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Characterization of gas station emissions during the CAREBeijing 2008 field study

J. Zheng¹, T. Zhu², R. Zhang^{1,2}, M. Wang², C.-C. Chang³, M. Shao², and M. Hu²

¹Department of Atmospheric Sciences, Texas A&M University, Texas 77843, USA

²State Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, 100871, China

³Research Center for Environmental Changes, Academia Sinica, Taipei 11529, Taiwan

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Correspondence to: T. Zhu (tzhu@pku.edu.cn)

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Abstract

A proton transfer-reaction mass spectrometer (PTR-MS) onboard a mobile laboratory was used to conduct emission measurements at eight gas stations in Beijing during the CAREBeijing 2008 campaign. Benzene, toluene, C₈-, C₉-aromatics, methanol, MTBE, butenes and pentenes were the major volatile organic compounds (VOCs) detected during the measurements. An inter-comparison between the PTR-MS and an on-line GC/MS/FID system was also conducted and the result showed good agreement between the two instruments (Interception < 0.08 ppbv, 0.72 < Slope < 0.95, and R² > 0.92). A Gaussian point source plume model was applied to evaluate the VOCs emission rates. The results showed that on average about 4.5 mt of gasoline were emitted from gas stations in Beijing per day. The estimated emission factor (EF) for gas stations due to refueling processes was about 0.5 kg t⁻¹, which was significantly lower than a value of 2.49 kg t⁻¹ obtained in 2002, indicating a successful implementation of vapor recovery system in the gas stations of Beijing. On average, about 18 ppbv of benzene has been detected at one gas station, twice as much as the US Environmental Protection Agency (EPA) recommended safe chronic exposure level and implying a potential public health concern. MTBE and aromatics were found to be the major antiknocking additives used in gasoline supplied in Beijing. Our results reveal that emissions from gas stations represent an important source for VOCs in megacity Beijing and need to be properly included in emission inventories to assess their roles in photochemical ozone production and secondary organic aerosol formation. Furthermore, promoting methanol-blended fuel in Beijing can be an effective way to reduce toxic air pollutants emission.

1 Introduction

Rapid urbanization in the Beijing area leads to a fast growth in automobile population. At an annual rate of 14.5 % (Hao et al., 2006), it is projected that the number of vehicles

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in Beijing will reach five million (Han and Hayashi, 2008) by 2020. Automobile-related air pollutants emissions account for more than 70% of volatile organic compounds (VOCs) and 40% of nitrogen oxides (NO_x) emissions in the Beijing metropolitan area (Liu et al., 2005; Hao et al., 2006), which trigger rapid ozone photochemical production (Finlayson-Pitts and Pitts, 1999; Zhang et al., 2004a) and lead to secondary organic aerosol formation (Zhao et al., 2009; Yue et al., 2010; Zhang, 2010). Consequently, severe air pollution episodes characterized by high O₃ concentration and particulate matter are often encountered in Beijing summertime (Tang, 2004), with the potential to impact regional and global climate (Zhang et al., 2007).

Gasoline emission due to fuel handing and storage at gas stations represents a major component of the VOC inventory in China. It was estimated that near 187.6 kt of VOCs were emitted into the atmosphere from gas stations all over China in 2002 (Shen et al., 2006). As the host of the 2008 Summer Olympic Games and due to international concerns on athletes' health during competition, the Beijing municipal administration pledged to improve Beijing's air quality and present a "Green Olympic Games". Since 2002, a series of emission control measures have been implemented in the Beijing City area, especially targeting at VOCs. By May 2008, the Beijing Environmental Protection Bureau (BEPB) has shut down 144 gas stations and storage facilities for failure to comply with the vapor recovery rule that requires all the gas pumps install specially designed nozzle to collect vapors from the vehicle's gas tank and return these collected vapors to the service station's underground storage tank.

Despite different refinery techniques and crude oil origins, typical gasoline mainly consists of C₄–C₁₂ hydrocarbons (i.e., paraffins, naphthenes, and olefins) and substantial amount of antiknocking additives, which prevent gasoline from autoignition under a high compression ratio to improve engine performance and achieve a higher fuel efficiency. Gasoline is typically classified by an octane number, a measure of resistance of gasoline to autoignition with references to iso-octane as No. 100 and *n*-heptane as No. 0. In this work, we consider the research octane numbers, i.e., RON. Currently, aromatics (i.e., benzene, toluene, xylenes, and ethylbenzene) and oxygenate

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compounds, such as methyl tertiary butyl ether (MTBE), methanol and ethanol, are the most widely used antiknocking additives. Most of the aromatics have adverse effects on human health after either chronic or acute exposure. Particularly, benzene is classified as a carcinogen by the world health organization (WHO) and is primary released into the atmosphere through fugitive emission due to its use in gasoline and industrial solvent. Moreover, aromatics are also considered as highly reactive VOCs (Suh et al., 2002, 2003; Atkinson and Arey, 2003; Zhao et al., 2005) and oxidation of aromatic hydrocarbons plays an important role in the nucleation and growth of secondary organic aerosols (Zhang et al., 2004b; Zhao et al., 2006; Wang et al., 2010). Thus, fugitive gasoline emission from gas stations can contribute significantly to O₃ production potential. Oxygenate additives can add "oxygen" into the fuel and help gasoline burn more completely, reducing toxic exhaust emissions. For example, methanol has been suggested to be a promising alternative fuel for gasoline (Reed and Lerner, 1973). Since methanol has only one carbon atom, it can burn much cleanly and exhaust nearly only carbon dioxide and water. Methanol blended gasoline can significantly reduce carbon monoxide (CO), NO_x, and aldehyde emissions. Despite the environmental benefits, oxygenate gasoline additives also cause health concerns. For instance, inhalation of MTBE vapor can cause damage to human organs and it is also considered as a possible carcinogen (US EPA report 600/R-94/217). Because methanol is practically odorless and has a high toxicity in human, people may be unaware of exposure to high level of methanol vapor and suffer metabolic acidosis and ocular toxicity (Tephly, 1991). Hence, speciation and quantification of VOCs in the gasoline plume from gas stations are of importance to establish accurate VOC emission inventories, to assess its impact on O₃ production potential, and to evaluate its effects on public health, especially for residents in the immediate vicinity of the gas stations.

As part of the 2008 Campaign of Air Quality Research in Beijing and Surrounding Regions (CAREBeijing 2008), measurements of VOC plumes originating from eight gas stations were conducted using a PTR-MS onboard a mobile laboratory to characterize emissions from gas stations. The performance of the PTR-MS has been validated by

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inter-comparison with an on-line GC system. The advantage of this work lies in the combination of the mobility of the mobile laboratory and the high sensitivity and fast time-response instrumentation. Aromatics and oxygenated additives in these gasoline plumes are the focus, because of their significant contribution to photochemical O₃ production, secondary organic aerosol formation, and public health concerns.

2 Experimental

2.1 Mobile Laboratory and PTR-MS

The PTR-MS was onboard a mobile laboratory (ML), which was modified from an IVECO Turin V diesel vehicle. A detailed description of the ML and the onboard instrumentation has been provided by Wang et al. (2009). Only information relevant to the present work is briefly introduced here. The ML was 6.6 m long, 2.4 m wide, and 2.8 m high, with a total payload of about 2.7 metric ton. Besides PTR-MS, the ML was equipped with a suite of research grade commercial instruments for both aerosol and gaseous species measurements. The NO_x data used in this work was measured by an ECOTECH 9841A chemiluminescence NO_x analyzer with a 0.4 ppbv detection limit at 1 s response time. To prevent self-contamination, the ML was powered by two sets of 12 V/110 Ah lead rechargeable batteries during on-road measurements, which lasted up to about four hours. All sampling inlets were mounted on the front top of the ML, about 3.2 m above the ground. The VOC inlet was made of a 1.5 m long 1.6 mm ID PFA tubing and the sampling rate was about 350 standard cubic centimeters per minute (sccm) to achieve a residence time less than 1 s.

The PTR-MS (Hansel et al., 1995) was a commercial instrument manufactured by Ionicon Analytik. In operation, water molecules were first ionized by a hollow cathode discharge ion source into hydronium ions (H₃O⁺), which then reacted with VOC molecules through proton-transfer reactions inside a drift-tube under a well-defined electric field. The protonated VOC species (R⁺) were further analyzed by a quadrupole

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mass spectrometer. The detailed PTR-MS operating conditions have been introduced by Fortner et al. (2009). Quantification of the VOC analytes was based on kinetic-limited calculations (Lindinger et al., 1998; Zhao and Zhang, 2004) and calibrations with commercial standard mixtures (Spectra Gases Inc.) from the USEPA TO-15 target compounds list. A custom made catalytic converter (Fortner et al., 2009) was used for both background checks and calibration, which was typically before or after each measurement trip.

In this work, pentenes, benzene, toluene, C₈-aromatics, C₉-aromatics, and methanol were identified and quantified at *m/e* 71, 79, 93, 107, 121, and 33, respectively (de Gouw and Warneke, 2007). Although the molecular weight of MTBE is 88, it exclusively fragments into *m/e* 57 after protonation, as confirmed by calibrations with commercial MTBE standards (Apel-Riemer Environmental Inc.). In addition, butenes were also detected at *m/e* 57 with a similar calibration factor. Based on the analysis of canister samples taken in Beijing during August 2005, Song et al. (2008) identified the gasoline emission profile, which contained about 4.1 % butenes and 4.7 % MTBE by volume. Accordingly, we attributed 47 % of the *m/e* 57 signal intensity to butenes and the other 53 % to MTBE. The detection limit (defined as 3σ of the background noise) of each VOC was less than 0.5 ppbv except for methanol, with a value of 2 ppbv due to its higher background level. Although gasoline contained significant portion of other hydrocarbons, most of them were alkane species and can not be detected by PTR-MS effectively (Arnold et al., 1998).

2.2 GC/MS/FID VOC measurement

An on-line automated gas chromatography system with mass spectrometry and flame ionization dual-detectors (GC/MS/FID, Varian CP-3800 and Saturn 2200 MS) was deployed to measure C₁-C₁₁ VOCs on the campus of Peking University during the campaign. The inlet of the system was set up on the roof of a six-story building (~25 m above ground). The on-line GC/MS system used here is a modification described by Chang et al. (2010). A built-in cryo-trap packed with fine glass beads was cooled with

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liquid nitrogen to -170°C for trapping. Air sample was drawn from the sample inlet through the cryo-trap at a rate of 12 ml min^{-1} for 20 min, which provided an aliquot of 240 ml air sample for each analysis. Desorption was made by flash heating of the trap to 85°C , and a stream of ultra-high purity helium (99.9999%) was used to flush the trapped hydrocarbons onto the columns. A glass Y-splitter separated the flow to two columns, i.e., a PLOT column (Chrompack; $30\text{ m} \times 0.32\text{ mm}$; $df = 5.0\text{ }\mu\text{m}$) connected to FID for separation and detection of $\text{C}_2\text{-C}_4$ hydrocarbons, and a DB-1 column (J&W; $60\text{ m} \times 0.32\text{ mm}$; $df = 1.0\text{ }\mu\text{m}$) connected to MS for the separation and detection of $\text{C}_5\text{-C}_{11}$ hydrocarbons, $\text{C}_1\text{-C}_3$ halogenated hydrocarbons, ethers, esters, and other VOCs. The GC oven started at -15°C for 1.5 min, ramped to 0°C at $10^{\circ}\text{C min}^{-1}$, to 140°C at $5^{\circ}\text{C min}^{-1}$, to 180°C at $20^{\circ}\text{C min}^{-1}$, and ended at 180°C for 9.5 min. The mass spectrometer detector was operated in the total ion current (TIC) mode, but only one or few ions (usually the primary ion or ions with less interference in chromatogram) for each target compound was used for quantitative analysis in order to reduce interference. Four internal standards (bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5, and 1-bromo-4-fluorobenzene) were blended in for each injection aliquot to confirm the stability of MS and to ensure data quality. Precision for measured species was evaluated by repeated 7 analyses of a standard mixture at around 1 ppbv. The precisions (one standard deviation) and detection limits of the upgraded method for most species were 0.5–2% and 5–20 pptv, and the time resolution for the NMHC dataset was 1 h.

2.3 Gas station plume measurement

Eight gas stations, located around the northwest corner of the 4th and 5th ring loops of the Beijing City (denoted as G1 to G8 in Fig. 2), were sampled by the ML on 6 and 10 August 2008. These gas stations were chosen since the traffic conditions were fairly smooth and plumes due to traffic jam could be avoided. The measurement time was between 8 a.m. and 12 p.m., when morning rush hours had passed and gas stations were engaged in typical business activity. Neither strong precipitation nor high wind speed (~ 0.3 to 0.6 m s^{-1}) were encountered during the measurements. Ambient

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temperature and relative humidity (RH) remained steady. The location, time of each measurement, and detailed meteorological conditions were summarized in Tables 1 and 2. Typically, the ML was selectively parked at the downwind side of the gas station, about 15 m from the fueling islands. Self-contamination was avoided by using the rechargeable battery sets. The PTR-MS was set in selective ion monitor mode (SIM) and scanned methanol, MTBE, benzene, toluene, C_8^- and C_9^- aromatic compounds, and twenty masses for 1 s each consecutively thus to achieve a time resolution of $\sim 25\text{ s}$. Other trace gases, including NO_x and meteorological parameters were also continuously monitored at 1 Hz. The detailed operating procedure of the ML has been provided by Wang et al. (2009).

2.4 Gaussian plume model

We considered a gas station as a point source emitter due to both refueling operations and evaporations from storage facility. As the plume travels downwind, it diffuses both vertically and horizontally and consequently its concentration is normally distributed in either direction. Therefore, a Gaussian plume model can be used to simulate the atmospheric diffusion process and to evaluate fugitive gasoline emission rate from the gas stations. Specifically, the model is based on the following assumptions: (1) the VOC concentrations in the plume are under steady state; (2) the mass within the plume is conserved; (3) wind and eddy diffusivities are constant as the plume traveled downwind. The Gaussian plume model is expressed as (Seinfeld and Pandis, 1998):

$$C(x, y, z) = \frac{Q}{2\pi u \sigma_y \sigma_z} \left\{ \exp\left(\frac{-(z-h)^2}{2\sigma_z^2}\right) + \exp\left(\frac{-(z+h)^2}{2\sigma_z^2}\right) \right\} \left\{ \exp\left(\frac{-(y)^2}{2\sigma_y^2}\right) \right\} \quad (1)$$

where C is the concentration of the VOC species at the point of observation denoted by coordinates (x, y, z) , Q is the source emission rate in g s^{-1} , u is the wind speed in m s^{-1} , and h is the height of the point source (taken as 1 m here). σ_z and σ_y are vertical and cross-wind plume distribution, respectively and are defined according to

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Figure 5 displays the box plots of the emission rates of VOCs in the plumes detected at the eight gas stations and Fig. 6 presents the corresponding bar plots of averaged VOC emissions at each gas station. Since alkanes cannot be detected by the PTR-MS, only eight VOC species are reported here, which account for about 34 % of the total gasoline emission (Song et al., 2008). It is shown that gasoline emissions from the gas stations vary significantly in terms of the emission rate and chemical composition. The observed highest and lowest emission rates are found at G3 and G6, respectively, with the values of 1.1×10^{-1} and $1.4 \times 10^{-3} \text{ g s}^{-1}$. From our observations at all the gas stations, one refueling process typically takes about 77 s and 16 vehicles are refueled per hour. Assuming all 1442 gas stations in Beijing (BEPB) are operated 24 h a day with the averaged work load, we estimate that about 4.5 mt of gasoline are emitted from gas stations per day or 1.6 kt yr^{-1} . Since about 3409 kt of gasoline have been consumed in Beijing during 2008 (National Bureau of Statistics of China, 2010), the VOC EF for gas stations in Beijing is evaluated as about 0.5 kg t^{-1} , i.e., 0.5 kg of every ton of gasoline supplied in Beijing are emitted into the atmosphere. Shen et al. (2006) reported a gasoline EF of 2.49 kg t^{-1} before the vapor recovery systems were mandatorily installed in all gas stations of Beijing. Hence, our measurements indicate that gasoline emission due to refueling process was significantly reduced during the Olympics period.

The aromatics and oxygenated hydrocarbons can significantly increase gasoline octane rating. The RON rating of MTBE, methanol, benzene, toluene, C_8 - and C_9 -aromatics (both are treated as xylene) are 116, 133, 101, 111, 117, and 117, respectively. In this work, the mass-weighted octane rating of the six detected VOCs is about 114, indicating that they are the major anti-knocking additives. In all cases a substantial amount of MTBE is found, accounting for 19 % to 36 % of the detected VOCs. Although MTBE does not participate in ozone production, its health risks are actively under debate. Currently, MTBE is not classified as a human carcinogen, but it has been suggested that MTBE can be a potential human carcinogen after high dose exposure, especially due to contamination of ground water by leakage from under-ground

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gasoline storage (US EPA, 2011).

Because benzene is a known carcinogen, its content in gasoline is regulated below 2.5 % by volume in China (GB17930-2006). At five gas stations, benzene is found to be more than 4.1 % of the detected VOCs, i.e., about 3 % of the total gasoline vapors, indicating that most gasoline supplied in China contains elevated benzene. Particularly, at G3, a maximum value of 164 ppbv or an average value of 18 ppbv for benzene is observed. In comparison, an average gasoline benzene content is about 1 % by volume in the US and the US EPA's inhalation reference concentration (RfC, i.e., an estimate of a continuous inhalation exposure concentration to people that is likely to be without risk of deleterious effects during a lifetime) for benzene is $3 \times 10^{-5} \text{ g m}^{-3}$ or $\sim 9 \text{ ppbv}$ under standard atmospheric conditions. Averaged benzene concentrations at most of the gas stations appear to cause no serious health concern, except that at G3 benzene concentration is twice as much as the RfC value.

In general, all aforementioned VOCs are detected in all gasoline vapor plumes with noticeable concentrations, except that a substantial amount of methanol is exclusively found in gasoline sold at G3 and G5. However, ethanol, a common additive used in the US, is not present in any brands of gasoline in Beijing and not detected by on-road PTR-MS measurements. Like other oxygenate gasoline additives, methanol has high octane number rating (RON = 133) and combusts at a lower temperature than gasoline, and addition of methanol into traditional gasoline can significantly lower exhaust emission. It is found that 76 % of antiknocking additives in gasoline sold at G3 and G5 are oxygenated in nature, while only 35 % of antiknocking additives are oxygenated in the other cases. Currently, the supplier of G3 and G5 is operating 10 gas stations in the Beijing region, accounting for less than 1 % of the Beijing region gasoline market. Potentially, promoting methanol-containing gasoline in Beijing area can significantly reduce emission inventory in the automobile sector, which contributes to more than half the VOC emission in Beijing (Liu et al., 2005).

Currently, VOC emissions from gas stations have not been properly included in the emission inventory (Streets et al., 2003). Although our results reveal that VOC emission

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from gas stations have been significantly reduced in Beijing due to the implementation of more strict regulations and the improvement in vapor recovery technologies, a substantial amount of gasoline is still emitted into the atmosphere. Therefore, an omission of emissions from gas stations may lead to a significant underestimate in VOC emissions in the Beijing megacity and consequently impacts simulations of photochemical ozone production and nucleation and growth of secondary organic aerosol in atmospheric models (Lei et al., 2004; Fan et al., 2006).

4 Conclusions

On 6 and 10 August 2008, eight gas stations in Beijing were sampled to characterize VOC emissions. This work represents the first in-situ measurements of gas station VOC emissions using a PTR-MS onboard a mobile laboratory. Aromatics, including benzene, toluene, C₈-, and C₉- aromatics, methanol, MTBE, butenes, and pentenes were the major VOCs observed by the PTR-MS. The emission rate of each VOC was calculated using a Gaussian point source plume model. On the basis of measurements at the eight gas stations, we estimated that about 4.5 mt d⁻¹ or 1.6 kt yr⁻¹ of gasoline were emitted from the gas stations in Beijing. The corresponding gasoline vapor emission factor was estimated as about 0.5 kg t⁻¹, showing that gasoline emissions during refueling processes have been decreased substantially since 2002. In addition, the results showed that, on average, the G2 and G6 gas stations were the most effective in fugitive gasoline vapor recovery while the others emitted about 10 times of gasoline as that of G2 and G6, indicating that further reduction of considerable gasoline vapor emissions can be achieved by improving the gasoline vapor recovery efficiency. The average benzene concentration at G3 was twice as much as the US EPA suggested RfC level. The type of octane rating enhancers was significantly different among all gas stations. G3 and G5 had the highest level of the oxygenated blend, about 112 % higher than the others. A noteworthy air pollution control strategy is to enforce methanol-blended fuel to reduce CO and other toxic automobile emissions. Our results indicate

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that emissions from gas stations represent an important source for VOCs in megacity Beijing and need to be properly included in emission inventory to assess their roles in photochemical ozone production and secondary organic aerosol formation.

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14735

Table 1. Summary of the gas station measurement trip on 6 August 2008.

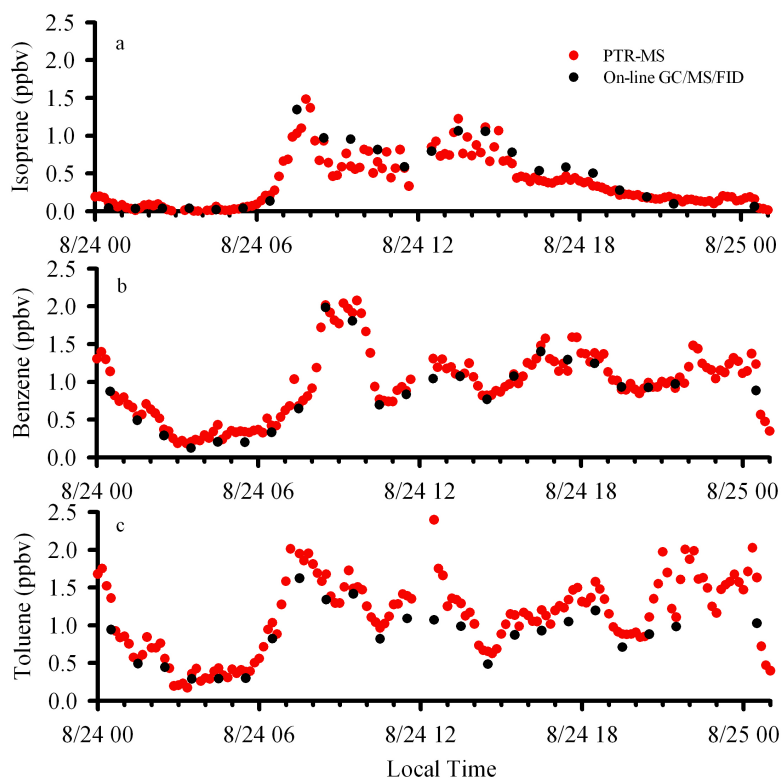
Gas station	Gas station location	Number of gasoline plumes	Duration measurement	Wind direction and speed	T (°C) and RH (%)
G1	116° 18' 34.6" E 39° 59' 56.94" N	4	08:14–08:29	N 0.58 m s ⁻¹	27.3 72.6
G2	116° 18' 29.74" E 40° 01' 14.74" N	5	08:41–09:01	N 0.56 m s ⁻¹	27.7 70.6
G3	116° 16' 33.71" E 40° 01' 15.92" N	3	09:16–09:31	N 0.34 m s ⁻¹	27.3 70.1

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Table 2. Summary of the gas station measurement trip on 10 August 2008.

Gas station	Gas station location	Number of gasoline plumes	Duration measurement	Wind direction and speed	T (°C) and RH (%)
G4	116° 17' 51.9" E 40° 02' 1.58" N	5	09:58–10:13	N 0.38 m s ⁻¹	26.8 84.3
G5	116° 19' 42.6" E 40° 02' 08" N	5	10:28–10:34	N 0.50 m s ⁻¹	26.9 80.8
G6	116° 19' 45.6" E 39° 58' 32.4" N	3	11:10–11:26	N 0.31 m s ⁻¹	26.1 84.1
G7	116° 19' 30.6" E 39° 57' 57" N	5	11:32–11:46	N 0.24 m s ⁻¹	26.7 82.1
G8	116° 18' 38.4" E 39° 58' 52.2" N	3	11:55–12:09	N 0.32 m s ⁻¹	27.0 83.1

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**Fig. 1.** Inter-comparison between the PTR-MS and the GC/MS/FID system in (a) isoprene, (b) benzene, and (c) toluene measurements on 24 August at the Peking University ground site.

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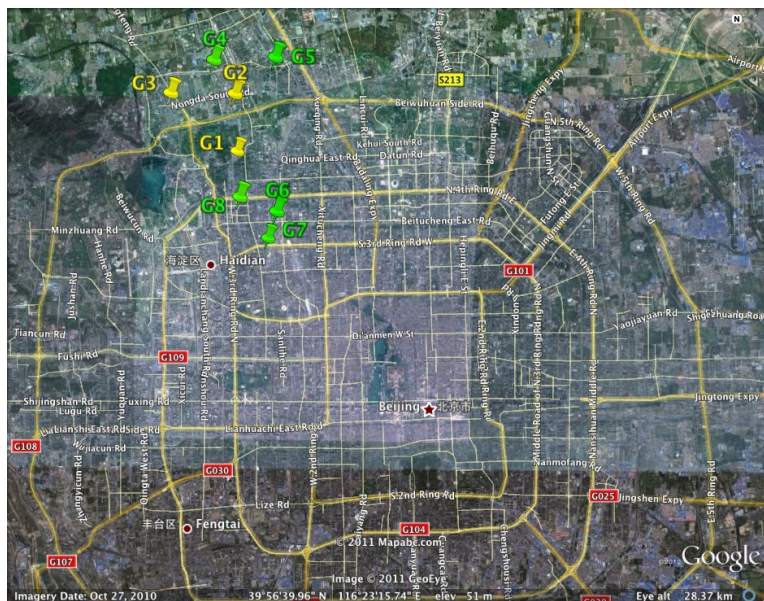


Fig. 2. Locations of the eight gas stations visited by the ML on 6 (yellow marker) and 10 August (green marker).

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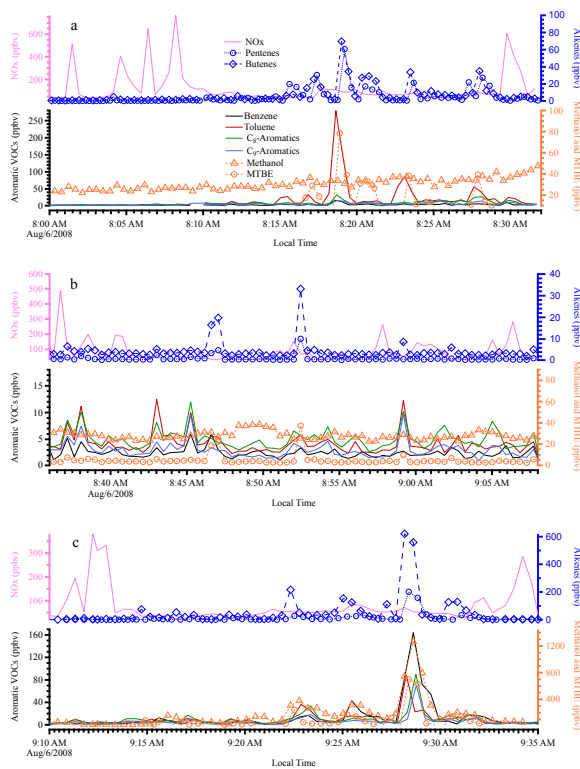


Fig. 3. Aromatics, methanol, MTBE, butenes, pentenes and NO_x observed at (a) G1, (b) G2 and (c) G3. Transient high levels of NO_x are due to fresh on-road emissions.

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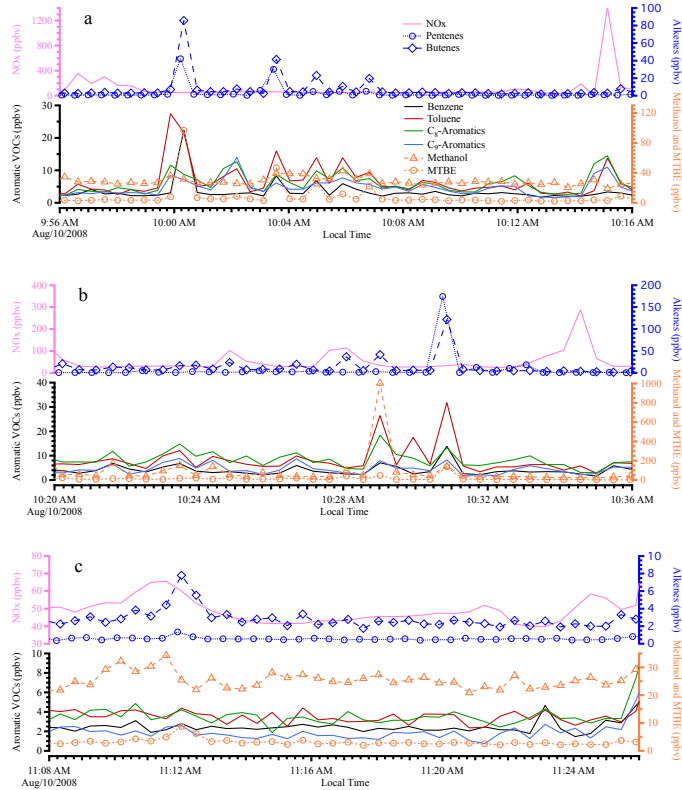


Fig. 4. Aromatics, methanol, MTBE, butenes, pentenes and NO_x observed at (a) G4, (b) G5, (c) G6, (d) G7, and (e) G8. Transient high levels of NO_x are due to fresh on-road emissions.

14741

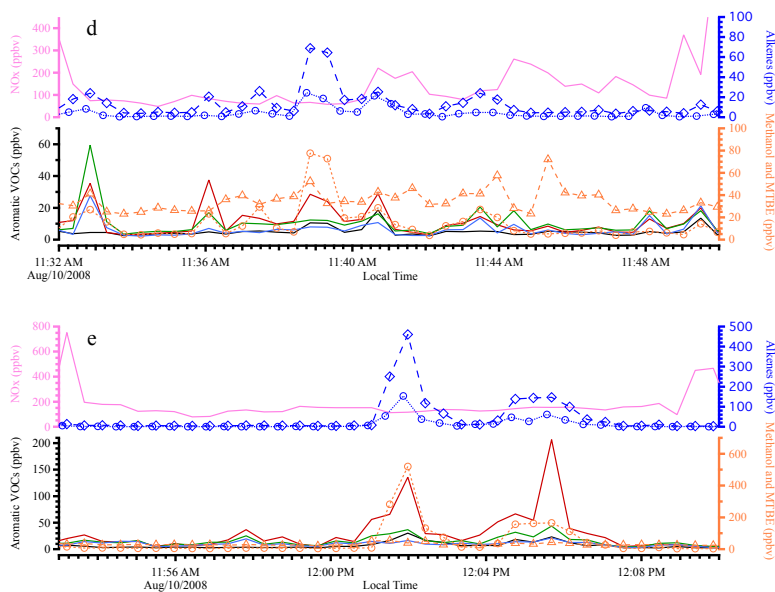


Fig. 4. Continued.

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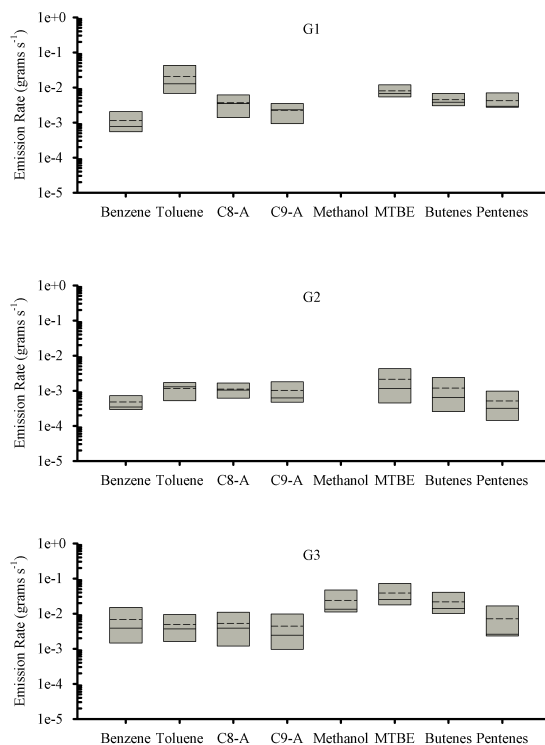


Fig. 5. Box plots of calculated emission rates (g s^{-1}) of benzene, toluene, C_8 -aromatics ($\text{C}_8\text{-A}$), C_9 -aromatics ($\text{C}_9\text{-A}$), methanol, MTBE, butenes and pentenes at all eight gas stations. Each box shows the minimum and maximum emission rates of the species and the dash and solid lines indicate the mean and median values, respectively.

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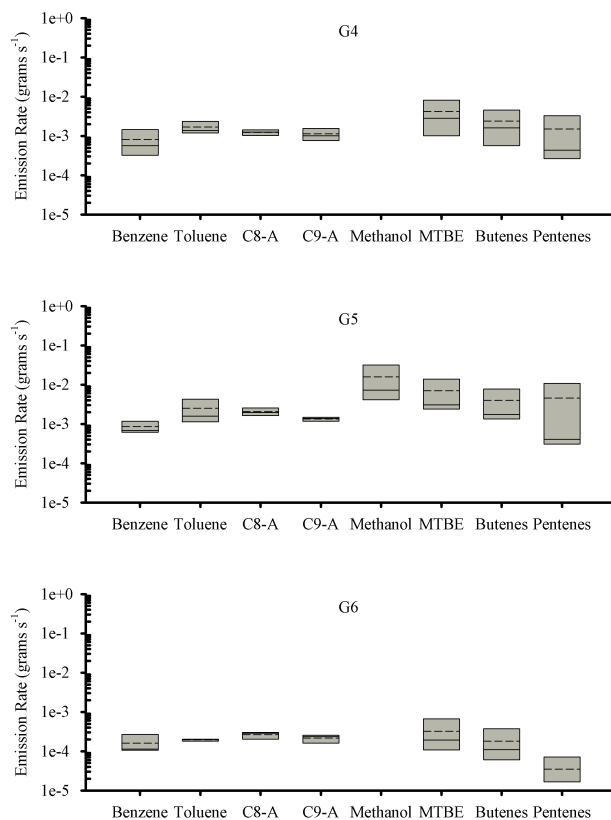


Fig. 5. Continued.

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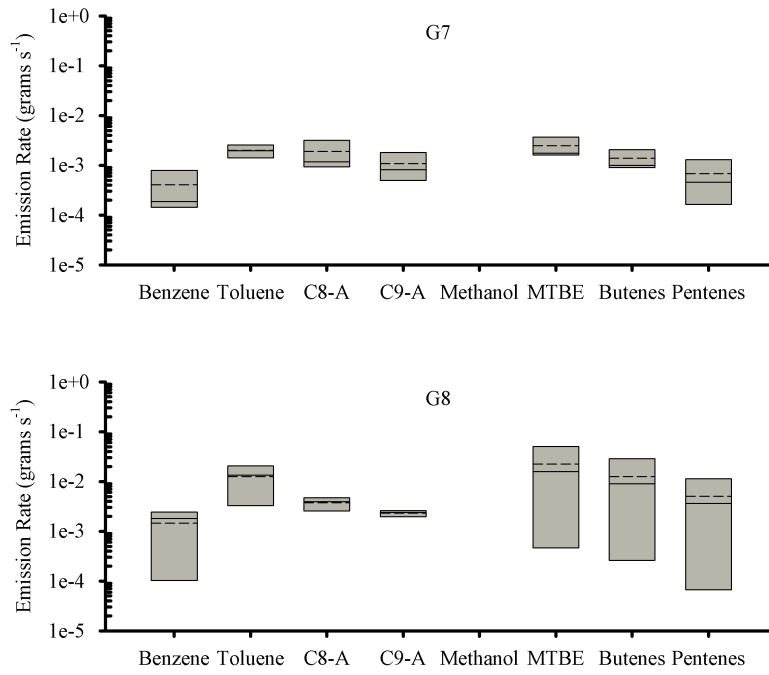


Fig. 5. Continued.

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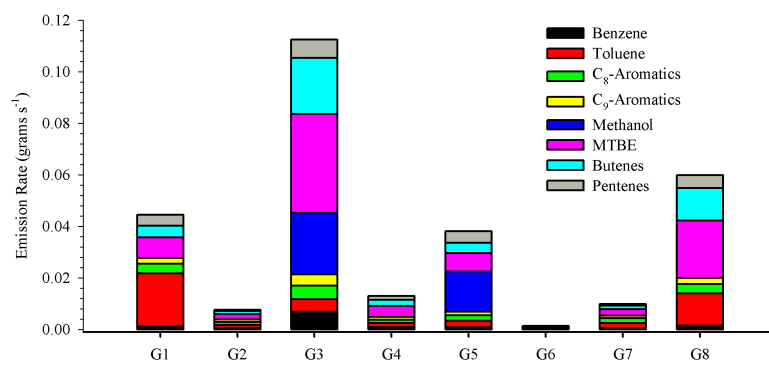


Fig. 6. Averaged total observed VOC emissions from the eight gas stations.

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