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Characterization and Source Apportionment of Volatile Organic Compounds in Urban and Suburban Tianjin, China

HAN Meng[1,2], LU Xueqiang*[1], ZHAO Chunsheng[3], RAN Liang[3,4], and HAN Suqin[5]

[1]*Tianjin Academy of Environmental Sciences, Tianjin* 300191

[2]*State Environmental Protection Key Laboratory of Odor Pollution Control, Tianjin* 300191

[3]*Department of Atmospheric and Oceanic Sciences, School of Physics, Peking University, Beijing* 100871

[4]*Key Laboratory of Middle Atmosphere and Global Environment Observation, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing* 100029

[5]*Tianjin Institute of Meteorology, Tianjin* 300074

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ABSTRACT

Tianjin is the third largest megacity and the fastest growth area in China, and consequently faces the problems of surface ozone and haze episodes. This study measures and characterizes volatile organic compounds (VOCs), which are ozone precursors, to identify their possible sources and evaluate their contribution to ozone formation in urban and suburban Tianjin, China during the HaChi (Haze in China) summer campaign in 2009. A total of 107 species of ambient VOCs were detected, and the average concentrations of VOCs at urban and suburban sites were 92 and 174 ppbv, respectively. Of those, 51 species of VOCs were extracted to analyze the possible VOC sources using positive matrix factorization. The identified sources of VOCs were significantly related to vehicular activities, which specifically contributed 60% to urban and 42% to suburban VOCs loadings in Tianjin. Industrial emission was the second most prominent source of ambient VOCs in both urban and suburban areas, although the contribution of industry in the suburban area (36%) was much higher than that at the urban area (16%). We conclude that controlling vehicle emissions should be a top priority for VOC reduction, and that fast industrialization and urbanization causes air pollution to be more complex due to the combined emission of VOCs from industry and daily life, especially in suburban areas.

Key words: volatile organic compounds, source apportionment, positive matrix factorization, ozone, megacity

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1. Introduction

Volatile organic compounds (VOCs), as ozone precursors, play a significant role in ozone formation (Atkinson, 2000). VOCs as a source of PM2.5 can also contribute to low-visibility incidents, which are increasingly common in the cities of northern China, including Beijing, Tianjin and Hebei. In 1990, the U.S Environmental Protection Agency (EPA) initiated the Photochemical Assessment Monitoring Stations (PAMS) for ozone nonattainment areas. Ozone and its precursors, especially for VOCs, have been systematically monitored. The 56 PAMS-target VOC species are mainly alkanes, alkenes and aromatic hydrocarbons. Therefore, understanding the emission sources of VOCs, especially PAMS-target VOCs, is crucial for ozone pollution control.

Receptor models such as PMF (positive matrix factorization) and CMB (chemical mass balance) are commonly used to identify emission sources and quantify their contribution to the ambient concentration of VOCs (Harley et al., 1992; Henry, 1997; Paatero and Tapper, 1994). For CMB, both ambient data and specific source profiles are needed. Because PMF is based on ambient data only, it is convenient to carry out VOC source identification and apportionment (Brown et al., 2007).

With the progress of industrialization and urbanization, high ozone and haze near the ground has become the biggest air quality problem in China, due to increasing emission of VOCs (Geng et al., 2007, 2008; Tie et al., 2009; Suthawaree et al., 2012; Yuan et al., 2012). It is necessary to reveal the sources of VOCs for regional ozone and haze control. Yuan et al. (2009) compared PMF-identified sources in urban and suburban areas in Beijing. Excluding the traffic contribution, the VOC sources were similar to what was found in Shanghai by Cai et al. (2010).

Tianjin is the third largest megacity in China. With the de-

* Corresponding author: LU Xueqiang
Email: xueqianglu@gmail.com

velopment of Tianjin Binhai New Area (TBNA), a national-level development area of 2270 km^2, Tianjin is becoming an economic center in northern China. The petrochemical industry is one of eight key industries in Tianjin and is mainly located in the TBNA. Although there is a high potential of ozone pollution due to the emission of VOCs from the petrochemical industry, the composition and sources of VOCs are unclear. Similarly, the status of ambient VOCs is also ambiguous in the suburban area despite the fast urbanization there.

Cities like Beijing, Milan and Paris have imposed driving restrictions to control VOC emissions. Such abatement measures for VOCs have often become doubtful without understanding the significance of different sources. Tianjin also initiated such restrictions on vehicles to improve air quality, although critics have disputed its effect.

During the HaChi (Haze in China) summer campaign period, we synchronously collected ambient air samples from urban and suburban areas in Tianjin. As many as 107 ambient VOC species were detected: a first in Tianjin. Lu et al. (2011) and Han et al. (2011) previously investigated the characteristics and possible sources for total VOCs in urban Tianjin and Ran et al. (2011) identified the reactivity of total VOCs in suburban Tianjin. Focusing on PAMS-target VOCs, the present paper aims to: (a) clarify the characteristics of VOCs in urban and suburban Tianjin; (b) identify the major sources of VOCs and their control priority; and (c) elucidate and compare the differences of VOCs between urban and suburban areas in Tianjin, and between Tianjin and other cities.

2. Materials and methods

2.1. *Sampling and measurement*

Urban and suburban sampling sites were located at the Meteorology Bureau Tower (MBT) of Tianjin downtown, and the Wuqing meteorology station of Tianjin Meteorology Bureau, respectively. The MBT site in the southwest of urban Tianjin was surrounded by a combination of dense commercial and residential facilities, and is close to an urban freeway. The Wuqing site is approximately 50 km northwest of Tianjin city center, near farmland and the Beijing–Tianjin highway. Samples were collected using SUMMA cans with a vacuum gauge. Samples were collected five times per day during 6–14 August 2009: 0730–0930, 1100–1300, 1400–1600, 1700–1900 and 2100–2300. The samples were analyzed within 24 hours.

Ambient air sample concentrations of total VOCs were measured following the U.S. EPA Compendium Method TO-14 and TO-15, using pre-concentration system (Entech Instruments Inc., US) and gas chromatography-mass spectrometry (Agilent technologies Inc., US). The analytical method and process have already been described in detail in Lu et al. (2011). All VOC concentrations were quantified by the internal standard method; the four internal standard compounds were bromochloromethane, 1, 4-difluorobenzene, chorobenzene-d5 and 4-bromofluorobenzene. Before analysis, 53 standard compounds were used to establish the calibration curve. Internal standard mixed gas and 53 species standard mixed gas were bought from Linde Spectragases with 1 ppm mixing ratio.

2.2. *Source apportionment*

VOCs sources were apportioned using the PMF model, which has been applied to analyze a wide range of data, including PM2.5, aerosol, deposition products, airborne toxic species, and VOCs (Kim et al., 2003; Brown et al., 2007; Heo et al., 2009). The method is briefly described here, and in greater detail elsewhere (Paatero, 1997; Paatero and Tapper, 1994).

The PMF model was used to identify the species profile of each source, and the mass contributed by each species. A speciated dataset can be viewed as a data matrix $\boldsymbol{x}$, with i by j dimensions, in which i number of samples and j chemical species were measured. The goal of PMF analysis is to identify a number of factors p, and a species profile f for each source, and the mass g contributed by each factor to each individual sample:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \ , \tag{1}$$

where e_{ij} is the residual for each sample/species. The PMF solution minimizes the object function Q based upon the uncertainties (u):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{if}} \right]^2 . \tag{2}$$

Each dataset was decomposed into profile and contribution matrices, and variability in the PMF solution was estimated using a bootstrapping technique. The PMF-resolved source profiles were identified by their composition to avoid biases and unrealistic interpretation.

During the HaChi campaign period, a total of 1855 were collected at MBT and 1802 at Wuqing. These samples were analyzed to detect PAMS-target VOCs. In order to avoid any unrealistic data distorting the source analysis result, some species that were not well-characterized in the sample, and were often at or below the method detection limit, such as 2, 2-dimethylbutane, were excluded. The species with high reactivity were also excluded, since they were quickly destroyed in the ambient atmosphere and including them may bias the model. However, although very reactive, isoprene was included as a marker for biogenic sources. The final dataset contained 21 VOC species at MBT and 25 at Wuqing.

Measurement uncertainties were used for the error estimates of the measured values. Missing data were replaced by the geometric mean of the corresponding species, and four times the geometric mean was taken as the corresponding error estimates. Half of the detection limit was used for the values below the detection limit and 5/6 of the detection limit was used for the corresponding error estimate (Polissar et al., 1998).

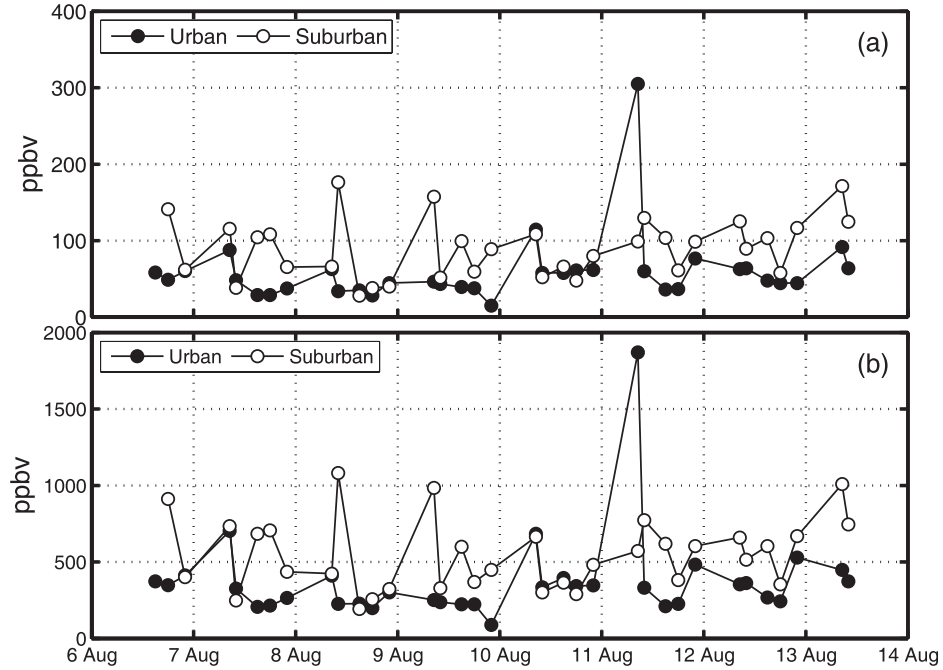

Fig. 1. Temporal variation of VOCs in urban and suburban Tianjin in August 2009.

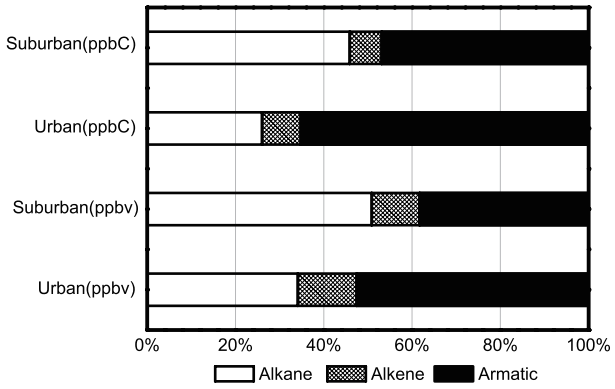

Fig. 2. Composition of VOCs in urban and suburban Tianjin.

3. Results and discussion

3.1. *Characteristics of VOCs at MBT and Wuqing*

A total of 107 species of ambient VOCs were detected, and the average concentrations of VOCs measured during the campaign was 92 at MBT and 174 ppbv at Wuqing. Fifty-one species of PAMS-target VOCs were extracted, 90% of the total 56 PAMS-target species determined by U.S. EPA. As shown in Fig. 1, the total PAMS-target VOCs had mixing ratios ranging from 15 ppbv to 305 ppbv, with an average of 59 ppbv at MBT, and the average carbon atom based mixing ratio was 372 ppb C with a maximum of 1870 ppb C. At Wuqing, the PAMS-target VOC mixing ratios ranged from 28 ppbv to 176 ppbv with an average of 90 ppbv, and the average carbon atom bashed mixing ratio was 551 ppb C with a maximum of 1081 ppb C. The total PAMS-target VOCs at Wuqing was higher than that at MBT. Figure 2 shows the mixing ratios of VOCs in ppbv and ppbC. For urban areas, aromatics were the most abundant VOC species, accounting for 52% of the mixing ratio (ppbv) and 65% of the ppbC. Alkanes were the second most abundant species, accounting for 34% of the ppbv mixing ratio, and 26% of the ppbC. In suburban areas, aromatics and alkanes were also the top two abundant VOCs. However, the alkane concentration was slightly higher than that in urban areas.

3.2. *Sources of VOCs at MBT*

Seven factors or sources were resolved for urban Tianjin. They were: (1) motor vehicle exhaust emission; (2) gasoline evaporation; (3) internal combustion engine emission; (4) diesel emission; (5) solvent usage; (6) industrial emission; and (7) biogenic emission. Among the seven sources, four sources (sources 1, 2, 3, and 4) were related to motor vehicle activities. Their profiles are shown in Fig. 3 as the percentage of each species loaded into each respective factor.

Motor vehicle exhaust contains abundant butane and aromatics, such as p-xylene, p-ethyltoluene, m-xylene, o-ethyltoluene, benzene, toluene, and 1, 2, 4-trimethylbenzene. Aromatics were reported as the main pollutant of motor vehicle exhausts (Ye et al., 2009). Moreover, the benzene to toluene ratio (0.6) is a typical tracer of the motor vehicle exhaust waste gas (Barletta et al., 2005). Evaporated liquid gasoline is dominated by C4–C5 alkanes such as isopentane, pentane, 2, 3-dimethylbutane, 2-methylpentane, and isobutene (Liu et al., 2005; 2008a, b). Internal combustion engine emission mostly consists of C3–C6 alkanes, benzene, toluene, ethylbenzene and xylene. These compounds come from both unburned and burned fuel

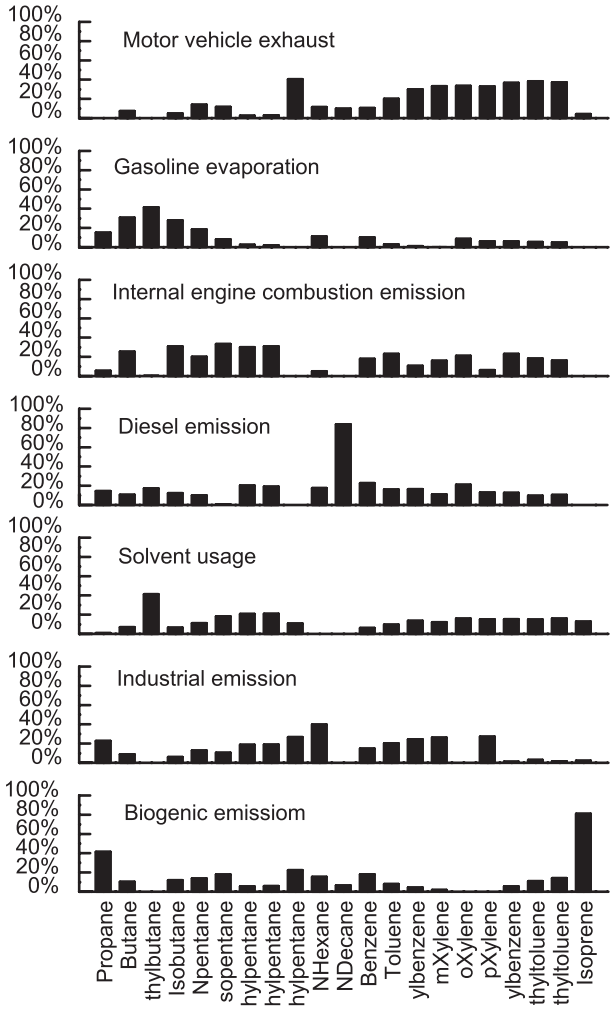

Fig. 3. Factor profiles (% of species) for VOCs in urban Tianjin (MBT).

(Grosjean et al., 1999; Guo et al., 2004). Diesel emission is characterized by a significant n-decane fraction (84%) (Watson et al., 2001; Song et al., 2007). Solvent usage emissions were identified due to its containing 50% 2, 3-dimethylbutane, a solvent for paint and coating. Abundant aromatic species also indicate solvent usage emissions.

High factor loadings of C3–C6 alkanes and BTEX (benzene, toluene, ethylbenzene and xylene) were found for source 6. Those compounds were mainly emitted by a petrochemical industry source (ATSDR, 1997; Guo et al., 2004; Liu et al., 2008a). Therefore, source 6 was identified as an industrial emission. For source 7, isoprene was the species with the highest factor loading (79%), a marker for biogenic emission (Atkinson, 2000).

3.3. *Sources of VOCs at Wuqing*

Figure 4 illustrates the source profiles at Wuqing, where five sources were identified. The justifications for source identification were very similar to those for MBT. Unlike MBT, the Wuqing site lacked the emissions from diesel and internal combustion engine sources. Serious traffic jams often happened near the MBT site, so diesel and gasoline vehicles idled frequently, but this did not happen at Wuqing. This made source apportion difficult.

The sampling periods were subdivided into two periods, depending on VOC composition or meteorological conditions (Ran et al., 2011). The VOCs were then classified into three categories. The first category had species with concentrations averaged over period 2 (after 10 August) higher than the double the concentrations averaged over period 1 (before 10 August), whereas species of the reversed situation were grouped into the second category. The third category contained all those species not in category 1 or 2, except for 21 species that were detected in neither period 1 nor period 2. The VOC species used for the above calculation were mostly within the third category, whose average concentrations of both periods were similar and therefore without the influence from meteorological conditions. This means the results of the source apportionment here can represent the

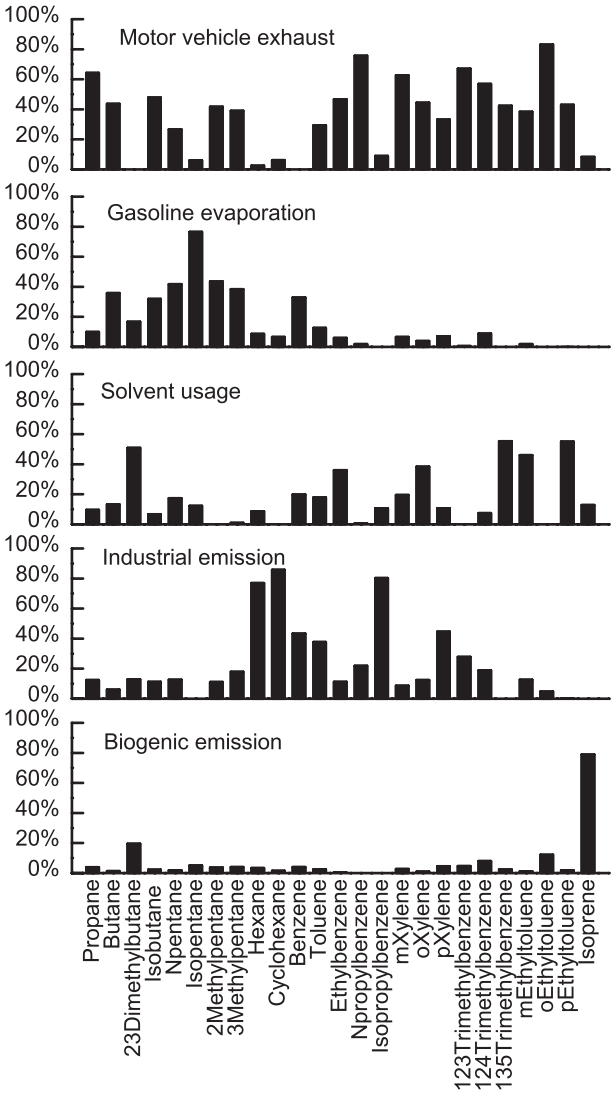

Fig. 4. Factor profiles (% of species) for VOCs in suburban Tianjin (Wuqing).

contribution from local sources, and the long-distance transportation of VOCs has negligible influence on the results.

3.4. *Source contributions*

Figure 5 shows the individual contributions for the two sites. The most important source was vehicle-related emissions, contributing 60% at MBT and 42% at Wuqing. The vehicle-related source contribution at MBT was generally similar to previously reported values for Beijing (64%) and urban Milan (60%–80%) (Song et al., 2007; Latella et al., 2005), and lower than that detected at traffic intersections (82%–87%) (Srivastava et al., 2005). The lower vehicle-related contribution (42%) at Wuqing was due to the lower traffic intensity of gasoline-powered vehicles. It is similar to the detected value at other rural sites (42%) or industrial sites (48%) previously found in China (Liu et al., 2008a).

Industry-related emission contributed 16% at MBT and 36% at Wuqing: the biggest difference between the sampling sites. There were many factories in Wuqing, which released a large number of VOCs. Although there were no large factories or industrial activities near the MBT site, the industrial VOCs were transported from surrounding areas such as Binhai New Area, on the dominant southeast wind in summer, and could have been consumed many ways during the long-distance transport.

The biogenic emission contribution at MBT (14%) was much higher than that at Wuqing (5%). It might have been caused by the different vegetation composition in urban and suburban Tianjin. The more broad-leaved plants, like *Fraxinus chinensis Roxb.*, in the urban area released more VOCs than the herbaceous plants, e.g. wheat, in the suburban area.

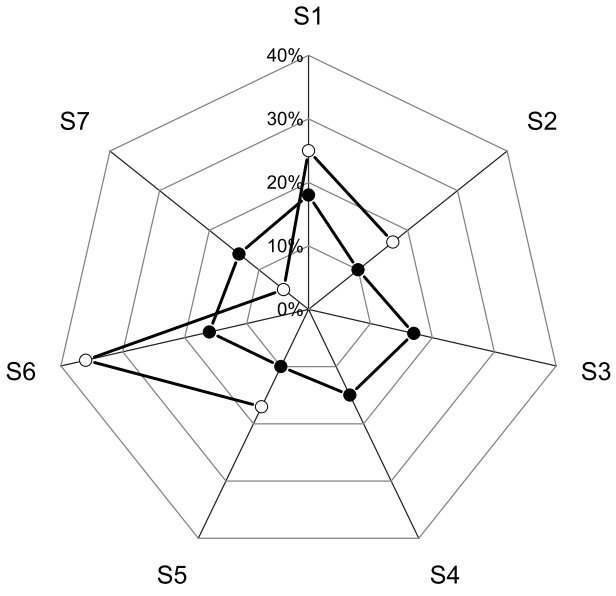

Fig. 5. Source-specific contribution to the measured VOCs in urban (closed circles) and suburban (open circles) Tianjin. S1 is motor vehicle exhaust; S2 is gasoline evaporation; S3 is internal combustion engine emission; S4 is diesel emission; S5 is solvent usage; S6 is industrial emission; and S7 is biogenic emission.

4. Concluding remarks

The first-ever source apportionment of VOC species collected simultaneously in suburban and urban locations of Tianjin was conducted using PMF. According to the characteristics of the factor loadings, seven VOC sources were identified at MBT of urban Tianjin, including: (1) motor vehicle exhaust emissions; (2) gasoline evaporation; (3) internal combustion engine emissions; (4) diesel emissions; (5) solvent usage; (6) industrial emission; and (7) biogenic emission. Except diesel emissions and internal combustion engine emissions, the same five sources were found at Wuqing, suburban Tianjin. The identified sources of VOCs in Tianjin were significantly related to vehicular activities, which contributed 60% and 42% to VOC loadings at MBT and Wuqing, respectively. Controlling vehicle emissions could be a top priority for VOC reduction in Tianjin. In addition, although the suburban area was fairly rural, fast industrialization and urbanization caused both industry- and vehicle-related VOC emissions. Due to the limitation of sampling locations and the short duration of this study, further studies are needed for a comprehensive ozone control strategy.

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