Response to anonymous referee #1

General comments:

This paper describes the measurement of higher alkanes by NO^+ PTR-ToF-MS at two sites in China and the authors showed the significant contribution of the higher alkanes to secondary organic aerosol (SOA) formation. I recognize that the measurement of the higher alkanes in ambient air is very challenging, so the data presented here would be precious. But I feel that there are two issues in the present paper.

Response: Thank you very much for your valuable comments and suggestions on our manuscript. These comments are all helpful for improving our article. All the authors have seriously discussed about all these comments. According to your comments, we have tried best to modify our manuscript to meet with the requirements for the publication in this journal. Point-by-point responses to the comments are listed below.

Firstly, the authors seemed to fail to suppress the formation of O_2^+ in the ion source (Figure S2). I think that the O_2^+ reaction could substantially interfere with the ion signals of alkanes. In addition, I feel that the ratio of O_2^+ to NO^+ was not stable as far as I looked at Figure S2. The authors should pay attention to the intensity of O_2^+ relative to the NO^+ intensity.

Response: In the submitted manuscript, we made a mistake on the **Fig. S2**, where we put a wrong number of Us=40 V (in fact Us=120 V) on the **Fig. S2(a)**. I think that might mislead you into thinking that we faild to suppress the formation of O_2^+. The corrected data and more experiment results were included in the revised **Fig. S2**. Before field campaigns, we did laboratory tests on the ion source voltages to find suitable volatage settings, where intensities of ion impurites (O_2^+, H_3O^+ and NO_2^+) are low. According to the laboratory results, we chose Us=40 V and Uso=100 V as ion source voltage settings for the field measurement of higher alkanes **(Fig. S2(a))**, under which condition (absolute humidity=~11.6 mmol/mol) the ratio of O_2^+ to NO^+ is ~10%.

We also included the data of NO^+, O_2^+, H_3O^+ and NO_2^+ during field campaigns in the revised supporting information. The intensities of primary ion NO^+ and impurites (O_2^+, H_3O^+ and NO_2^+) (**Fig. S3**) and the ratio of O_2^+ to NO^+ (**Fig. S4**) fluctuate during two campaigns. The ratio of O_2^+/NO^+ (**Fig. S4(a)**) is basically stable at 2-4% during the PRD campaign except a little high values of 7-10% for Oct. 26-Nov. 2, 2018. While, for the NCP campaign, the ratio of O_2^+/NO^+ (**Fig. S4(b)**) fluctuates between 10-40% in the early stage of campaign and keeps stable at ~20% in the late stage of campaign. When comparing the O_2^+/NO^+ ratio with the ambient abosolute humidity during campaigns (**Fig. S5**), we find that there was an obvious negative correlation between O_2^+/NO^+ ratio and ambient abosolute humidity (**Fig. S5**), which is also consistent with laboratory humidity experiments. As the result, the fluctuations of O_2^+/NO^+ ratios are attributed to the changes of humidity during the two campaigns.

We agree with the comment that O_2^+ could interfere with the ion signals of alkanes. According to the study from Amador et al. (2016), the reactions of O_2^+ with alkanes can be proceeded by charge transfer and hydride abstraction that might affect the ion signals of alkanes with NO^+ reactions in our study. As we got the alkanes standard at the very late period of the PRD campaign, we did not have the daily calbirations for this campaign. However, the O_2^+/NO^+ ratios were small with a genaral range of 2-4% (**Fig. S4(a)**), we think the interfence of O_2^+ in this campaign is negligible. During the NCP camaign, we conducted calibrations every 1-2 days under both dry conditions and ambient humidity conditions. In the revised manuscript, we add a figure (**Fig. 2**) to show the correlation of sensitivities of *n*-alkanes and O_2^+/NO^+ ratios. As showned in **Fig. 2**, the sensitivities of *n*-alkanes (C8-C15) varied significantly with the fluctuations of O_2^+/NO^+ ratios in both dry conditions and ambient conditions during the NCP campaign. This indicate that the interference of O_2^+ should be considered. Therefore, we use the daily ambient calibrations results to quantify the concentration of higher alkanes for the NCP campaign.

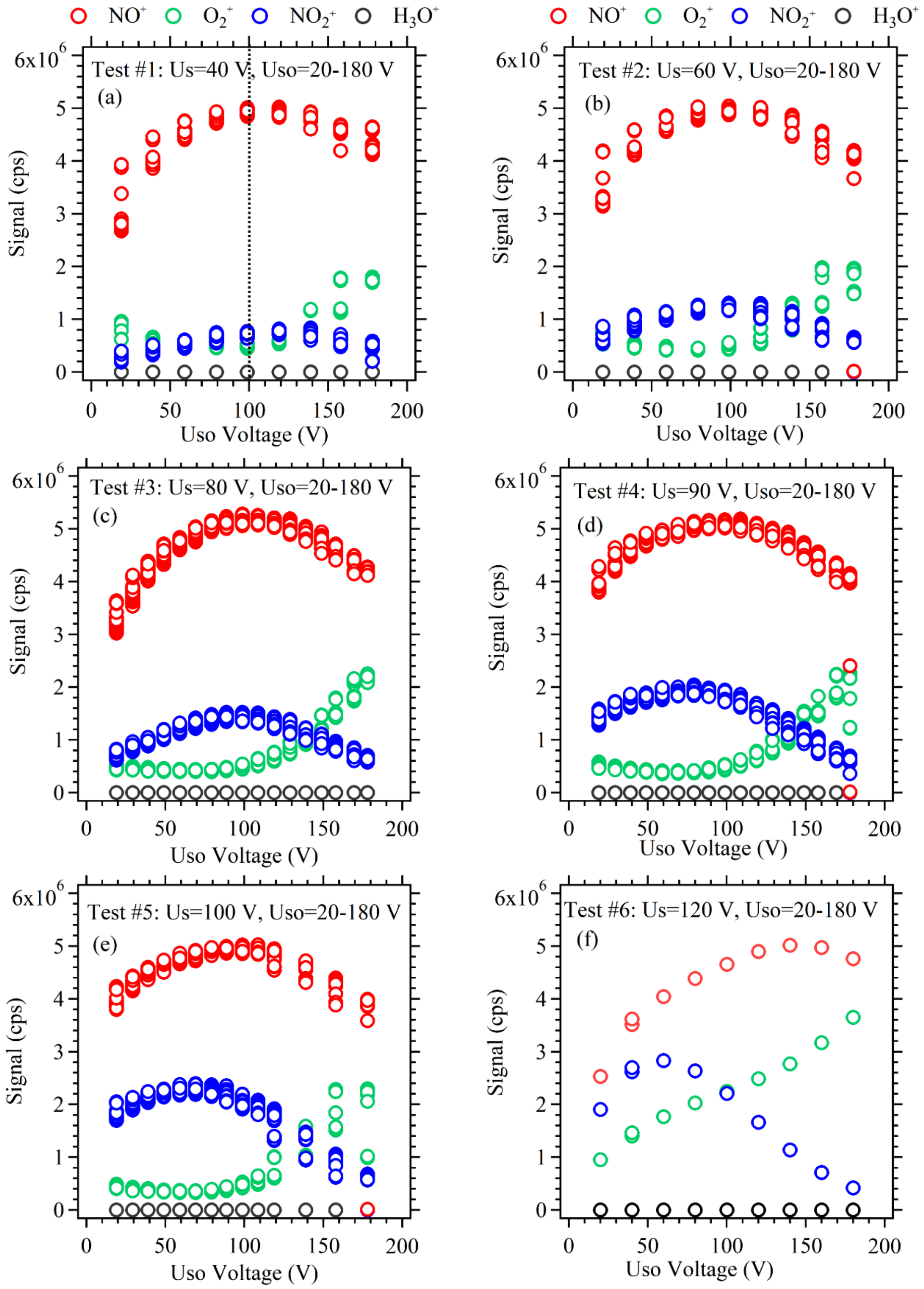

Figure S2. The variations of NO^+, H_3O^+, O_2^+ and NO_2^+ ions on the voltages of ion source (Us and Uso) for NO^+ PTR-ToF-MS. For each experiment, either Us or Uso is fixed at a voltage and the other was varied to explore the best setting for NO^+ PTR-ToF-MS. For example, test #1 in (a), we fix Us at 40 V and change Uso from 20 V to 180 V. The dashed line in (a) indicate the setting point in this study (Us=40 V and Uso=100 V).

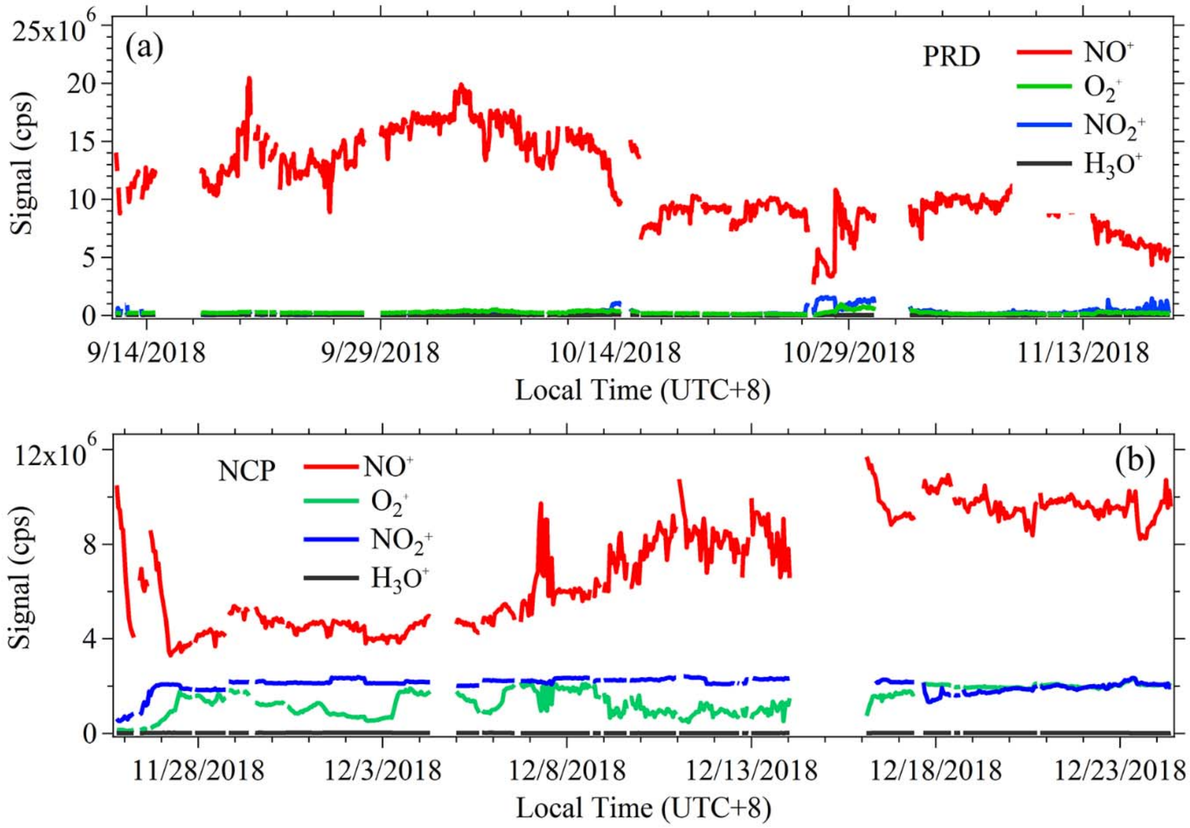

Figure S3. Time series of NO^+, H_3O^+, O_2^+, NO_2^+ during the PRD **(a)** and the NCP **(b)** campaigns, respectively.

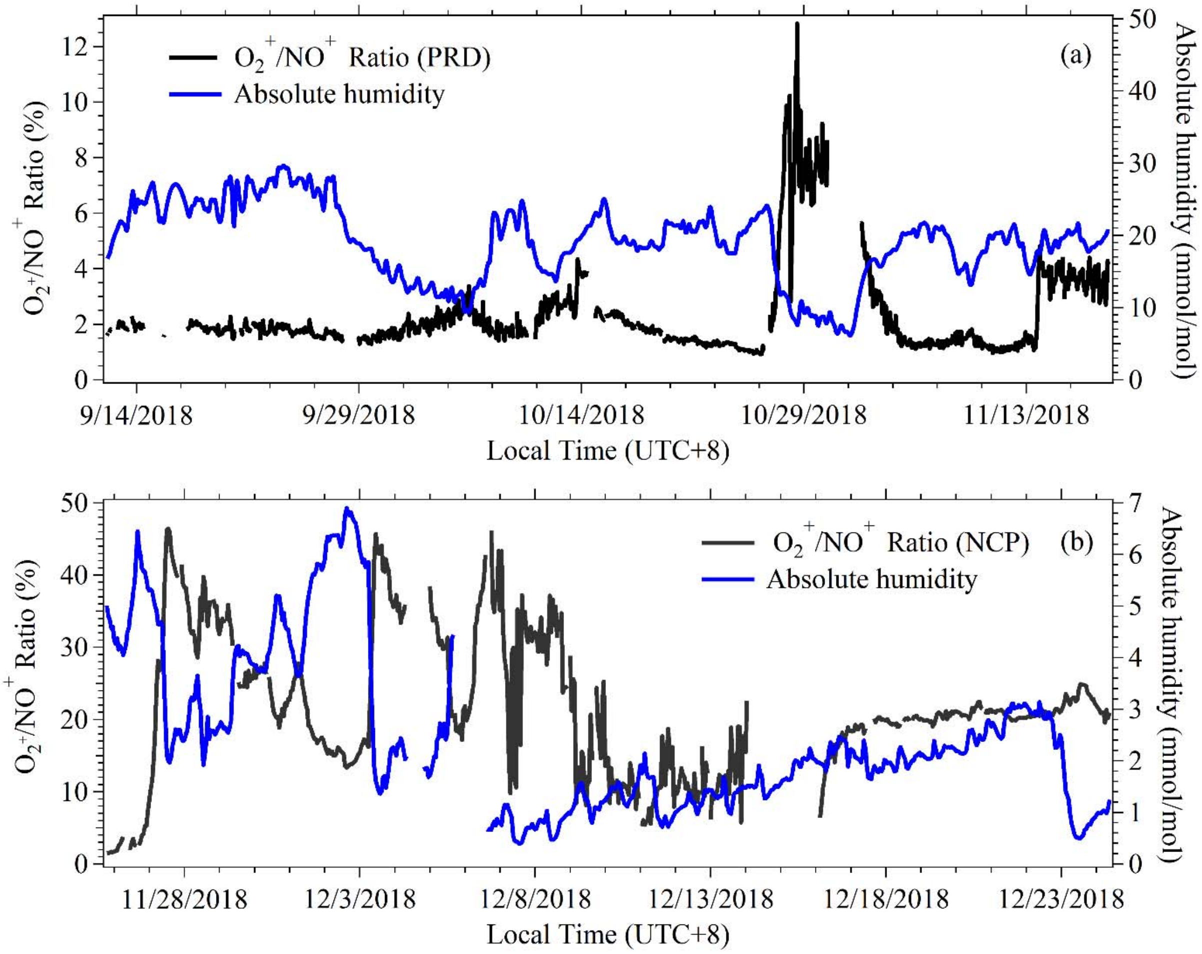

Figure S4. Time series of O_2^+ to NO^+ ratios and absolute humidity during the PRD (a) and the NCP (b) campaigns, respectively.

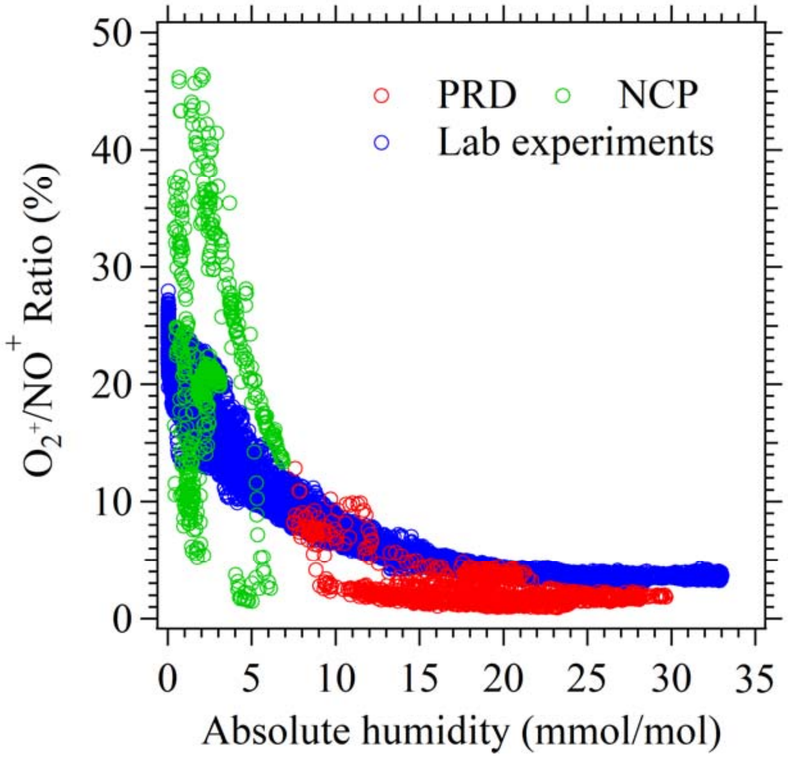

Figure S5. Humidity dependence of O_2^+ to NO^+ ratios during the lab experiment and the two field campaigns.

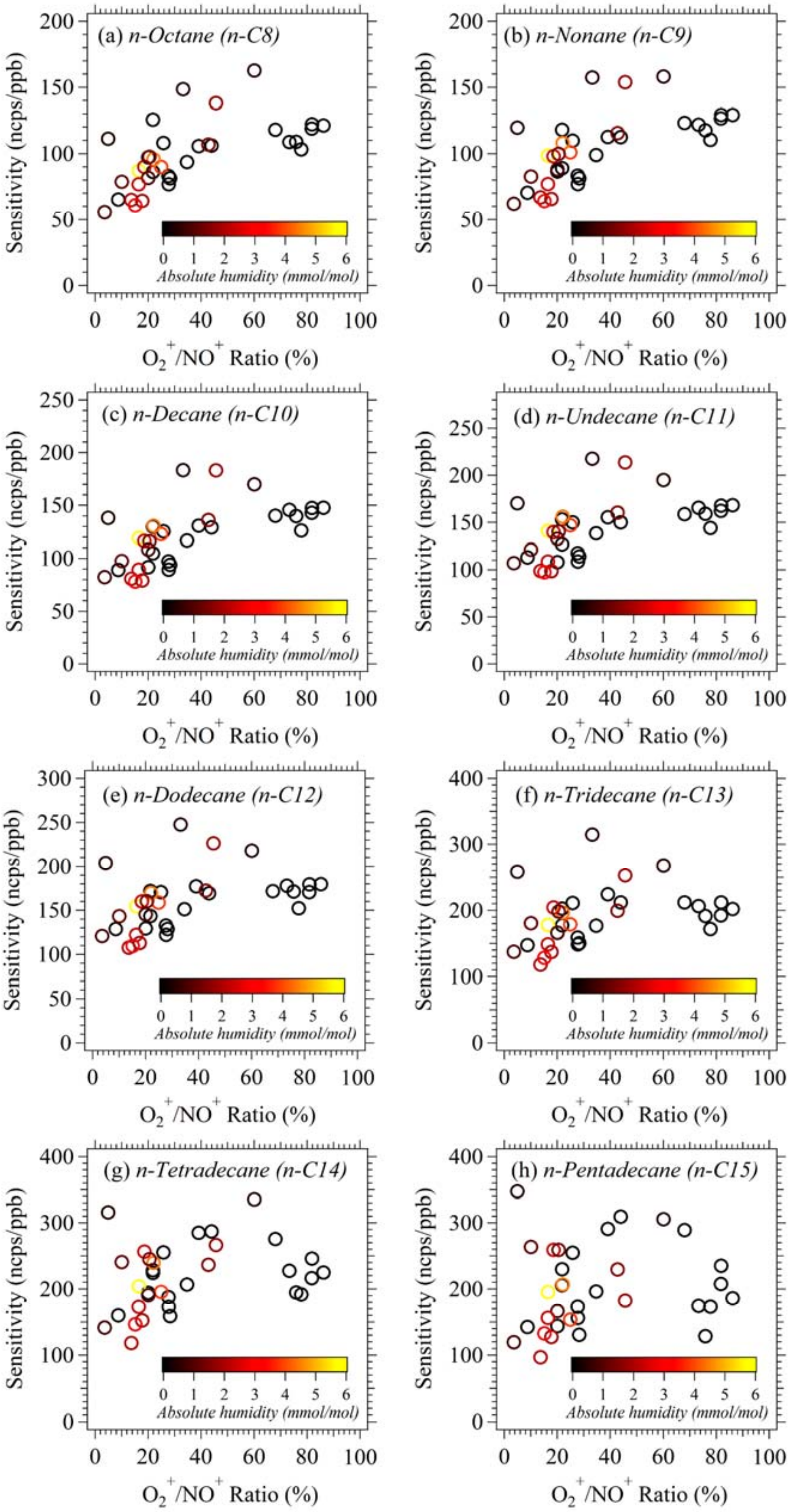

Figure 2. The relationship of sensitivities of *n*-alkanes (C8-C15) versus O_2^+/NO^+ ratios during the NCP campaign. The data points are color-coded using absolute humidity during the calibration.

In the revised manuscript, part of the section of “2.1 NO$^+$ PTR-ToF-MS measurement” are modified as follows:

Line 122-131 on Page 6: “Voltages of ion source and drift chamber were explored (Figure S2) in the laboratory to optimize the generation of NO$^+$ ions relative to H_3O^+, O_2^+, and NO_2^+ and minimize alkane fragmentation. The intensities of primary ion NO$^+$ and impurities (O_2^+, H_3O^+ and NO_2^+) and the ratio of O_2^+ to NO$^+$ during two campaigns are shown in Figure S3 and Figure S4, respectively. The ratio of O_2^+/NO$^+$ (Figure S4 (a)) is basically stable at 2-4% during the PRD campaign except during Oct. 26-Nov. 2, 2018 (7-10%). For the NCP campaign, the ratio of O_2^+/NO$^+$ (Figure S4 (b)) fluctuates between 10-40% in the early stage of campaign and keeps stable at ~20% in the later stage of the campaign. Such fluctuations are atrributed to the humidity effect in the ambient air (Figure S5).”

Line 147-161 on Page 7: “Sensitivities of *n*-alkanes (C8-C15) standards were obtained during the campaign (Figure S6), which is defined as the normalized signal of hydride abstraction ions for each higher alkane at 1 ppbv with a unit of ncps/ppb. The fluctuations of sensitivities during the NCP campaign may be influenced by the variations of O_2^+ signals (Figure 2), because the reactions of O_2^+ with alkanes can be proceeded by both charge transfer and hydride abstraction (Amador et al., 2016) that may affect the ion signals of alkanes with NO$^+$ reactions. Therefore, we use the daily ambient calibrations results to quantify the concentration of higher alkanes during the NCP campaign to reflect the variations of sensitivity from day to day. For the measurements without daily calibrations, we used closest calibration results according to corresponding ambient O_2^+/NO$^+$ ratios and ambient humidity. Since we got the alkanes standard at the very late period of the PRD campaign, we did not have the daily calibrations for this campaign. Therefore, we use the sensitivity of each alkane under corresponding O_2^+/NO$^+$ condition obtained from lab experiments after this campaign and also consider the humidity effects (Figure 3(b, c)) to quantify the concentration of higher alkanes during the PRD campaign.”

Secondly, I feel that the diurnal variation of the OH exposure derived from isoprene chemistry method is strange (Figure S9). I cannot understand why the value is low during daytime compared with that in nighttime. The authors indicated two reference (Apel et al., 2002; Carlton et al., 2009), but I could not find the derivation of the OH exposure by "the isoprene chemistry method" in the references. The authors should show how the OH exposure by the isoprene chemistry method was calculated. I think that the low OH exposure during the daytime causes the low SOA formation from isoprenoids during the daytime, as shown in Figure 8(c).

Response: The isoprenoids (i.e. isoprene and monoterpenes in this study) are dominantly emitted from biogenic sources during the PRD campaign and reach the maximam concentration during daytime. These species have less photochemical oxidation time during daytime than that in nighttime. The lower OH exposure of the isoprenoids during daytime than that of nighttime is as a result of much fresh emission during daytime and the aging time is smaller than that of nighttime. We calculated the OH exposure of isoprenoids based on isoprene chemistry for the PRD campaign. The calculation method can be found in Roberts et al. (2006). We will also add a short introduction about the calculation in the supporting information of the revised manuscript.

Isoprene are mainly photo-oxidized through the reactions with OH radical in the atmosphere and its primary first-generation reaction products are formaldehyde, MVK and MACR (Apel et al., 2002) . The reaction processes of isoprene oxidized by OH radical are mainly as follows:

$$Isoprene + OH \rightarrow 0.63HCHO + 0.32MVK + 0.23MACR \quad k_1=1.0\times10^{-10}\,cm^{-3}\,s^{-1} \quad \textit{(Eq. S1)}$$

$$MVK + OH \rightarrow Products \quad k_2=1.9\times10^{-11}\,cm^{-3}\,s^{-1} \quad \textit{(Eq. S2)}$$

$$MACR + OH \rightarrow Products \quad k_3=3.3\times10^{-11}\,cm^{-3}\,s^{-1} \quad \textit{(Eq. S3)}$$

where k_1, k_2, k_3 are the rate constants of the reactions. According to above reactions, the relationship between MVK/Isoprene, MACR/Isoprene, (MVK+MACR)/Isoprene and the reaction time Δt can be decribed as follows (Apel et al., 2002):

$$\frac{MVK}{Isoprene} = \frac{0.32k_1}{k_2-k_1}\left(1-\exp((k_1-k_2)[OH]\Delta t)\right) \qquad \textit{(Eq. S4)}$$

$$\frac{MACR}{Isoprene} = \frac{0.23k_1}{k_3-k_1}\left(1-\exp((k_1-k_3)[OH]\Delta t)\right) \qquad \textit{(Eq. S5)}$$

$$\frac{MVK+MACR}{Isoprene} = \frac{0.32k_1}{k_2-k_1}\left(1-\exp((k_1-k_2)[OH]\Delta t)\right) + \frac{0.23k_1}{k_3-k_1}\left(1-\exp((k_1-k_3)[OH]\Delta t)\right) \quad \textit{(Eq. S6)}$$

where $\frac{MVK+MACR}{Isoprene}$ can be derived from the measurements by PTR-ToF-MS. Then the OH exposure ($[OH]\Delta t$) of isoprenoids can be obtaind from Eq. S6. SOA production of isoprenoids can be calculated from the following equation.

$$[SOA_i]_t = [VOC_i]_t \times (e^{k_{VOC_i} \times ([OH] \times \Delta t)} - 1) \times Yield_i \quad (Eq.\ S7)$$

Where $[SOA_i]_t$ is the calculated SOA production (μg m^{-3}) for a given specific compound VOC_i at time *t*, $[VOC_i]_t$ is the VOC_i concentration measured at time *t* (μg m^{-3}), $Yield_i$ is the SOA yield data summarized from chamber studies, k_{VOC_i} is the rate constant of VOC_i with the OH radical (cm^3 molecule^{-1} s^{-1}). $[OH] \times \Delta t$ is the OH exposure (molecules cm^{-3} s). Therefore, the diurnal variations of SOA formation are as result of the combing effects of concentration, the rate constant with OH radical, OH exposure and SOA yield for each compound.

Specific comments:

(1) Page 6, Line 113: In Figure S2, the authors showed that the relative intensity of O_2^+ to that of NO^+ was ~50 % (Fig. S2(a)) and ~15 % (Fig. S2(b)) under the conditions of Us = 40 V and Uso = 120V. These conditions are not good because I think that the O_2^+ reaction could substantially interfere with the ion signals of alkanes. I am concerned that the ratio of O_2^+ to NO^+ was not stable. The authors should mention the quality of the data of the alkanes presented in this paper.

Response: In the originally submitted manuscript, we made a mistake on the Figure S2. The corrected one is shown as follows. Based on the laboratory results, we chose Us=40 V and Uso=100 V as ion source voltage settings for the field measurement of higher alkanes **(Fig. S2(a))**, under which condition (absolute humidity=~11.6 mmol/mol) the ratio of O_2^+ to NO^+ is ~10%. The more details about the O_2^+ interference are replied above on pages 1-8.

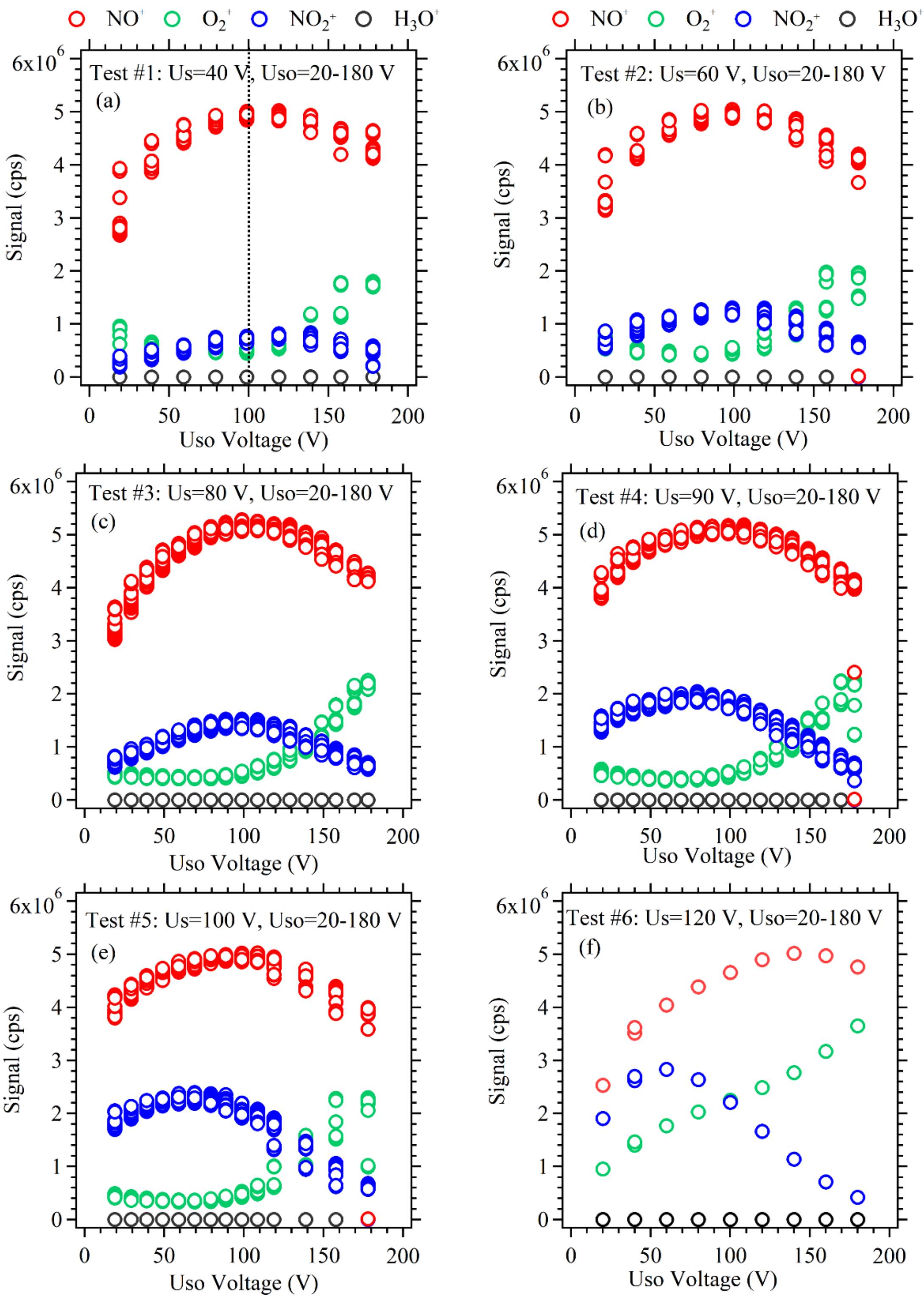

Figure S2. The variations of NO^+, H_3O^+, O_2^+ and NO_2^+ ions on the voltages of ion source (Us and Uso) for NO^+ PTR-ToF-MS. For each experiment, either Us or Uso is fixed at a voltage and the other was varied to explore the best setting for NO^+ PTR-ToF-MS. For example, test #1 in (a), we fix Us at 40 V and change Uso from 20 V to 180 V. The dashed line in (a) indicate the setting point in this study (Us=40 V and Uso=100 V).

(2) Page 6, Lines 130-131: I cannot agree to the argument by the authors that calibration factors were stable during the campaigns, because the normalized sensitivities of the n-C15 alkane were scattered with a factor of 2. As far as I experienced, the normalized sensitivity is very stable. I feel that this instability of the normalized sensitivity may be related to the interference of the O_2^+ reaction.

Response: We agree with that the instability of the normalized sensitivity might be related to the interference of O_2^+ reaction. As showned in **Fig. 2**, the sensitivities of *n*-alkanes (C8-C15) varied significantly with the fluctuations of O_2^+/NO^+ ratios in both dry conditions and ambient conditions during the NCP campaign. This indicate that the interference of O_2^+ should be considered. In the revised manuscript, the **Fig. 2** was added to explain the fluctuations of sensitivities of *n*-alkanes. During the NCP camaign, we conducted calibrations every 1-2 days under both dry conditions and ambient humidity conditions. The daily ambient calibrations results were used to quantify the concentration of higher alkanes for the NCP campaign. For the measurements without daily calibrations, we used the closest calibration results according to the corresponding ambient O_2^+/NO^+ ratios and the ambient humidity.

In the revised manuscript, part of the section of "2.1 NO^+ PTR-ToF-MS measurement" are modified as follows:

Line 147-161 on Page 7: "Sensitivities of *n*-alkanes (C8-C15) standards were obtained during the campaign (Figure S6), which is defined as the normalized signal of hydride abstraction ions for each higher alkane at 1 ppbv with a unit of ncps/ppb. The fluctuations of sensitivities during the NCP campaign may be influenced by the variations of O_2^+ signals (Figure 2), because the reactions of O_2^+ with alkanes can be proceeded by both charge transfer and hydride abstraction (Amador et al., 2016) that may affect the ion signals of alkanes with NO^+ reactions. Therefore, we use the daily ambient calibrations results to quantify the concentration of higher alkanes during the NCP campaign to reflect the variations of sensitivity from day to day. For the measurements without daily calibrations, we used closest calibration results according to corresponding ambient O_2^+/NO^+ ratios and ambient humidity. Since we got the alkanes standard at the very late period of the PRD campaign, we did not have the daily calibrations for this campaign. Therefore, we use the sensitivity of each alkane under corresponding O_2^+/NO^+ condition obtained from lab experiments after this campaign and also consider the

humidity effects (Figure 3(b, c)) to quantify the concentration of higher alkanes during the PRD campaign.”

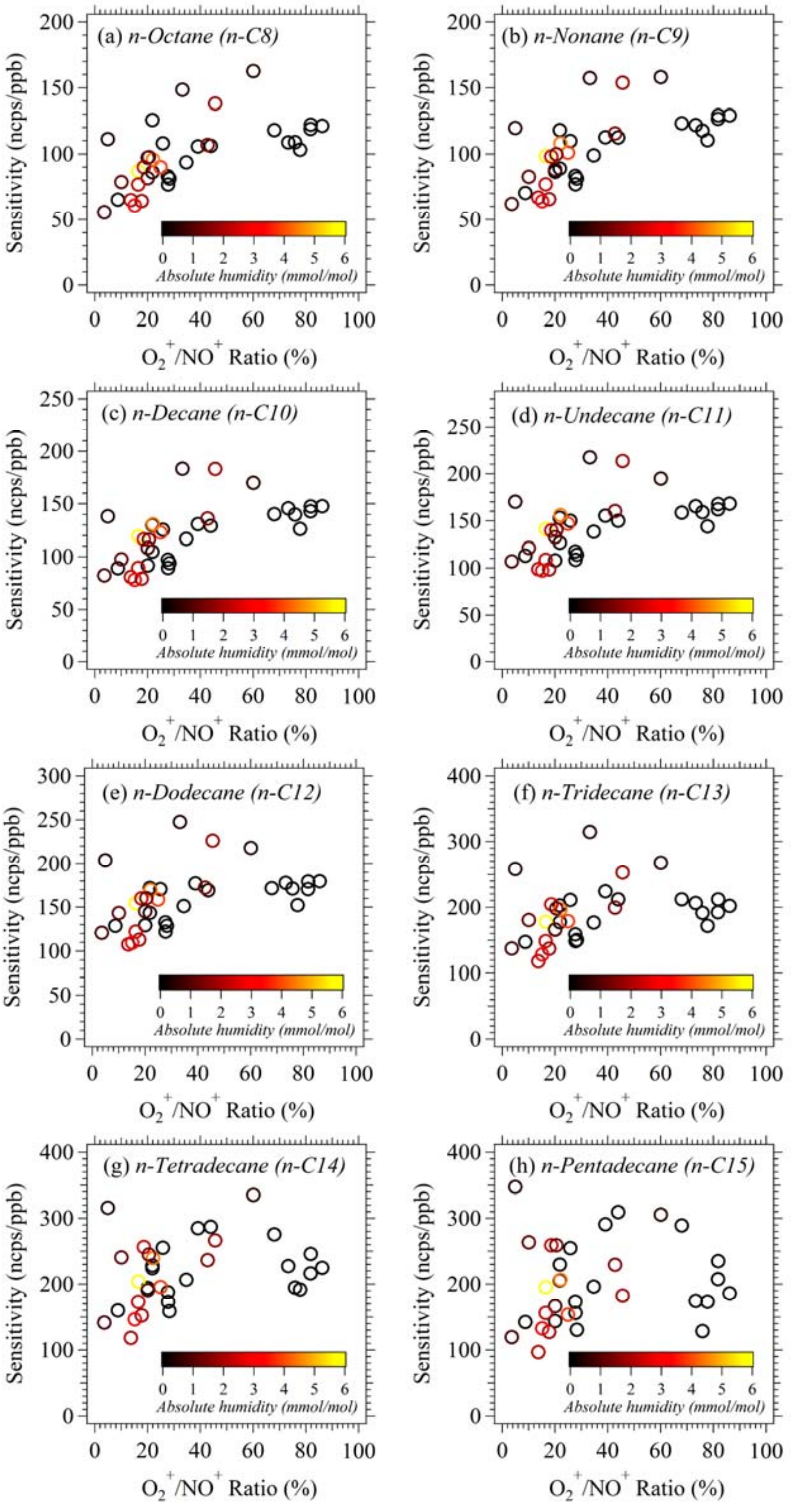

Figure 2. The relationship of sensitivities of *n*-alkanes (C8-C15) versus O_2^+/NO^+ ratios during the NCP campaign. The data points are color-coded using absolute humidity during the calibration.

(3) Page 7, Lines 137-139: When I looked at the mass spectra in Figure S4, I found that the signal intensities of 13C-isotopologue of [M-1]+ are low. For example, the signal at m/z 282 should be 20 % of the intensity at m/z 281 for n-Eicosane. I wonder if the quantitation was guaranteed or not in the present measurements using the NO^+ PTR-ToF-MS instrument.

Response: We obtained the mass spectra (Fig. S4) and the fragmentation patterns (Fig. 3(a)) for each high alkane by introducing commercially acquired pure chemicals with NO^+ PTR-ToF-MS measurement. The mass spectra shown in Fig. S4 represent the distributions of product ions of each higher alkane reacted with NO^+. As shown in the attached figure below, the isotopic signals (green lines) are subtracted when performing the high-resolution peak-fitting using Tofware software (Tofwerk AG). That is to say, the signals of masses shown in Fig. S4 are the results after subtracting the isotopic signals during the high resolution peak fitting of the mass spectra.

The title of Fig. S4 was modified to "**Mass spectra of the distributions of product ions from *n*-Dodecane (a), *n*-Pentadecane (b) and *n*-Eicosane (c) with NO^+ PTR-ToF-MS. The signals of masses shown in the graph are the results after subtracting the isotopic signals during the high resolution peak fitting of the mass spectra.**"

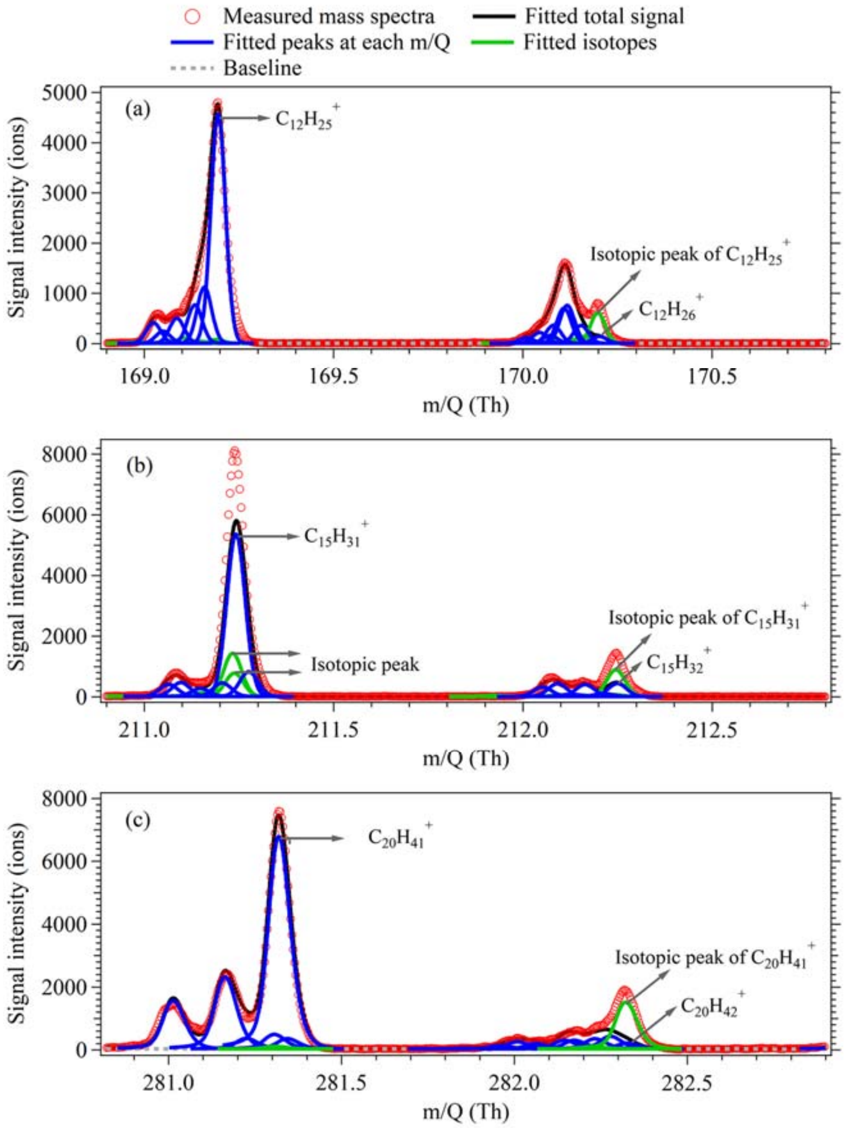

Figure. High-resolution (HR) peak-fitting to the averaged mass spectra during lab experiments for m/z 169, m/z 170 (a), m/z 211, m/z 212 (b) and m/z 281, m/z 282 (c), at which masses produced by dodecane ($C_{12}H_{25}^+$, $C_{12}H_{26}^+$), pentadecane ($C_{15}H_{31}^+$, $C_{15}H_{32}^+$) and eicosane ($C_{20}H_{41}^+$, $C_{20}H_{42}^+$) produced in NO^+ PTR-ToF-MS.

(4) Page 9, Lines 187-190: Some are good, but some are not good. The authors should mention the results correctly and explain the disagreement for some species. Were the concentrations from PTR-ToF-MS in Figs. S6 and S7 calibrated or calculated?

Response: The concentrations mentioned in the Figs. S6 and S7 were all calibrated with the commercial gas standards. Benzene measurements in H_3O^+ chemistry show large difference with benzene measured from NO^+ chemistry in the earlier period of PRD campaign (11 Sep.-14 Oct. 2018), but good agreement was obtained for the rest of measurement period.

Considering good agreement of benzene between NO^+ PTR-ToF-MS and GC-MS/FID, we used benzene data from NO^+ measurement in this study.

The sentences on lines 237-244 on page 11 are modified to:

"Overall, good agreements between PTR-ToF-MS (both H_3O^+ and NO^+ chemistry) and GC-MS/FID are obtained for aromatics and oxygenated VOCs except benzene (Figure S12, S13). Benzene measurements in H_3O^+ chemistry show large difference with benzene measured from NO^+ chemistry in the earlier period of PRD campaign (11 Sep.-14 Oct. 2018), but good agreement was obtained for the rest of measurement period. Considering good agreement of benzene between NO^+ PTR-ToF-MS and GC-MS/FID, we used benzene data from NO^+ measurement in this study."

(5) Page 10, Lines 219-221: The degree of the chemical removal of hydrocarbons by the OH reaction was quite different at two sites, when we consider the concentration of OH (Figure S19). The authors should mention the results accurately.

Response: We modified these sentences to "**Such diurnal patterns are consistent with other primary VOCs species (e.g. aromatics). In PRD, the diurnal variations of higher alkanes are as the result of faster chemical removal in the daytime and shallow boundary layer heights at night. While, since the OH concentrations in NCP during winter are much lower than that in PRD during autumn (Figure S16), the diurnal variations of higher alkanes in NCP are mainly influenced by the boundary layer effect.**"

(6) Page 10, Line 226: The data of naphthalenes were not shown anywhere in this paper.

Response: Naphthalenes are measured with H_3O^+ PTR-ToF-MS in these two campaigns. The details about the H_3O^+ PTR-ToF-MS measurement can be found in our companion paper (Wu et al., 2020). We added the sentences on line 310-314 of page 14 and a figure of time series of naphthalenes in the revised supporting information.

"**The concentration data of higher alkanes, isoprenoids and benzene were taken from measurements of NO^+ PTR-ToF-MS. The concentration data of naphthalenes (Figure S18) and monoaromatics except benzene were taken from measurements of H_3O^+ PTR-ToF-MS. The detail about the H_3O^+ PTR-ToF-MS measurements can be found in Wu et al. (2020)**"

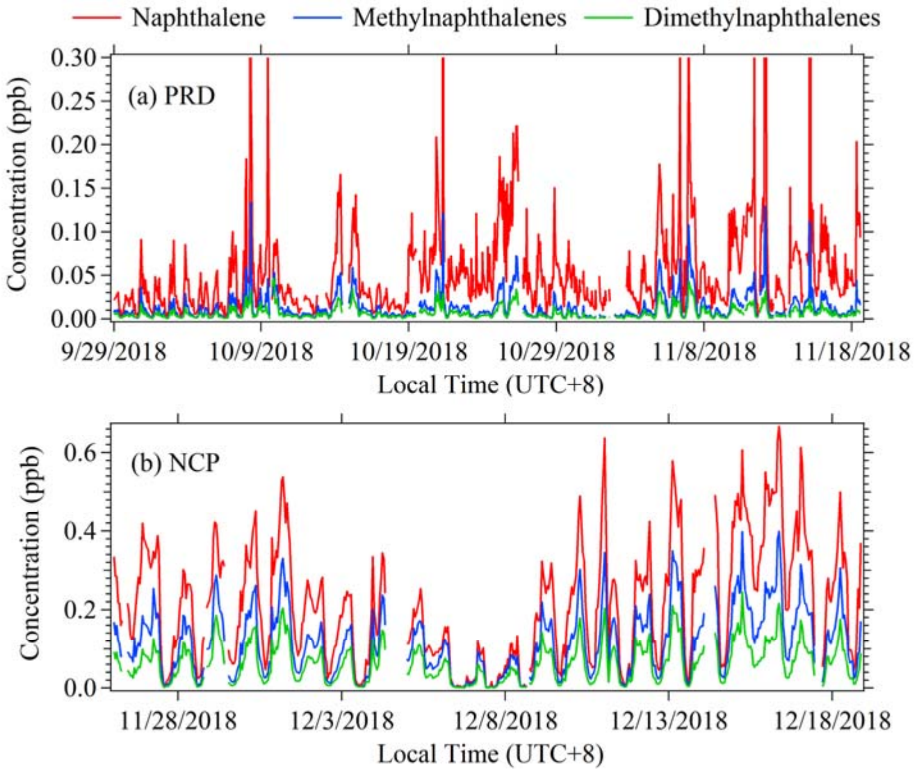

Figure S18. Time series of naphthalene, methylnaphthalenes, dimethylnaphthalenes in PRD (a) and NCP (b), respectively.

(7) Page 11, Lines 239-242: I could not understand how the authors estimated the OH exposure clearly. Which value was used as the ratio of m+p-xylene to ethylbenzene at t = 0 (the emission ratio)? How was the OH exposure estimated by the oxidation process of isoprene? Why was the OH exposure estimated by the oxidation process of isoprene low during daytime compared with that in nighttime?

Response: We included more detail about the calculation of OH exposure in the revised supporting information (**Appendix 4, SI**). The initial emission ratios of m+p-xylene/ethylbenzene were estimated according to the correlation of m+p-xylene with ethylbenzene during campaigns. As shown in the attached figure, diurnal variation of m+p-xylene/ethylbenzene concentration ratios (a) and the correlation of m+p-xylene with ethylbenzene (b) were studied in 2018 PRD campaign. Red dots are measured ratios during the campaign. Blue line indicates hourly geometric average, and gray areas are geometric standard deviations. The dashed line in both graphs indicate the estimated initial emission ratio of m+p-xylene/ethylbenzene. Details can also be found in Fig. S11 from Wu et al. (2020).

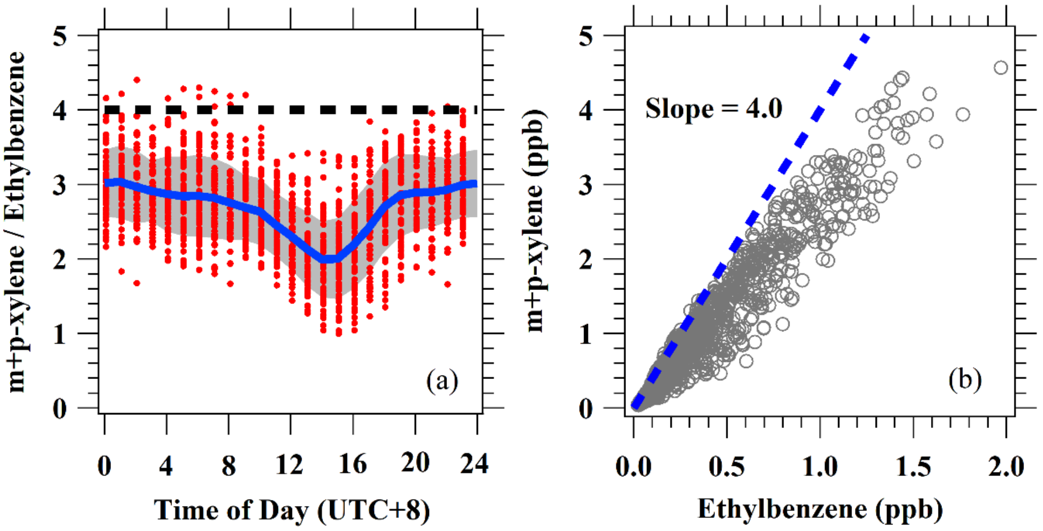

Figure S11. Diurnal variations of m+p-xylene/ethylbenzene concentration ratios. Red dots are measured ratios during 2018 PRD. Blue line indicates hourly geometric average, and gray areas are geometric standard deviations. (b) Correlation of m+p-xylene with ethylbenzene. The dashed lines in both graphs indicate the estimated initial emission ratio of m+p-xylene/ethylbenzene. (Wu et al., 2020)

The OH exposure estimated by the oxidation process of isoprene are added in the revised supporting information as follows. **Isoprene are mainly photo-oxidized through the reactions with OH radical in the atmosphere and its primary first-generation reaction products are formaldehyde, MVK and MACR (Apel et al., 2002). The reaction processes of isoprene oxidized by OH radical are mainly as follows:**

$$\boldsymbol{Isoprene + OH \rightarrow 0.63HCHO + 0.32MVK + 0.23MACR} \quad k_1=1.0\times10^{-10}\,cm^{-3}\,s^{-1}$$ ***(Eq. S1)***

$$\boldsymbol{MVK + OH \rightarrow Products} \quad k_2=1.9\times10^{-11}\,cm^{-3}\,s^{-1}$$ ***(Eq. S2)***

$$\boldsymbol{MACR + OH \rightarrow Products} \quad k_3=3.3\times10^{-11}\,cm^{-3}s^{-1}$$ ***(Eq. S3)***

where k_1, k_2, k_3 are the rate constants of the reactions. According to above reactions, the relationship between MVK/Isoprene, MACR/Isoprene, (MVK+MACR)/Isoprene and the reaction time Δt can be decribed as follows (Apel et al., 2002):

$$\frac{MVK}{Isoprene} = \frac{0.32k_1}{k_2-k_1}\left(1-\exp((k_1-k_2)\,[OH]\Delta t)\right)$$ ***(Eq. S4)***

$$\frac{MACR}{Isoprene} = \frac{0.23k_1}{k_3-k_1}\left(1-\exp((k_1-k_3)\,[OH]\Delta t)\right)$$ ***(Eq. S5)***

$$\frac{MVK+MACR}{Isoprene} = \frac{0.32k_1}{k_2-k_1}\left(1-\exp((k_1-k_2)[OH]\Delta t)\right) + \frac{0.23k_1}{k_3-k_1}\left(1-\exp((k_1-k_3)[OH]\Delta t)\right) \quad (Eq.\ S6)$$

where $\frac{MVK+MACR}{Isoprene}$ can be derived from the measurements by PTR-ToF-MS. Then the OH exposure ($[OH]\Delta t$) of isoprenoids can be obtaind from Eq. S6.

As shown in the attached figure below, isoprene is mainly emitted by vegetation in the PRD campaign with the highest concentration around noon. The lower OH exposure during daytime than that of nighttime is as a result of much fresh emission during daytime and the aging time is smaller than that of nighttime. The photochemical age of the air mass after mixing is the nonlinear addition of the photochemical age before mixing. Generally, the photochemical age of the mixed air mass is closer to that of the fresh air mass (Parrish et al., 1992). The OH exposure values in this study represent the average "photochemical age" that are calculated by some properly chosen VOCs ratios. Parrish et al. (2007) compared the calculated photochemical age of different NMHCs species with the transport time calculated by a back trajectory model, and concluded that the calculated photochemical age could better describe the average transport time of VOCs species by selecting suitable hydrocarbon species pairs.

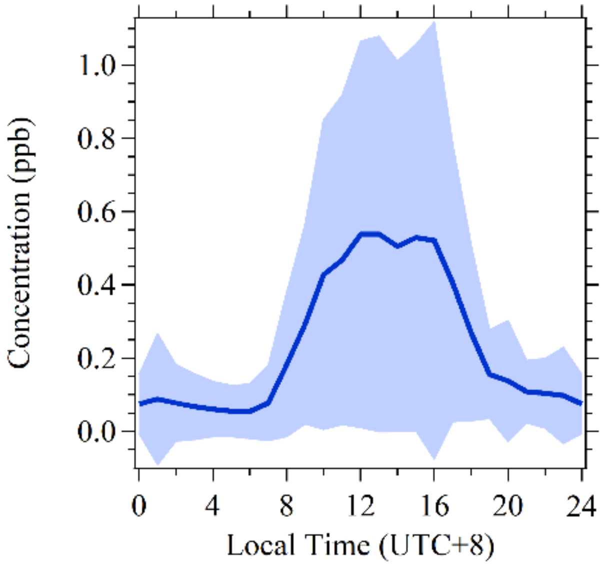

Figure. Diurnal variations of isoprene during the PRD campaign. Blue lines and shaded areas represent averages and standard deviations, respectively.

(8) Page 13, Lines 288-89: The diurnal variation of the estimated SOA produced from isoprenoids shown in Figure 8(c) is strange to me. In addition, I cannot understand the diurnal variations of the calculated SOA produced from higher alkanes, monoaromatics, naphthalenes, and isoprenoids in Figure 8(d). Why were those concentrations

low during the daytime in spite of the fact that the production rates were calculated to be positive during the daytime (Figure S18(d)). Did the authors consider the dynamics (e.g., the movement of the boundary layer) into the calculation? If so, explain in the text.

Response: The SOA productions in the Figure 8 are calculated based on the following formula:

$$[SOA_i]_t = [VOC_i]_t \times (e^{kvoc_i \times ([OH]\times\Delta t)} - 1) \times Yield_i$$

This means the SOA production for each compound is determined by the concentration, OH exposure, and rate constant with OH and yield the SOA yield. In the Figure 8(c), the SOA productions of isoprenoids present the sum of that from isoprene and monoterpenes. As shown in the attached figure below, the diurnal variations of the SOA production from isoprene exhibit a high level during the daytime and a low level during nighttime. While, the diurnal pattern of isoprenoids which is shown in Figure 8(c) is mainly influenced by that of monoterpenes with a relatively low level during the daytime.

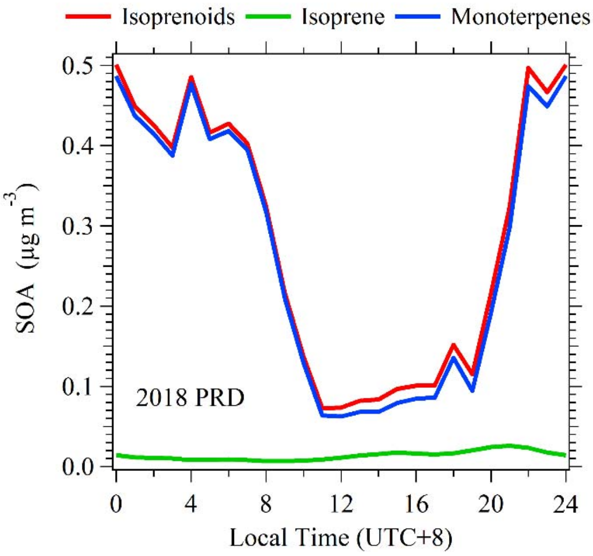

Figure. Diurnal variations of SOA productions from isoprene, monoterpenes and isoprenoids (sum of isoprene and monoterpenes) in PRD.

The low SOA productions during the daytime from higher alkanes, monoaromatics, naphthalenes, and isoprenoids in NCP (Figure 8(d)) are mainly due to the low SOA yields of these compounds during daytime (Figure S27). As shown in Figure 8(c, d), there are still a lot of missing SOA sources in both regions, which implies that some other SOA precursors or formation pathways (e.g. aqueous reactions) (Kuang et al., 2020) are contributing significantly to SOA formation in these regions. In this manuscript, we didn't consider the movement of the boundary layer into the calculation because we don't have the measurement of the boundary layer.

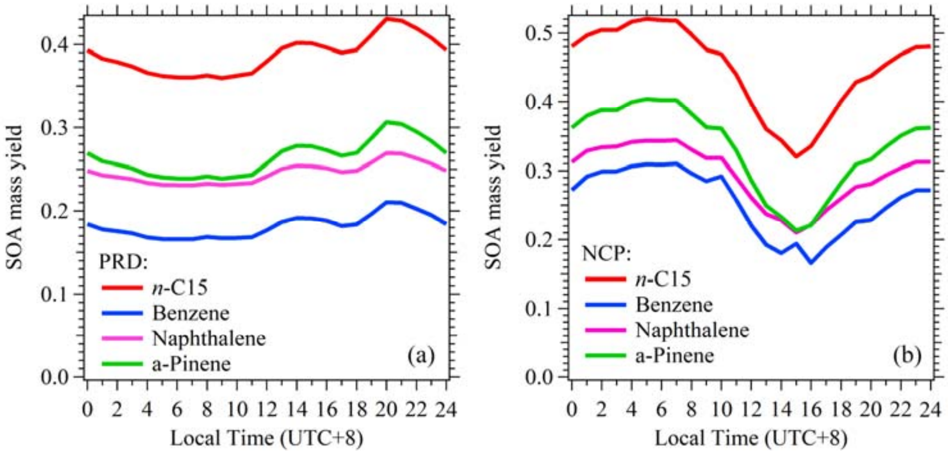

Figure S27. Diurnal variations of SOA yields of *n*-C15 alkane, benzene, naphthalene and *α*-pinene in PRD (a) and NCP (b).

(9) Page 32, Figure 8(d): The diurnal variation of the measured SOA in Figure 8(d) seems to be different from that in Figure S11(b). Is it OK?

Response: The duration in the original Figure S11(b) is different from that in Figure 8(d). In the original submitted manuscript, the durations in the Figure S11(b) and Figure 8(d) are 11.25-12.18 and 11.26-12.14, respectively. We modified the Figure S11(b) in the revised supporting information as follows, in which the duration is consistent with that in Figure 8(d).

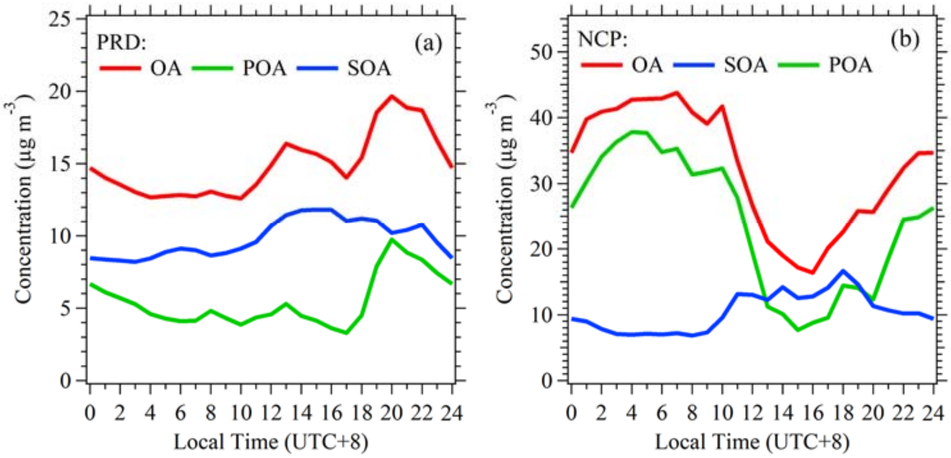

Figure S19. Diurnal variations of concentrations of organic aerosols (OA), secondary organic aerosols (SOA) and primary organic aerosols (POA) in PRD **(a)** and NCP **(b)**. POA and SOA were determined by positive matrix factorization (PMF) analysis of OA measured by AMS.

(10) Page S5, Line 106: Explain “isoprene chemistry method”.

Response: **Isoprene are mainly photo-oxidized through the reactions with OH radical in the atmosphere and its primary first-generation reaction products are formaldehyde, MVK and MACR (Apel et al., 2002) . The reaction processes of isoprene oxidized by OH radical are mainly as follows:**

$$Isoprene + OH \rightarrow 0.63HCHO + 0.32MVK + 0.23MACR \quad k_1=1.0\times10^{-10}\,cm^{-3}\,s^{-1} \quad \textit{(Eq. S1)}$$

$$MVK + OH \rightarrow Products \quad k_2=1.9\times10^{-11}\,cm^{-3}\,s^{-1} \quad \textit{(Eq. S2)}$$

$$MACR + OH \rightarrow Products \quad k_3=3.3\times10^{-11}\,cm^{-3}s^{-1} \quad \textit{(Eq. S3)}$$

where k_1, k_2, k_3 are the rate constants of the reactions. According to above reactions, the relationship between MVK/Isoprene, MACR/Isoprene, (MVK+MACR)/Isoprene and the reaction time Δt can be decribed as follows (Apel et al., 2002):

$$\frac{MVK}{Isoprene} = \frac{0.32k_1}{k_2-k_1}\left(1-\exp((k_1-k_2)[OH]\Delta t)\right) \qquad \textit{(Eq. S4)}$$

$$\frac{MACR}{Isoprene} = \frac{0.23k_1}{k_3-k_1}\left(1-\exp((k_1-k_3)[OH]\Delta t)\right) \qquad \textit{(Eq. S5)}$$

$$\frac{MVK+MACR}{Isoprene} = \frac{0.32k_1}{k_2-k_1}\left(1-\exp((k_1-k_2)[OH]\Delta t)\right) + \frac{0.23k_1}{k_3-k_1}\left(1-\exp((k_1-k_3)[OH]\Delta t)\right) \quad \textit{(Eq. S6)}$$

where $\frac{MVK+MACR}{Isoprene}$ can be derived from the measurements by PTR-ToF-MS. Then the OH exposure ($[OH]\Delta t$) of isoprenoids can be obtaind from Eq. S6.

(11) Page S7, Line 129: Which equation was used in the present paper, eqn. (1) in Page 11, Line 235 or eqn. (7) in Page S7, Line 129? Don’t make readers confused.

Response: In this manuscript, we used two methods to evaluate the importance of higher alkanes to SOA. One is estimated by eqn. (1) in the main body. The other one is estimated by eqn. (7) in the supporting information. In the revised supporting information, we added “S” before all equation numbers. For example, eqn. (7) was modified to eqn. (S7).

Technical comments:

(1) Page 4, Line 72: Anh et al., 2008. ("et al." is missing)

Response: We added "et al.".

(2) Page 4, Line 83-84: Erickson et al. (2014) did not use NO+ as the reagent ion.

Response: We deleted this citation.

Don't make readers misread. Same comment to Page 5, Line 108.

Response: We deleted the citation from Erickson et al. (2014).

(3) Page 6, Line 125: Corbin et al., 2015. (Delete "C.")

Response: We deleted "C."

(4) Page 9, Line 208: Table 1→Table 2

Response: Corrected

(5) Page 14, Line 319-Page 15, Line 347: I feel it strange that some papers are cited in "Conclusions". If the authors want to cite the papers, I think that the authors change"Conclusions" to "Concluding remarks".

Response: We changed "Conclusions" to "Concluding remarks".

(6) Page 17, Line 404: "C. Corbin, J." → "Corbin, J. C."

Response: Corrected

(7) Page S6, Line 107: Figure S8 →Figure S9

Response: Corrected

(8) Page S7, Lines 134-143: These are mentioned in the text (Page 11, Line 249-Page 12, Line 259)

Response: Here are descriptions for another method to calculate SOA production rate, some of the parameters used in this method are same as those in the text.

(9) Page S17, Figure S9: "expousre" → "exposure"

Response: Corrected

Reference:

Amador, O., Misztal, P., Weber, R., Worton, D., Zhang, H., Drozd, G., and Goldstein, A.: Sensitive detection of n -alkanes using a mixed ionization mode proton-transfer-reaction mass spectrometer, Atmospheric Measurement Techniques, 9, 5315-5329, 10.5194/amt-9-5315-2016, 2016.

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