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How does the OH reactivity affect the ozone production efficiency: case studies in Beijing and Heshan

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Abstract

Total OH reactivity measurements have been conducted in August 2013 on the Peking University campus, Beijing and from October to November 2014 in Heshan, Guangdong Province. The daily median result for OH reactivity was 19.98 ± 11.03 s^{-1} in Beijing and 30.62 ± 19.76 s^{-1} in Heshan. Beijing presented a significant diurnal variation with maxima over 27 s^{-1} in the early morning and minima below 16 s^{-1} in the afternoon. Measurements in Heshan gave a much flatter diurnal pattern. Missing reactivity was observed at both sites, with 21% missing in Beijing and 32% missing in Heshan. Unmeasured primary species, such as branched-alkenes could contribute to missing reactivity in Beijing, especially in morning rush hour. An observation-based model with the Regional Atmospheric Chemical Mechanism 2 was used to understand the daytime missing reactivity in Beijing by adding unmeasured oxygenated volatile organic compounds and simulated intermediates of primary VOCs degradation. However, the model failed to explain the missing reactivity in Heshan, where the ambient air was found to be more aged, and the missing reactivity was presumably to

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attribute to oxidized species, such as aldehydes, acids and di-carbonyls. The ozone production efficiency was 27% higher in Beijing and 35% higher in Heshan when constrained by the measured reactivity, compared to the calculation with measured and modeled species included, indicating the importance of quantifying the OH reactivity for better understanding ozone chemistry.

1. Introduction

Studies on total OH reactivity in the atmosphere have been increasing over the last two decades. The instantaneous total OH reactivity, is defined as

$$k_{OH} = \sum_i k_{OH+X_i}[x_i] \quad (1\text{-}1)$$

where X represents a reactive species (CO, NO_2 etc.) and k_{OH+X_i} is the rate coefficient for the reaction between X and OH radicals. Total OH reactivity is an effective index for evaluating the amounts of reductive pollutants in terms of ambient OH loss and hence their role in atmospheric oxidation (Williams, 2008; Williams and Brune, 2015; Yang et al., 2016). It also provides a constraint for OH budget researches in both field campaigns and lab studies (Stone et al., 2012; Fuchs et al., 2013).

There are three major total OH reactivity measuring techniques, two laser-induced-fluorescence (LIF) based techniques (Calpini, et al., 1999; Kovacs and Brune, 2001) and one proton-transfer-reaction mass spectrometry (PTR-MS) based technique, comparative reactivity method (CRM) (Sinha et al., 2008). A brief comparison of these techniques and known interferences has been summarized previously (Yang et al., 2016). In parallel with the developments of measuring techniques, total OH reactivity measurements have been intensively conducted in urban and suburban areas worldwide. Details of these campaigns are compared in Table 1 and Table 2, following similar summaries from previous papers (Lou et al., 2010; Dolgorouky et al., 2012; Yang et al., 2016). Most of the campaigns exhibited similar diel variations with higher reactivity in the late night and early morning rush hour, and lower results in the afternoon, which could be explained by the variations of the boundary layer height, the temporal change

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in emissions and oxidation processes. Anthropogenic volatile organic compounds (VOCs) and inorganics, such as CO and NO_x ($NO + NO_2$) are major known OH sinks in urban areas.

However, a substantial difference between measured and calculated or modelled OH reactivity, which is termed missing reactivity, has been revealed in many campaigns. Compared to the high percentages of missing reactivity in forested areas (Sinha et al., 2010; Nölscher et al., 2012; 2016; Edwards et al., 2013, Williams et al., 2016), most campaigns reported relatively lower percentages of missing reactivity in urban and suburban areas except for the 75% missing reactivity in Paris in MEGAPOLI under continental air masses influences.

Different researchers have applied various methods in pursuit of origins of missing reactivity. Unmeasured primary species are important candidates. Sheehy et al. (2010) discovered a higher percentage of missing reactivity in morning rush hour and found unmeasured primary species, including organics with semi and low-volatility could contribute up to 10% reactivity. Direct measurements on reactivity of anthropogenic source emissions were conducted, such as vehicle exhaust and gasoline evaporation. An average of 17.5% missing reactivity was found in vehicle exhaust measurements (Nakashima et al., 2010), while good agreements were obtained for gasoline evaporation, by adding primary emitted branched-chained alkenes into consideration (Wu et al., 2015). All these experiments require more comprehensive measurements covering branched hydrocarbons as well as semi-volatile organic compounds (SVOCs). Besides primary substances, unknown secondary species are also not negligible. Yoshino et al. (2006) found a good correlation between missing reactivity and measured oxygenated VOCs (OVOCs) in three seasons except for winter, assuming that the unmeasured OVOCs could be major contributors of missing reactivity. The observation-based model (OBM) is widely used to evaluate the measured reactivity (Lee et al., 2010; Lou et al., 2010; Whalley et al., 2016), confirming the important contribution from OVOCs and undetected intermediate compounds, in one case could increase reactivity by over 50% (Lou et al., 2010).

Ground-level ozone has been of increasing concern in China. While the ozone

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concentration exceeds Grade II of China National Ambient Air Quality Standards (2012) frequently in summer in Beijing-Tianjin-Hebei area and Pearl River Delta (PRD) region (Wang et al., 2006; Zhang et al., 2008), it appears there is an increasing trend for ozone in Beijing and other area (Zhao et al., 2009; Zhang et al., 2014). Due to the non-linearity relationship between the precursors (NO_x and VOCs) and ozone, revealing the contribution of VOCs to ozone formation has become a difficult but key question for researchers. Compared to traditional empirical kinetic model approach (EKMA) (Dodge et al., 1977), the OH reactivity due to VOCs (termed VOCs reactivity) rather than VOCs mixing ratio has certain advantages in the calculation of ozone production rate (Geddes et al., 2009; LaFranchi et al., 2011; Sinha et al, 2012; Zhang et al., 2014). However, due to species and chemistry deficiencies in measurements and model, the conception of VOCs reactivity was conventionally limited to the OH reactivity from measured species. Species, those have not yet been typically measured, hence unaccounted for, have laid a great uncertainty in ozone production prediction as well as in control strategy formulation. By directly measuring the total OH reactivity, VOCs reactivity can be obtained by deducting the inorganic reactivity from total OH reactivity, which provides a good constrain for the evaluation (Yang et al., 2016).

This paper presents two intensive observation datasets conducted in August 2013 in Beijing, and October to November 2014 in Heshan, Guangdong, focusing on OH reactivity and related species. The variations of total OH reactivity at both sites were compared with similar observations in urban and suburban areas worldwide. Thereafter, a zero dimensional box model based on Regional Atmospheric Chemical Mechanism 2 (RACM2) was employed for OH reactivity simulations. The possible missing reactivity was discussed and its importance for the ozone production calculation was also provided.

2. Methods

2.1 Total OH reactivity measurements

2.1.1 Measuring principles

Total OH reactivity was measured by the comparative reactivity method first

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developed at Max Planck Institute for Chemistry (Sinha et al., 2008). An introduction to the measurement system and principle is provided in brief below. The CRM system consisted of three major components, inlet and calibration system, reactor, and measuring system as in Fig 1. Ambient air was pumped through a 14.9m Teflon 3/8 inch inlet at about 7 L·min^{-1} rate.

In this method, pyrrole (C_4H_5N) was used as the reference substance and quantified by a quadrupole PTR-MS (Ionicon Analytic, Austria). There are four working modes for the whole measuring procedure. In the C0 mode, pyrrole (Air Liquid Ltd, U.S.) is introduced into the reactor with dry synthetic air (99.99%, Chengweixin Gas Ltd, China). A mercury lamp (185nm, used for OH radicals generation) is turned off and high-pure dry nitrogen (99.99%, Chengweixin Gas Ltd, China), is mixed into the reactor through a second arm. In this mode, the highest signals of m/z 68 (protonated mass of pyrrole) c0 are obtained. Then in the C1 mode, the nitrogen and synthetic air is still dry but the mercury lamp is turned on. The mixing ratio of pyrrole decreased to c1. The difference between c0 and c1 is mainly due to the photolysis of pyrrole (Sinha et al., 2008). C2 mode is the "zero air" mode in which synthetic air and nitrogen are humidified before being introduced into the reactor. The photolysis of water vapor generates OH radicals which react with pyrrole in the reactor to c2 level. Then C3 mode is the measuring mode in which the automatic valve switches from synthetic to ambient air. The ambient air is pumped into the reactor to react with OH radicals, competing with pyrrole molecules. The mixing ratio of pyrrole is detected as c3. Total OH reactivity is calculated as below, based on equations from Sinha et al. (2008):

$$k_{OH} = c1 \times k_{Pyr+OH} \times \frac{c3-c2}{c1-c3} \quad (2\text{-}1)$$

2.1.2 Calibrations and tests

We performed two calibrations for the measurements. First, PTR-MS was calibrated by diluted dry pyrrole standard gas ranging from less than 10 ppbV to over 160 ppbV (presented in Fig S1). Additionally, we conducted a comparison calibration with humidified pyrrole dilution gas. The sensitivity was about 3% to 5% higher than dry calibration, which was considered for later calculation (Sinha et al., 2009). The other calibration was to test the CRM system performance, in which single standard

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gases, such as CO, propane, propene (Huayuan Gas Ltd, China) or a mixture 56 non-methane hydrocarbons (NMHCs) (SpecialGas Ltd, U.S.) were introduced into the CRM reactor instead of the ambient air samples. Examples of these calibrations are presented in Fig 2. Measured and calculated OH reactivity matched well within uncertainty range for all calibrations.

A major factor influencing the measurement results is the stability of OH radical generation. One potential interference is the difference in relative humidity between C2 mode and C3 mode. During the experiment, we used one single needle valve to control the flow rate of synthetic air going through the bubbler, so that the relative humidity during C2 mode could be adjusted to match humidity during ambient sampling (C3 mode). Meanwhile, the remaining minor difference could be corrected by factors derived from the OH reactivity-humidity correction experiment. The details of the OH-correction experiment and the figures are presented in the supporting information (Fig. S1 and S2).

Another interference is the variations of ambient NO, producing unconstrained OH radicals by recycling simultaneously genrated HO_2 radicals, as described in previous studies (Sinha et al., 2008; Dolgorouky et al., 2012; Michoud et al., 2015). In the morning rush hour or on polluted cloudy days, NO can rise to over 30 ppbV in both Beijing and Heshan, which can potentially introduce high uncertainties for reactivity measurements. The NO-correction experiment was conducted by introducing known amounts of standard gases into the reactor. When the stable concentrations for c2 were obtained, different levels of NO were injected into the reactor and the "measured" reactivity decreased as the NO mixing ratio increased. Then a correction curve was fitted between the differences in reactivity and NO mixing ratios. Several standard gases and different levels of base reactivity (from less than $30s^{-1}$ to over $180s^{-1}$) have been tried and the curve was quite consistent for all tested gases, as shown in Fig 3. The correction derived from the curve was used later to correct ambient measurements according to simultaneous detected NO levels. The correction was necessary when NO mixing ratio was larger than 5 ppbV, which was quite often observed in the morning time as well as cloudy days in Beijing and Heshan. The relative change for reactivity

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results could be over 100 s^{-1} when NO mixing ratio was about 30 ppbV.

A further potential interference from nitrous acid (HONO) on total OH reactivity measurement with CRM was first discovered and corrected during the Heshan campaign. The photolysis of HONO in the reactor can generate the same amount of unconstrained OH radicals and NO molecules, as shown in R1. The additional OH radicals and NO molecules can be both interferences with the reactivity measurements. Similar correction experiments were conducted as the same with the NO correction experiment. HONO were added stepwise in several mixing ratios (1-10 ppbV), generated by a HONO generator (Liu et al., 2016) and thus introduced into the reactor. A curve was fitted between the differences in reactivity and HONO mixing ratios, as presented in Fig 4. The correction associated with this curve was also applied later in the ambient measurements.

$$\mathrm{HONO} \xrightarrow{h\gamma} \mathrm{OH+NO} \qquad \text{(R1)}$$

To make sure the production of OH radicals was stable during the experiments, C1 mode was measured for 1-2 hour every other day and C2 mode was measured for 20-30 minutes every two hours. With above calibrations and tests into consideration, the detection limits of CRM methods in two campaigns was around 5 s^{-1} (2δ). The total uncertainty of the method was about 20%, due to rate coefficient of pyrrole reactions (15%), flow fluctuation (3%), instrument precision (6% when measured reactivity > 15 s^{-1}), standard gases (5%) and corrections for relative humidity (5%).

2.2 Field measurements

2.2.1 Measuring sites and periods

The urban measurements started from August 10th to August 27th, 2013 at Peking University (PKU) Site (116.18°E, 39.99°N), which was set on the roof laboratory of a 6-floor building. The site is about 300 m from the 6 lane main road to the east and 500 m off the 8 lane 4th ring of Beijing to the south. This site is a typical urban site and significantly impacted by vehicle emissions. Detailed information about this site can be found in a previous paper (Yuan et al., 2012).

Suburban measurements were conducted from October 20th to November 22nd

2014 at Heshan (HS) site, Guangdong (112.93°E, 22.73°N). The site is located on top of a small hill (60 m above ground) in Jiangmen, which is 50km from a medium size city Foshan (with a population of about 7 million) and 80 km from a megacity Guangzhou. Detailed information about this site can also be found in a separate paper (Fang et al., 2016)

2.2.2 Simultaneous measurements

During both intensive campaigns, fundamental meteorological parameters and trace gas were measured simultaneously. Meteorological parameters, such as temperature, relative humidity, pressure, wind speed, wind direction were measured. NO and NO_x mixing ratios were measured by chemi-luminescence (model 42i, Thermo Fischer Inc, U.S.), and O_3 was measured by UV absorption (model 49i, Thermo Fischer Inc, U.S.). CO was measured by Gas Filter Correlation (model 48i, Thermo Fischer Inc, U.S.), and SO_2 was measured by pulsed fluorescence (model 43C, Thermo Fischer Inc, U.S.). The photolysis frequencies were measured by a spectral radiometer (SR) including 8 photolysis parameters. These parameters were all averaged into 1-minute resolution. The performances of these instruments are presented in Table S1 and Table S2.

VOCs were measured by a cryogen-free online GC-MSD/FID system, developed by Peking University (Yuan et al., 2012; Wang et al., 2014a). The time resolution is 1 hour but the sampling time starts from the 5th minute to 10th minute every hour. The system was calibrated by two sets of standard gases: 56 NMHCs including 28 alkanes, 13 alkenes and alkynes, 15 aromatics; EPA TO-15 standards (http://www.epa.gov/ttnamti1/les/ambient/airtox/to-15r.pdf), including additional OVOCs and halocarbons. The detection limits ranged from 10ppt-50ppt, depending on the species. Formaldehyde was measured by the Hantzsch method with time resolution of 1 minutes. Detailed information about this instrument is described in one previous paper (Li et al., 2014).

2.3 Model description

2.3.1 Box model

A zero-dimensional box model was applied to simulate the unmeasured secondary

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products and OH reactivity for both field observations. The chemical mechanism employed in the model was RACM2 (Stockwell et al., 1997, Goliff et al., 2013), with implementation of the additional isoprene mechanism Mainz Isoprene Mechanism (MIM, Pöschl et al., 2000) and update by Geiger et al. (2003) and Karl et al. (2006). The model was constrained by measured photolysis frequencies, ancillary meteorology and inorganic gases measurements, as well as VOCs results. Mixing ratios of methane and H_2 were set to be 1.8 ppmV and 550 ppbV. The model was calculated in a time-dependent mode with 5 min time resolution. In the model run, all input data were constant in the time interval. Each model run started with 3 days spin-up time to reach steady-state conditions for long-lived species. Additional loss by dry deposition was assumed to have a corresponding lifetime of 24 hours to avoid the accumulation of secondary productions.

2.3.2 Ozone production efficiency

Ozone production efficiency (OPE) is defined as the number of molecules of total oxidants produced photochemically when a molecule of NO_x was oxidized (Kleinman, 2002, Chou et al., 2011). It helps to evaluate the impacts of VOCs reactivity on ozone production in various NO_x regimes. In this model work, the OPE could be calculated as the ratio of ozone production rate (i.e. $P(O_3)$) to NO_x consumption rate (i.e. $D(NO_x)$). NO_z, calculated as the difference between NO_y (sum of all odd-nitrogen compounds) and NO_x, was assumed to be the oxidation products of NOx. Thus the OPE could be also calculated as $P(O_3)/P(NO_z)$. The ozone production rate is obtained as 2-2, and the $P(NO_z)$ is approximately as $P(HNO_3)$, which is given as 2-3.

$$P(O_3) = k_{HO_2+NO}\,[HO_2][NO] + \sum_i k_{RO_{2_i}+NO}\,[RO_{2_i}][NO] \qquad (2\text{-}2)$$

$$P(NO_z) = k_{NO_2+OH}\,[NO_2][OH] \qquad (2\text{-}3)$$

3. Results

3.1 Time series of meteorology and trace gases

In Fig 5, the time series of selected meteorological parameters and inorganic trace gases are presented in 5 minute averages. The median values of the inorganic trace gases were 0.715 ± 0.335 ppmV for CO, 6.3 ± 5.75 ppbV for NO and 36.5 ±

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21.3 ppbV for NO_2, 57 ± 44 ppbV for O_3 in Beijing. In Heshan, the median results were 0.635 ± 0.355 for CO, 9.7 ± 6.95 for NO, 29.6 ± 12.6 for NO_2, and 55.7 ± 34.9 for O_3. Both results were within the range of literature reports (Zhang et al., 2008; Zheng et al., 2010; Zhang et al., 2014). However, daytime averaged O_3 mixing ratio in Beijing 2013 was a little lower than the medium results (about 60 ppbV) in normal years (Zhang et al., 2014). This can be explained by higher frequencies of cloud and rains during the observations, taking up for one third of the measuring times. With weaker sunshine, the photolysis rate decreased significantly as the peak values of J (O1D) on cloudy days could be only half the values of sunny days. Even with these factors into consideration, pollution episodes with ozone exceeding Grade II of China National Ambient Air Quality Standards (93 ppbV) existed in both campaigns.

Measured mixing ratios of VOCs in both campaigns are presented in Table S3 and Table S4 in the supporting information. In summer Beijing, alkanes made up over 60% of the summed VOCs during most of the time, while in Heshan the contribution from aromatics was 6% higher than that in Beijing. This could be explained by stronger emissions from solvent use and paint industry in the PRD region (Zheng et al., 2009). The ratio of toluene to benzene, which is typically used qualitatively as an indicator for aromatics emission sources also supported this assumption. While this ratio in Beijing was close to 2, similar to vehicle emissions (Barletta et al., 2005), the ratio in Heshan is higher than 3 due to strict control of benzene in solvent usage these days (Barletta et al., 2005; Liu et al., 2008). In the ozone polluted episode in Fig 5, the mixing ratios of most species were about twice to three times higher than the daily average results.

Comparing diurnal variations of NO_x, O_3 and photochemical age, which are presented in Fig 6 and Fig 7, differences are apparent between both sites. Both sites presented similar diurnal patterns for O_3 and NO. However, the highest 1-hour average O_3 value at PKU site came in the afternoon and stayed in the high level till the dawn. However, O_3 pattern at Heshan site did not have the same “plateau” in the afternoon. An additional similarity was that NO peaks were present at similar times for both sites. But NO decreased at a slower rate in Heshan that even when it was

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12:00 p.m., there was still over 1 ppbV. This was because NO observed at PKU site was mainly from local vehicle emissions while NO_x at Heshan site was significantly influenced by transported air masses.

VOCs measurements provided us a good comparison of the oxidation state at two sites. Based on the OH exposure calculation methods (de Gouw et al., 2005), we chose a pair of VOCs species: m,p-xylene and ethylbenzene to calculate the photochemical age, as shown in 3-1

$$[\mathrm{OH}]\Delta t = [\ln(\frac{[E]}{[X]})_t - \ln(\frac{[E]}{[X]})_0]/(k_E - k_x) \quad (3\text{-}1)$$

Here, [E] and [X] represents the mixing ratios of ethylbenzene and m,p-xylene, k_E and k_X means the OH reaction rate coefficient of ethylbenzene and m,p-xylene. As presented in Fig 7, we chose 1.15 ppbV $ppbV^{-1}$ and 2.3 ppbV $ppbV^{-1}$ as emission ratios of ethylbenzene to m,p-xylene in Beijing and Heshan, as they were the largest ratios in diurnal variations for the campaign. The largest OH exposure in Beijing 2013 was calculated as 0.71×10^{11} mole s cm^{-3} in 13:00 LTC, while the largest OH exposure in Heshan 2014 was calculated to be 1.69×10^{11} mole s cm^{-3} in 14:00 LTC. The results in Beijing was comparable to previous reports (Yuan et al., 2012). Under the assumption that ambient OH concentration was 8.0×10^6 mole cm^{-3} (Lu et al., 2013), the photochemical age in Beijing was about 3 h at most. With measured peak OH concentration as 1.2×10^7 mole cm^{-3} in Heshan (Tan et al., in preparation), the photochemical age in Heshan was about 5 h to 6 h, which was about twice the photochemical age of the Beijing observations, indicating a more aged atmospheric environment in Heshan.

3.2 Measured reactivity

Total OH reactivity ranged from less than 10 s^{-1} to over 100 s^{-1} in Beijing summer 2013 (Fig 5a). The daily median value was 19.98 ± 11.03 s^{-1}, and presented a slight diel variation, despite the large variations between different days (Fig 8). Total OH reactivity was higher in the late night to morning rush hour with an hourly median value of 27.15 s^{-1}, and decreased to a lower value in the afternoon, median value of 17.33 s^{-1}. This diurnal pattern was similar to the variations of NO_x mixing ratios,

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which was also presented in a previous study (Williams et al., 2016). The morning rush hour peak was mostly due to the stronger vehicle emissions from close roads. The difference between midnight reactivity and afternoon levels is the results of the variations of boundary layer height, vertical mixing and chemical reaction rates.

In contrast, measured total OH reactivity in Heshan was higher in median but the diel variation was not significant. The daily median value was 30.62 ± 19.76 s^{-1}. The OH reactivity was much less variable in the daily variation. This could result from several "clean" periods with little variations for the whole day, during which ozone and $PM_{2.5}$ concentrations were relatively low. Two pollution episodes were identified between Octber 24th to 27th and November 14th to 17th, 2014. Both episodes showed accumulating pollution with increasing concentrations of ozone and $PM_{2.5}$. The reactivity level was also significantly higher than ordinary days (Fig 5b).

3.3 Variations in missing reactivity

Significant differences between measured and calculated reactivity have been obtained for both measurements in Beijing and Heshan. While the measured reactivity was obtained by direct measurement, the calculated reactivity was derived from mixing ratios of different species multiplied by their rate coefficients with OH radicals. Taking all measured species into consideration, NO_x and NMHCs contributed the most, which were 45%-55% of total OH reactivity (Fig 9). However, measured OVOCs played a more significant role in Beijing rather than in Heshan, due to higher levels of formaldehyde and acetaldehyde observed in Beijing. This could be partially explained by the seasonal difference and thus faster photochemical productions in August in Beijing than October and November in Heshan.

Missing reactivity was on average 21 ± 17% of the total OH reactivity in Beijing and 32 ± 21% in Heshan. However, the missing reactivity presented different temporal patterns. In Beijing, the missing reactivity was extremely high during pollution episodes. On some occasions during the morning rush hour, the missing percentage reached over 50%. In contrast, missing reactivity was quite consistent for the whole campaign at the Heshan site, similar to measured reactivity patterns. Even for clean days with reactivity levels of less than 20 s^{-1}, a 20%-30% percentage of missing

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reactivity still existed.

4. Discussion

4.1 Reactivity levels in Beijing and Heshan

While the absolute VOCs reactivity was high for both sites, the relative reactivity compared to NMHCs mixing ratios were higher. Compared to other urban and suburban measurements, the measured VOCs reactivity (obtained by subtracting inorganic reactivity from total OH reactivity) was not very high (Beijing 2013 as 11.2s^{-1} and Heshan 2014 as 18.3s^{-1}), as in Fig 10. Tokyo presented a similar level of VOCs reactivity (Yoshino et al., 2006) and Paris had an even higher level of VOCs reactivity despite the observation was conducted in the winter (Dolgorouky et al., 2012). The measured NMHCs levels (obtained by adding all hydrocarbon mixing ratios together) were also not very high, with Beijing 2013 being around 20 ppbV and Heshan 2014 higher than 35 ppbV. However, when the VOCs reactivity was divided by the measured NMHCs mixing ratios to obtain the ratio, values for both Beijing and Heshan were higher than results from similar observations. This indicated that with a similar level of hydrocarbons, VOCs in Beijing and Heshan would provide higher reactivity than in other areas.

There could be several explanations for this phenomenon. One possible explanation is the higher contribution from highly-reactive VOCs. Compared to other campaigns, both observation sites in this study had a slightly higher loading of alkenes and aromatics (Yuan et al., 2012; Wang et al., 2014b). These species significantly increased the VOCs reactivity due to relatively higher OH reaction rate coefficients. The other probable reason is contribution from OVOCs. In Beijing and PRD, formaldehyde could accumulate to over 10 ppbV during some periods, which was significantly higher than levels found in other observations (Li et al., 2013; Chen et al., 2014). Another possible explanation is unmeasured species, whether primary hydrocarbons or secondary products, which will be discussed later.

4.2 Contributions to the missing reactivity: primary VOCs

As missing reactivity was observed at Beijing and Heshan site during both

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campaigns, the species causing these missing phenomena were examined. One possible explanation could be unmeasured primary VOCs species.

Throughout the whole campaign at the PKU site, missing reactivity was normally found in the morning, as for an example in August 16th and 17th 2013 in Fig 11. Between 5 a.m. to 10 a.m., primary emissions were strong due to vehicle-related sources, but the chemical reactions were relatively slow owing to comparatively weak sunshine, and thus low concentrations of oxidants. Unmeasured primary VOCs species were therefore assumed to be the most likely contributors to missing reactivity in this time range. Specially unmeasured branched-alkenes were paid attention to, for their high reactivity and previously observed emissions from vehicle exhaust (Nakashima et al., 2010) and gasoline evaporation (Wu et al., 2015). We found only one dataset in 2005 measured by NOAA (Liu et al., 2009). We chose the diurnal patterns of missing reactivity in Beijing 2013 and compared to the diel cycles of four measured branched-alkenes in 2005. Good correlations were found as presented in Fig 11. However, even with mixing ratios of 2005, the reactivity contribution was less than 2.5s^{-1}. With observed decreasing trends in mixing ratios of most NMHCs species in Beijing (Zhang et al., 2014; Wang et al., 2015), the branched-alkenes were insufficient to explain the missing reactivity. Unmeasured semi-volatile organic compounds (SVOCs) and intermediate volatile organic compounds (IVOCs), such as alkanes between C12 to C30, and polycyclic aromatic hydrocarbons (PAHs) could be also important. Sheehy (2010) found SVOCs and IVOCs contributed to about 10% in morning time in Mexico City. A more comprehensive characterization of VOCs covering high-volatility to low-volatility is required for future budget closure experiments of total OH reactivity.

4.3 Contributions to the missing reactivity: secondary VOCs

Due to limitations in chemistry mechanisms as well as measuring techniques, secondary products are not fully quantified in ambient air and could probably contribute significantly to the observed missing reactivity, especially in the urban or suburban sites receiving chemically complex aged air masses.

Besides the large missing reactivity during the morning rush hour, there was about 25% difference between measured and calculated reactivity from August 16th to 18th,

2013 at PKU site. Considering high levels of oxidants in daytime, the mixing ratios of branched-alkenes could be lower than 0.1 ppbV, which could not explain the observed missing reactivity. Constrained by measured parameters (meteorology, inorganic gases, VOCs including measured carbonyls), modeled reactivity was about 20-25% higher than calculated reactivity and could agree with measured reactivity in most of the daytime, as presented in Fig 11. Major contributors from modeled species were unmeasured aldehydes, glyoxal and methyl glyoxal. Average values of major secondary contributors to modelled reactivity are provided in Table S5. In the model, the higher secondary contribution on August 17th 2013 morning was owing to isoprene oxidation products due to unusual high levels of isoprene over 1.5 ppbV at 8:00 a.m. However, there remained over 40% missing reactivity at 7:00 and 8:00 a. m. unexplained within the model.

The similar OBM was applied for the Heshan observation to simulate the unmeasured secondary species, as shown in Fig 12. During the heavy polluted episode between October 24th and 27th 2014, a 30% missing reactivity existed for most time between the measured reactivity and the calculated reactivity. However, the modeled reactivity was only about 10-20% higher than calculated reactivity, and not enough to explain the measured reactivity. The major contributors among modeled species were also unmeasured aldehydes, glyoxal, methyl glyoxal and other secondary products, as shown in Table S6. Due to strong emissions of aromatics from solvent use and petroleum industry in PRD region (Zheng et al., 2009), high levels of glyoxal and methyl glyoxal in this region have been observed from space borne measurements (Liu et al., 2012) and ground-based measurements (Li et al., 2013). Compared to the 2006 measurements in Backgarden, a semi-rural site in PRD region, the modeled glyoxal was twice as high as around 0.8 ppbV (Li et al., 2013). This difference possibly resulted from higher levels of precursors in 2014 measurements, where the measured reactivity was about 50% higher than the results in Backgarden 2006 (Lou et al., 2010).

4.4 Implications for ozone production efficiency

While the missing reactivity raises our interests in looking for unknown organic species in measurements and simulations, it also provides a useful constrain for ozone

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modelling, which lead us to wonder how much the unconstrained VOCs species will contribute to ozone production. To evaluate this contribution, we employed the OBM model to calculate the OPE. We set two scenarios for the model run: 1) The base run was constrained with measured species, including all inorganic compounds, PAMS 56 hydrocarbons, TO-15 OVOCs and formaldehyde. This is how we obtained the modelled reactivity as presented above. With the model's help, some intermediates and oxidation products were reproduced. 2) The other scenario was constrained by measured reactivity. However, due to the difference between measured and modeled reactivity, we allocated the missing reactivity into several groups. For the primary species, we assumed the ratio between total chain-alkenes and branched-alkenes were the same in Beijing 2013 and in Heshan 2014 as the ratio in Beijing 2005, so we got the assumed mixing ratios of branched-alkenes at both sites. For secondary species, we allocated the remaining missing reactivity into different intermediates or products based on weights obtained in the model base run. Under both assumptions, we ran the OBM and calculated the OPE, as presented in Fig 13.

For both sites, the OPE constrained by measured reactivity were significantly higher than the OPE we calculated from modeled reactivity. In Beijing, the OPE from measured reactivity was about 27% higher in average. The value was 35% higher at Heshan site under similar assumptions. This percentage was close to the percentage of missing reactivity, indicating the ignorance of unmeasured or unknown organic species can cause significant underestimation in ozone production calculation.

Compared to other similar calculations worldwide, the OPE results for Beijing and Heshan were significantly higher (Fig 14). The comparison was made for NO_x = 20 ppbV which was in the range of most observation results. For urban measurements, only the results from Mexico City in MCMA-03 were close to the Beijing results in basic model run (Lei et al., 2008). For suburban measurements, the OPE in Heshan 2014 was higher than all other three campaigns, even including the results from Shangdianzi station in CAREBEIJING-2008 campaigns (Ge et al., 2012). While taking missing reactivity into consideration, the OPE results were even higher, indicating more ozone was produced by the reactions of the same quantity of NO_x molecules.

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5. Conclusions

In this study, total OH reactivity measurements employing CRM system were conducted at PKU site in Beijing 2013, and Heshan site 2014 in PRD region. Comparisons between measured and calculated, as well as modelled reactivity were made and possible reasons for the missing reactivity have been investigated. The contribution of missing reactivity to ozone production efficiency was evaluated.

In Beijing 2013, daily median result for measured total OH reactivity was 19.98 ± 11.03 s^{-1}. Similar diurnal variation with other urban measurements was found with peaks over 25 s^{-1} during the morning rush hour and lower reactivity than 16 s^{-1} in the afternoon. In Heshan 2014, total OH reactivity was 30.62 ± 19.76 s^{-1} on daily median result. The diurnal variation was not significant. Both sites have experienced OH reactivity over 80 s^{-1} during polluted episodes.

Missing reactivity was found at both sites. While in Beijing the missing reactivity made up 21% of measured reactivity, some periods even reached a higher missing percentage as 40%-50%. In Heshan, missing reactivity's contribution to total OH reactivity was 32% on average and quite stable for the whole day. Unmeasured primary species, such as branched-alkenes could be important contributor to the missing reactivity in Beijing, especially in morning rush hour, but they were not enough to explain Aug 17th morning's event. With the help of RACM2, unmeasured secondary products were calculated and thus the modelled reactivity could agree with measured reactivity in Beijing in the noontime. However, they were still not enough to explain the missing reactivity in Heshan, even in daytime. This was probably because of the relatively higher oxidation stage in Heshan than in Beijing.

Missing reactivity could impact the estimation of atmospheric ozone production efficiency. Compared to modeled reactivity from base run, ozone production efficiency would rise 27% and 35% in Beijing and Heshan with measured reactivity applied. Both results were significantly higher than similar observations worldwide, indicating the relatively faster ozone production at both sites.

However, in order to further explore the OH reactivity in both regions, more

species need to be included in measurements and modeling to close the total OH reactivity budget. Moreover, a thorough way with more detailed mechanisms should be established to connect the missing reactivity to the evaluation of ozone production.

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826 Table 1 Total OH reactivity measurements in urban areas

Campaign	Site	Year	method	$k_{OH(measured)}$ (s^{-1}) [a]	$k_{OH\ (calculated)}$ (s^{-1} if it is a value) [b]	Measured species [c]	Reference
SOS	Nashville, US	summer, 1999	LIF-flow tube	11.3	7.2	SFO	Kovacs et al., 2001; 2003;
PMTACS-NY 2001	NY, US	summer, 2001	LIF-flow tube	15~25	within 10%	SFO	Ren et al., 2003
PMTACS-NY 2004	NY, US	winter, 2004	LIF-flow tube	18-35	statistically lower	SF	Ren et al., 2006a
MCMA-2003	Mexico City, Mexico	spring, 2003	LIF-flow tube	10~120	30% less than	-[d]	Shirley et al., 2006
TexAQS	Houston, US	summer, 2000	LIF-flow tube	7~12	agree well	SFO	Mao et al., 2010
TRAMP2006	Houston, US	summer, 2006	LIF-flow tube	9-22	agree well	SFOB	Mao et al., 2010
	Tokyo, Japan	2003-2004	LP-LIF	10~100	30% less than	SFOB	Sadanaga et al., 2004; Yoshino et al., 2006
	Tokyo, Japan	summer, 2006	LP-LIF	10~55	30% less than	SFOB	Chatani et al., 2009
	Tokyo, Japan	spring, 2009	LP-LIF	10~35	22% less than	SFOB	Kato et al., 2011
	Tokyo, Japan	winter, 2007, autumn, 2009	LP-LIF	10~80	10~15 less than	SFOB	Yoshino et al., 2012

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Table 1 Total OH reactivity measurements in urban areas (continued)

	Mainz, German	summer, 2005	CRM	10.4		-	Sinha et al.,2008
MEGAPOLI	Paris, France	winter, 2010	CRM	10~130	10~54% less than	SO	Dolgorouky et al., 2012
ClearfLo	London, England	summer, 2012	LP-LIF	10-116	20~40%	SFOB	Whalley et al., 2016
	Lille, France	autumn , 2012	CRM, LP-LIF	~70	Reasonable agreement	SFO	Hansen et al., 2015
	Dunkirk, France	summer, 2014	CRM	10-130		-	Michoud et al., 2015

a. For sources from different studies, the measured reactivity was presented as the averaged results, or ranges of diurnal variations, or the ranges of the whole campaign.
b. For sources of different studies, the calculated reactivity was presented within an uncertainty range, as a percentage reduction or s^{-1} reduction.
c. Measured species that have been used for the calculated reactivity (following Lou et al., 2010): S = inorganic compounds (CO, NO_x, SO_2 etc) plus hydrocarbons (including isoprene); F = formaldehyde; O = OVOCs other than formaldehyde; B = BVOCs other than isoprene;
d. "-" means a lack of information regarding what has been measured or how long it has been measured.

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Table2 Total OH reactivity measurements in suburban and surrounding areas

Campaign	Site	Year	method	$k_{OH(measured)}$ (s^{-1})	$k_{OH\ (calculated)}$ (s^{-1} if it is a value)	Measured Species	Reference
	Central Pennsylvania, US	spring, 2002	LIF-flow tube	6.1		-	Ren et al., 2005
PMTACS-NY2002	Whiteface Mountain, US	summer, 2002	LIF-flow tube	5.6	within 10%	-	Ren et al., 2006b
TORCH-2	Weybourne, England	spring, 2004	LIF-flow tube	4.85	2.95	SFO	Ingham et al., 2009 Lee et al., 2010
CareBeijing-2006	Yufa, China	summer, 2006	LP-LIF	10-30	agree well	S	Lu et al., 2010; 2013
PRIDE-PRD	Backgarden, China	summer, 2006	LP-LIF	10~120	50% less than	S	Lou et al., 2010
DOMINO	El Arenosillo, Spain	winter, 2008	CRM	6.3~85		SF	Sinha et al., 2012

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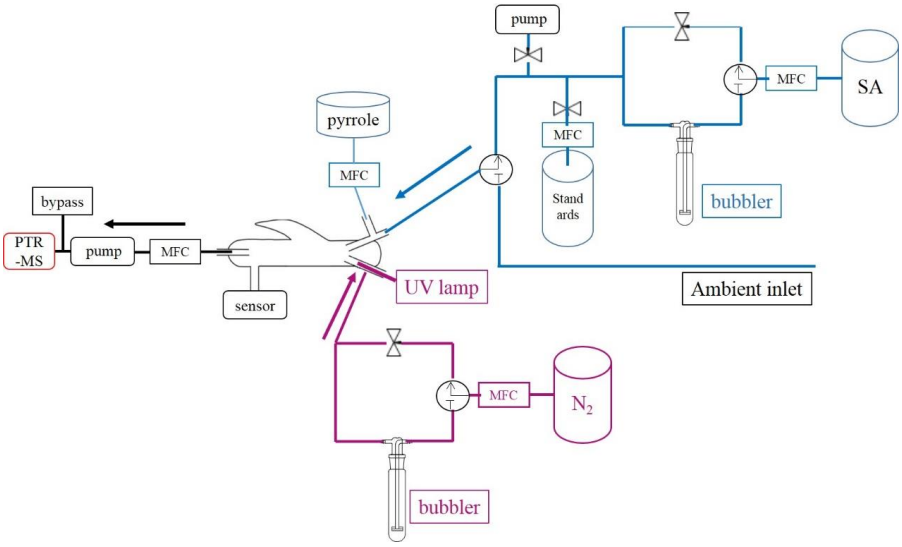

Fig 1 Schematic figures of CRM system in Beijing and Heshan observations.
Blue color represents ambient air or synthetic air injection system, purple color represents OH generating system, black color represents the detection system.
Pressure is measured by the sensor connected to the glass reaction.

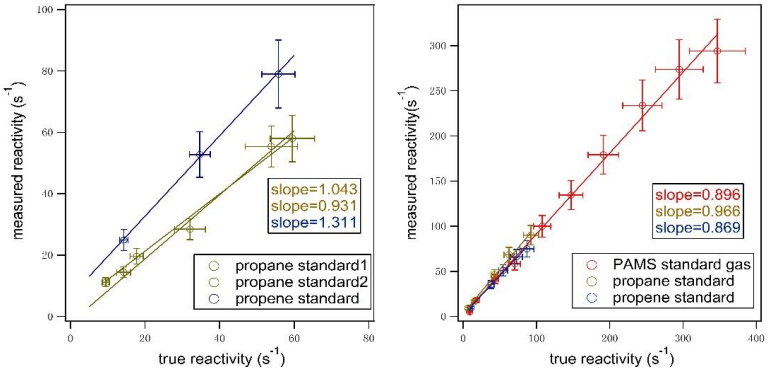

Fig 2 OH reactivity calibration in Beijing (left) and Heshan (right).
Left: Calibration in Beijing used two single standards: propane, propene;
Right: Calibration in Heshan used three standards: propane, propene, mixed PAMS 56 NMHCs.
Error bars stand for estimated uncertainty on the measured and true reactivity.

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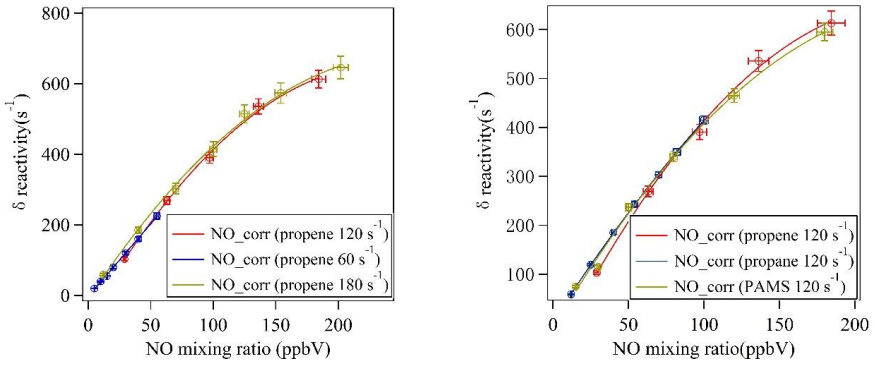

Fig 3 NO-correction experiments and fitting curves in Heshan 2014.

Left: NO-correction experiments with different mixing ratios of propene standard gas; Right: NO-correction experiments with different standard gases at the same reactivity level: 120 s^{-1}.

Error bars stand for estimated uncertainty on the NO mixing ratios and difference in reactivity.

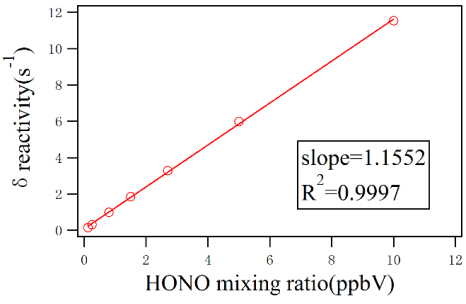

Fig 4 HONO-correction experiments and the fitting curve in Heshan 2014.

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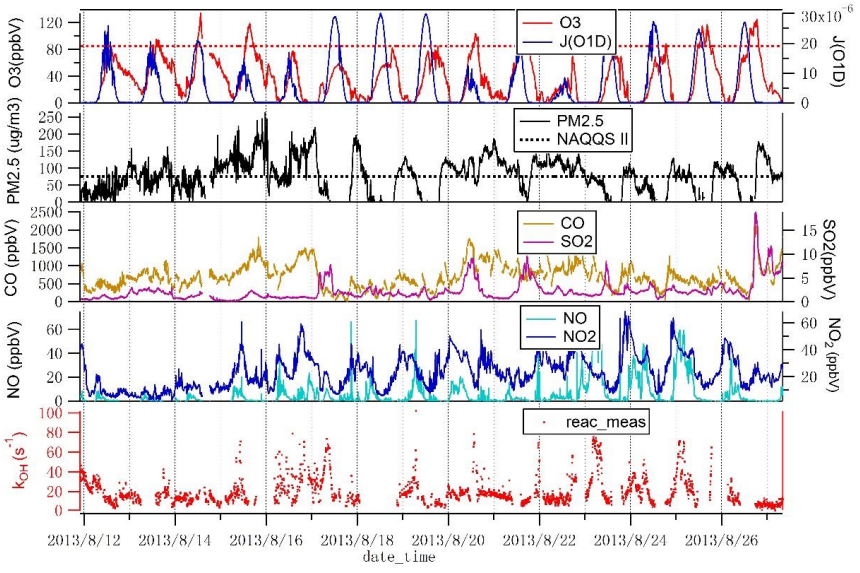

Fig 5-a Time series of meteorological parameters and inorganic trace gases during August 2013 in Beijing.

Red and black dashed lines are Grade II of National Ambient Air Quality Standard.

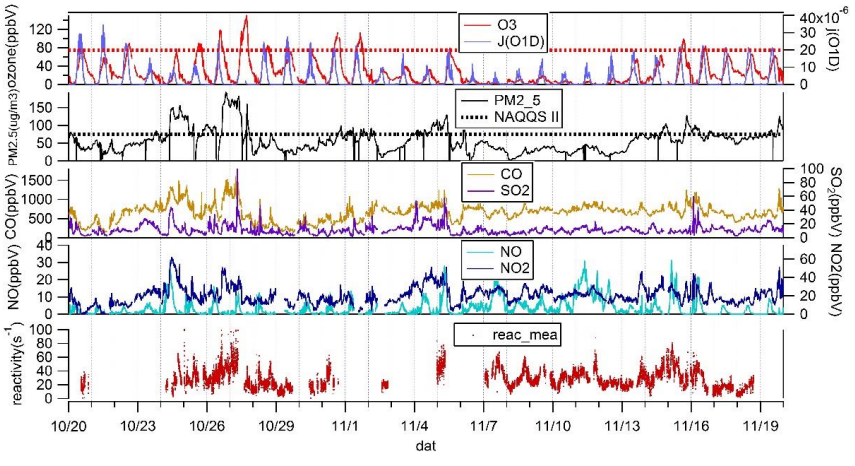

Fig 5-b Time series of meteorological parameters and inorganic trace gases during October-November, 2014 in Heshan.

Red and black dashed lines are Grade II of National Ambient Air Quality Standard.

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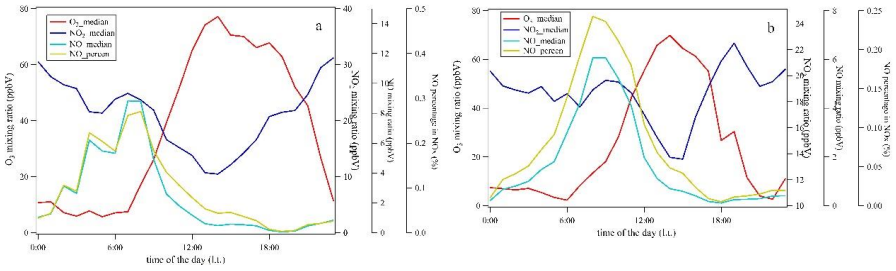

Fig 6 Diurnal variations of O_3, NO, NO_2 and relative contribution of NO to NO_x in Beijing 2013 (a) and Heshan 2014 (b)

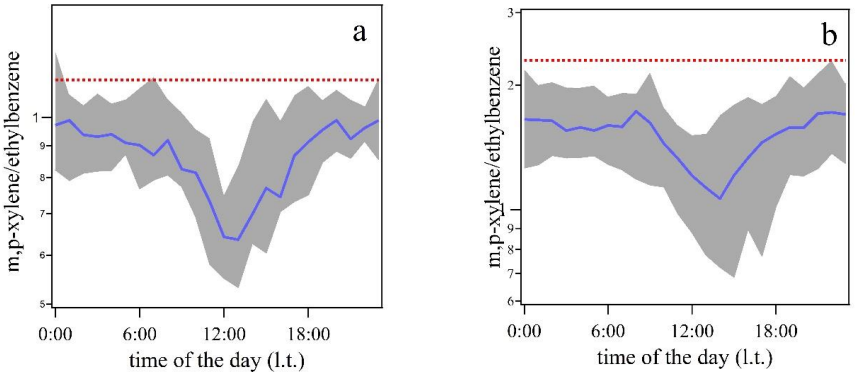

Fig 7 Ratios of m,p-xylene to ethylbenzene in Beijing 2013 (a) and Heshan 2014 (b)

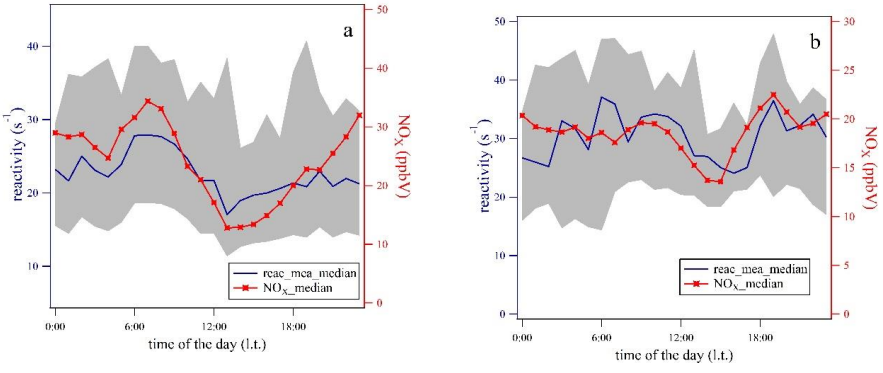

Fig 8 Diurnal variation of hourly median results of measured OH reactivity and NO_x mixing ratios in Beijing (a) and Heshan (b)

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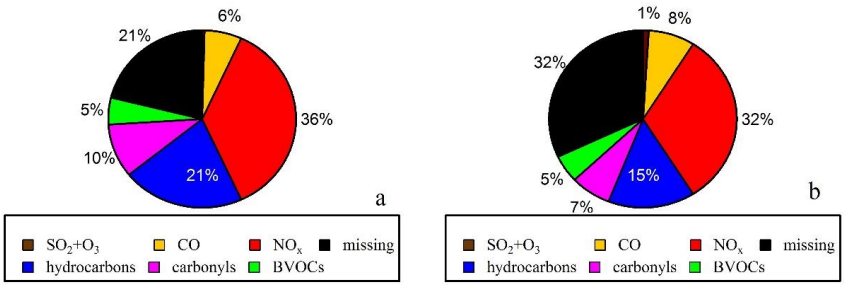
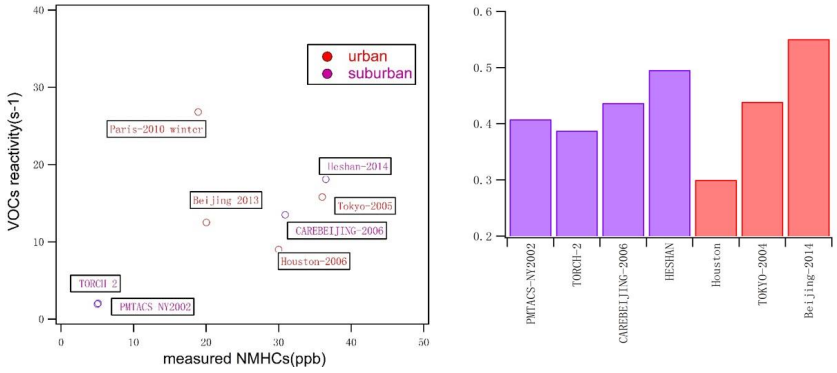
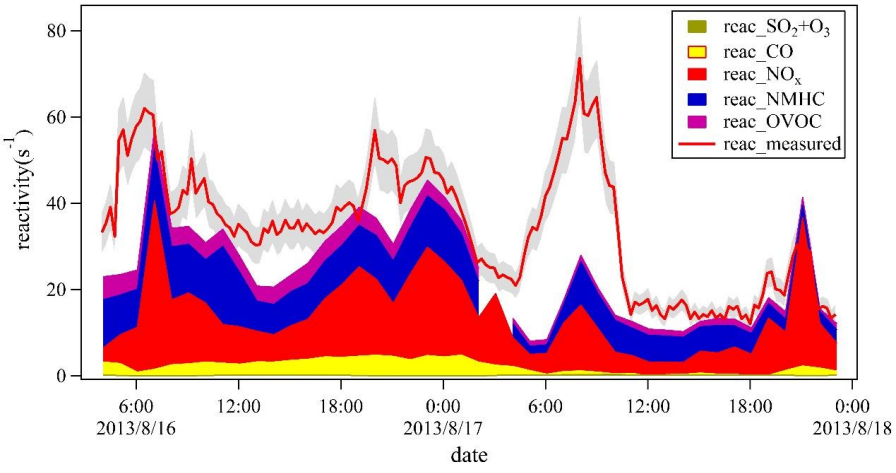


Fig 9 Composition of measured reactivity in Beijing (a) and Heshan (b)



a b

Fig 10 a: Comparison of VOCs reactivity and measured NMHCs in urban and suburban observations.
b: Comparison of the ratio between VOCs reactivity and measured NMHCs in urban and suburban observations



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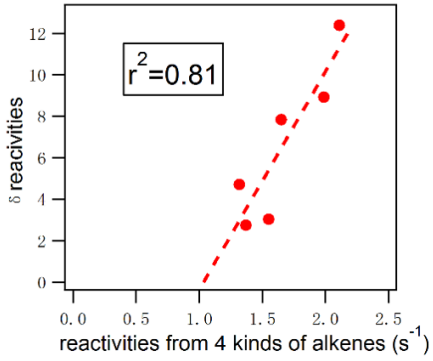

Fig 11 Upper panel: Comparison between measured and calculated reactivity in Beijing August 16th to 18th 2013.
Lower panel: Correlation between missing reactivity and reactivity assumed from branched-chain alkenes in diurnal patterns.

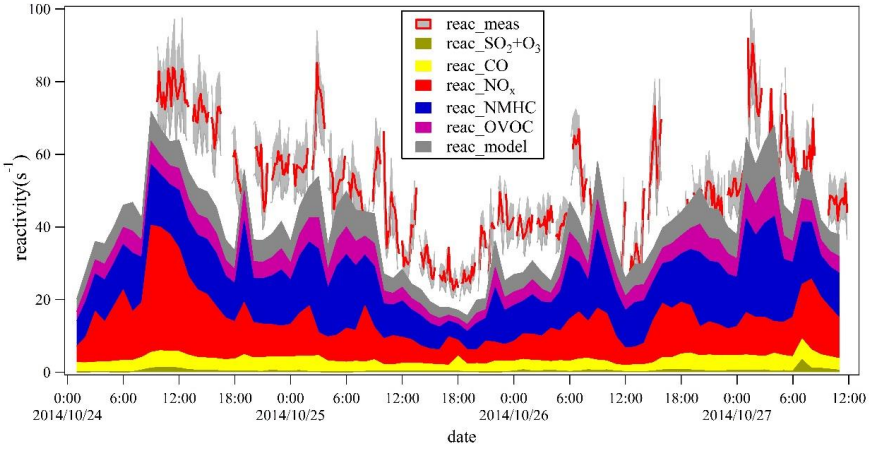

Fig 12 Comparison between measured reactivity and calculated reactivity as well as modelled reactivity in Heshan between October 24th and 27th 2014.

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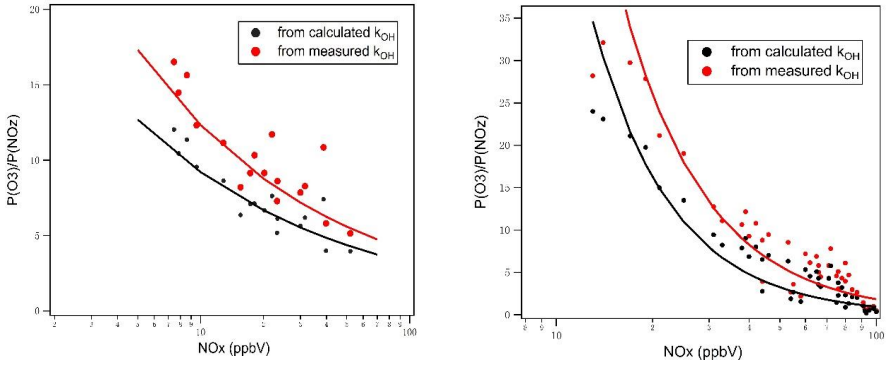

a b

Fig 13 Comparison between OPE calculated from measured reactivity and calculated reactivity in Beijing (a) and Heshan (b).

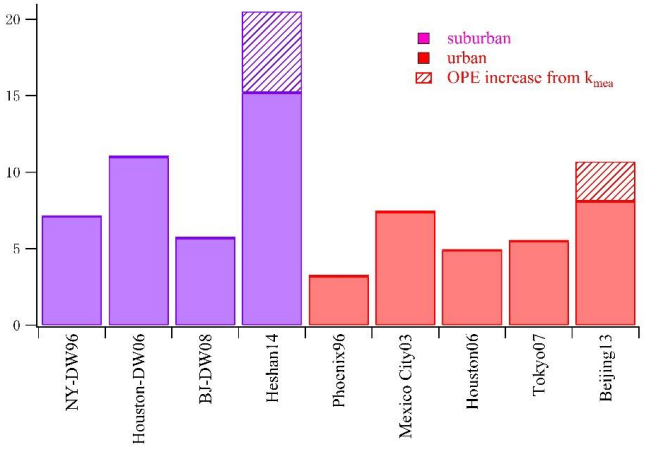

Fig 14 Comparison between the OPE results in this study and other results from literatures. The comparison is made with the NO_x = 20 ppbV. "DW" is in abbreviation of downwind.