k th source, e_{ij} is the residual matrix for the j th species in the i th sample, and p is the total number of independent sources (Paatero, 1997).

PMF can identify the potential source categories for VOCs without emission source profiles of VOCs. No samples can obtain a negative source-contribution because of results constrained. Data below method detection limit (MDL) can be retained for using in PMF model with the related uncertainty adjusted based on the characteristics that PMF model admits data points to be signally weighed, therefore, these data points have less effect on the solution than measurements above MDL.

The object function Q can be allowed to review the distribution of each species in order to evaluate the stability of the solution, which is defined as:

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