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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

Zhuoran He[1,2], Xuemei Wang[3], Zhenhao Ling[1,2*], Jun Zhao[1,2], Hai Guo[4], Min Shao[3], Zhe Wang[4,*]

[1]School of Atmospheric Sciences, Sun Yat-sen University, Guangzhou, China
[2]Guangdong Province Key Laboratory for Climate Change and Natural Disaster Studies, Sun Yat-sen University, Guangzhou, China
[3] Institute for Environmental and Climate Research, Jinan University, Guangzhou, China
[4] Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hong Kong, China

Correspondence to: lingzhh3@mail.sysu.edu.cn (Zhenhao Ling); z.wang@polyu.edu.hk (Zhe Wang)

Abstract. Volatile organic compounds (VOCs) are key precursors of photochemical smog. Quantitatively evaluating the contributions of VOCs sources to ozone (O_3) formation could provide valuable information for emissions control and photochemical pollution abatement. This study analysed the continuously measured VOCs during the photochemical season in 2014 at a receptor site (Heshan site, HS) in the Pearl River Delta (PRD) region, where photochemical pollution has been a long-standing issue. The averaged mixing ratio of measure VOCs was 34 ± 3 ppbv, with the largest contribution from alkanes (17 ± 2 ppbv, 49%), followed by aromatics, alkenes, and acetylene. The positive matrix factorization (PMF) model was applied to resolve the anthropogenic sources of VOCs, coupled with a photochemical-aged-based parameterization that better considers the photochemical processing effects. Four anthropogenic emission sources were identified and quantified, with gasoline vehicular emission as the most significant contributor to the observed VOCs, followed by diesel vehicular emissions, biomass burning, and solvent usage. The O_3 photochemical formation regime at HS was identified as VOCs-limited by a photochemical box model with the master chemical mechanism (PBM-MCM). The PBM-MCM model results also suggested that vehicular emission was the most important source to the O_3 formation, followed by biomass burning and solvent usage. Sensitivity analysis indicated that in order to prevent the increment

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of O_3 concentration, the abatement ratios of the individual VOC source vs. NO_x should be higher than 3.8, 4.6, 4.6, and 3.3, respectively, for diesel vehicular emission, solvent usage, biomass burning, and gasoline vehicular emission, respectively. Based on the above results, a brief review on the policies on the controlling of vehicular emissions and biomass burning in the PRD region from a regional perspective were also provided in this study. It reveals that different policies have been/being implemented and formulated could help to alleviate the photochemical pollution in the PRD. Nevertheless, evaluation on the cost-benefit of each policy is still needed to improve the air quality.

Key words: Anthropogenic emissions; Ozone formation; Pearl River Delta region; Policy implications

1 Introduction

Atmospheric volatile organic compounds (VOCs) have significant impact on air quality. Due to their high chemical activity, VOCs are key precursors of ozone (O_3) and secondary organic aerosol (SOA). In addition, some VOCs and their oxidation products are harmful to human health, which further deteriorates air quality (Seinfeld and Pandis, 2006; ATSDR, 2007; Huang et al., 2014). VOCs have a variety of natural and anthropogenic sources, including biogenic emissions and emissions from human activities (*i.e.,* fuel and biomass combustion, fuel evaporation, solvent usage, industrial processes, etc.). It is relatively well known that the two key ozone precursors (VOCs and NO_x) synergize complex, nonlinear effects on ozone formation. For a given region, depending on which precursor is the limiting factor for controlling ozone formation, the ozone isopleth diagram (the mixing ratios of VOCs and NO_x as two coordinates) can be classified into VOCs and NO_x limited regimes. In the VOCs-limited regime, the effective measure for reducing ozone production is to control the VOC emissions and vice versa for the NO_x-limited regime (Jenkin and Clemitshaw, 2000).

In recent years, with rapid urbanization and industrialization, high O_3 mixing ratios were frequently observed in the Pearl River Delta region (e.g., Zheng et al., 2010; Li et al., 2014; Wang et al., 2017).

Many previous studies have shown that photochemical O_3 formation was generally VOCs-limited in the PRD region, and suggested that the reduction of VOC emission could effectively alleviate photochemical O_3 formation (Guo et al., 2017). Therefore, source identification and quantification of VOCs are prerequisites for the formulation and implementation of the most effective control measures of photochemical pollution in the PRD region. Indeed, many efforts have been made to perform the source apportionments of VOCs in this region by using different methods, including tunnel measurements, receptor models, emission-based measurements, and emission inventory. Ho et al. (2009) quantified the emission factors of 92 VOCs from gasoline, diesel, and LPG vehicles from a tunnel study in Hong Kong. Guo et al. (2011b) and Zheng et al. (2013) characterized the source profiles of VOCs emitted from industrial and vehicular sectors through samples collected directly from the plumes of the above sources. These emission-based measurements provided clear attributions of VOCs from different sources and emission factors for the emission-inventory to estimate the total amount of VOCs emitted from those sources. In particular, Zheng et al. (2009) and Ou et al. (2015b) established a specific VOC emission inventory to estimate the abundance of VOCs and to provide input data for different air quality models. The inventory was applied to quantify the strength of vehicular emissions, solvent usage, and biogenic emissions in the PRD.

In contrast to emission inventory, which estimates the emission strength based on emission factors and emission activity, receptor models are useful for source apportionment of VOCs without any prior knowledge of the emissions. As a widely used receptor model, positive matrix factorization (PMF) has been employed in the source apportionment of VOCs in the PRD region (Guo et al., 2011a; Ling et al., 2011; Lau et al., 2010; Ou et al., 2015a). For example, Ling et al. (2011) identified 10 sources of VOCs at a receptor site in the PRD region and concluded that solvent usage and vehicular exhaust were the most significant sources with average contributions of 51% and 37%, respectively. Results from source apportionment using the PMF model demonstrated the important roles of vehicular emissions in ambient VOCs in urban (65 ± 36%) and suburban (50 ± 28% and 53 ± 41%) environments of Hong Kong (Lau et

al., 2010; Ou et al., 2015a). However, uncertainties existed in the PMF analysis due to the assumption of mass conservation during the transport of pollutants from emissions to the receptor site. To investigate the influence of photochemical processes on the factorization of VOCs by the PMF model, Yuan et al. (2012b) applied a photochemical age-based parameterization method to analyze the measured VOC data at an urban site in Beijing. They found that the PMF-resolved factors were influenced by VOCs from a common source at different stages of the photochemical processing, thus the independent source could not be clearly identified. The results further suggested that when using the PMF model for VOC source apportionments, it is necessary to assess if photochemical processing could influence the source signatures of VOCs at the receptor site. Although many previous studies reported source apportionment of VOCs in the PRD region using the PMF model, they did not take the influence of photochemical processing into account, leading possibly to uncertainties in identifying and quantifying the source attribution of VOCs.

In this study, the PMF model coupled with a photochemical-age-based parameterization method was applied to the continuous real-time VOCs data from an intensive field campaign at a receptor site in PRD. The model provides a more detailed and accurate description of the source characteristics of VOCs in the PRD region. Furthermore, the contribution of different sources of VOCs to the photochemical O_3 formation and the sensitivity of ozone and its precursors were evaluated through a photochemical box model coupled with the master chemical mechanism. Our results could provide valuable information, facilitating local and regional policy-makers for proposing appropriate strategies and effective control measures of VOCs and photochemical pollution.

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2 Methodology

2.1 Measurements

The field measurement was conducted at the Heshan (HS) Atmospheric Supersite (22.728°N, 112.929°E, at an altitude of 60 m) in the western PRD region from October 22 to November 20, 2014. Figure 1 shows the surrounding environment at the sampling site. A detailed description of the Heshan site can be found in previous studies (Zhou et al., 2013, 2014). Briefly, the site is located in a rural area of the PRD region, about 50-80 km northeast of the urban central cities (i.e., Guangzhou and Foshan) of the PRD region. In addition to local emissions, the abundances of air pollutants at the HS during autumn and winter seasons are frequently affected by the outflow of air masses from the central cities, thus this site can be used as a representative of regional emissions in the PRD region (Zhou et al., 2014).

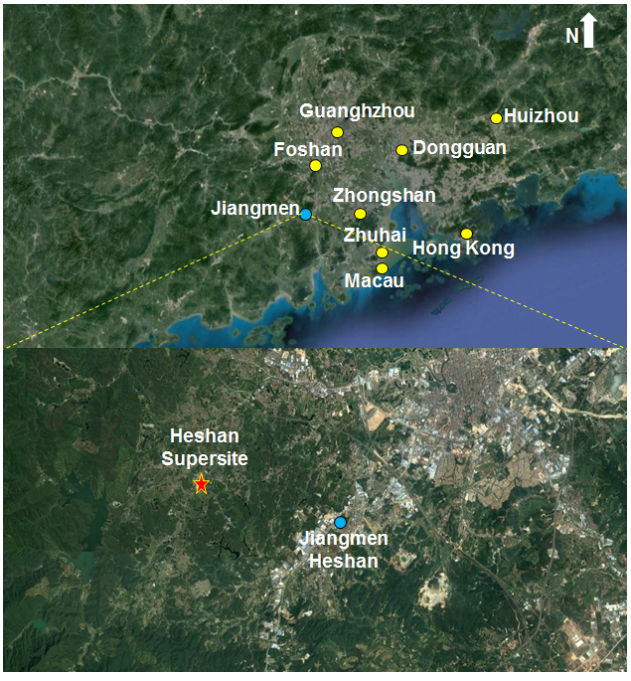

Figure 1. The sampling site and its surrounding environment in the Pearl River Delta region (top panel: overview of the site location; bottom panel: zoomed-in view, red star denotes the site location)

An automated online gas chromatography-flame ionization detector (GC-FID) system measured hourly concentrations of 58 VOC species at the site from October 22 to November 20, 2014. Detailed descriptions of the configuration of the GC-FID system, the detection limits, and precision of VOCs can be found elsewhere (Wang et al., 2008; Zhang et al., 2008a; Ling et al., 2017). Air-quality related trace gases, including O_3, NO-NO_2-NO_x, CO, and SO_2, together with meteorological data, *i.e.,* temperature, solar radiation, precipitation, relative humidity, wind speed, and wind direction were continuously measured by the Guangdong Environmental Monitoring Center.

2.2 Positive matrix factorization (PMF) model

The Positive Matrix Factorization (PMF) (US Environmental Protection Agency (USEPA) version 5.0) model was applied to the observed data for source apportionments of the VOCs. The PMF model is a multivariate factor analysis tool that decomposes a matrix of speciated sample data into two matrices, factor contributions, and factor profiles, which can be interpreted by an analyst as to explore the source types and their contributions based on the measured data at the receptor site (Paatero and Tapper, 1994; Paatero, 1997). It could be simplified as

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

where x_{ij} is the jth species concentration measured in the ith sample, g_{ik} the species contribution of the kth source to the ith sample, f_{kj} the jth species fraction from the kth source, e_{ij} the residual for each species, and p the total number of independent sources (Paatero, 1997). The model could provide the number of emission sources (p) and the distributed profiles (f) of each species in the individual source after simulation.

The description of the model input was provided elsewhere (Guo et al., 2011a). In this study, the selection of species for the model input followed several criteria: 1) The chosen species had relatively high concentrations and/or were typical tracers for specific emissions. 2) Species with low abundance and/or high uncertainties were excluded, *i.e.*, *cis*-2-pentene, diphenyl methane, and 1,3-diethylbenzene, because more than a quarter of the samples for those species were below the detection limit. 3) Species related to biogenic emissions, i.e., isoprene and *α*/*β*-pinene, were excluded as this study focused on the source characteristics of anthropogenic emissions in the PRD region (Fuentes et al., 1996; Sanadze, 2004). A total of 49 species, including 47 VOCs, MTBE (methyl tert-butyl ether), and acetonitrile (ACN) were selected for the input data.

For the PMF modeling run, different numbers of factors were tested and an optimal number of factors was determined based on both a good fit to the data and the most meaningful results. The uncertainty for each species was determined to be sum of 10% of the VOC concentration and two times the detection limit of the species (Paatero, 2000a; Lau et al., 2010). Concentrations below the detection limit were replaced with half of the detection limit and their uncertainties were set to be 5/6 of the detection limit. Missing concentrations were replaced by the geometric mean of the measured values and their corresponding uncertainties were set to be four times the geometric mean values (Paatero, 2000b).

2.3 PBM-MCM model

The photochemical box model coupled with the master chemical mechanism (PBM-MCM) was applied to quantify the contributions of VOC emission sources to in-situ O_3 formation. The PBM-MCM model uses the concentrations of VOCs and trace gases, and the meteorological data as input to simulate the total amount of photochemical O_3 formation at the site based on the master chemical mechanism (version 3.2), which consists of 5900 chemical species and 16500 reactions. Note that the physical processes, including horizontal and vertical transport, were not considered in the model. Details of the model setup and configuration can be found in previous studies (Saunders et al., 2003; Lam et al., 2013). In this study,

the hourly data of VOCs, five trace gases (i.e., O_3, NO, NO_2, CO, and SO_2) and two meteorological parameters (*i.e.,* temperature and relative humidity) measured during the campaign were used as model input.

In addition, the PBM-MCM model can be used to assess the sensitivity of O_3 photochemical production to the changes in the concentrations of its precursors by calculating the relative incremental reactivity (RIR) without a detailed or accurate knowledge of these emissions (Carter and Atkinson, 1989; Cardelino and Chameides, 1995). The RIR is defined as the percent change in O_3 production per percent change in the precursors. The RIR of a specific precursor *X* at site *S* is given by

$$RIR^S(X) = \frac{\left[P^S_{O_3-NO}(X) - P^S_{O_3-NO}(X-\Delta X)\right]/P^S_{O_3-NO}(X)}{\Delta S(X)/S(X)} \quad (2)$$

where $S(X)$ represents the measured concentration of precursor *X*, including the amounts emitted at the site and those transported to the site and ΔX is the change in the concentration of precursor *X* caused by a hypothetical change $\Delta S(X)$ (10% $S(X)$ in this study). Here, $P^S_{O_3-NO}$ represents the O_3 formation potential, which is the net O_3 production and NO consumed during the evaluation period and can be calculated by the output from the PBM-MCM. A large positive RIR value of a specific precursor suggests that the O_3 production could be decreased significantly if the emissions of this precursor were controlled.

In addition, the average RIR function of precursor *X* can be calculated from

$$\overline{RIR}(X) = \frac{\sum_1^N [RIR^S(X) P^S_{O_3-NO}(X)]}{\sum_1^N P^S_{O_3-NO}(X)} \quad (3)$$

where *N* means the number of days simulated.

In addition, considering both the reactivity and abundance of VOC species in different sources, the relative contributions of the precursor *X* can be calculated by (Ling et al., 2011; Ling and Guo, 2014).

$$Contribution(X) = \frac{\overline{RIR}(X) \times conc(X)}{\sum[\overline{RIR}(X) \times conc(X)]} \times 100\% \quad (4)$$

where $conc(X)$ was obtained from the measurement and PMF resolutions.

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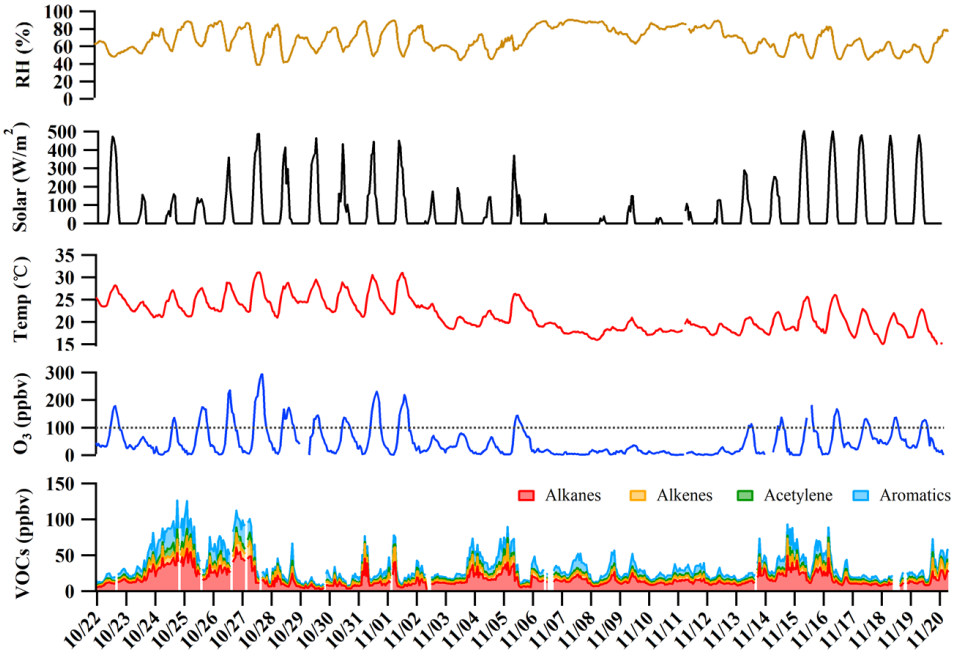
3 Results and discussion

3.1 General statistics

Figure 2 shows the time series of O_3 and total VOCs (TVOCs), as well as meteorological parameters (i.e., temperature, relative humidity) observed at Heshan site from 22 October to 20 November. It was found that two major episodes of high O_3 mixing ratios (maximum hourly-averaged mixing ratio > 100 ppbv, China II Standard) appeared during 24 October ~ 01 November and 13~19 November, respectively. Consistent with higher O_3 levels, the mixing ratios of TVOCs in O_3 episode days were higher, with the average values of 38 ± 3 ppbv and 30 ± 2 ppbv (mean ± 95% intervals) observed during O_3 episode and non-episode days, respectively, indicating that O_3 formation at Heshan site was probably VOC-limited. The measured 58 VOC species included 30 alkanes, 10 alkenes, 17 aromatics, and acetylene. Table 1 summarizes the average mixing ratios of the major VOC groups measured at the site from 22 October to 20 November, 2014. The average mixing ratio of total VOCs was 34 ± 3 ppbv, with the highest contributions from alkanes (17 ± 2 ppbv, 49%), followed by aromatics (9 ± 1 ppbv, 26%), alkenes (5 ± 1 ppbv, 15 %) and acetylene (3 ± 1 ppbv, 10%). This is consistent with previous measurements in this region (Guo et al., 2011a; Yuan et al., 2012a; Zou et al., 2015). The VOC mixing ratio at the Heshan site was similar to that in urban Shanghai and Beijing, with a range of 30.3-38.7 ppbv (Geng et al., 2009; Cai et al., 2010) and 29.4-43.4 ppbv (Song et al., 2007; Duan et al., 2008; Shao et al., 2009; Li et al., 2015), respectively. However, it was much higher than that in background areas of the North China Plain region, Yangtze River Delta region, and PRD (< 20 ppbv) (Tang et al., 2009; Yuan et al., 2012b; Zhu et al., 2016). The most abundant VOC species was ethane (3.86 ± 0.10 ppbv), followed by toluene (3.74 ± 0.22 ppbv), acetylene (3.42 ± 0.17 ppbv), propane (3.01 ± 0.14 ppbv), and ethene (2.94 ± 0.25 ppbv). The composition and the variations of VOCs suggest that the air masses arriving at the Heshan site may be through photochemical processing. In addition, incomplete combustion was likely to be the dominant source of VOCs at this site (Yuan et al., 2012a; Zhang et al., 2014; Yang et al., 2017), because typical tracers of

98 incomplete combustion (i.e., ethane, acetylene, ethene, and propane) were present with high
99 concentrations due to relatively lower photochemical reactivity of alkane (*i.e.,* ethane and propane) than
00 other VOCs. Indeed, the average diurnal variations of VOCs (Figure 3) presented relative higher mixing
01 ratios during the early morning and from the evening to midnight, which may be related to elevated traffic
02 emissions during rush hours and the constrained mixing height (Yuan et al., 2009). On the other hand, the
03 mixing ratios of VOCs started to decrease at 0900 LT (local time) and presented a broad trough during
04 daytime hours (0900-1900 LT), which were probably due to strong photochemical reactions, increased
05 mixing height and/or less VOC emissions (Yuan et al., 2009; Lau et al., 2010).



06
07 Figure 2. Time series of O_3, VOCs, and meteorological parameters observed at Heshan site
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Table 1. Average, range, and standard deviation of concentrations for the eight most abundant VOCs measured at the Heshan site, together with a sum of the mixing ratios for each hydrocarbon category (i.e., alkanes, aromatics, and alkenes)

Species	Average ± standard deviation (ppbv)	Range (ppbv)
Ethane	3.86 ± 1.34	1.08 - 10.44
Toluene	3.74 ± 2.89	0.56 - 15.80
acetylene	3.42 ± 2.33	0.11 - 28.22
Propane	3.01 ± 1.82	0.45 - 10.70
Ethene	2.94 ± 3.34	0.37 - 64.56
i-Pentane	1.90 ± 2.20	0.22 - 16.16
n-Butane	1.85 ± 1.28	0.20 - 10.10
m/p-Xylene	1.62 ± 1.44	0.17 - 12.74
Alkanes	17.04 ± 10.64	2.04 - 61.01
Aromatics	9.07 ± 7.01	1.46 - 40.12
Alkenes	5.29 ± 5.01	0.67 - 77.39

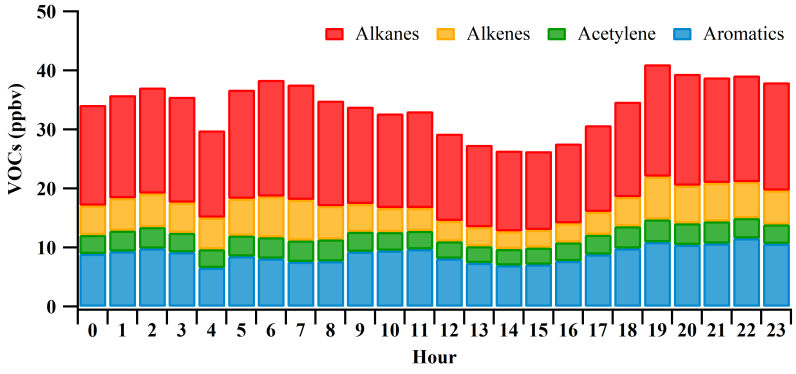

Figure 3. Diurnal variations of VOCs observed at Heshan site

3.2 Sources of VOCs

3.2.1 The influences of photochemical processing on VOCs concentration

To investigate the source attributions of VOCs, the PMF model was applied to the observed concentrations of VOCs at the Heshan site. As mentioned above, to more accurately identify and quantify

the source contributions, it is necessary to evaluate whether the photochemical processing could influence the source signatures of VOCs.

Correlation analysis between two VOC species from the same emissions with different photochemical reactivity, *i.e.,* propane vs butanes and ethylbenzene vs xylenes, has been widely used in previous studies to evaluate the photochemistry impacts (Ling et al., 2011). If the two species are involved in photochemical reactions, their correlation will weaken due to their different reactivity. In the present study, excellent correlation was found for ethylbenzene vs *o*-xylene (R^2 = 0.95, p < 0.01) and propane vs *i*-butane (R^2 = 0.91, p < 0.01) (figure not shown), indicating the insignificant influence of photochemical processing on the correlations and clear source signatures for the selected species.

To evaluate further the influence of photochemical processing on the observed levels, a photochemical-aged-based parameterization method was used to estimate the initial concentrations of VOCs after emissions (Eq. (5)). This method was first introduced by de Gouw et al. (2005) and was applied to VOC measured data in different environments (Liu et al., 2009; Shao et al., 2009; Yuan et al., 2012b).

Through the photochemical-aged-based parameterization method, photochemical age, representing the photochemical processing time, could be calculated by the ratio between the concentrations of two VOCs with relatively strong correlation and different OH reaction rates, *i.e.,* the ratio of ethylbenzene and *m/p*-xylene. In this study, high correlation was found between ethylbenzene and *m/p*-xylene (R^2 = 0.96, p < 0.01). Furthermore, the OH reaction rate constants for the above species were 7.10×10^{-12} (ethylbenzene), 1.90×10^{-11} (*m/p*-xylene, obtained from the average OH reaction rate constants of *m*- and *p*-xylene) $cm^3\cdot molecule^{-1}\cdot s^{-1}$, respectively. It has been demonstrated that ratios of above species could be used to estimate the effect of photochemical processing on VOC variations (Shiu et al., 2007; Shao et al., 2009; Chang et al., 2010). The OH exposure ([OH]△t) is calculated and used to represent photochemical age, as [OH] and △t always appear together in the parameterization equation (Jimenez et al., 2009). The OH exposure is calculated from the ratio of VOCs concentrations by

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$$[\mathrm{OH}]\Delta t = \frac{1}{(k_E - k_X)} \times \left[ln\frac{[E]}{[X]}|_{t=0} - ln\frac{[E]}{[X]} \right] \quad (5)$$

The $[\mathrm{OH}]$ term represents the concentration of the OH radical and its reaction time △t for VOCs between the emission sources and the observation site. The parameters k_E and k_X are the reaction rate constants of ethylbenzene and *m/p*-xylene, 7.10×10^{-12} and 1.90×10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, respectively (Atkinson et al., 2006). $\frac{[E]}{[X]}$ is the average measured concentration ratio of ethylbenzene to *m/p*-xylene. $\frac{[E]}{[X]}|_{t=0}$ is the initial concentration ratio of ethylbenzene to *m/p*-xylene.

In the present study, the initial concentration ratio of ethylbenzene to *m/p*-xylene ($\frac{[E]}{[X]}|_{t=0}$) is calculated to be 0.62 using the methods suggested by Yuan et al. (2012b) and Shao et al. (2009), consistent with those calculated at other urban and rural environments (Shao et al., 2009), and the OH exposure ($[\mathrm{OH}]\Delta t$) calculated by Eq. (5) was 6.47×10^9 $molecule \cdot cm^{-3} \cdot s$.

On the other hand, the initial concentration of VOCs could be described by

$$[VOC]_{initial} = [VOC]_{measured} \times \exp(-k_{NMHC} \cdot [\mathrm{OH}]\Delta t) \quad (6)$$

Here, $[VOC]_{initial}$ and $[VOC]_{measured}$ are the initial and measured concentration of particular VOC, respectively. k_{VOC} is the reaction rate constant of the specific VOC.

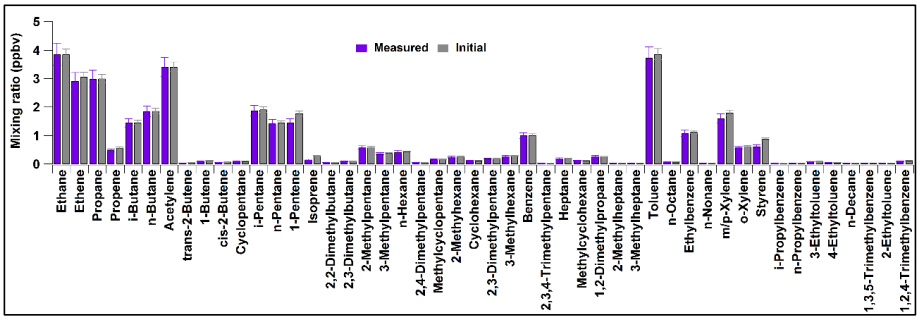

Figure 4. Average measured and initial concentrations of VOCs

Figure 4 shows the comparison between the observed levels and the initial concentrations of VOCs at the Heshan site. In general, the variations between the observed levels and the initial concentrations of VOCs were small for most of the VOC species, with the OH reaction rate < 5.64×10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, and the ratio of initial/observed concentrations ranging from 1.00-1.23. However, for those species with relatively higher photochemical reactivity (with the OH reaction rate ranging from 5.64×10^{-11}-6.40×10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$), the initial concentrations were 1.44-1.51 times of the observed levels. It should be noted that these relatively higher reactive species only accounted for a small fraction of the concentrations and the ozone formation potential (OFP) of all the observed VOCs due to their relatively lower abundance (data not shown).

Therefore, to consider the influence of photochemical processing on source apportionment results, the concentrations for the species with relatively higher reactivity (the ratio of initial/observed concentrations > 1.3, *i.e., trans*-2-butene, *cis*-2-butene, styrene, and 1,3,5-trimethylbenzene) were compensated by the difference between observed levels and initial concentrations. They were further used as input to the PMF model, together with the observed concentrations of rest species to investigate the source attributions of VOCs at the Heshan site in the following section.

3.2.2 Source apportionments of VOCs

In this study, the data matrix for PMF model was composed of 682 samples and 47 VOCs together with ACN and MTBE. The solution of four factors was obtained. Figure 5 presents the source profiles (in percentages of species total) extracted from the PMF model, while Figure 6 presents the relative contributions of different sources to ambient VOCs at the Heshan site. It was found that factor 1 and 4 were both associated with high percentages of aromatics. In addition to the solvent usage, aromatics were mainly related to vehicle emissions in the PRD region (Zhang et al., 2013; Ou et al., 2014). The relatively higher loadings of C_2-C_4 alkenes in factor 1 suggest that this source was mainly related to diesel vehicular emission (Guo et al., 2011a; Ou et al., 2014), which accounts for about 25 ± 3% (mean ± 95% intervals)

of the total observed VOCs. On the other hand, factor 4 was characterized by high levels of *n*/*i*-pentane and MTBE, the typical tracers for gasoline vehicular emissions (Song et al., 2006; Ho et al., 2009; Ou et al., 2014). As such, factor 4 was assigned to gasoline vehicular emission and its contribution to the observed VOCs was 33 ± 5%. Factor 2 was characterized by high percentages of C_6-C_7 alkanes and certain amounts of aromatics, while the contributions of other combustion tracers were insignificant in this factor, suggesting that this factor was related to solvent usage. It is consistent with previous studies that aromatics and C_6-C_7 could be used as solvents in the printing and paint industry (He et al., 2002, Chan et al., 2006; Liu et al., 2008). 18 ± 2% of the observed VOCs, were identified to be associated with solvent use. Factor 3 was represented by high percentages of ethane (~65%), acetylene (~51%), benzene (~52%), and ethene (~ 31%), together with some C_3-C_5 alkanes and alkenes, which are typically tracers of incomplete combustion such as vehicular exhaust and biomass burning (Nelson et al., 1984; Wadden et al., 1986; Blake et al., 1994; Rudolph, 1995; Guo et al., 2011a, 2011b). The high percentage of acetonitrile in factor 3 suggests that this factor was associated with biomass burning (Holzinger et al., 1999; Yuan et al., 2010), which was responsible for 24 ± 3% of the observed VOCs. Figure 7 shows the diurnal variations of VOCs emitted from different sources extracted from PMF. Different diurnal patterns were found for different sources, which may be related to the variations in emission strength, the concentrations of species in different source profiles, as well as the influence of mixing height. For example, relatively higher levels were found for the diesel and gasoline vehicular emissions in the early morning and in the evening, corresponding well with traffic emissions during rush hours, while a broad peak during daytime hours may be related to the increased mixing height and photochemical loss, and decreased emission strength (Zheng et al., 2010; Yuan et al., 2009). Different from vehicular emissions, the concentrations of solvent usage started to increase in the early morning and reached maximum value at noon, and then decreased gradually and presented a broad peak until midnight. The increased levels of solvent usage from early morning to midday was associated with the increased emissions from human production activities and the increased temperature which would accelerate VOCs evaporated during the use of solvent. The diurnal

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variations of biomass burning were much weaker compared with other sources, with peak values occurred in the early morning, which was consistent with the diurnal patterns of plumes of biomass burning at Heshan site (Yuan et al., 2010).

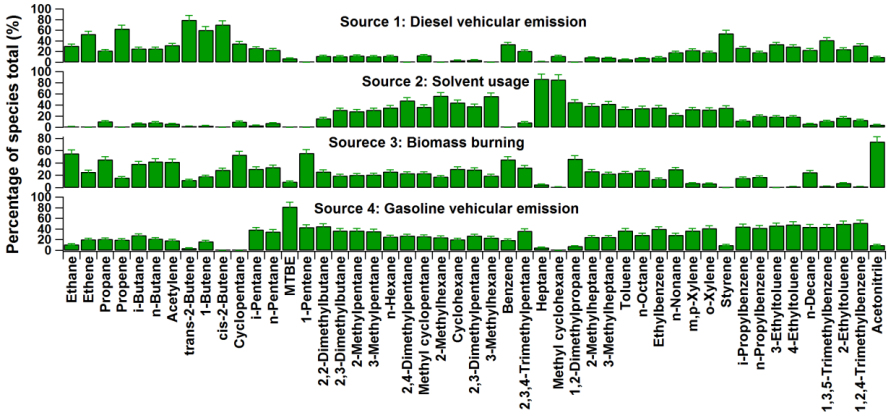

Figure 5. Factor profile (in percentage of species total) attributed from PMF

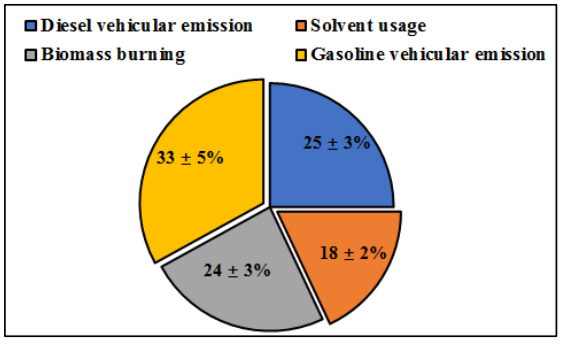

Figure 6. Contributions of different sources to ambient VOCs extracted from PMF

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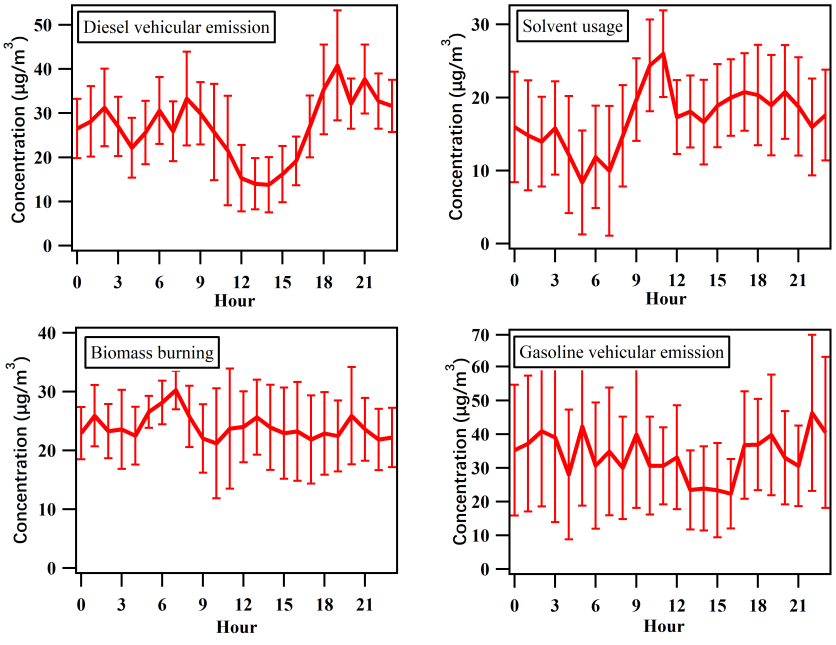

Figure 7. Diurnal variations of VOCs emitted from different sources extracted from PMF

3.3 The contributions of VOCs sources to ozone photochemical formation

To evaluate the roles of the different VOCs emissions for O_3 formation, we applied the PBM-MCM model to the PMF-extracted VOC concentrations. Figure 8(a) shows the average RIR values of different VOC sources and NO, together with the contributions of different VOC sources to photochemical O_3 formation. The average RIR values of various VOC sources were positive, while that of NO was negative, suggesting that O_3 formation at Heshan site was located in the VOC-limited regime. Among the four main anthropogenic sources of VOCs, relative higher average RIR values of vehicular emissions and biomass burning than that of solvent usage were found. Furthermore, considering both the reactivity and abundance of VOCs in different sources, the relative contributions of the four anthropogenic sources were

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calculated by Eq. (3) and the results are shown in Figure 8(b). It shows that the vehicular emissions, including diesel and gasoline vehicular emissions, made the most important contributions to photochemical O_3 production, with an average percentage of 58%, followed by biomass burning (28%) and solvent usage (14%), suggesting that controlling vehicular emissions and biomass burning could be more effective way for reduction of O_3 pollution at Heshan.

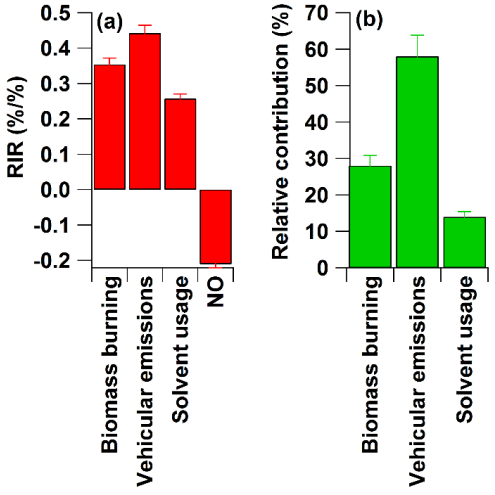

Figure 8. The average RIR values of VOC sources and NO, together with the contributions of different VOC sources to photochemical O_3 formation at Heshan

3.4 Improvement for the reduction of VOCs and NO_x to photochemical O_3 formation

3.4.1 Sensitivity analysis of ozone formation

Changes in the concentrations of VOCs and NO_x will affect O_3 formation, leading to a great variation of the O_3 concentration, which can be illustrated from the ozone isopleth plot. The PBM-MCM model was employed to perform a sensitivity study based on the average diurnal variations of the observed air pollutants (*i.e.*, 58 VOCs, O_3, NO, NO_2, CO, and SO_2.) at the site. We followed the procedures suggested

by Lyu et al. (2016) to investigate the O_3 variations related to the changes of precursors. A total of 520 reduction scenarios (26 NO_x × 20 VOCs) were simulated and the maximum O_3 value in each scenario was selected. Figures 9 shows the obtained ozone isopleth based on the observed levels of VOCs and NO_x at Heshan site.

The two ozone isopleths (Figures 9(a) and (b)) show distinct characteristics of O_3 variations. For a 0-60% reduction of NO_x (corresponding to 40-100% of original NO_x), the O_3 mixing ratio decreases significantly with VOCs for a certain NO_x condition but increases slightly with decreasing NO_x for a fixed mixing ratio of VOCs (Figure 9(a)). This clearly indicates a VOC-limited regime for O_3 formation in this region and is consistent with previous results found in the urban, suburban, and even some rural environments, as well as the downwind site of the PRD region (Zhang et al., 2008b; Cheng et al., 2010; Ling et al., 2011; Zheng et al., 2013; Ling and Guo, 2014). However, it is different from the results found in the northern rural areas of the PRD region based on the measured ratios of O_3/NO_x (Zheng et al., 2010). Here, we introduce the absolute value of RIR (|RIR|) to evaluate the sensitivity of the O_3 formation to VOCs and NO_x. It turns out that the |RIR| decreases with VOCs for a fixed NO_x, while it fluctuates at first and then increases with decreasing NO_x for a fixed VOCs. This implies that the efficiency of O_3 reduction by cutting down VOC emissions alone would decrease gradually (data not shown) and we may need to pay attention to the counter effects caused by decreasing NO_x. For NO_x reduction to 0-40% of the original level, a clear ridge can be seen (Figure 9(b)), dividing the isopleth into two parts: VOCs-limited (right) and NO_x-limited (left). In the VOCs-limited regime, the effects of both VOCs and NO_x on O_3 formation are linear, and the ozone concentration is apparently proportional to the amounts of VOCs (and NO_x): the higher the VOCs mixing ratio (or the lower the NO_x), the higher the O_3 concentration. On the other side of the ridge, for the reduced NO_x to 7.5-15% of original mixing ratio, O_3 concentration decreases with NO_x concentration, but VOCs decrease would lead to O_3 increase. Ideally, the NOx reduction to its 1-7.5%, a regime with "pure" NO_x-limited would occur, where ozone formation is solely controlled by the

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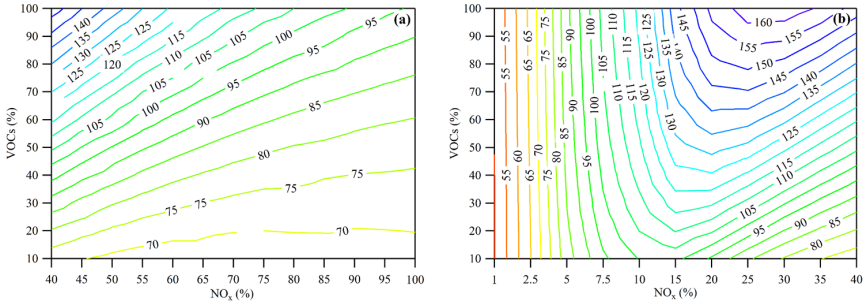
63 NO_x concentrations and insensitive to the change of VOCs. The reduction of NO_x emissions in this case
64 will be the most effective measure for mitigating ozone production.



65

66 Figure 9. The ozone isopleth in term of percentage changes of VOCs and NOx: the percentage change of NO_x from 0 to
67 60% (a) and from 60 to 99% (b). The ozone mixing ratios are in ppbv. The horizontal and vertical axes correspond to
68 the percentage of the measured average mixing ratios of NO_x and VOCs, respectively.

69 **3.4.2 Development of the most optimum control measures on both VOCs and NO_x**

70 Though it was found that the O_3 formation was located in the VOCs-limited regime at the Heshan site
71 (with 100% of NO_x and VOCs as input), it is unknown how much VOCs should be controlled for the
72 most efficient O_3 reduction, especially in society where VOCs and NO_x frequently are controlled
73 simultaneously. To achieve this goal and provide detailed information about the amounts of VOCs and
74 NO_x that need to be controlled, we simulated the net O_3 increment (the total increase of average O_3
75 concentrations when both VOCs and NO_x are reduced) with the reduction of both VOCs and NO_x. This
76 is shown in Figure 10. The horizontal and vertical axis corresponds, respectively, to the reduction
77 percentages of NO_x (e.g., 10% means that the mixing ratios of NO_x were reduced by 10%) and the net
78 increments of O_3 (positive and negative values represent the increase and decrease of O_3 compared to the
79 base case with no reduction of VOCs and NO_x, respectively). The different curves correspond to scenarios
80 with different cutting percentages of VOCs. It shows that the net O_3 increments increased as the reduction
81 percentages of NO_x increased from 0 to 70% regardless of the reduction of VOCs, while the net O_3

increment decreased gradually, starting from the NO_x reduction percentage of ~70%. However, an optimum control measure for VOCs and NO_x was that when this control measure was conducted, the O_3 mixing ratios would be reduced or at least the O_3 mixing ratios would not increase (*i.e.,* the value of the net O_3 increment was less than or equal to zero, the highlighted area in Figure 10). It was found that when the mixing ratios of VOCs were reduced from 0 to 99.5%, the appropriate reduction percentages of NO_x should be located between 0 and 88% or between 90 and 99.5% for zero O_3 increment. However, it was interesting to find that when the reduction percentages of NO_x ranged from 90 to 99.5%, the O_3 formation reduced with the reduction of NO_x regardless of the reduction of VOCs, though reducing NO_x by 90~99.5% is probably unrealistic. Therefore, this section only focused on the range of 0~88% of NO_x reduction for devising optimum controlling measures of VOCs and NO_x. It was determined that when the reduction percentages of NO_x ranged from 0 to 88%, the minimum abatement ratio of VOCs/NO_x for zero O_3 increment changed from ~1 to 1.1 (i.e., the cutting ratios of VOCs/NO_x at the intersections of the curves and the horizontal axis). This suggests that the abatement ratio of VOCs/NO_x should be more than 1.1 to prevent the increase of the O_3 levels at Heshan.

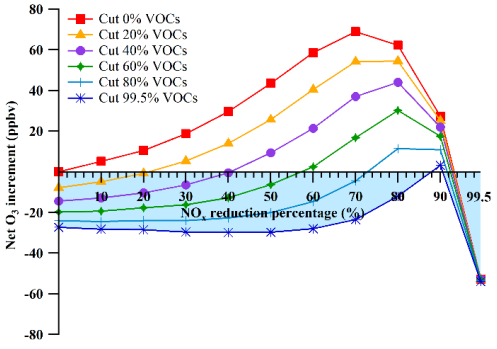


Figure 10. Net O_3 increment as function of the reduction percentages of NO_x and VOCs. The highlighted area represents zero O_3 increment

Furthermore, to determine the appropriate cutting ratios of the individual source of VOCs vs NO_x when both VOC sources and NO_x were reduced, O_3-VOC sources-NO_x sensitivity analysis was conducted. The net O_3 increments as a function of the reduction percentages of NO_x for the individual VOC source are shown in Fig. 11. For different VOC sources, the patterns of the net O_3 increment as a function of different NO_x reductions are similar, with O_3 increments increased when the mixing ratios of NO_x was reduced by 0~80% and decreased with the reduction percentages of NO_x ranging from 80 to 99.5%. It was found that when the cutting percentages of VOCs increased from 0 to 99.5%, the appropriate reduction percentages of NO_x for zero O_3 increment were located in the ranges of 0~30% and 90~99.5%. It was interesting to find that when the reduction percentages of NO_x ranged from 90 to 99.5%, the O_3 formation reduced with the reduction of NO_x regardless of the reduction of VOCs, though reducing NO_x by 90~99.5% is probably unrealistic in the near future. Therefore, here we only focus on the range of 0~30% of NO_x reduction to provide appropriate reduction ratios for devising optimum controlling measures of VOCs and NO_x.

It was found that the specific appropriate reduction percentages of NO_x for zero O_3 increment was 0~27%, 0~22%, 0~22%, and 0~30% for diesel vehicle emission, solvent usage, biomass burning, and gasoline vehicular emission, respectively, while the abatement ratio of individual sources of VOC vs NO_x should be more than 3.8, 4.6, 4.6, and 3.3 for diesel vehicular emission, solvent usage, biomass burning, and gasoline vehicular emission, respectively. For example, if the mixing ratios of NO_x were reduced by 10%, more than 38% of diesel vehicular emission, 46% of solvent usage or biomass burning, or 33% of gasoline vehicular emission needs to be cut to prevent increase of O_3 levels at Heshan. Furthermore, the above ratios demonstrate that reducing VOCs from gasoline vehicular emission has the highest efficiency for both reductions of VOCs and NO_x without increasing O_3 levels, followed by diesel vehicular emission, biomass burning, and solvent usage.

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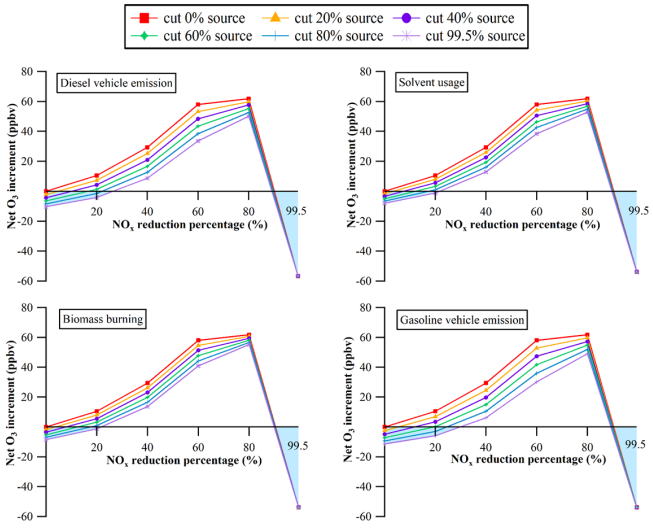

Figure 11. Net O_3 increment as a function of the reduction percentages of NO_x for individual sources of VOC. The highlighted area represents zero O_3 increment

4 Conclusion

The PRD region has long been facing severe photochemical air pollution, and VOCs has been the limiting factor of ozone formation in this region. To better understand the contribution of different anthropogenic VOCs to the ozone formation in this region, we performed in-depth analysis on the data of intensive measurement of VOCs and related species conducted at a downwind rural site (the HeShan site) of the PRD region during October to November of 2014. Overall the mixing ratio of total measured VOCs was high and similar to other urban cluster regions. By using the PMF model with consideration of photochemical processing effects, four anthropogenic emissions sources were identified. The vehicular emission was the most important source of VOCs and also the major contribution to O_3 formation at Heshan site, followed by biomass burning. The PBM-MCM model analysis confirms that the ozone formation at Heshan was VOC-limited, and the regime would not transform until the NO_x is reduced to ≤

25% of the current concentration. The O_3-VOCs-NO_x sensitivity analysis in the whole air suggested that >1.1 of the abatement ratio of VOCs/NO_x was the most appropriate abatement ratio when both the VOC and NO_x were reduced to prevent net O_3 increment. Furthermore, O_3-VOC sources-NO_x sensitivity analysis suggested that the cutting ratios of individual source of VOC vs NO_x should be more than 3.8, 4.6, 4.6, and 3.3 for diesel vehicular emission, solvent usage, biomass burning, and gasoline vehicular emission, respectively, for the more effective control of the O_3 formation, which providing important scientific support for the management department for better formulation and implementation of measures on photochemical pollution.

Indeed, more and more policies on VOCs were/are being implemented and formulated in the PRD region and/or the whole country. A series of policies regarding the control of vehicular emissions have been conducted in the PRD region, which can be mainly divided into two categories: 1) Improve the environment standards of the main air pollutants, *e.g.*, the National Ambient Air Quality Standard of GB 3095-2012; 2) Improve the quality of the fuel used in vehicles, *e.g.* the fifth phase of the vehicle emission standards (GB 18176-2016, GB 14622-2016, GB 19755-2016, and HJ 689-2014). It should be noted that the fifth phase of the vehicle emission standards have limited the emissions of total VOCs from vehicles (IGES, 2014) compared with those of the fourth phase. On 26 December 2017, the Monitoring Plan on the Ambient Volatile Organic Compounds (VOCs) in Key Areas in 2018 was issued by the Ministry of Environmental Protection, which will help to better supervise and provide more observed data for exploring the effective pathways to alleviate VOCs and photochemical O_3 pollution. In addition, "new energy automobiles" are promoted widely in urban cities of the PRD region, such as Guangzhou and Shenzhen, and the eight civil conduct codes of "Breath and Struggle together" were released to raise the public's concern about how to improve the air quality. However, the policies on controlling biomass burning are relatively limited when compared to those for vehicular emissions. For biomass burning, straw return and collected integrated agricultural machinery have been encouraged and widely promoted, and the outdoor burning of straw was forbidden according to the Law of the Prevention and Control of

Atmospheric Pollution. The emission standards for biomass burning are included in the latest version of "Air pollution emission standard for boilers" (GB 13271-2014), where emission standards of coal-fired boilers were applied to biomass briquettes. Furthermore, the emissions from biomass forming fuel boilers and the biomass-molded fuel used in Guangdong should meet DB44/765-2017 and DB44/T 1052-2012, respectively.

Nevertheless, it is expected that these measures could help alleviate the photochemical pollution and improve air quality and visibility, but most of them only control the total mass of VOCs. Therefore, evaluation on the benefits of these measures on VOCs and photochemical pollution is still needed. Overall, the findings of this study provide quantitative information on devising appropriate measures on the VOCs, NO_x, and O_3 pollution at the receptor site of PRD, which could be extended to other regions in China.

Competing interests

The authors declare that they have no conflict of interest.

Author Contributions

In this study, the analysis methods were developed and the whole structure for the manuscript was designed by Dr. Zhenhao Ling, Dr. Zhe Wang and Prof. Jun Zhao. Ms. Zhuoran He conducted the data process and wrote the original copy of the manuscript. Prof. Xuemei Wang and Prof. Min Shao provided the data and revised the manuscript. Furthermore, the simulation of PBM-MCM model was conducted by Dr. Zhenhnao Ling and Prof. Hai Guo. Finally, the manuscript was finalized by Dr. Zhenhao Ling and Dr. Zhe Wang.

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