Ambient Volatile Organic Compounds in a Suburban Site between Beijing and Tianjin: Concentration Levels, Source Apportionment and Health Risk Assessment

Yuan Yang[1, 2], Dongsheng Ji[1], Jie Sun[1], Yinghong Wang[1], Dan Yao[1], Shuman Zhao[1], Xuena Yu[3], Limin Zeng[3], Renjian Zhang[1], Hao Zhang[5], Yonghong Wang[1,4], Yuesi Wang[1,2,6*]

[1] Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

[2] University of the Chinese Academy of Sciences, Beijing 100049, China

[3] State Joint Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

[4] Institute for Atmospheric and Earth System Research / Physics, Faculty of Science, P.O.Box 64, 00014 University of Helsinki, Helsinki, Finland

[5] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, China

[6] Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

Revised to: Science of The Total Environment

Corresponding author: wys@mail.iap.ac.cn; yonghong.wang@helsinki.fi

Abstract

Volatile organic compounds (VOCs) have vital implications for secondary pollutants, atmospheric oxidation and human health. Ambient VOCs were investigated using an online system, gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID), at a suburban site in Xianghe in the North China Plain from 6 November 2017 to 29 January 2018. Positive matrix factorization (PMF) receptor model was applied to identify the major VOC contributing sources. Four-step health risk assessment method was used to estimate risks of all risk-posing VOC species. A total of 101 VOCs were quantified, and the mean concentration of total VOCs was 61.04±65.18 ppbv. The VOCs were dominated by alkanes (38.76%), followed by alkenes, aromatics, halocarbons, OVOCs, acetylene and acetonitrile. The results of PMF revealed that vehicle exhaust, industrial emissions, liquefied petroleum gas & natural gas, solvent utilization and secondary and long-lived species contributed 31.0%, 26.4%, 18.6%, 13.6% and 10.4%, respectively, to the total VOCs. Pollutant-specific and source-specific noncarcinogenic and carcinogenic risk estimates were conducted, which showed that acrolein and vehicle exhaust had evident noncarcinogenic risks of 4.9 and 0.9, respectively. The carcinogenic risks of specific species (1,3-butadiene, acetaldehyde, benzene, chloroform and 1,2-dichloroethane) and identified sources were above the United States Environmental Protection Agency (USEPA) acceptable level (1.0×10^{-6}) but below the tolerable risk level (1.0×10^{-4}). Vehicle exhaust was the largest contributor (56.2%) to noncarcinogenic risk, but solvent utilization (32.6%) to carcinogenic risk. Moreover, with the evolution of pollution levels, almost all VOC species, contributions of alkenes, aromatics, solvent utilization and vehicle exhaust, and pollutant-specific and source-specific risks increased continuously and noticeably. Collectively, our findings unraveled the importance of alkenes, aromatics, solvent utilization and vehicle exhaust in the evolution of pollution levels. Future studies should consider targeting these VOC groups and sources when focusing on effective reduction strategies and assessing public health risks.

Keywords: VOCs; source apportionment; health risk assessment; vehicle exhaust; solvent utilization

1 Introduction

Overwhelming quantities of VOCs are emitted into the troposphere from anthropogenic sources and biogenic sources (Chen et al., 2019; Li et al., 2019b). VOCs are not merely critical precursors to ground-level ozone (O_3), secondary organic aerosol (SOA), peroxyacetyl nitrate (PAN) and polycyclic aromatic hydrocarbons (PAHs), which have a strong influence on the oxidation capacity of the troposphere (Gentner et al., 2017; McDonald et al., 2018), but are unequivocally harmful to human health and are occurring in close proximity to populated areas (Bolden et al., 2015). For instance, benzene, the simplest aromatic VOC, is listed as a toxic air contaminant under the USA Clean Air Act (CAA) in section 112 (https://www3.epa.gov/airtoxics/orig189.html) and is even classified as a known human carcinogen (IARC Group 1[1]) by the International Agency for Research on Cancer (IARC). Chronic exposure to elevated levels of benzene can reduce the production of both red and white blood cells from bone marrow in humans, resulting in aplastic anaemia (http://www.inchem.org/documents/ehc/ehc/ehc150.htm). Epidemiological studies have shown that toluene (IARC Group 3), ethylbenzene (IARC Group 2B) and xylenes (IARC Group 3) could increase the odds of low birth weight, rhinitis and cardiovascular disease (Bolden et al., 2015; Halliday et al., 2016). Consequently, vast multitudes of studies on VOCs are being conducted globally, covering measurement techniques (Wang et al., 2014; Bourtsoukidis et al., 2017), chemical mechanisms (Atkinson and Arey, 2003; Atkinson et al., 2006), reactivity scales (Carter, 1994; Derwent et al., 1998), emission inventories (Bo et al., 2008; Huang et al., 2011; Wu and Xie, 2017; Zhao et al., 2017; Zhou et al., 2017), health risk assessment (Li et al., 2014b; Bari and Kindzierski, 2017) and removal technology (Domeno et al., 2010; Sui et al., 2016; Wolowiec et al., 2017).

---

[1] Group 1: Carcinogenic to humans; Group 2A: Probably carcinogenic to humans; Group 2B: Possibly carcinogenic to humans; Group 3: Not classifiable in terms of its carcinogenicity to humans; Group 4: Probably not carcinogenic to humans.

Rising anthropogenic interferences due to astonishing economic growth and rapid industrialization and urbanization in China have triggered a dramatic increase in VOCs since the Chinese Economic Reform began in 1978 (Wu and Xie, 2017), particularly in some highly industrialized and densely populated regions, e.g., North China Plain (NCP) (Li et al., 2015b; Qi et al., 2017), Yangtze River Delta (YRD) (Shao et al., 2016; Xu et al., 2017), Pearl River Delta (PRD) (Lu et al., 2013; Ou et al., 2015) and Sichuan Basin (SB) regions (Li et al., 2014a). Over the past several decades, the abundance and speciation of VOCs, source apportionment of VOCs and the relationship of VOCs with O_3 and SOA in NCP, which are mainly concentrated in the megacities of Beijing and Tianjin, have been comprehensively studied (Guo et al., 2017). The common findings in the NCP region were that alkanes and aromatics were the most abundant VOCs (Duan et al., 2008; Wang et al., 2015); vehicle-related emissions were the most predominant contributor to VOCs (Song et al., 2007; Shao et al., 2009); the photochemical O_3 formation in Beijing was VOC-limited (Guo et al., 2017). To tackle the problem of severe air pollution, China has implemented active clean air policies in recent years. As a consequence, the emissions of major air pollutants have decreased during 2010–2017 as follows: -62% for SO_2, -17% for NO_x, -27% for CO, -38% for PM_{10}, -35% for $PM_{2.5}$, -27% for BC and -35% for OC (Zheng et al., 2018). However, nonmethane volatile organic compounds (NMVOCs) emissions are estimated to have increased by 11% because China lacked effective emission control measures on NMVOCs (Zheng et al., 2018).

The average annual concentrations of PM_{10}, $PM_{2.5}$, SO_2, NO_2 and CO in Langfang in 2017 (http://www.lfhbj.gov.cn/) were 102, 60, 14, 48 and 2900 ug/m^3, dropping 8.93%, 9.09%, 22.22%, 7.69% and 17.14%, respectively, compared with 2016. These official statistics showed that the air quality has substantially improved in Langfang. However, relatively few research studies concerning the current situation of VOCs pollution in Xianghe have been completed (Xin et al., 2015; Li and Lu, 2017). Limited available studies have mainly focused on the determination of the concentration levels and seasonal variation of VOCs. For example, the study conducted from 12 September to 10 October 2012, in which 56 VOCs were measured, reported that the average concentration of total VOCs in Xianghe was 28.2 ppbv with the highest concentration being 79.4 ppbv in April and the lowest being 5.8 ppbv in August, and aromatics were the highest abundant, accounting for 37.1%, followed by halocarbons (30.2%), alkanes (26.8%), and alkenes (10.5%) (Xin et al., 2015). These measurements provided the first snapshot of VOC concentrations in Xianghe. However, field measurements online of VOCs in Xianghe remain scarce. To further advanced our understanding of VOCs pollution, more measurements of ambient VOCs in Xianghe are still needed.

In this study, a three-month campaign was carried out at Xianghe, a typical suburban site located between the megacities of Beijing and Tianjin from 6 November 2017 to 29 January 2018. Continuous measure atmospheric VOCs was made using an electronic cryogenic technology for preconcentration and a GC-FID/MS for separation and detection. The objectives of the present study are to (1) determine the ambient VOC pollution level, (2) identify and apportion the major sources, and (3) screen the human health risk assessment of risk-posing VOC species and sources. To our knowledge, this study represents the first online field observations of VOCs in Xianghe. The data collected here are unique and valuable. The results from this work can provide useful information for policy-makers to develop strategies to alleviate air contamination in Xianghe.

2 Methodology

2.1 Sampling-site description

The sampling site is located at the Xianghe Atmospheric Observatory (39.798°N, 116.958°E; 15m above sea level). The sampling site is a typical suburban site in the serious pollution region, the Beijing–Tianjin–Hebei large urban region, which is approximately 50 km southeast of Beijing, 75 km northwest of Tianjin, and 35 km northeast of Langfang in Hebei province. The unique geographical location makes it an indispensable platform in Beijing air pollution warning system and plays an important strategic role in regional air pollution research. The sampling site is approximately 4 km west of the downtown center and is surrounded by residential areas and agricultural land (see Figure 1).

2.2 VOCs Measurements

Ambient VOC samples were analyzed with a time resolution of 1 h using a custom-built gas chromatography-mass spectrometry/flame ionization detector (GC-MS/FID). A complete analysis cycle for ambient VOC measurements by the online GC-MS/FID system includes five stages: preparation, sampling and preconcentration, injection/GC analysis, idle/GC analysis, and back purge/GC analysis (Wang et al., 2014). In the preparation stage, air samples were vented from the sampling and pre-concentration system via the pump, which could reduce or avoid interferences by previous samples. In addition, temperatures for H_2O and enrichment traps during the preparation stage were set at their corresponding values for the sampling and pre-concentration stage. In the sampling and preconcentration stage, air samples were drawn into the FID channel and MS channel for VOCs enrichment. The temperatures of the enrichment traps for both channels were set at -150℃. In the injection/GC-analysis stage, The concentrated VOCs in the enrichment traps were volatilized by thermal desorption at 110℃ and were injected into the GC system by Helium carrier gas. After the 1 minute injection, GC analysis was continued for VOCs separation and detection. Moreover, the sampling and pre-concentration system shifted to the idle condition. Twenty minutes after the injection/GC-analysis stage, a 5 minutes back purge for the sampling and pre-concentration system was programmed for removing residues in the water management traps and cleaning sampling lines to prevent samples carryover effects. Briefly, samples are collected into GC-MS/FID for 5 min every 1 h at a flow of 60 mL min^{-1}. Both the CO_2 and H_2O were removed in an electronic cryogenic pre-concentrator (TH300, Wuhan Tianhong Environmental protection industry co., LTD, Wuhan, China) before VOC analysis. The air was then thermally desorbed at 100 °C and transferred for analysis in a gas chromatography (GC, 7820A, Agilent Technologies, Santa Clara, CA, USA) coupled with mass spectrometric detector (MSD)/flame ionization detector (FID) (5977E, Agilent Technology, Santa Clara, CA, USA). Dual columns and detectors were applied for the simultaneous analysis of C2-C12 hydrocarbons. C2-C5 hydrocarbons were separated on a PLOT-Al_2O_3 column (15 m×0.32 mm ID×3 µm, J&W Scientific, USA) and were measured by the FID channel. Other compounds were separated on a semipolar column (DB624, 60 m×0.25 mm ID×1.4 µm, J&W Scientific, USA) and were quantified using a quadrupole MS detector. The VOC species measured by GC-MS/FID are listed in Table S1. Several OVOCs species are also measured by the MS channel, including acetaldehyde, acrolein, acetone, propanal, methyl tert-butyl ether (MTBE), n-butanal, methyl ethyl ketone (MEK), methyl vinyl ketone (MVK), methacrolein (MACR), 2-pentanone, pentanal, 3-pentanone and hexanal. Good agreements were found between GC-MS/FID and high-sensitivity proton-transfer-reaction mass spectrometry (PTR-MS) for C3-C4 carbonyls and MVK+MACR, with correlation coefficients larger than 0.90 and slopes ranging from 0.7 to 1.4

(Yuan et al., 2012; Chen et al., 2014; Wang et al., 2014). The GC was programmed for a 35 min run time, with a temperature program as follows: staying in 35°C for 3 minutes, then rising to 180°C at a heating rate of 6°C min^{-1} and keeping it for 5 minutes, then rising to 185°C at a heating rate of 6°C min^{-1} and keeping it for 2 minutes. The MSD was operated with the electron ionization (EI) impact (70 eV), where the ions were detected in the selected ion monitoring (SIM) mode with a minimum of two and maximum of eleven ions being monitored for each time window.

The analyzed compounds were subjected to rigorous quality assurance and quality control procedures (QA/QC). The VOCs detected by FID were quantified by the external standard method, and the components detected by MS were quantified by the internal standard method. Four compounds, i.e., bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5, and bromofluorobenzene, were used as internal standards (Li et al., 2015a). Specifically, the system was calibrated at multiple concentrations in the range of 0.8-8 ppbv by two gas standards, i.e., a mixture of 57 PAMS (provided by Spectra Gases Inc., USA), and a mixture of oxygenated VOCs (OVOCs) and halocarbons (provided by Spectra Gases Inc., USA). Daily calibrations were performed every day, and the variations of target species responses were required to be within ±20% from the calibration curve. R^2 values for calibration curves ranged from 0.941 (n-dodecane) to 1.000 for VOCs, indicating that integral areas of peaks were proportional to the concentrations of target compounds. The method detection limit (MDL) of the online GC-FID/MS system for all measured compounds ranged from 0.003 to 0.092 ppbv and the relative standard deviation (RSD) for measured compounds ranged from 2.1% to 14.9% (Table S1). To check the stability of the instrument, routine calibration was operated periodically, by using a calibration gas with a mixing ratio of 2 ppbv and consisting of 56 kinds of VOC components. The variations between measured and nominal concentrations of the periodically calibration was within 10%. The signal variations of each targeted compound due to system instability were corrected by the signal of CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane) due to its long atmospheric lifetime and quite stable anthropogenic emissions (Yuan et al., 2013; Chen et al., 2014).

2.3 Source apportionment: PMF model analysis

US PMF 5.0 (U.S. EPA, 2014) was comprehensively applied to identify the initial contribution of sources to samples based on the composition or fingerprints of the sources. The method is described in greater detail elsewhere (Paatero and Tapper, 1994; Paatero, 1997) and reviewed briefly here. The PMF is a multivariate factor analytical tool that decomposes the speciated measurement data matrix x of i by j dimensions into two matrices-factor profiles (f) and factor contributions (g):

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

where p is the total number of independent sources, g_{ik} stands for the contribution of k^{th} factor in the i^{th} sample, f_{kj} is the load of j^{th} compound in the k^{th} source and e_{ij} is the relevant residual for each sample/species. Factor contributions and profiles are derived by the PMF model minimizing the objective function Q:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{\sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right] \quad (2)$$

where m and n are the numbers of samples and chemical species, respectively, u represents the uncertainty of each data. The theoretical Q ($Q_{theoretical}$) can be calculated as Eq. (3), and the best PMF solution should have $Q/Q_{theoretical}$ with the value of~1.

$$Q_{theoretical} = i \times j - p \times (i + j) \qquad (3)$$

Two files including species concentrations and uncertainty file are required to be introduced into the EPA PMF 5.0 model. The concentrations file is a matrix (X matrix) of number of samples (column) plus the number of species (row), i.e., 2040×49 in this study. PMF analysis requires a complete data set; in order to reduce the error, the samples with missing values for individual species were excluded rather than replaced by the mean concentrations of the remaining observations (Huang et al., 2017). The equation-based uncertainty dataset is constructed according to the method detection limit (MDL) and error fraction (%). If the concentration is less than or equal to the MDL provided, the uncertainty is calculated using a fixed fraction of the MDL, as Uncertainty=5/6×MDL. If the concentration is greater than the provided MDL, the calculation is defined as $\mathrm{Uncertainty} = \sqrt{(\mathrm{Error\ \ Fraction\ \ } \times \mathrm{concentration})^2 + (0.5 \times \mathrm{MDL})^2}$. Not all 101 measured VOCs are introduced into the PMF model, there are some rules to decide which species should be included or excluded from the PMF model: 1) the chosen species had relatively high concentrations (i.e., ethane, ethylene and propane, the top three species in this study) and/or were typical tracers for specific emissions (i.e., acetylene is marker of combustion sources); 2) highly collinear species, such as iso-butane & n-butane, iso-pentane& iso-pentane, benzene & toluene, m/p-Xylene & o-Xylene are included (Figure S1); 3) species that are highly reactive are excluded, except for the source markers, since they are rapidly reacted away in the ambient atmosphere (Shao et al., 2016; Zheng et al., 2017; Li et al., 2019a); 4) species were incorporated in PMF analysis based on their potential toxicity (e.g., 1,3-butadiene, tetrachloroethylene, bromoform). Finally, a total of 48 species, including 9 alkanes, 5 alkenes, 7 OVOCs, 10 aromatics and 15 halocarbons, acetylene and acetonitrile were selected for the input data. In addition, the total measured VOC was included as an input variable in the PMF model to directly obtain source contribution instead of using post-hoc regression analysis in this study. Prior to the PMF model run, the retained species are firstly classified into strong, weak, and bad based on their signal-noise-ratios (S/N). Species with S/N ratios less than 0.5 are grouped into bad and into weak if S/N ratios are in the range of 0.5-1.0 (US EPA, 2014). Finally, 41 species were categorized as strong and seven species (bromomethane, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, 1,2-Dibromoethane, bromoform, 1,1,2,2-Tertrachloroethane and 1,4-Dichlorobenzene) were characterized as weak. Choosing the optimal number of factors in modeling is a critical question. Too many factors will result in meaningless factor profiles, while too few factors will make it difficult to segregate the mixing sources (Bressi et al., 2014; Zheng et al., 2017). The Q-values, source profiles and scaled residuals distributions were examined to obtain the most reasonable factor solutions (Ji et al., 2018; Li et al., 2019a). The uncertainties of the results were assessed by bootstrapping (BS) and displacement (DISP) (Belis et al., 2015; Brown et al., 2015; Debevec et al., 2017). The detailed information as to how to find the optimum factor solutions and the uncertainty estimation are described in the Supplementary material.

Significantly, previous studies have shown that the emissions from biogenic emissions are very limited in wintertime because emission from biogenic sources, eg., isoprene, the most abundant compound from biogenic emissions, is sensitive to a number of environmental parameters, especially temperature and light intensity (Guenther et al., 1993; Pacifico et al., 2009; Ding et al., 2014; Saunier et al., 2017). A latest source apportionment study conducted at the atmospheric monitoring site in the northeast of Langfang city from April 2016 to March 2017 revealed that the contributions of biogenic emission contributed to ambient VOCs in November, December and January were only 0.7%, 0.8% and 2.3%, respectively (Song et al., 2019). In addition, in this study, the linear correlation between isoprene and temperature was extremely poor, fairly correlations between isoprene and three short-lived unsaturated hydrocarbons, i.e., 1,3-butadiene, trans-2-butene and propylene, as showed in Figure S2, which is partial evidence that isoprene produced from local vehicular exhaust may be responsible for wintertime isoprene mixing ratio at Xianghe. Therefore, this study only focused on the source characteristics of anthropogenic emissions.

2.4 Human health risk assessment of VOCs species and sources

A screening-level health risk assessment is the process to characterize the nature and magnitude of health risks to humans and ecological receptors from chemical contaminants and other stressors that may be present in the environment (https://www.epa.gov/risk). To assess public health risks associated with chronic inhalation exposure, a four-step health risk assessment method proposed by the U.S. National Academy of Sciences has become an internationally recognized health risk assessment method and has been used in several studies to screen ambient concentrations of hazardous air pollutants (Bari et al., 2016; Bari and Kindzierski, 2017, 2018).

The USEPA's risk assessment methods are generally used in studies to evaluate carcinogenic and non-carcinogenic risks of pollutant-specific (Li et al., 2014b; Zhang et al., 2017). However, pollutant-specific risk estimates may provide limited information for air quality management due to contributions of multiple sources to each compound. Source-specific risk estimates may add valuable information for understanding potential control strategies for particular sources (Bari and Kindzierski, 2018). Source-risk apportionment, which is a combination of risk assessment and receptor modeling using actual measurements, has been applied in several studies worldwide to determine relative source contributions to human health risks (Wu et al., 2009; Liao et al., 2015; Bari and Kindzierski, 2017).

In this study, out of all detected species, only 31 VOC species with known toxicity values were considered, including 27 noncarcinogenic species and 13 carcinogenic species. Target VOCs and associated toxicity values of health risk assessment can be found in Table S2. Carcinogenic and non-carcinogenic risks of all risk-posing VOC species were evaluated using the EPA inhalation unit risk (IUR, μg m^{-3}) and reference concentrations (RfCs, mg m^{-3}) associated with the exposure concentration (EC) based on the investigation of the Chinese behavior pattern for each trace element. Noncarcinogenic and carcinogenic risk from inhalation exposure to the i^{th} source was estimated as the sum of cancer and noncancer risks of all available n risk-posing VOC species in PMF-derived profiles. Detail information on the health risk estimate procedures are presented in the Supplementary material.

3 Results and discussion

3.1 Overall concentration characteristics of VOCs

In this study, we identified and quantified approximately 101 VOCs from C2 to C12, including 29 alkanes, 11 alkenes, 13 OVOCs, 16 aromatics, 30 halocarbons, acetylene and acetonitrile, as presented in Table S1. The time series and fractions of the hourly VOC category concentrations determined by GC-FID/MS from 6 November 2017 to 29 January 2018 are presented in Figure 2. The gaps in the data were due to maintenance and calibration of GC-FID/MS or power failure.

Over the entire period of the study, the mean concentration of total VOCs was 61.04±65.18 ppbv. Taking the study period as a whole, it was observed that the average composition of VOCs was mainly characterized by alkanes (23.66±23.90 ppbv; 38.76% of the total VOCs), followed by alkenes (12.27±16.47 ppbv; 20.10%), aromatics (8.27±10.30 ppbv; 13.55%), halocarbons (8.47±9.52 ppbv; 11.62%) and OVOCs (5.18±4.80 ppbv; 8.49%) and to a lesser extent by acetylene (4.24±5.20 ppbv; 6.95%) and acetonitrile (0.32±0.84 ppbv; 0.53%)， as presented in Figure 2.

Alkanes were dominated by a strong presence of ethane (9.60±10.08 ppbv), propane (5.07±5.71 ppbv), n-butane (2.63±3.27 ppbv), iso-butane (1.49±1.75 ppbv) and iso-pentane (1.02±1.22 ppbv), representing 93.07% of the alkanes. Approximately 90.82% of the alkenes were mainly characterized by ethylene, propylene and 1-butene, with corresponding average mixing ratios of 8.73±11.73, 2.02±2.99 and 0.39±0.77 ppbv, respectively. M/p-xylene (1.99±2.83 ppbv), benzene (1.98±2.72 ppbv), toluene (1.91±2.35 ppbv), ethylbenzene (0.74±1.09 ppbv) and o-xylene (0.67±1.00 ppbv), collectively called BTEX, together contributed to 88.10% of the aromatics. The top five halocarbon species were methylene chloride (2.71±5.61 ppbv), 1,2-dichloroethane (1.55±2.71 ppbv), chloromethane (0.69±0.56 ppbv), chloroform (0.68±1.27 ppbv) and 1,2-dichloropropane (0.61±1.42 ppbv). These five species accounted for 87.98% of the halocarbons. Among the OVOCs, acetone and acetaldehyde were the two most abundant species with average mixing ratios of 1.79±1.83 ppbv and 1.53±1.49 ppbv, respectively. The top ten VOCs measured in this study are presented in Figure S3 and Table S3 for comparison with those from cities in China. In general, the average concentrations of the top ten VOCs fell within the ranges reported for other Chinese cities (Geng et al., 2010; Guo et al., 2011; An et al., 2014; Zou et al., 2015; Liu et al., 2016a; Wu et al., 2016; Liu et al., 2017). During the entire sampling period, the average concentrations of the top ten VOCs in winter in Xianghe were remarkably greater than those reported in fall in Beijing (Wu et al., 2016) but comparable with those observed in winter in Beijing (Liu et al., 2017). The discrepancies in the VOC average concentrations can be explained by the strong intensity of pollution emissions and the fluctuations in meteorological conditions, such as wind speed, relative humidity, air temperature and pressure, atmospheric stability, the height of the planetary boundary layer, and air mass origins (Song et al., 2018; Yang et al., 2018; Zheng et al., 2018; Li et al., 2019a).

3.2 Source profiles and apportionments of VOCs

In this campaign, a solution of five factors was chosen to best represent VOCsources at Xianghe from 6 November 2017 to 29 January 2018. Figure 3 presents the source profiles i.e., chemical composition of emission sources of each of the identified source factors from the base runs and the average contributions (in ppbv and percentage) of PMF-derived sources to ambient VOCs. The regression relationship between modeled and measured total VOCs concentrations (Figure S4) showed a good fit with square of the correlation coefficient (R^2) of 0.97 suggesting that statistically, observed VOC concentrations at Xianghe were well represented by the PMF model-resolved source factors. Bootstrapping mapping of PMF factor solutions are shown in Table S4, indicating the results were more stable with all factors mapped in BS in 100%, and there are no unmapped BS factors and no swaps with DISP. In order to further determine if source contributions are really different, we summary the error estimation of concentrations and percentages for TVOCs, as showed in Table S5. For each factor, the median bootstrap value is typically within ±5% of the base run value and the interquartile range of the bootstrap run values is mostly within ±5% of the bootstrap median, except for industrial emissions where the interquartile range of the bootstrap run values is 22.7% of the bootstrap median, showing that the percentages were reasonable. The presences of discrepancies of the concentrations/percentages of base value, BS 5th, BS 25th, BS 50th, BS 75th and BS 95th among factors, as showed in Table S5, demonstrate that these contributions are really different. In conclusion, the analysis of uncertainty revealed that the identified source profiles are reasonable in this study.

Factor 1 was characterized by 82.4% of the total 1,4-Dichlorobenzene mixing ratios, 81.8% of the total bromoform mixing ratios, 79.7% of the total 1,1,1-Trichloroethane mixing ratios and 73.6%

of the total carbontetrachloride mixing ratios, which have a long lifespan in the atmosphere (Mccarthy et al., 2007; Li et al., 2015a). Factor 1 also included high mixing ratios of pentanal (72.7%) and hexanal (68.5%). Based on the abundances of long-lived compounds and carbonyls, factor 2 was assigned to secondary and long-lived species, and its contribution to the observed VOCs was 10.4%. Previous studies also reported that secondary formation was still an important source of carbonyls, although carbonyls mainly came from direct anthropogenic emissions in winter (Chen et al., 2014; Li et al., 2015a). Factor 2 consisted of abundant 2-methylhexane, cyclohexane and n-hexane, which are widely used solvents and adhesives in paints (Cai et al., 2010). The loadings of aromatics, including o-xylene, m/p-xylene and ethylbenzene , were high, accounting for 68.1% of o-xylene, 66.8% of m/p-xylene, 62.7% of ethylbenzene, respectively, in the atmosphere; these species are the dominant components of organic paint solvents (Ying et al., 2008; Li et al., 2015a; He et al., 2019). Consequently, we believe that the loadings of VOC species in this source were related to solvent utilization, which contributed 13.6% of the observed VOCs. Factor 3 accounted for 26.4% of the total observed VOCs and for more than 91.7% of our measured 1-pentene, which is often considered as a tracer for industrial emissions (Gao et al., 2014), so we attributed this factor to industrial emissions. Factor 4 was abundant in 1,3-butadiene, propylene, ethylene and benzene, which accounted for 78.3%, 68.7%, 68.3% and 61.4% of the total 1,3-butadiene, propylene, ethylene and benzene, respectively. These chemicals are typical VOCs observed in vehicle exhaust (Ying et al., 2008; Chen et al., 2014; Jun-Lin et al., 2014; Song et al., 2018), suggesting that this factor was associated with vehicle exhaust and was responsible for 31.0% of the total VOCs. Factor 5 contributed 63.1% of measured n-butane, 62.3% of measured n-pentane, 61.8% of measured iso-butane, 58.1% of measured iso-pentane, 40.0% of measured MTBE and 38.1% of measured propane.

It has been reported that these chemicals are representative species in liquefied petroleum gas & natural gas (Wang et al., 2015; Li et al., 2019a). Totally, 18.6% of the observed VOCs were associated with liquefied petroleum gas & natural gas.

The source apportionment results showed that the dominant source in this study was vehicle exhaust (18.7 ppbv, 31.0%), followed by industrial sources (15.9 ppbv, 26.4%), liquefied petroleum gas & natural gas (11.2 ppbv, 18.6%), solvent utilization (8.2 ppbv, 13.6%) and secondary and long-lived species (6.3 ppbv, 10.4%). Comparable results can be found in latest source apportionment study conducted at the atmospheric monitoring site in the northeast of Langfang city (Xianghe city belong to Langfang district) from April 2016 to March 2017 (Song et al., 2019). The source apportionment results in this study were compared with former studies, as listed in Table S6. In these studies, vehicle exhaust was the major source in urban and industrial areas, contributing approximately 27.8-58.3% to the total VOCs. Among the compared Chinese cities, the contribution of vehicle exhaust in this study was lower than that in other cities due to the huge vehicle flows in megacities. The contribution of industrial emissions in this study was higher than the values reported for various Chinese cities. The contribution of liquefied petroleum gas & natural gas was comparable with that in Tianjin, Hong Kong and Wuhan but much lower than that in the Junggar Basin. Given that there are no LPG-fueled vehicles in Xianghe, the emissions of LPG-related VOCs from household and catering were considerable. The contribution of solvent utilization to VOCs in Xianghe is higher than that in Tianjin (Liu et al., 2016b), , lower than that in Lanzhou, Wuhan, Baoji, Chengdu, Nanjing and Hong Kong (Guo et al., 2004; Gao et al., 2014; Jia et al., 2016; Lyu et al., 2016; Xue et al., 2017; Song et al., 2018), and comparable with that in Beijing (Li et al., 2015a). The contribution of secondary and long-lived species was much higher than that in Beijing.

Nevertheless, source identification and source contributions strongly depend upon the model, the study period, and the species and profiles used for source apportionment (Pandolfi et al., 2008; Yuan et al., 2012; Lyu et al., 2016). In summary, the comparison suggests a general characteristic of source apportionments of VOCs, where vehicle-related emissions, industrial sources and solvent utilization were the major contributors to ambient VOCs.

3.3 Pollutant- and source-specific health risk assessment

The HQs and carcinogenic risks of hazardous VOC species via inhalation exposure in the present study and in other cities in China were estimated and are presented in Figure 4 and listed in Table S7. Apart from benzene, o-xylene, bromomethane, trichloroethylene and 1,4-dichlorobenzene, the HQ of other noncarcinogens was higher than that in Beijing (Zhang et al., 2017). With the exception of styrene, the HQ of other aromatics was basically within the values reported for other Chinese cities (Cai et al., 2010; Li et al., 2013; Zhang et al., 2017), as showed in Figure 4a. A noncarcinogenic risk is represented by hazard index (HI). US EPA states that if HI <1, there is no appreciable risk of adverse health effects, while HI >1 indicates a chance of noncancer effects occurring (USEPA, 2009). In our study, HI of the observed noncarcinogenic species was 5.2, so they had significant non-carcinogenic risk. Specifically, among the noncarcinogens, only the HQ of acrolein (4.9) exceeded the value of 1, indicating a obvious noncarcinogenic risk. In contrast, the HI of other noncarcinogens was lower than the value of 1, suggesting no chance of noncancer effects occurring.

Among the carcinogens, as illustrated in Figure 4b and Table S7, with the exception of benzene, trichloroethylene, tetrachloroethylene and vinylchloride, the carcinogenic risks of the four other carcinogens in this study were evidently greater than those reported in Beijing (Zhang et al., 2017).

The excess cancer risk range recommended by the (USEPA, 2009) for public health protection is one in a million (1.0×10^{-6}) acceptable risk level to one in ten thousand (1.0×10^{-4}) tolerable risk level. The carcinogenic risks of 1,3-butadiene, acetaldehyde, benzene, chloroform and 1,2-dichloroethane were above the acceptable level of 1.0×10^{-6} but below a tolerable risk of 1.0×10^{-4}, showing a potential carcinogenic risk (Dutta et al., 2009; Zhang et al., 2012). The cancer risks of other VOC species were below the acceptable level of 1.0×10^{-6}, which means that there might be no obvious cancer risk from these VOC species. In this study, the average cumulative carcinogenic risk (the summation of available individual compound risks) based on personal exposure was 5.4×10^{-5}. Compared with other studies using the same IURs, cumulative carcinogenic risks for personal exposure were higher than average estimates in Tianjin (3.0×10^{-5}) (Zhou et al., 2011) and South Baltimore (4.3×10^{-5}) (Payne-Sturges et al., 2004). The difference in the cumulative cancer risk among these studies may be the result of VOCs species and individual activities magnifying the variability in personal exposure concentrations (Payne-Sturges et al., 2004; Zhou et al., 2011), eg., 13 VOCs in this stuy, but 9 VOCs in Payne-Sturges' study and 5 VOCs in Zhou's study. In short, from pollutant-specific health risk perspective, much more attention should be paid to acrolein, 1,3-butadiene, acetaldehyde, benzene, chloroform and 1,2-dichloroethane.

In addition, health risk was apportioned to the five identified sources by summing the carcinogenic and noncarcinogenic risks of all available risk-posing VOC species in a particular source (Bari and Kindzierski, 2017, 2018). The source-specific noncarcinogenic and carcinogenic risk values are shown in Figure 5a-5b and Table S8. Noncarcinogenic risks of different sources ranged from 0.01 (solvent utilization) to 0.9 (vehicle exhaust), and all noncarcinogenic values were lower than the USEPA safe level (1.0), except for vehicle exhaust, where the noncarcinogenic value was comparable with the safe level, as illustrated in Figure 5a. The source-specific carcinogenic risk of different sources ranged from 1.0×10^{-6} (secondary and long-lived species) to 3.1×10^{-6} (solvent utilization), and all risk values were above the USEPA acceptable level (1.0×10^{-6}) but below the tolerable risk (1.0×10^{-4}). In general, vehicle exhaust posed the greatest noncarcinogenic risk to public health (56.2%), followed by secondary and long-lived species (23.1%), industrial emissions (17.7%) and liquefied petroleum gas & natural gas (2.2%). Solvent utilization posed a relatively low noncarcinogenic risk (0.8%) to public health. Solvent utilization was the largest contributor (32.6%) to carcinogenic risk, followed by vehicle exhaust (30.3%), industrial emissions (15.0%) and Liquefied petroleum gas & natural gas (11.5%). Secondary and long-lived species posed a relatively low carcinogenic risk (10.6%) to public health, as depicted in Figure 5b. In brief, from source-specific health risk perspective, much more attention should be paid to vehicle exhaust and solvent utilization.

It should be mentioned that there are some limitations to our health risk assessment. Noncarcinogenic and carcinogenic risks were calculated based solely on 27 and 13 detected hazardous VOCs, respectively, whereas other potentially important hazardous VOCs, for example, formaldehyde, acetophenone, and cresols/cresylic acid, in the USEPA list of 187 air toxins (https://www3.epa.gov/airtoxics/orig189.html) and 30 urban air toxins (https://www.epa.gov/urban-air-toxics/urban-air-toxic-pollutants) were not measured in this study. It is reported that formaldehyde and BTEX are more serious indoors than outdoors (Wang et al., 2007), and according to the exposure parameters of the Chinese population, the Chinese population spends most of their day indoors (1213 min/day); hence, the estimations can only represent the lower limits. Overall, the resultant inhalation noncarcinogenic and carcinogenic risks estimated here are a reasonable first step for understanding ambient VOC risks to public health in Xianghe.

3.4 Evolution at different pollution levels

Theoretically, determining high and low pollution levels from total VOCs concentrations are more common and reasonable than that from $PM_{2.5}$ concentrations. However, determining pollution levels using total VOCs concentrations are random and unfounded. $PM_{2.5}$ (fine particulate matter with a diameter of less than 2.5 μm) is the premier pollutant of atmosphere pollution in winter in NCP and $PM_{2.5}$ pollution grading standards is clear and specific in the Air Quality Index (AQI) technical regulations (HJ 633-2012) formulated by the Chinese Ministry of Environmental Protection. In view of the above-mentioned facts, in this study, drawing on the $PM_{2.5}$ concentrations as a reference and considering the quantity of samples analyzed, days with average concentrations of $PM_{2.5} <75$, $75 \leq PM_{2.5} <150$, and $PM_{2.5} \geq 150$ μg m^{-3} were defined as clean (C), moderate pollution (MP), and heavy pollution (HP) days, respectively. $PM_{2.5}$ was measured continuously using RP1400-$PM_{2.5}$ instruments at the Xianghe site. The time series of the $PM_{2.5}$ concentrations during the entire observational period are presented in Figure S5.

3.4.1 Concentration variations at different pollution levels

The mean concentrations and fractional contributions of VOC groups at different pollution levels during the entire observational period are shown in Figure 6a-6b. The statical analysis of the results was performed using IBM SPSS Statistics 22. Seen from Figure 6a, the results showed that there was significant difference of the seven VOC groups at $p<0.01$ at same pollution level. At different pollution levels, there was significant difference of alkanes and alkenes at $p<0.001$, but aromatics, OVOCs, halocarbons and acetonitrile at $p<0.01$, and acetylene at $p<0.05$. The statical analysis suggested that the differences are statistically significant.

Figure 6a indicates that nearly all the VOC groups increased continuously and noticeably with the deterioration of the air quality. The mixing ratios of the total VOCs in Xianghe were relatively low on clean days, with an average value of 33.09 ±30.55 ppbv, but increased to 164.12±94.49 ppbv on average on heavy pollution days, among which alkanes were the most abundant chemical groups, accounting for 34.48% (56.59±33.71 ppbv) of the total VOCs. Alkenes and aromatics were two other major components. Their average mixing ratios increased by 576.13% and 485.23%, respectively, on heavy pollution days. Acetylene, which mainly comes from incomplete combustion, and acetonitrile, which is a typical tracer of biomass burning, increased dramatically to 11.67±8.19 ppbv and 1.02±1.43 ppbv on average, i.e., by 477.48% and 540.10%, respectively, compared with that on clean days. The fractional contributions of VOC groups to the total VOCs at different pollution levels are presented in Figure 6b. Visibly, the fractional contribution of alkanes decreased from clean days to heavy pollution days, whereas alkenes and aromatics increased and the others remained nearly constant, indicating the significance of alkenes and aromatics in the evolution process of pollution (Guo et al., 2014).

Table S1 summarizes the average mixing ratios of all 101 VOC species measured in this campaign. It is evident that the average concentrations of alomost all quantified individual species remarkably increased from clean days to heavy pollution days, and their average concentrations on heavy pollution days were 1-8 times higher than those on clean days, which is in good agreement with previous studies (Zhang et al., 2014; Wu et al., 2016; Liu et al., 2017), except for several halocabons (e.g., CFC-113, 1,4-dichlorobenzene and trichloroethylene), where the mixing ratios remained constant. As each hydrocarbon source has its own characteristic chemical composition, variations in chemical compositions may indicate differences in the source contributions (Wang et al., 2010). As listed in Table S9, tracers of gasoline vehicle exhaust, diesel vehicle exhaust, petrochemical industry, paint solvent usage, industrial sources and secondary and long-lived species comprised the top 20 most increased species, suggesting the importance of these sources in the evolution of pollution. Of note, among the top 20 VOC species, eight are toxic hydrocarbons, including 1,3-butadiene, styrene, benzene, methylene chloride, 1,2-dichloropropane, chloroform, 1,1,2-trichloroethane and ethylbenzene, as shown in Table S2. This finding suggested a potential health risk to the public on pollution days. Parallel results were observed in October 2014 in Beijing (Wu et al., 2016).

3.4.2 Source contributions at different pollution levels

Figure 6c-6d illustrates the evolution of source factors to the total VOCs mixing ratios at different pollution levels. In order to determine the significance of the difference in relationships to the uncertainties found for the different contributions, we summary the bootstrap calculation (with 100 bootstraps and using a minimum correlation R-value of 0.6) with the variability in the concentrations and percentages of TVOCs for the factors at different pollution levels, as showed in Table S10 and Table S11. For each factor, the median bootstrap value is typically within ±15% of the base run value (Table S10) and the interquartile range of the bootstrap run values is mostly within ±15% of the bootstrap median at different pollution levels (Table S11), showing that the percentages were reasonable. The presences of discrepancies of the concentrations/percentages of base value, BS 5th, BS 25th, BS 50th, BS 75th and BS 95th among factors at different pollution levels, as showed in Table S10 and Table S11, demonstrate that the differences of these contributions are significant. In conclusion, the evolution of mean concentrations and fractional contributions of PMF-derived sources at different pollution levels in this study was reasonable.

As showed in Figure 6c, nearly all of the source mixing ratio contributions increased continuously with the aggravation of pollution. Industrial emissions and vehicle exhaust were the largest contributors to the total VOCs mixing ratios on clean days, but vehicle exhaust and liquefied petroleum gas & natural gas on moderate pollution days, vehicle exhaust, industrial emissions and solvent utilization on heavy pollution days. The fractional contributions of vehicle exhaust and solvent utilization increased continuously over time, whereas the fractional contributions of industrial emissions and secondary and long-lived species decreased continuously, liquefied petroleum gas & natural gas kept constant on clean days and heavy pollution days, as showed in Figure 6d. On clean days, industrial emissions was the largest contributor (30.2%) to the total VOCs mixing ratios, contributing 10.4 ppbv, followed by vehicle exhaustsolvent utilization (8.6 ppbv, 25.0%) and liquefied petroleum gas & natural gas (5.8 ppbv, 16.7%). Solvent utilization and secondary and long-lived species contributed 4.8 and 4.8 ppbv, accounting for 14.0% and 14.0%, respectively, of the total VOCs. On moderate pollution days, the largest contributor was vehicle exhaust, with 30.3 ppbv, accounting for 26.5% of total VOCs, followed by liquefied petroleum gas & natural gas (29.2 ppbv, 25.6%), solvent utilization (20.7 ppbv, 18.1%), secondary and long-lived species (17.7 ppbv, 15.5%) and industrial emissions (16.4 ppbv, 14.3%). On heavy pollution days, the largest contributor was vehicle exhaust, with 59.0 ppbv, accounting for 28.6% of total VOCs. The second largest contributor was industrial emissions (44.8 ppbv, 21.7%) and solvent utilization (44.6 ppbv, 21.6%). The contributions from liquefied petroleum gas & natural gas and secondary and long-lived species were 35.0 ppbv and 22.7 ppbv, accounting for 17.0 and 11.0%, respectively, of the total VOCs. Compared with that on clean days, the contribution of vehicular exhaust increased to the greatest extent, with a value of 50.4 ppbv, followed by solvent utilization (39.7 ppbv) and

Industrial emissions (34.4 ppbv).

Increases in vehicular exhaust and solvent utilization, industrial emissions, liquefied petroleum gas & natural gas and secondary and long-lived species were responsible for 29.4, 23.2, 20.0, 17.0 and 10.4%, respectively, of the increases in ambient VOCs, indicating that vehicle exhaust, solvent utilization and industrial emissions played a key role in the development of pollution levels in Xianghe. The evidently elevated contributions of vehicle exhaust and solvent utilization can be accounted for by the following facts: 1) Vehicle-related emission was an important source, although more stringent emission standards for new vehicles have been implemented in Beijing-Tianjin-Hebei. As of the end of 2016, the number of vehicles reached 19.22 million, accounting for 32.03% in Beijing-Tianjin-Hebei and its surrounding areas, and the vehicle output in Hebei Province reached 1.29 million, with 29.1% in the Jing-Jin-Ji region (http://www.hetj.gov.cn/res/nj2017/indexch.htm). 2) Solvent use is a major contributor to the increase in VOC emissions, which is estimated to have increased by 52% since 2010, making solvents the largest contributor (36%) to VOC emissions in 2017 in China (Zheng et al., 2018). According to the China Furniture Yearbook, as of the end of 2016, the number of brands in Xianghe was as high as 1500. Consequently, emission reductions of vehicle exhaust and solvent usage are the optimal scheme to reduce the mixing ratio of VOCs in Xianghe.

3.4.3 Health risk assessment at different pollution levels

Noncarcinogenic risk assessment results of VOC species at different pollution levels are shown in Figure 7 and Table S12. HI was 2.7, 7.4 and 15.1, respectively, on clean days, moderate pollution days and heavy pollution days, suggesting a increasing noncarcinogenic risk (Table S12) with the aggravation of pollution. Specifically, compared with that on clean days, the HQ of methylene chloride, 1,3-butadiene, styrene, 1,2-dichloropropane and benzene increased remarkably by a factor of 8.3, 8.2, 7.9, 7.8 and 6.7, respectively, on heavy pollution days. Noticeably, the HQ of acrolein was higher than a safe level (=1) on clean days, posing a clear risk to public health, which should be paid more attention. In contrast, the HI of the other noncarcinogens was lower than a safe level, although it increased gradually with the degradation of air quality.

Carcinogenic risk assessment results of VOC species at different pollution levels are shown in Figure 7 and Table S12. Cumulative cancer risk was 2.8×10^{-5}, 8.3×10^{-5} and 1.5×10^{-4}, respectively, on clean days, moderate pollution days and heavy pollution days, suggesting a increasing cumulative cancer risk (Table S12) with the aggravation of pollution. Cumulative cancer risk estimates on clean days were lower than average estimates in Tianjin and South Baltimore. However, Cumulative cancer risk estimates on moderate pollution days and heavy pollution days were much higher than average estimates in Tianjin and South Baltimore (Payne-Sturges et al., 2004; Zhou et al., 2011). Specifically, the risks of 1,3-butadiene, benzene, chloroform and 1,2-dichloroethane on celan days were above the acceptable level of 1×10^{-6} but below a tolerable risk of 1×10^{-4}, showing a potential carcinogenic risk. The cancer risk of acetaldehyde increased gradually until it exceeded the acceptable level of 1×10^{-6} but below a tolerable risk of 1×10^{-4} on heavy pollution days. Apart from the above-mentioned potentially toxic VOC species, the cancer risks of the others were lower than the acceptable level of 1×10^{-6}, although they increased continuously with the aggravation of pollution.

In addition to the evolution of the noncarcinogenic and carcinogenic risks of VOC species at different pollution levels, significant variations in noncarcinogenic and carcinogenic risks of predicted VOC sources were also observed. As presented in Figure 5c-5d, Table S13 and Table S14, the noncarcinogenic and carcinogenic risks of predicted VOC sources increased noticeably with increasing pollution levels. For the noncarcinogenic risk of predicted sources, as showed in Figure 5c and Table S13 ,vehicle exhaust, industrial emissions and secondary and long-lived species eventually exceeded acceptable safe levels during the transitions from clean days to heavy pollution days, whereas the other sources remained lower than safe levels at different pollution levels. For the carcinogenic risk of predicted sources, as showed in Figure 5d and Table S14, all sources eventually exceeded the USEPA acceptable level (1×10^{-6}) but remained lower than the tolerable risk (1×10^{-4}). These findings revealed that predicted sources exerted increasing noncarcinogenic and carcinogenic risks on the public with the evolution of pollution levels.

4 Conclusions

This study represents the first field online observations of VOCs in Xianghe, focusing on concentration levels and sources of ambient VOCs and their associated risk to public health. Over the entire period of the study, the total VOCs varied greatly from 4.61 ppbv to 511.98 ppbv. The most dominant compounds were alkanes, followed by alkenes, aromatics, halocarbons, OVOCs, acetylene and acetonitrile. Source apportionment analysis identified five sources, namely, vehicle exhaust (31.0%), industrial emissions (26.4%), liquefied petroleum gas & natural gas (18.6%), solvent utilization (13.6%)and secondary and long-lived species (10.4%). Health risk assessment screening indicated that the noncarcinogenic risk of acrolein (4.9) exceeded 1.0, and the carcinogenic risks of all selected VOCs were lower than the tolerable risk (1×10^{-4}). Estimated noncarcinogenic risks for all sources were below a safe level (= 1), with vehicle exhaust (56.2%) was the largest contributor to noncarcinogenic risk. Estimated carcinogenic risks for nearly all sources were above the USEPA acceptable level (1×10^{-6}) but below the tolerable risk (1×10^{-4}), with solvent utilization (32.6%) was the largest contributor to carcinogenic risk. With the aggravation of pollution, the fractional contribution of alkenes, aromatics, vehicle exhaust and solvent utilization increased during the transition, indicating the significances of these VOC groups and sources in the evolution process of pollution. The noncarcinogenic risks of vehicle exhaust, industrial emissions and secondary and long-lived species eventually exceeded acceptable safe levels, and the carcinogenic risks of nearly all sources eventually exceeded the USEPA acceptable level (1×10^{-6}) but remained lower than the tolerable risk (1×10^{-4}), suggesting predicted sources exerted increasing noncarcinogenic and carcinogenic risks on the public with the evolution of pollution levels. We recommend that the priorities for the control of VOC groups and sources include alkenes, aromatics, vehicle exhaust and solvent utilization because of their larger emissions and health risks in Xianghe.

Acknowledgements

This work was supported by the Ministry of Science and Technology of China (No: 2017YFC0210000) and Beijing Major Science and Technology Project (Z181100005418014). All referenced supplemental figures and tables can be found in the supporting information. The authors are grateful to all staff and workers from the Xianghe Atmospheric Observatory of Institute of Atmospheric Physics (IAP) of the Chinese Academy of Sciences for their support during the sampling campaign. We also acknowledge Dr. Tengyue Yu from Beijing Pengyu Changya Environmental Protection Technology Co., Ltd. for technical support.

References

An, J., Zhu, B., Wang, H., Li, Y., Lin, X., Yang, H., 2014. Characteristics and source apportionment of VOCs measured in an industrial area of Nanjing, Yangtze River Delta, China. Atmos Environ 97, 206-214.

Atkinson, R., Arey, J., 2003. Atmospheric Degradation of Volatile Organic Compounds. Chemical Reviews 103, 4605-4638.

Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Rossi, M.J., Troe, J., 2006. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species. Atmos Chem Phys 6, 3625-4055.

Bari, M.A., Kindzierski, W.B., 2017. Concentrations, sources and human health risk of inhalation exposure to air toxics in Edmonton, Canada. Chemosphere 173, 160-171.

Bari, M.A., Kindzierski, W.B., 2018. Ambient volatile organic compounds (VOCs) in Calgary, Alberta: Sources and screening health risk assessment. Sci Total Environ 631-632, 627-640.

Bari, M.A., Kindzierski, W.B., Spink, D., 2016. Twelve-year trends in ambient concentrations of volatile organic compounds in a community of the Alberta Oil Sands Region, Canada. Environ Int 91, 40-50.

Belis, C.A., Karagulian, F., Amato, F., Almeida, M., Artaxo, P., Beddows, D.C.S., Bernardoni, V., Bove, M.C., Carbone, S., Cesari, D., Contini, D., Cuccia, E., Diapouli, E., Eleftheriadis, K., Favez, O., El Haddad, I., Harrison, R.M., Hellebust, S., Hovorka, J., Jang, E., Jorquera, H., Kammermeier, T., Karl, M., Lucarelli, F., Mooibroek, D., Nava, S., Nøjgaard, J.K., Paatero, P., Pandolfi, M., Perrone, M.G., Petit, J.E., Pietrodangelo, A., Pokorná, P., Prati, P., Prevot, A.S.H., Quass, U., Querol, X., Saraga, D., Sciare, J., Sfetsos, A., Valli, G., Vecchi, R., Vestenius, M., Yubero, E., Hopke, P.K.,

2015. A new methodology to assess the performance and uncertainty of source apportionment models II: The results of two European intercomparison exercises. Atmos Environ 123, 240-250.

Bo, Y., Cai, H., Xie, S.D., 2008. Spatial and temporal variation of historical anthropogenic NMVOCs emission inventories in China. Atmos Chem Phys 8, 7297-7316.

Bolden, A.L., Kwiatkowski, C.F., Colborn, T., 2015. New Look at BTEX: Are Ambient Levels a Problem? Environ Sci Technol 49, 5261-5276.

Bourtsoukidis, E., Helleis, F., Tomsche, L., Fischer, H., Hofmann, R., Lelieveld, J., Williams, J., 2017. An aircraft gas chromatograph–mass spectrometer System for Organic Fast Identification Analysis (SOFIA): design, performance and a case study of Asian monsoon pollution outflow. Atmos Meas Tech 10, 5089-5105.

Bressi, M., Sciare, J., Ghersi, V., Mihalopoulos, N., Petit, J.E., Nicolas, J.B., Moukhtar, S., Rosso, A., Féron, A., Bonnaire, N., Poulakis, E., Theodosi, C., 2014. Sources and geographical origins of fine aerosols in Paris (France). Atmos. Chem. Phys. 14, 8813-8839.

Brown, S.G., Eberly, S., Paatero, P., Norris, G.A., 2015. Methods for estimating uncertainty in PMF solutions: examples with ambient air and water quality data and guidance on reporting PMF results. Sci Total Environ 518-519, 626-635.

Cai, C., Geng, F., Tie, X., Yu, Q., An, J., 2010. Characteristics and source apportionment of VOCs measured in Shanghai, China. Atmos Environ 44, 5005-5014.

Carter, W.P.L., 1994. Development of Ozone Reactivity Scales for Volatile Organic-Compounds. J Air Waste Manage 44, 881-899.

Chen, W.T., Shao, M., Lu, S.H., Wang, M., Zeng, L.M., Yuan, B., Liu, Y., 2014. Understanding primary and secondary sources of ambient carbonyl compounds in Beijing using the PMF model.

Atmos Chem Phys 14, 3047-3062.

Chen, X., Millet, D.B., Singh, H.B., Wisthaler, A., Apel, E.C., Atlas, E.L., Blake, D.R., Brown, S.S., Crounse, J.D., de Gouw, J.A., Flocke, F., Fried, A., Heikes, B.G., Hornbrook, R.S., Mikoviny, T., Min, K.-E., Müller, M., Neuman, J.A., amp, apos, Sullivan, D.W., Peischl, J., Pfister, G.G., Richter, D., Roberts, J.M., Ryerson, T.B., Shertz, S., Treadaway, V., Veres, P.R., Walega, J., Warneke, C., Washenfelder, R.A., Weibring, P., Yuan, B., 2019. On the sources and sinks of atmospheric VOCs: An integrated analysis of recent aircraft campaigns over North America. Atmospheric Chemistry and Physics Discussions, 1-39.

Debevec, C., Sauvage, S., Gros, V., Sciare, J., Pikridas, M., Stavroulas, I., Salameh, T., Leonardis, T., Gaudion, V., Depelchin, L., Fronval, I., Sarda-Esteve, R., Baisnée, D., Bonsang, B., Savvides, C., Vrekoussis, M., Locoge, N., 2017. Origin and variability of volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus). Atmos Chem Phys 17, 11355-11388.

Derwent, R.G., Jenkin, M.E., Saunders, S.M., Pilling, M.J., 1998. Photochemical ozone creation potentials for organic compounds in northwest Europe calculated with a master chemical mechanism. Atmos Environ 32, 2429-2441.

Ding, X., He, Q.-F., Shen, R.-Q., Yu, Q.-Q., Wang, X.-M., 2014. Spatial distributions of secondary organic aerosols from isoprene, monoterpenes,β-caryophyllene, and aromatics over China during summer. Journal of Geophysical Research: Atmospheres 119, 11,877-811,891.

Domeno, C., Rodriguez-Lafuente, A., Martos, J.M., Bilbao, R., Nerin, C., 2010. VOC removal and deodorization of effluent gases from an industrial plant by photo-oxidation, chemical oxidation, and ozonization. Environ Sci Technol 44, 2585-2591.

Duan, J., Tan, J., Yang, L., Wu, S., Hao, J., 2008. Concentration, sources and ozone formation potential of volatile organic compounds (VOCs) during ozone episode in Beijing. Atmos Res 88, 25-35.

Dutta, C., Som, D., Chatterjee, A., Mukherjee, A.K., Jana, T.K., Sen, S., 2009. Mixing ratios of carbonyls and BTEX in ambient air of Kolkata, India and their associated health risk. Environmental Monitoring & Assessment 148, 97-107.

Gao, M., Jun-Lin, A.N., Hang, Y.X., Yong-Yu, L.I., 2014. Comparison of PMF and PCA /APCS for VOCs source apportionment in north suburb of Nanjing. Journal of Meteorology & Environment 30, 43-50.

Geng, F., Cai, C., Tie, X., Yu, Q., An, J., Peng, L., Zhou, G., Xu, J., 2010. Analysis of VOC emissions using PCA/APCS receptor model at city of Shanghai, China. J Atmos Chem 62, 229-247.

Gentner, D.R., Jatha, S.H., Timothy D. Gordon, Bahreini, R., Day, D.A., Haddad, I.E., Hayes, P.L., Pieber, S.M., Platt, S.M., Gouw, J.d., Goldstein, A.H., Harley, R.A., Jimenez, J.L., Prevot, A.H., Robinson, A.L., 2017. Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions. Environ Sci Technol 51, 1074-1093.

Guenther, A.B., Zimmerman, P.R., Harley, P.C., Monson, R.K., Fall, R., 1993. Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses. Journal of Geophysical Research 98, 12609-12617.

Guo, H., Ling, Z.H., Cheng, H.R., Simpson, I.J., Lyu, X.P., Wang, X.M., Shao, M., Lu, H.X., Ayoko, G., Zhang, Y.L., Saunders, S.M., Lam, S.H.M., Wang, J.L., Blake, D.R., 2017. Tropospheric volatile organic compounds in China. Sci Total Environ 574, 1021-1043.

Guo, H., Wang, T., Louie, P.K.K., 2004. Source apportionment of ambient non-methane hydrocarbons in Hong Kong : Application of a principal component analysis/absolute principal component scores (PCA/APCS) receptor model. Environ Pollut 129, 489-498.

Guo, S., Hu, M., Zamora, M.L., Peng, J.F., Shang, D.J., Zheng, J., Du, Z.F., Wu, Z., Shao, M., Zeng, L.M., Molina, M.J., Zhang, R.Y., 2014. Elucidating severe urban haze formation in China. P Natl Acad Sci USA 111, 17373-17378.

Guo, S., Tan, J., Ma, Y., Yang, F., Yu, Y., Wang, J., 2011. Characteristics of atmospheric non-methane hydrocarbons during high PM10 episodes and normal days in Foshan, China. Atmos Res 101, 701-710.

Halliday, H.S., Thompson, A.M., Wisthaler, A., Blake, D.R., Hornbrook, R.S., Mikoviny, T., Müller, M., Eichler, P., Apel, E.C., Hills, A.J., 2016. Atmospheric benzene observations from oil and gas production in the Denver-Julesburg Basin in July and August 2014. Journal of Geophysical Research: Atmospheres 121, 11,055-011,074.

He, Z., Wang, X., Ling, Z., Zhao, J., Guo, H., Shao, M., Wang, Z., 2019. Contributions of different anthropogenic volatile organic compound sources to ozone formation at a receptor site in the Pearl River Delta region and its policy implications. Atmospheric Chemistry and Physics Discussions, 1-34.

Huang, C., Chen, C.H., Li, L., Cheng, Z., Wang, H.L., Huang, H.Y., Streets, D.G., Wang, Y.J., Zhang, G.F., Chen, Y.R., 2011. Emission inventory of anthropogenic air pollutants and VOC species in the Yangtze River Delta region, China. Atmos Chem Phys 11, 4105-4120.

Huang, X., Liu, Z., Liu, J., Hu, B., Wen, T., Tang, G., Zhang, J., Wu, F., Ji, D., Wang, L., Wang, Y., 2017. Chemical characterization and source identification of PM2.5 at multiple sites in the Beijing–Tianjin–Hebei region, China. Atmospheric Chemistry and Physics Discussions, 1-34.

Ji, D., Cui, Y., Li, L., He, J., Wang, L., Zhang, H., Wang, W., Zhou, L., Maenhaut, W., Wen, T., Wang, Y., 2018. Characterization and source identification of fine particulate matter in urban Beijing during the 2015 Spring Festival. Sci Total Environ 628-629, 430-440.

Jia, C., Mao, X., Tao, H., Liang, X., Wang, Y., Shen, Y., Jiang, W., Wang, H., Bai, Z., Ma, M., 2016. Non-methane hydrocarbons (NMHCs) and their contribution to ozone formation potential in a petrochemical industrialized city, Northwest China. Atmos Res 169, 225-236.

Jun-Lin, A.N., Zhu, B., Wang, H.L., Yang, H., 2014. Characteristics and Source Apportionment of Volatile Organic Compounds (VOCs) in the Northern Suburb of Nanjing. Environmental Science 35, 4454.

Li, B., Ho, S.S.H., Gong, S., Ni, J., Li, H., Han, L., Yang, Y., Qi, Y., Zhao, D., 2019a. Characterization of VOCs and their related atmospheric processes in a central Chinese city during severe ozone pollution periods. Atmos Chem Phys 19, 617-638.

Li, J., Xie, S.D., Zeng, L.M., Li, L.Y., Li, Y.Q., Wu, R.R., 2015a. Characterization of ambient volatile organic compounds and their sources in Beijing, before, during, and after Asia-Pacific Economic Cooperation China 2014. Atmospheric Chemistry and Physics Discussions 15, 12453-12490.

Li, L., Chen, Y., Zeng, L., Shao, M., Xie, S., Chen, W., Lu, S., Wu, Y., Cao, W., 2014a. Biomass burning contribution to ambient volatile organic compounds (VOCs) in the Chengdu–Chongqing Region (CCR), China. Atmos Environ 99, 403-410.

Li, L., Li, H., Wang, X.Z., Zhang, X.M., Wen, C., 2013. Pollution characteristics and health risk assessment of atmospheric VOCs in the downtown area of Guangzhou, China. Huanjing Kexue 34, 4558-4564.

Li, L., Li, H., Zhang, X., Wang, L., Xu, L., Wang, X., Yu, Y., Zhang, Y., Cao, G., 2014b. Pollution characteristics and health risk assessment of benzene homologues in ambient air in the northeastern urban area of Beijing, China. J Environ Sci-China 26, 214-223.

Li, L., Lu, Y., 2017. The sources apportionment andactivity evaluationof volatile organic compounds (VOCs) of Langfang City. Environment & Development 4, 42-44.

Li, L.Y., Xie, S.D., Zeng, L.M., Wu, R.R., Li, J., 2015b. Characteristics of volatile organic compounds and their role in ground-level ozone formation in the Beijing-Tianjin-Hebei region, China. Atmos Environ 113, 247-254.

Li, M., Zhang, Q., Zheng, B., Tong, D., Lei, Y., Liu, F., Hong, C., Kang, S., Yan, L., Zhang, Y., Bo, Y., Su, H., Cheng, Y., He, K., 2019b. Persistent growth of anthropogenic NMVOC emissions in China during 1990&ndash;2017: dynamics, speciation, and ozone formation potentials. Atmospheric Chemistry and Physics Discussions, 1-29.

Liao, H.T., Chou, C.C., Chow, J.C., Watson, J.G., Hopke, P.K., Wu, C.F., 2015. Source and risk apportionment of selected VOCs and PM2.5 species using partially constrained receptor models with multiple time resolution data. Environ Pollut 205, 121-130.

Liu, B., Liang, D., Yang, J., Dai, Q., Bi, X., Feng, Y., Yuan, J., Xiao, Z., Zhang, Y., Xu, H., 2016a. Characterization and source apportionment of volatile organic compounds based on 1-year of observational data in Tianjin, China. Environ Pollut 218, 757-769.

Liu, B., Liang, D., Yang, J., Dai, Q., Bi, X., Feng, Y., Yuan, J., Xiao, Z., Zhang, Y., Xu, H., 2016b. Characterization and source apportionment of volatile organic compounds based on 1-year of observational data in Tianjin, China ☆. Environ Pollut 218, 757-769.

Liu, C., Ma, Z., Mu, Y., Liu, J., Zhang, C., Zhang, Y., Liu, P., Zhang, H., 2017. The levels, variation characteristics, and sources of atmospheric non-methane hydrocarbon compounds during wintertime in Beijing, China. Atmos Chem Phys, 10633-10649.

Lu, Q., Zheng, J., Ye, S., Shen, X., Yuan, Z., Yin, S., 2013. Emission trends and source characteristics of SO2, NOx, PM10 and VOCs in the Pearl River Delta region from 2000 to 2009. Atmos Environ 76, 11-20.

Lyu, X.P., Chen, N., Guo, H., Zhang, W.H., Wang, N., Wang, Y., Liu, M., 2016. Ambient volatile organic compounds and their effect on ozone production in Wuhan, central China. Sci Total Environ 548-549, 483-483.

Mccarthy, M.C., Hafner, H.R., Chinkin, L.R., Charrier, J.G., 2007. Temporal variability of selected air toxics in the United States. Atmos Environ 41, 7180-7194.

McDonald, B.C., de Gouw, J.A., Gilman, J.B., Jathar, S.H., Akherati, A., Cappa, C.D., Jimenez, J.L., Lee-Taylor, J., Hayes, P.L., McKeen, S.A., Cui, Y.Y., Kim, S.W., Gentner, D.R., Isaacman-VanWertz, G., Goldstein, A.H., Harley, R.A., Frost, G.J., Roberts, J.M., Ryerson, T.B., Trainer, M., 2018. Volatile chemical products emerging as largest petrochemical source of urban organic emissions. Science 359, 760-764.

Ou, J., Zheng, J., Li, R., Huang, X., Zhong, Z., Zhong, L., Lin, H., 2015. Speciated OVOC and VOC emission inventories and their implications for reactivity-based ozone control strategy in the Pearl River Delta region, China. Sci Total Environ 530-531, 393-402.

Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. Chemometr Intell Lab 37, 23-35.

Paatero, P., Tapper, U., 1994. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. Environmetrics 5, 111-126.

Pacifico, F., Harrison, S.P., Jones, C.D., Sitch, S., 2009. Isoprene emissions and climate. Atmos

Environ 43, 6121-6135.

Pandolfi, M., Viana, M., Minguillón, M.C., Querol, X., Alastuey, A., Amato, F., Celades, I., Escrig, A., Monfort, E., 2008. Receptor models application to multi-year ambient PM10 measurements in an industrialized ceramic area: Comparison of source apportionment results. Atmos Environ 42, 9007-9017.

Payne-Sturges, D.C., Burke, T.A., Breysse, P., Diener-West, M., Buckley, T.J., 2004. Personal exposure meets risk assessment: a comparison of measured and modeled exposures and risks in an urban community. Environ Health Perspect 112, 589-598.

Qi, J., Zheng, B., Li, M., Yu, F., Chen, C., Liu, F., Zhou, X., Yuan, J., Zhang, Q., He, K., 2017. A high-resolution air pollutants emission inventory in 2013 for the Beijing-Tianjin-Hebei region, China. Atmos Environ 170, 156-168.

Saunier, A., Ormeño, E., Boissard, C., Wortham, H., Temime-Roussel, B., Lecareux, C., Armengaud, A., Fernandez, C., 2017. Effect of mid-term drought on Quercus pubescens BVOCs' emission seasonality and their dependency on light and/or temperature. Atmos Chem Phys 17, 7555-7566.

Shao, M., Lu, S., Liu, Y., Xie, X., Chang, C., Huang, S., Chen, Z., 2009. Volatile organic compounds measured in summer in Beijing and their role in ground‐level ozone formation. Journal of Geophysical Research 114, D00G06.

Shao, P., An, J., Xin, J., Wu, F., Wang, J., Ji, D., Wang, Y., 2016. Source apportionment of VOCs and the contribution to photochemical ozone formation during summer in the typical industrial area in the Yangtze River Delta, China. Atmos Res 176-177, 64-74.

Song, C., Liu, B., Dai, Q., Li, H., Mao, H., 2019. Temperature dependence and source apportionment of volatile organic compounds (VOCs) at an urban site on the north China plain.

Atmos Environ 207, 167-181.

Song, M., Tan, Q., Feng, M., Qu, Y., Liu, X., An, J., Zhang, Y., 2018. Source Apportionment and Secondary Transformation of Atmospheric Nonmethane Hydrocarbons in Chengdu, Southwest China. Journal of Geophysical Research: Atmospheres 123, 9741-9763.

Song, Y., Shao, M., Liu, Y., Lu, S.H., Kuster, W., Goldan, P., Xie, S.D., 2007. Source apportionment of ambient volatile organic compounds in Beijing. Environ Sci Technol 41, 4348-4353.

Sui, H., Zhang, T., Cui, J., Li, X., Crittenden, J., Li, X., He, L., 2016. Novel off-Gas Treatment Technology To Remove Volatile Organic Compounds with High Concentration. Ind Eng Chem Res 55, 2594-2603.

USEPA, 2009. Guidance for Superfund Volume I Human Heatlh Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment). EPA-540-R-070-002, OSWER 9285.9287-9282.

Wang, B., Lee, S.C., Ho, K.F., 2007. Characteristics of carbonyls: Concentrations and source strengths for indoor and outdoor residential microenvironments in China. Atmos Environ 41, 2851-2861.

Wang, B., Shao, M., Lu, S.H., Yuan, B., Zhao, Y., Wang, M., Zhang, S.Q., Wu, D., 2010. Variation of ambient non-methane hydrocarbons in Beijing city in summer 2008. Atmos Chem Phys 10, 5911-5923.

Wang, M., Shao, M., Chen, W., Lu, S., Liu, Y., Yuan, B., Zhang, Q., Zhang, Q., Chang, C.C., Wang, B., Zeng, L., Hu, M., Yang, Y., Li, Y., 2015. Trends of non-methane hydrocarbons (NMHC) emissions in Beijing during 2002–2013. Atmos Chem Phys 15, 1489-1502.

Wang, M., Zeng, L., Lu, S., Shao, M., Liu, X., Yu, X., Chen, W., Yuan, B., Zhang, Q., Hu, M., Zhang, Z., 2014. Development and validation of a cryogen-free automatic gas chromatograph system (GC-MS/FID) for online measurements of volatile organic compounds. Anal. Methods 6, 9424-9434.

Wolowiec, M., Muir, B., Zieba, K., Bajda, T., Kowalik, M., Franus, W., 2017. Experimental Study on the Removal of VOCs and PAHs by Zeolites and Surfactant-Modified Zeolites. Energ Fuel 31, 8803-8812.

Wu, C.F., Wu, S.Y., Wu, Y.H., Cullen, A.C., Larson, T.V., Williamson, J., Liu, L.J., 2009. Cancer risk assessment of selected hazardous air pollutants in Seattle. Environ Int 35, 516-522.

Wu, R., Li, J., Hao, Y., Li, Y., Zeng, L., Xie, S., 2016. Evolution process and sources of ambient volatile organic compounds during a severe haze event in Beijing, China. Sci Total Environ 560-561, 62-72.

Wu, R., Xie, S., 2017. Spatial Distribution of Ozone Formation in China Derived from Emissions of Speciated Volatile Organic Compounds. Environ Sci Technol 51, 2574-2583.

Xin, J.Y., Wang, Y.S., Pan, Y.P., Ji, D.S., Liu, Z.R., Wen, T.X., Wang, Y.H., Li, X.R., Sun, Y., Sun, J., Wang, P.C., Wang, G.H., Wang, X.M., Cong, Z.Y., Song, T., Hu, B., Wang, L.L., Tang, G.Q., Gao, W.K., Guo, Y.H., Miao, H.Y., Tian, S.L., Wang, L., 2015. The Campaign on Atmospheric Aerosol Research Network of China Care-China. B Am Meteorol Soc 96, 1137-1155.

Xu, Z., Huang, X., Nie, W., Chi, X., Xu, Z., Zheng, L., Sun, P., Ding, A., 2017. Influence of synoptic condition and holiday effects on VOCs and ozone production in the Yangtze River Delta region, China. Atmos Environ 168, 112-124.

Xue, Y., Ho, S.S.H., Huang, Y., Li, B., Wang, L., Dai, W., Cao, J., Lee, S., 2017. Source apportionment of VOCs and their impacts on surface ozone in an industry city of Baoji, Northwestern China. Sci Rep 7, 9979.

Yang, W.Q., Zhang, Y.L., Wang, X.M., Li, S., Zhu, M., Yu, Q.Q., Li, G.H., Huang, Z.H., Zhang, H.N., Wu, Z.F., Song, W., Tan, J.H., Shao, M., 2018. Volatile organic compounds at a rural site in Beijing: influence of temporary emission control and wintertime heating. Atmos Chem Phys 18, 12663-12682.

Ying, L., Min, S., Fu, L., Lu, S., Zeng, L., Tang, D., 2008. Source profiles of volatile organic compounds (VOCs) measured in China: Part I. Atmos Environ 42, 6247-6260.

Yuan, B., Hu, W.W., Shao, M., Wang, M., Chen, W.T., Lu, S.H., Zeng, L.M., Hu, M., 2013. VOC emissions, evolutions and contributions to SOA formation at a receptor site in eastern China. Atmos Chem Phys 13, 8815-8832.

Yuan, B., Shao, M., de Gouw, J., Parrish, D.D., Lu, S., Wang, M., Zeng, L., Zhang, Q., Song, Y., Zhang, J., Hu, M., 2012. Volatile organic compounds (VOCs) in urban air: How chemistry affects the interpretation of positive matrix factorization (PMF) analysis. Journal of Geophysical Research: Atmospheres 117, 24302.

Zhang, H., Li, H., Zhang, Q., Zhang, Y., Zhang, W., Wang, X., Bi, F., Chai, F., Gao, J., Meng, L., Yang, T., Chen, Y., Cheng, Q., Xia, F., 2017. Atmospheric Volatile Organic Compounds in a Typical Urban Area of Beijing: Pollution Characterization, Health Risk Assessment and Source Apportionment. Atmosphere-Basel 8, 61.

Zhang, Y., Mu, Y., Liu, J., Mellouki, A., 2012. Levels, sources and health risks of carbonyls and BTEX in the ambient air of Beijing, China. J Environ Sci-China 24, 124-130.

Zhang, Y., Mu, Y., Meng, F., Li, H., Wang, X., Zhang, W., Mellouki, A., Gao, J., Zhang, X., Wang, S., Chai, F., 2014. The pollution levels of BTEX and carbonyls under haze and non-haze days in Beijing, China. Sci Total Environ 490, 391-396.

Zhao, Y., Mao, P., Zhou, Y.D., Yang, Y., Zhang, J., Wang, S.K., Dong, Y.P., Xie, F.J., Yu, Y.Y., Li, W.Q., 2017. Improved provincial emission inventory and speciation profiles of anthropogenic non-methane volatile organic compounds: a case study for Jiangsu, China. Atmos Chem Phys 17, 7733-7756.

Zheng, B., Tong, D., Li, M., Liu, F., Hong, C., Geng, G., Li, H., Li, X., Peng, L., Qi, J., Yan, L., Zhang, Y., Zhao, H., Zheng, Y., He, K., Zhang, Q., 2018. Trends in China's anthropogenic emissions since 2010 as the consequence of clean air actions. Atmos Chem Phys 18, 14095-14111.

Zheng, H., Kong, S., Xing, X., Mao, Y., Hu, T., Ding, Y., Li, G., Liu, D., Li, S., Qi, S., 2017. One year monitoring of volatile organic compounds (VOCs) from an oil-gas station in northwest China. Atmospheric Chemistry and Physics Discussions 18, 1-57.

Zhou, J., You, Y., Bai, Z., Hu, Y., Zhang, J., Zhang, N., 2011. Health risk assessment of personal inhalation exposure to volatile organic compounds in Tianjin, China. Sci Total Environ 409, 452-459.

Zhou, Y., Xing, X., Lang, J., Chen, D., Cheng, S., Wei, L., Wei, X., Liu, C., 2017. A comprehensive biomass burning emission inventory with high spatial and temporal resolution in China. Atmos Chem Phys 17, 2839-2864.

Zou, Y., Deng, X.J., Zhu, D., Gong, D.C., Wang, H., Li, F., Tan, H.B., Deng, T., Mai, B.R., Liu, X.T., Wang, B.G., 2015. Characteristics of 1 year of observational data of VOCs, NOx and O3 at a suburban site in Guangzhou, China. Atmos Chem Phys 15, 6625-6636.