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Supplement of

Measurements of higher alkanes using NO^+ chemical ionization in PTR-ToF-MS: important contributions of higher alkanes to secondary organic aerosols in China

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95 et al., 2016;Tajuelo et al., 2019) (a-e), naphthalenes (naphthalene, methylnaphthalene,

96 dimethylnaphthalenes) (Chan et al., 2009) (f-h) and isoprenoids (isoprene and α-

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136

1. Description of sampling sites

The sampling site of Guangzhou Campaign (23.13º N, 113.26 º E) was on the top of a nine-story building (25 m above ground level) at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. This site is a typical urban site surrounded by residential areas, campus and urban transport arteries with a strong influence of vehicle emissions. Field measurements of site Baoding (38.85º N, 115.48º E) were performed on the top of a sea container (3.5 m above ground level) located at a Meteorological Auto-Monitoring Station in the rural area of North China Plain. This rural site was surrounded by farmlands and villages, with several national roads and railways nearby, where air masses are influenced from local emissions and regional transport.

2. Estimation of SOA production from individual precursors

It is assumed that VOCs are removed from the atmosphere mainly by reaction with OH radical(Atkinson and Arey, 2003), then the VOCs are assumed to follow a pseudo first-order kinetic reaction, such as

$$-\frac{d[VOC_i]}{dt} = k_{VOC_i}[VOC_i][OH] \quad (S1)$$

Where $[VOC_i]$ is the concentration of a given VOC (μg m^{-3}), [OH] is the concentration of OH radical (molecule cm-^{3}), k_{VOC_i} is the rate constant of VOC_i with the OH radical (cm^3 molecule^{-1} s^{-1}). The initial concentration of a given VOC, $[VOC_i]_{t=0}$ can be retrieved from Eq. (1) as follows:

$$[VOC_i]_{t=0} = [VOC_i]_t \times (e^{k_{VOC_i} \times [OH] \times \Delta t}) \quad (S2)$$

$[VOC_i]_t$ is the VOC_i concentration measured at time t (μg m^{-3}), The OH exposure, $[OH] \times \Delta t$ (molecules cm^{-3} s), is estimated by the ratio of 1,2,4-trimethylbenzene to benzene(de Gouw et al., 2017;Hayes et al., 2013) for anthropogenic VOCs and by isoprene chemistry method

160 for biogenic VOCs, respectively (Apel et al., 2002;Roberts et al., 2006) (see details in SI,

161 Appendix 4 and Figure S19).Then consumed concentration of a given VOC, $\Delta[VOC_i]$, can

162 be estimated as follows:

163 $$\Delta[VOC_i] = [VOC_i]_{t=0} - [VOC_i]_t \qquad\qquad (S3)$$

164 $$\Delta[VOC_i] = [VOC_i]_t \times (e^{k_{VOC_i} \times ([OH] \times \Delta t)} - 1) \qquad\qquad (S4)$$

165 Then for a given VOC, the SOA production (µg m^{-3}) at time t, $[SOA_i]_t$, can be estimated

166 using the consumed concentration multiply the SOA yield, $Yield_i$, as follows:

167 $$[SOA_i]_t = [VOC_i]_t \times (e^{k_{VOC_i} \times ([OH] \times \Delta t)} - 1) \times Yield_i \qquad\qquad (S5)$$

168 **3. Estimation of contributions of individual precursors to SOA production**

169 We calculated the relative contribution of each compound to the total SOA

170 concentration at time *t* by

171 $$[Fraction_i]_t = \frac{[SOA_i]_t}{[SOA_{measured}]t} \times 100 \qquad\qquad (S6)$$

172 where $[Fraction_i]_t$ (%) is the relative contribution of a given compound VOC_i to the

173 measured SOA total concentration, $[SOA_i]_t$ is the SOA production of VOC_i at time t by the

174 equation (S6), $[SOA_{measured}]_t$ is the SOA concentration at time *t*, which is determined by

175 positive matrix factorization (PMF) analysis of organic aerosol measured by aerosol mass

176 spectrometry (µg m^{-3}).
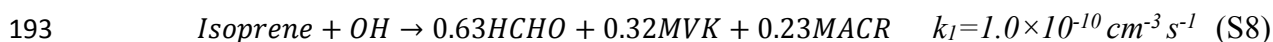
177 **4. Calculation of OH exposure**

178 The observed ratios between m+p-xylene and ethylbenzene were used to estimate the

179 OH exposure ($[OH] \times \Delta t$) for anthropogenic compounds by Roberts et al. (1984):

180 $$[OH] \times \Delta t = \frac{1}{k_{\text{m+p−xylene}} - k_{ethylbenzene}} \times [ln(\frac{\text{m+p−xylene}}{ethylbenzene})_{t=0} - ln(\frac{\text{m+p−xylene}}{ethylbenzene})_t], \qquad (S7)$$

181   where the initial emission ratios of m+p-xylene/ethylbenzene were estimated according to the

182   correlation of m+p-xylene with ethylbenzene during campaigns. The ratio of 4 and 1.5 were

183   used in the PRD campaign and the NCP campaign, respectively (Figure S31).

184   During 2018 PRD campaign, isoprenoids (i.e. isoprene and monoterpenes in this study)

185   are dominantly emitted from biogenic sources, which are different from anthoprogenic

186   compounds such as higher alkanes, monoaromatics and naphthalenes. Therefore, we calculated

187   the OH exposure of isoprenoids based on isoprene chemistry for 2018 PRD campaign. The

188   calculation method can be found in Roberts et al. (2006).

189   Isoprene are mainly photo-oxidized through the reactions with OH radical in the

190   atmosphere and its primary first-generation reaction products are formaldehyde, MVK and

191   MACR (Apel et al., 2002) . The reaction processes of isoprene oxidized by OH radical are

192   mainly as follows:

193         $Isoprene + OH \rightarrow 0.63HCHO + 0.32MVK + 0.23MACR$ $k_1 = 1.0 \times 10^{-10}\, cm^{-3}\, s^{-1}$ (S8)

194         $MVK + OH \rightarrow Products$ $k_2 = 1.9 \times 10^{-11}\, cm^{-3}\, s^{-1}$ (S9)

195         $MACR + OH \rightarrow Products$ $k_3 = 3.3 \times 10^{-11}\, cm^{-3}\, s^{-1}$ (S10)

196   where k_1, k_2, k_3 are the rate constants of the reactions. According to above reactions, the

197   relationship between MVK/Isoprene, MACR/Isoprene, (MVK+MACR)/Isoprene and the

198   reaction time Δt can be decribed as follows (Apel et al., 2002):

199         $\frac{MVK}{Isoprene} = \frac{0.32 k_1}{k_2 - k_1} \left(1 - \exp((k_1 - k_2)[OH]\Delta t)\right)$ (S11)

200         $\frac{MACR}{Isoprene} = \frac{0.23 k_1}{k_3 - k_1} \left(1 - \exp((k_1 - k_3)[OH]\Delta t)\right)$ (S12)

201    $\frac{MVK + MACR}{Isoprene} = \frac{0.32 k_1}{k_2 - k_1} \left(1 - \exp((k_1 - k_2)[OH]\Delta t)\right) + \frac{0.23 k_1}{k_3 - k_1} \left(1 - \exp((k_1 - k_3)[OH]\Delta t)\right)$ (S13)

202   where $\frac{MVK+MACR}{Isoprene}$ can be derived from the measurements by ToF-MS. Then the OH exposure

203   ($[OH]\Delta t$) of isoprenoids can be obtaind from Eq. S13.

204   ## 5. Estimation of SOA production rate from individual precursors

205   Here we calculated the SOA production rate associated with OH radicals for each SOA

206   precursors based on the diurnal variation of each species. Here, only the oxidation of OH

207   radicals is considered(Atkinson and Arey, 2003). The SOA production rate represents the

208   instant SOA production amount by oxidation reaction with atmospheric OH radical at a

209   certain time for a specific precursor, which can be characterized as follows:

210   $$[SOA_i]_t = [VOC_i]_t \times [OH]_t \times k_{VOC_i} \times Yield_i, \qquad\qquad (S14)$$

211   where for a given specific compound VOC_i, $[SOA_i]_t$ is the instant SOA production rate for

212   the species (μg m^{-3} s^{-1}), $[VOC_i]_t$ is the concentration measured at time t (μg m^{-3}), $[OH]_t$ is

213   the OH concentration at time t (molecules cm^{-3}), k_{VOC_i} is the rate constant of VOC_i with the

214   OH radical (cm^3 molecule^{-1} s^{-1}) and $Yield_i$ is the SOA yield.

215   Based on equation (S14), SOA instant production for higher alkanes (C8-C20),

216   monoaromatics (benzene, toluene, C8 aromaics, C9 aromaics), naphthalenes (naphthalene,

217   methylnaphthalenes, dimethylnaphthalenes) and isoprenoids (isoprene, monoterpenes) were

218   calculated. The OH reaction rate constant of each compound was taken literature (Atkinson,

219   2003). SOA yield data used here for alkanes (Lim and Ziemann, 2009;Presto et al.,

220   2010b;Loza et al., 2014;Lamkaddam et al., 2017a), monoaromatics (Li et al., 2016;Tajuelo

221   et al., 2019;Ng et al., 2007), naphthalenes (Chan et al., 2009) and isoprenoids (Ahlberg et al.,

222   2017;Carlton et al., 2009;Edney et al., 2005;Kleindienst et al., 2006;Pandis et al., 1991) were

223   summarized from reported values in the literature, with the consideration on the influence of

224   organic aerosol concentration (Figure S20) to SOA yield (Figure S21-22). OH

225 concentrations are derived from an observation-constrained box model utilizing MCM

226 v3.3.1 as the chemical mechanisms(Wolfe et al., 2016).

227 As shown in Figure S29, the total mean SOA production rate of higher alkanes (C8-C20)

228 is much higher compared to other VOCs classes, ~1.9 times of monoaromatics, ~7.8 times

229 of naphthalenes and ~2.4 times of isoprenoids at the urban site in PRD. At the rural site in

230 NCP, the total mean SOA production rate of higher alkanes (C8-C20) is comparable to

231 monoaromatics and slightly higher than that of naphthalenes and isoprenoids. Strong diurnal

232 variations are observed in both sites. In comparison with the rural site in NCP, SOA

233 production rates of VOCs are much higher at the urban cite in PRD. This is mainly due to

234 the higher OH concentrations (Figure S16) by strong solar radiation under high humidity

235 conditions in PRD during autumn, compared to dry and cold environment during the

236 measurements in NCP.
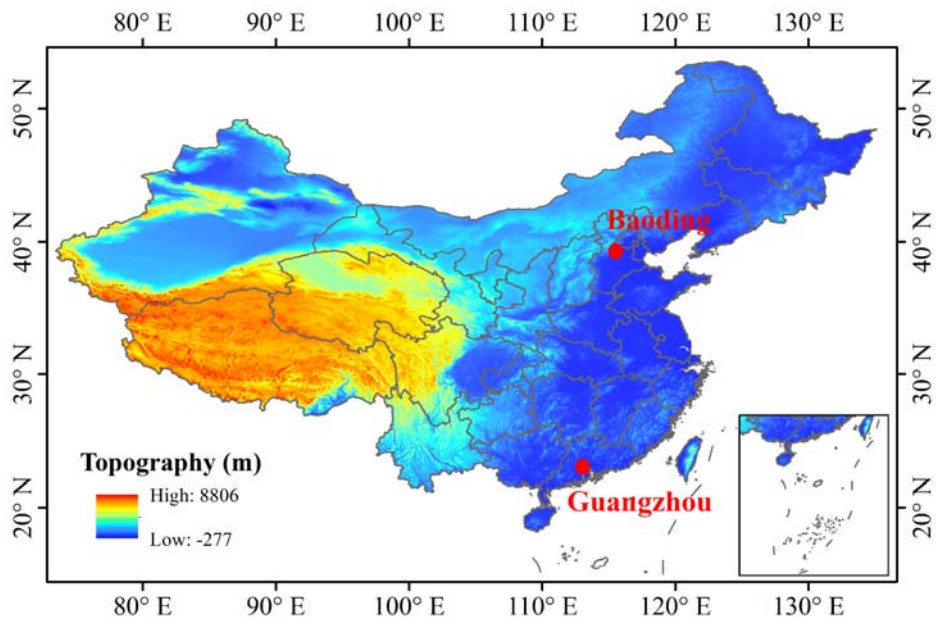
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Figure S1. Sampling site locations of Guangzhou Campaign in PRD and Baoding Campaign

in NCP of China.

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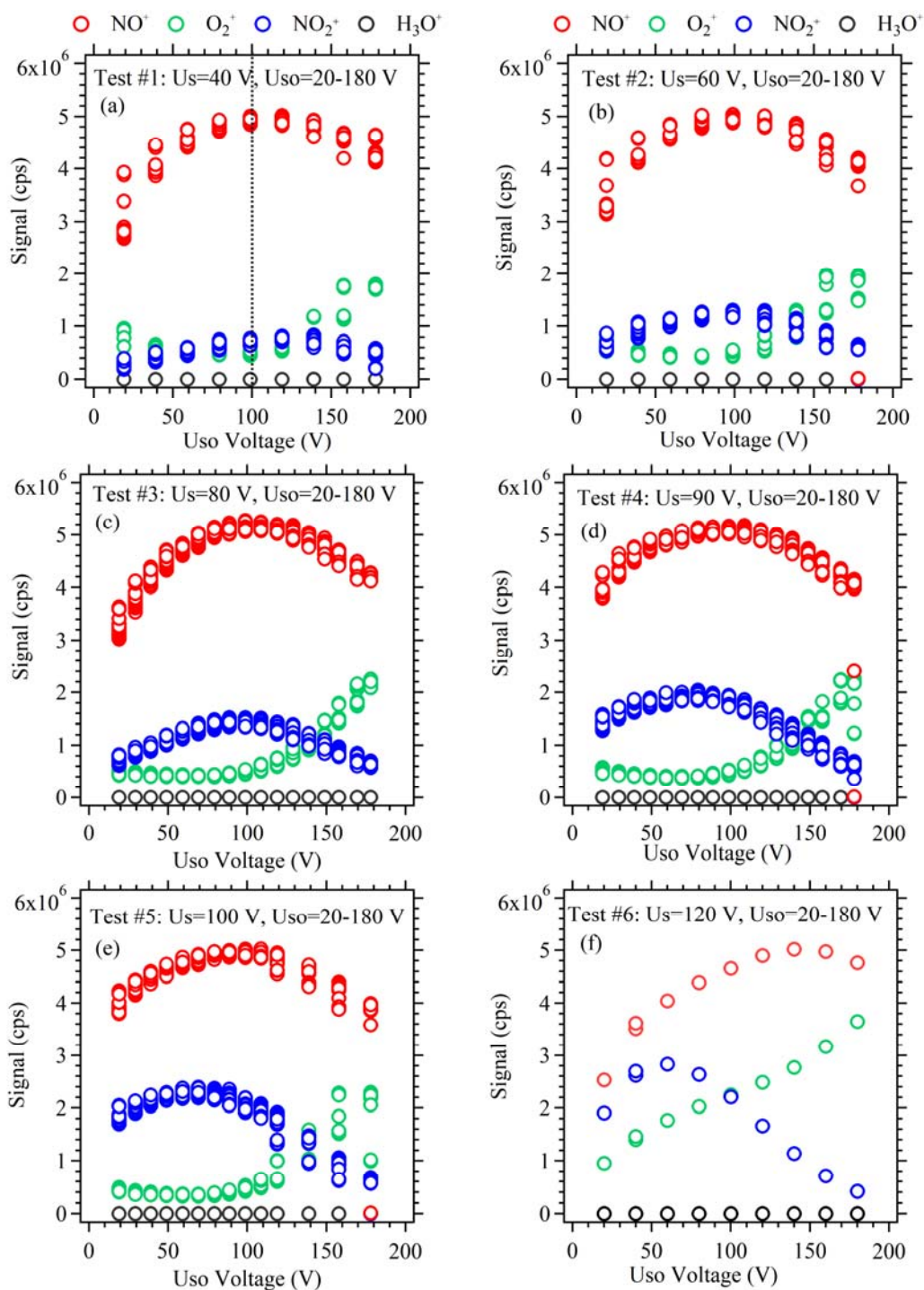
Figure S2. The variations of NO^+, H_3O^+, O_2^+ and NO_2^+ ions on the voltages of ion source (Us and Uso) for NO^+ PTR-ToF-MS. For each experiment, either Us or Uso is fixed at a voltage and the other was varied to explore the best setting for NO^+ PTR-ToF-MS. For example, test #1 in (a), we fix Us 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).
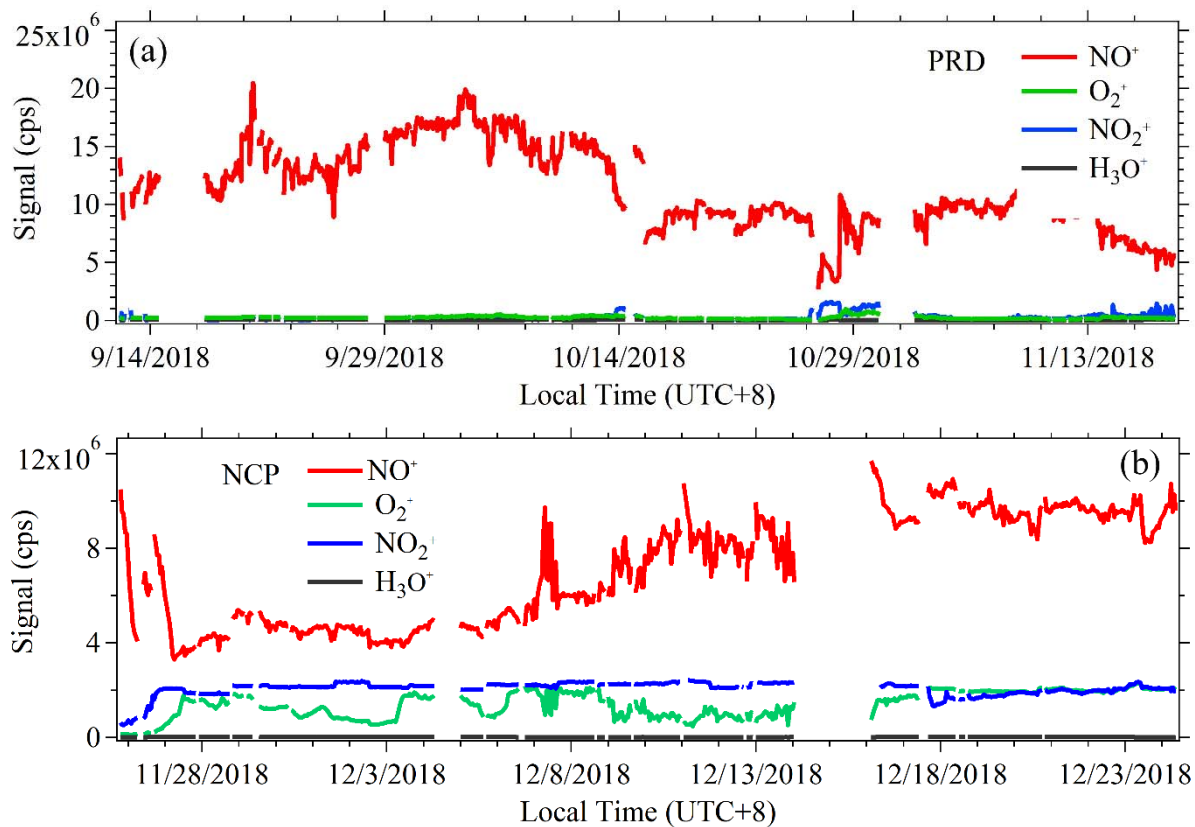
Figure S3. Time series of NO^+, H_3O^+, O_2^+, NO_2^+ during the PRD **(a)** and the NCP **(b)** campaigns, respectively.

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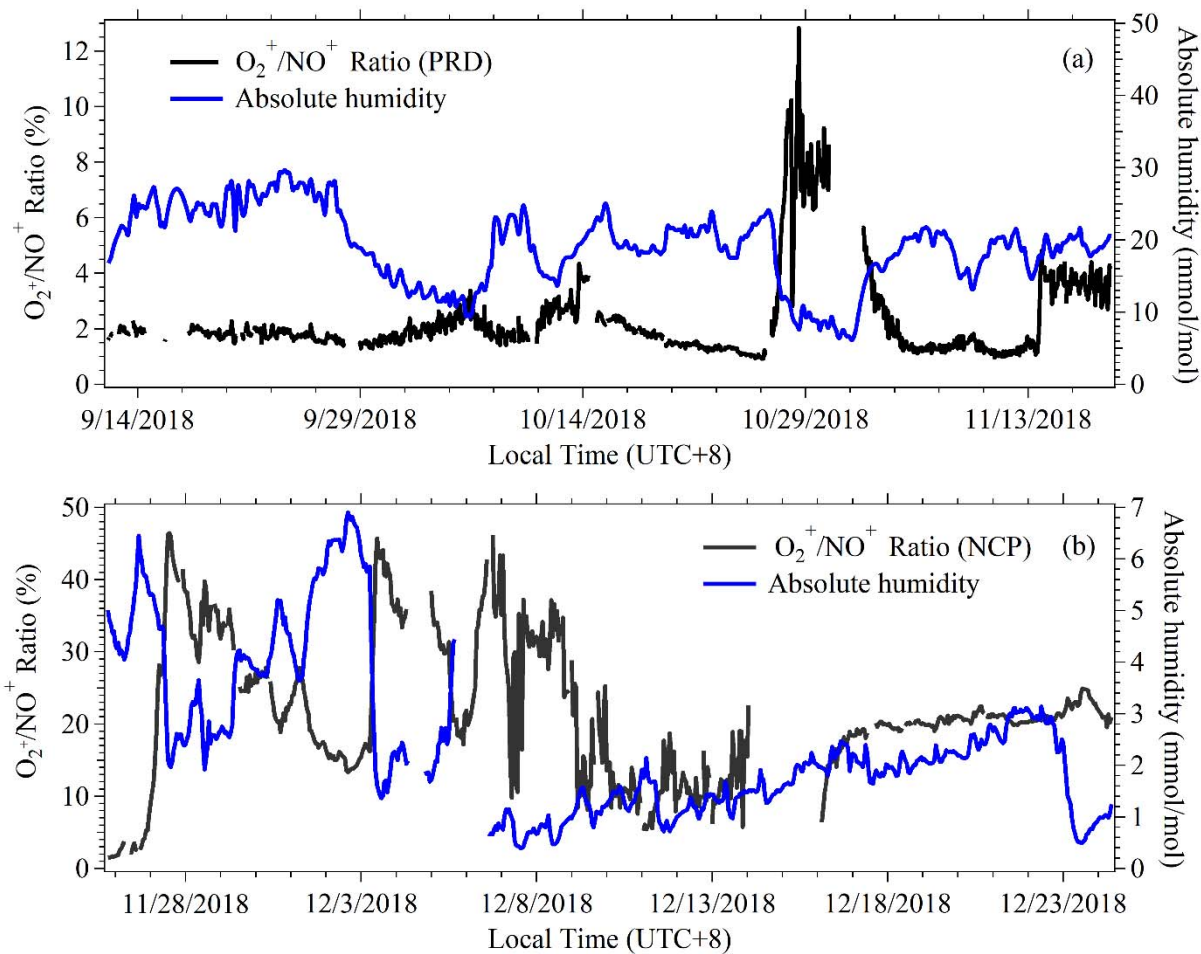
Figure S4. Time series of O_2^+ to NO^+ ratios and absolute humidity during the PRD **(a)** and

253 the NCP **(b)** campaigns, respectively.

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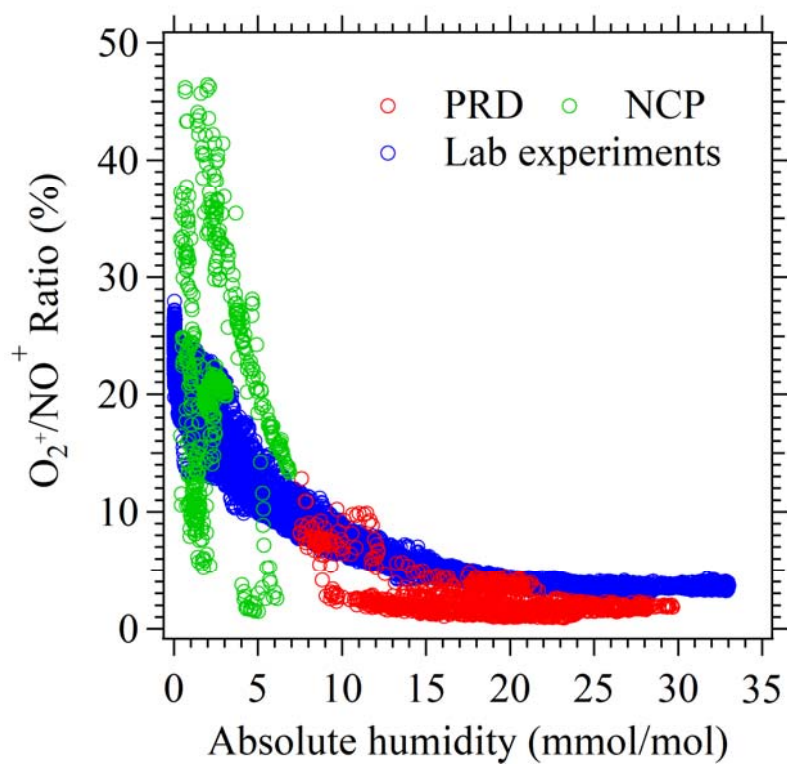
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Figure S5. Humidity dependence of O_2^+ to NO^+ ratios during the lab experiment and the two field campaigns.

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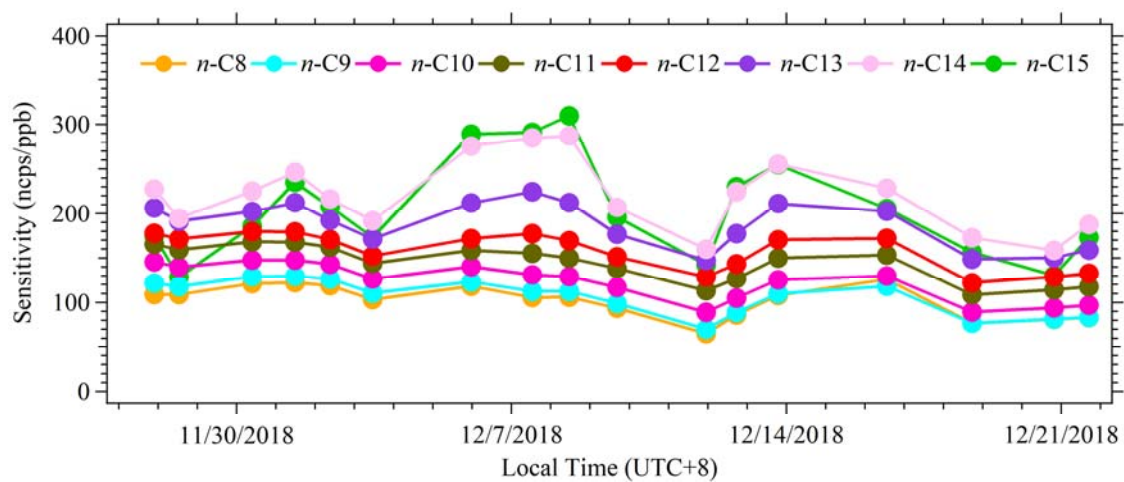
Figure S6. Calibration factors of C8-C15 *n*-alkanes under dry conditions (RH<1%) during

the two field campaigns.

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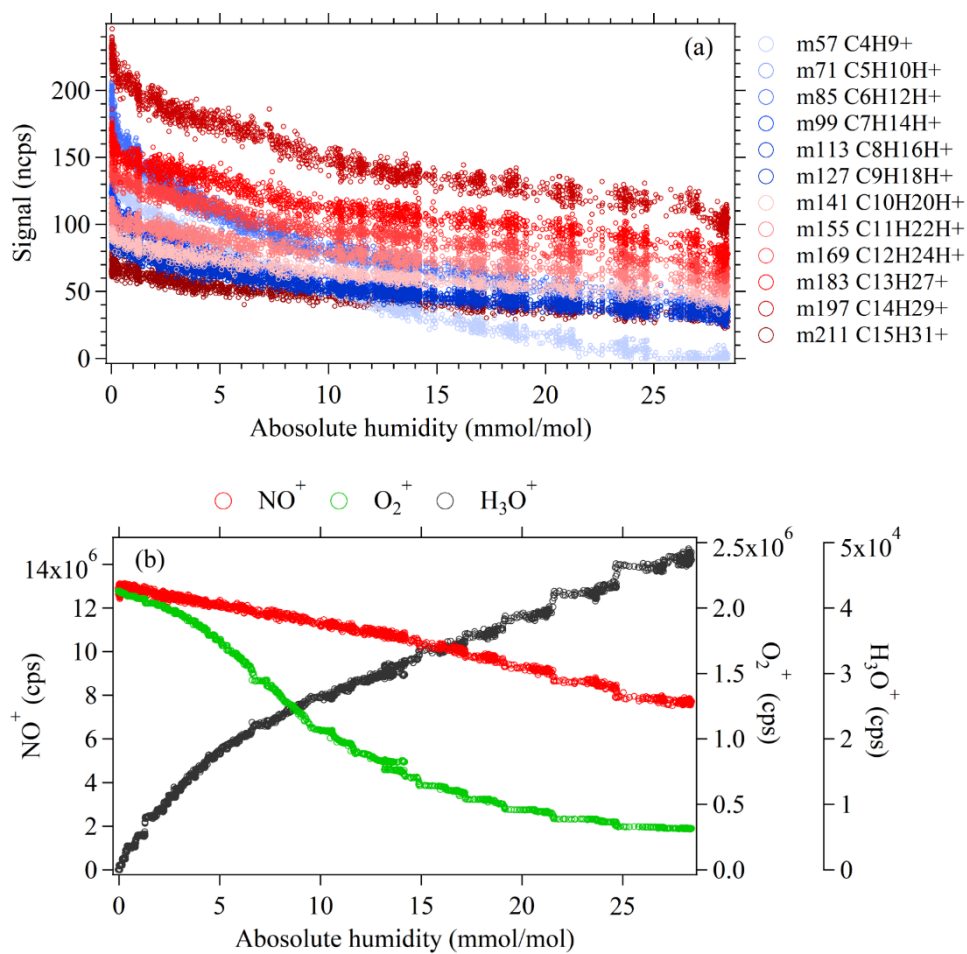
Figure S7. Humidity dependence of all product ions and the fragment ions for *n*-alkanes (C8-C15) **(a)**, and primary ions (NO$^+$, O$_2^+$, H$_3$O$^+$) **(b)**.
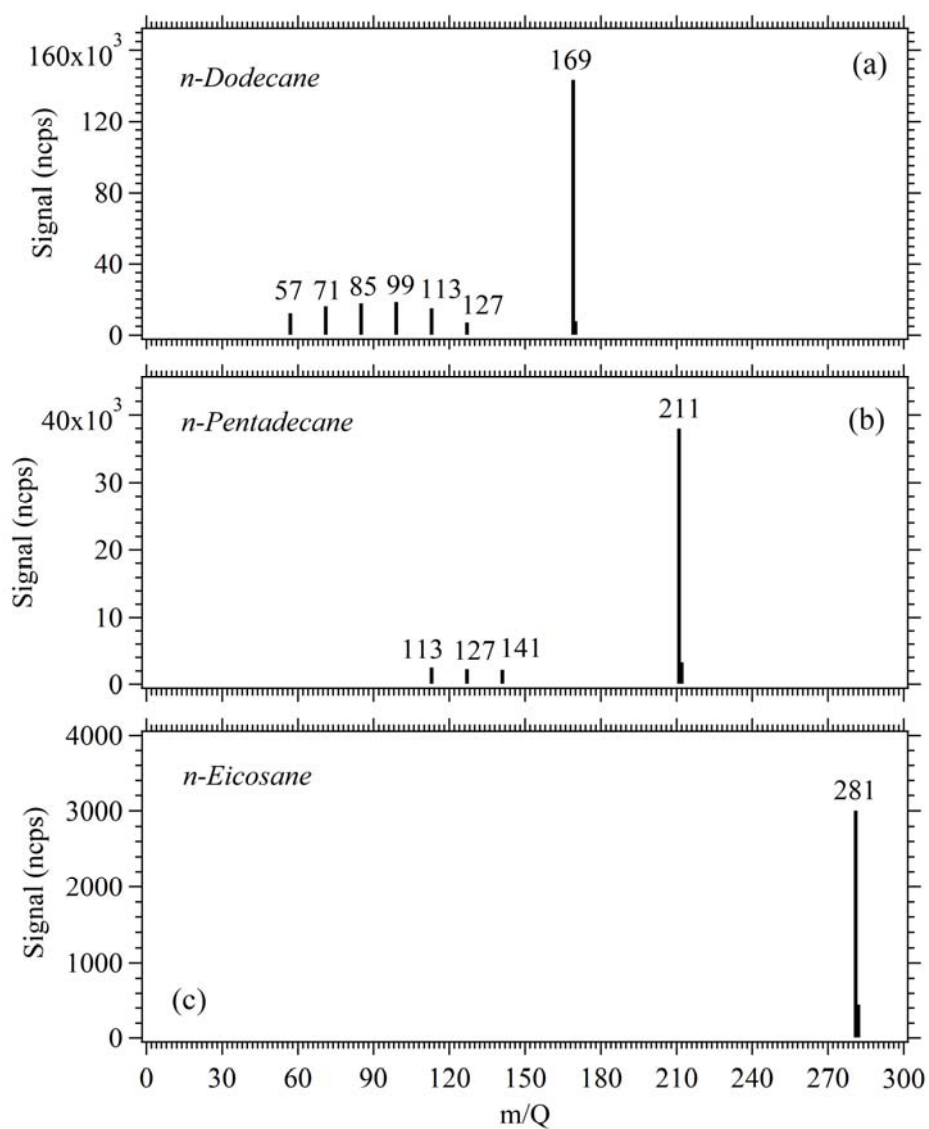
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Figure S8. Mass spectra of the distributions of product ions from *n*-Dodecane **(a)**, *n*-Pentadecane **(b)** and *n*-Eicosane **(c)** with NO^+ PTR-ToF-MS. The signals of masses shown in the graph are the results after subtracting the isotopic signals during the high resolution peak fitting of the mass spectra.
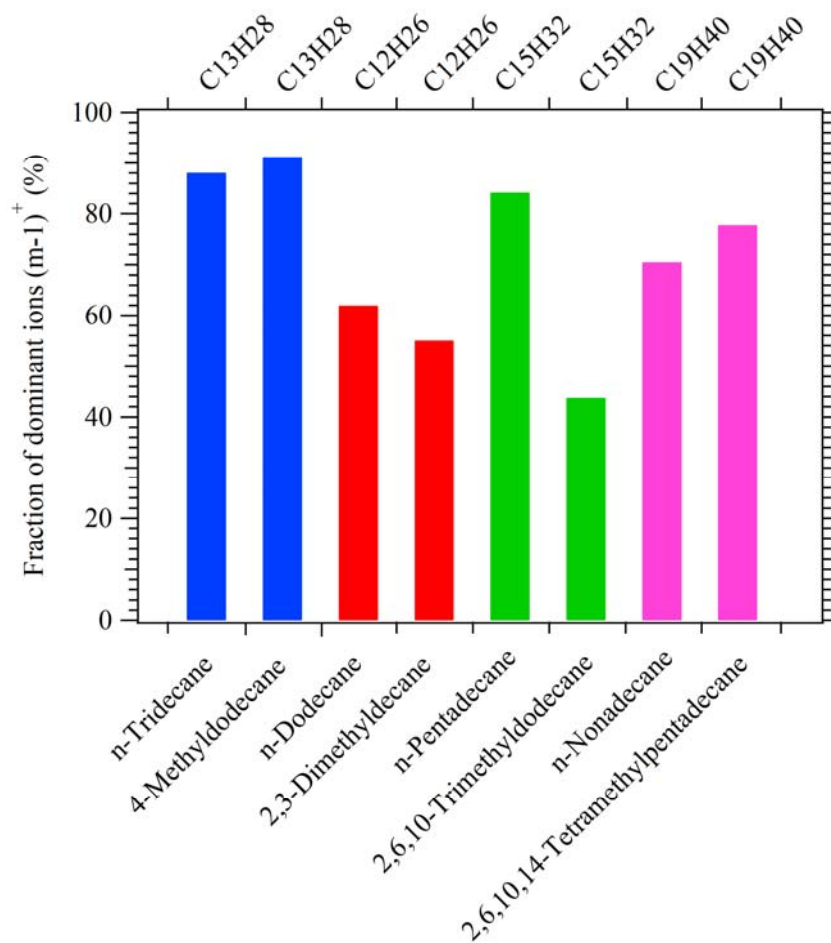
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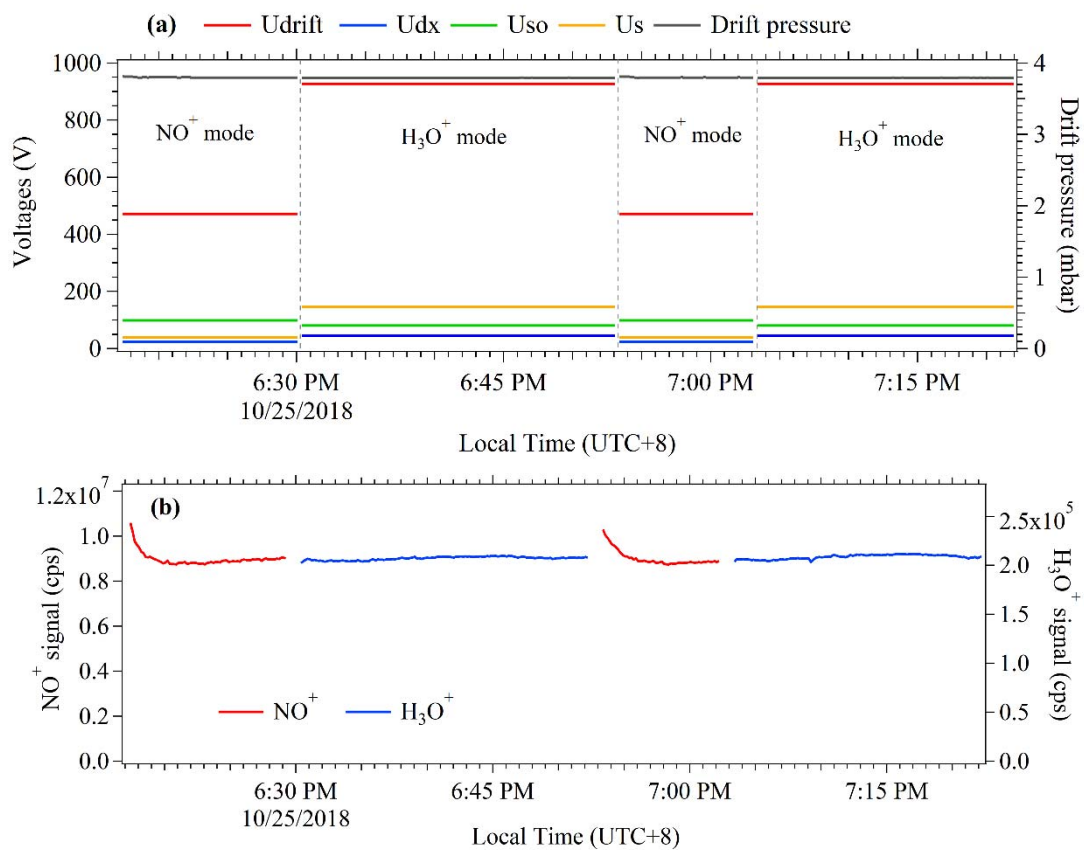**Figure S9**. Fraction of product ions $(m-1)^+$ in the mass spectra of *n*-alkanes and their isomers with different number of substituted methyl groups in NO^+ PTR-ToF-MS.

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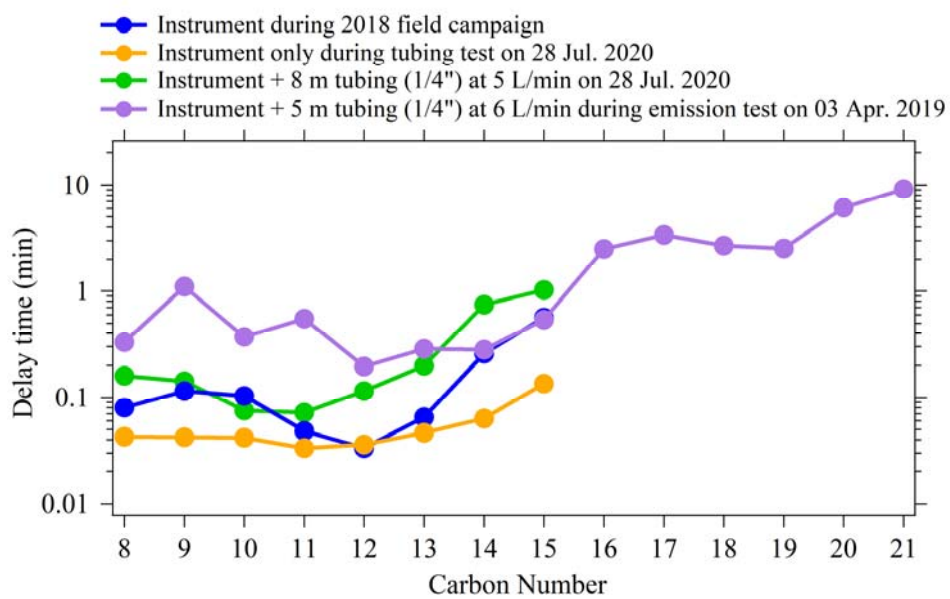
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Figure S10. Delay times of higher alkanes for the field campaigns, emission source measurements and tubing losses test in the laboratory.
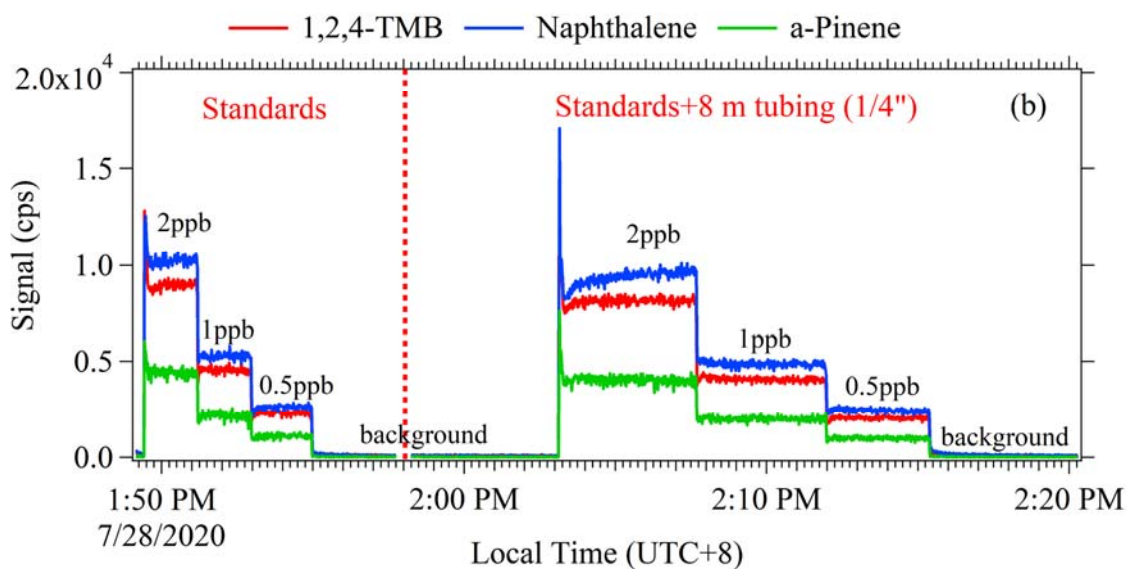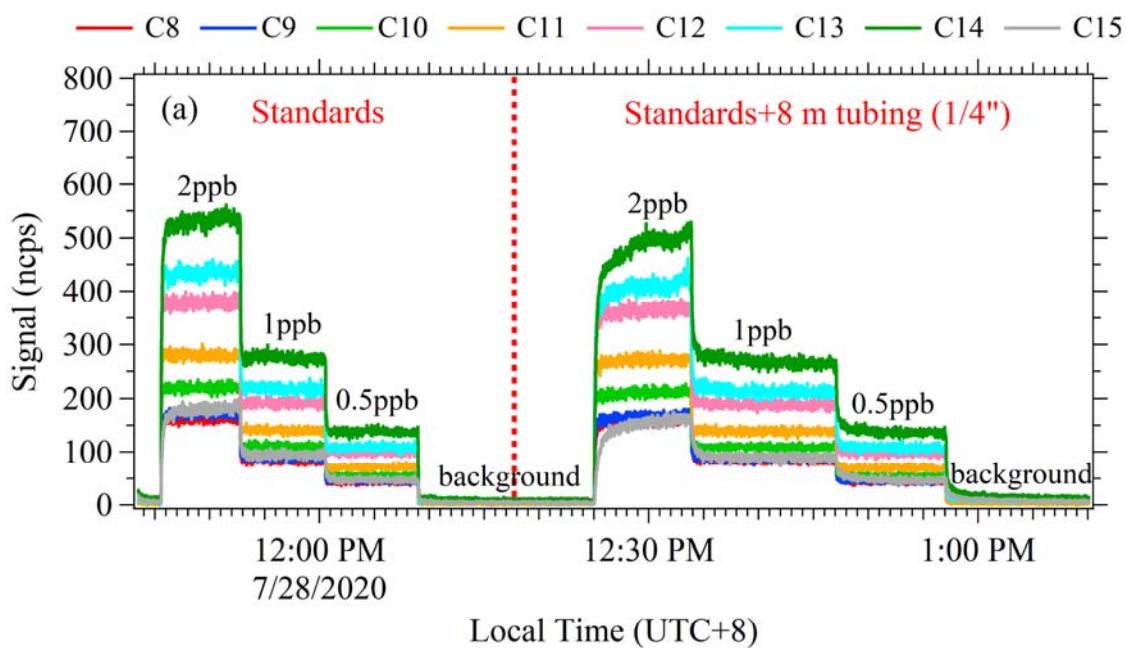
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Figure S11. An example of voltages of ion source voltages (Us, Uso), drift tube (Udrift, Udx)

and pressure of drift tube **(a)**, and the signal changes of primary ions **(b)** during automatical
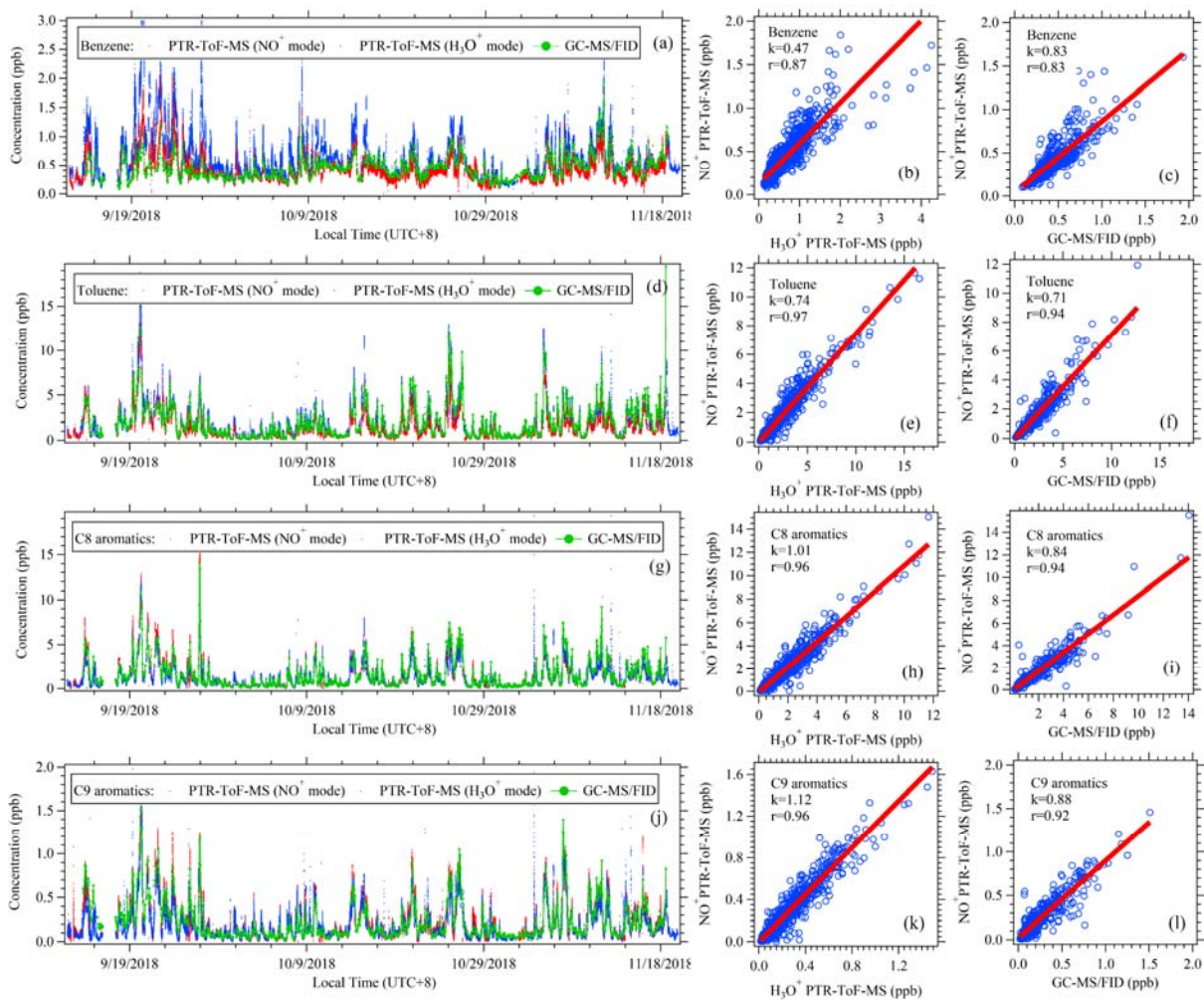
switching between NO$^+$ mode and H$_3$O$^+$ mode, respectively.

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Figure S12. The tubing loss experiments of higher alkanes (*n*-C8-C15), 1,2,4-trimethylbenzene, α-pinene and naphthalene at room temperature using PTR-ToF-MS with an external pump at 5.0 L/min.
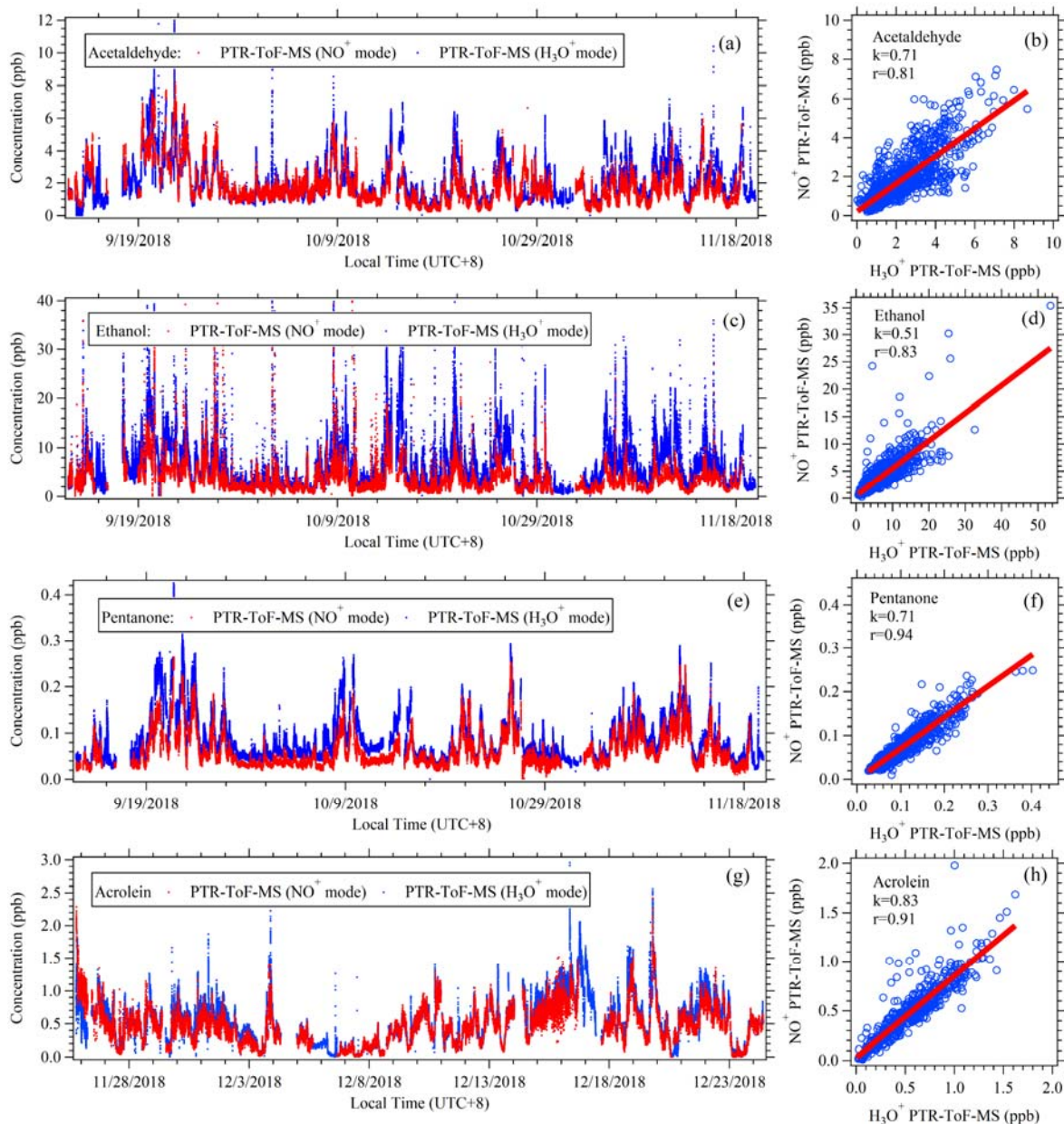
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Figure S13. Comparisons of benzene, toluene, C8 aromatics and C9 aromatics measured by

NO$^+$ PTR-ToF-MS (red dots), H$_3$O$^+$ PTR-ToF-MS (blue dots) and GC-MS/FID (green lines
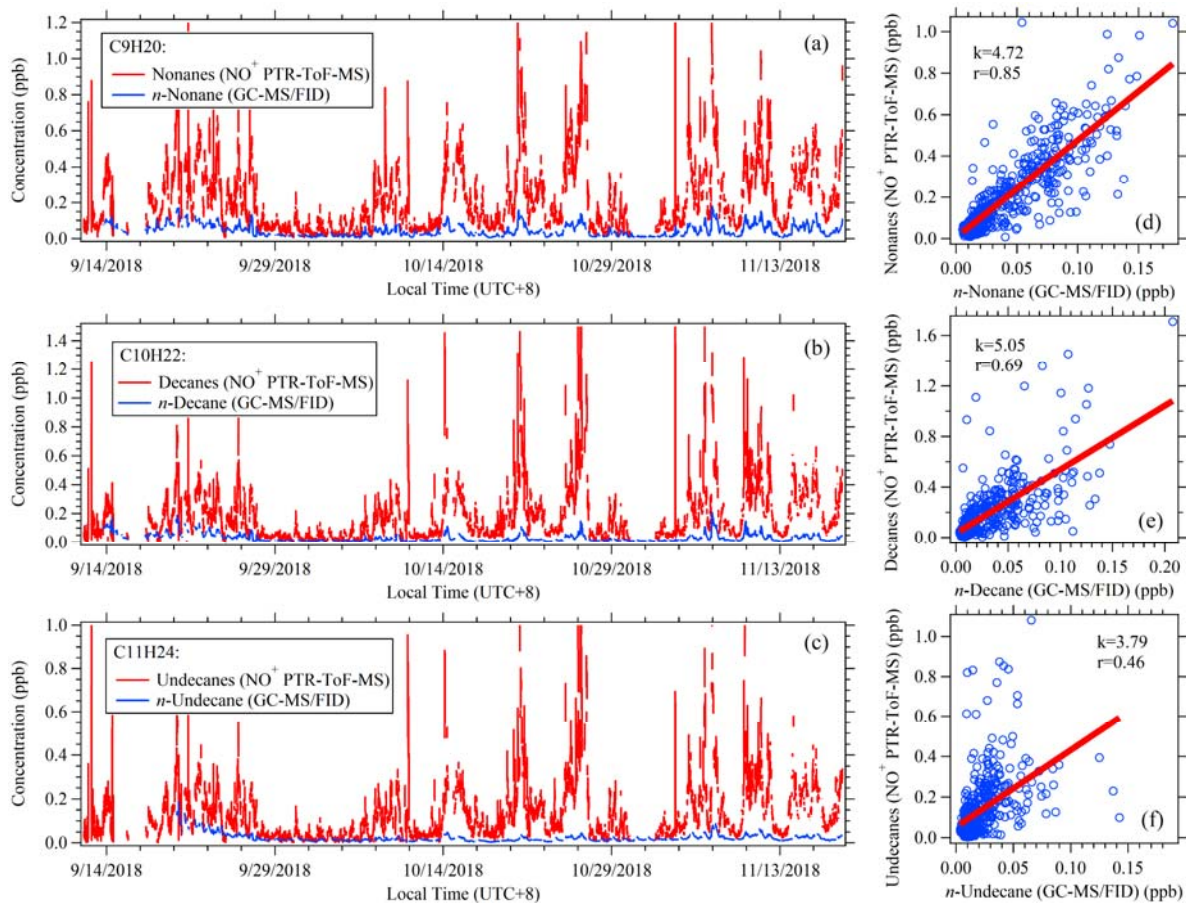
and dots) during the PRD campaign.

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Figure S14. Comparisons of acetaldehyde, pentanone, ethanol and acrolein measured by NO+ PTR-ToF-MS (red dots) and H3O+ PTR-ToF-MS (blue dots) during the PRD and NCP campaigns.
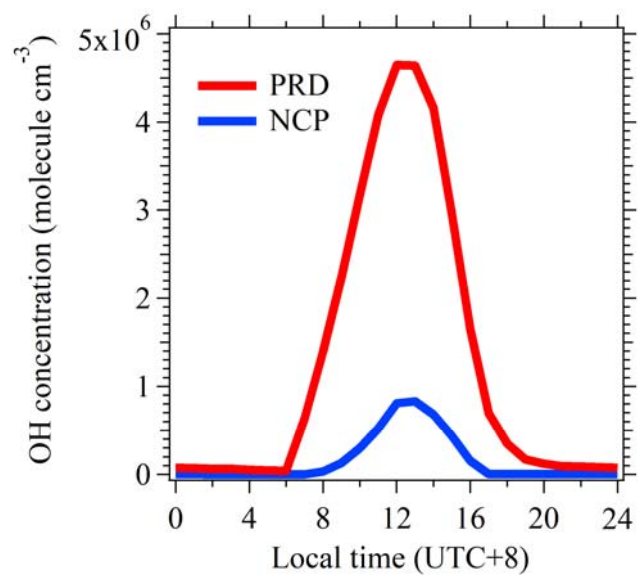
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Figure S15 Comparisons of C9-C11 alkanes measured by NO[+] PTR-ToF-MS and GC-MS/FID during PRD campaign.
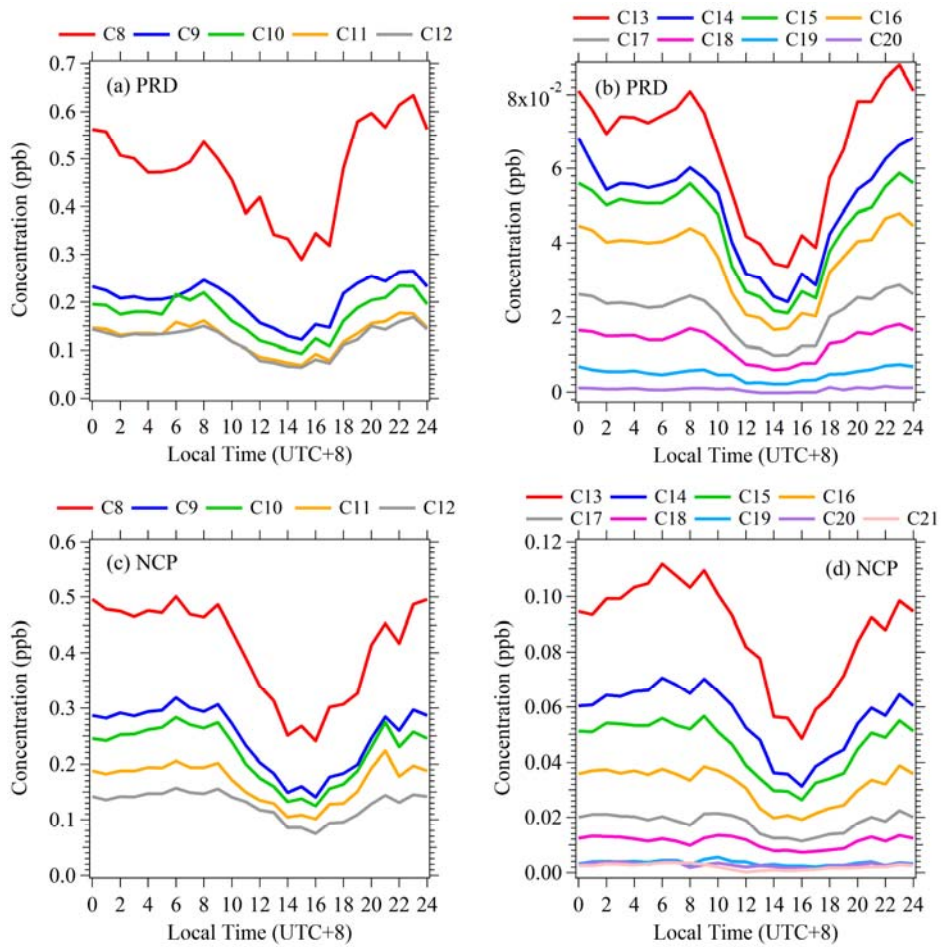
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302 **Figure S16**. Diurnal variations of OH concentrations in PRD and NCP, respectively. OH

303 concentrations are derived from an observation-constrained box model utilizing MCM v3.3.1

304 as the chemical mechanisms(Wolfe et al., 2016).
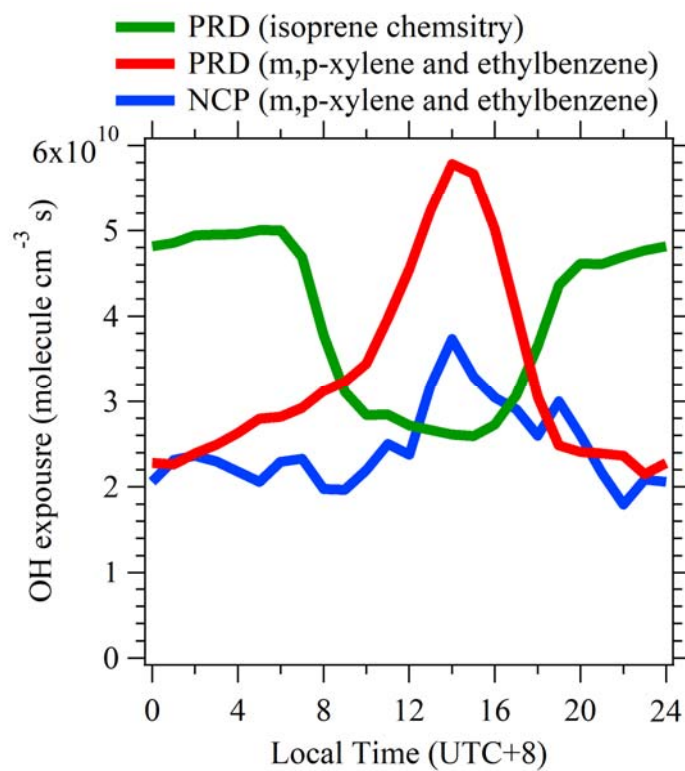
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Figure S17. Similar diurnal profiles of C8-C21 alkanes during campaigns in PRD (a, b) and

308   NCP (c, d).

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Figure S18. Comparisons of average diurnal variations of OH exposure calculated from the ratio of m+p-xylene and ethylbenzene for anthropogenic compounds in PRD and NCP and isoprene chemistry in PRD for biogenic compounds.

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Figure S19. **(a)** Time series of isoprene and monoterpenes in NCP. **(b)** Diurnal variation of isoprene, monoterpenes and benzene in NCP. **(c)** Scatter plot of isoprene and monoterpenes versus CO in NCP.

Figure S20. Time series of naphthalene, methylnaphthalenes, dimethylnaphthalenes in PRD **(a)** and NCP **(b)**, respectively.

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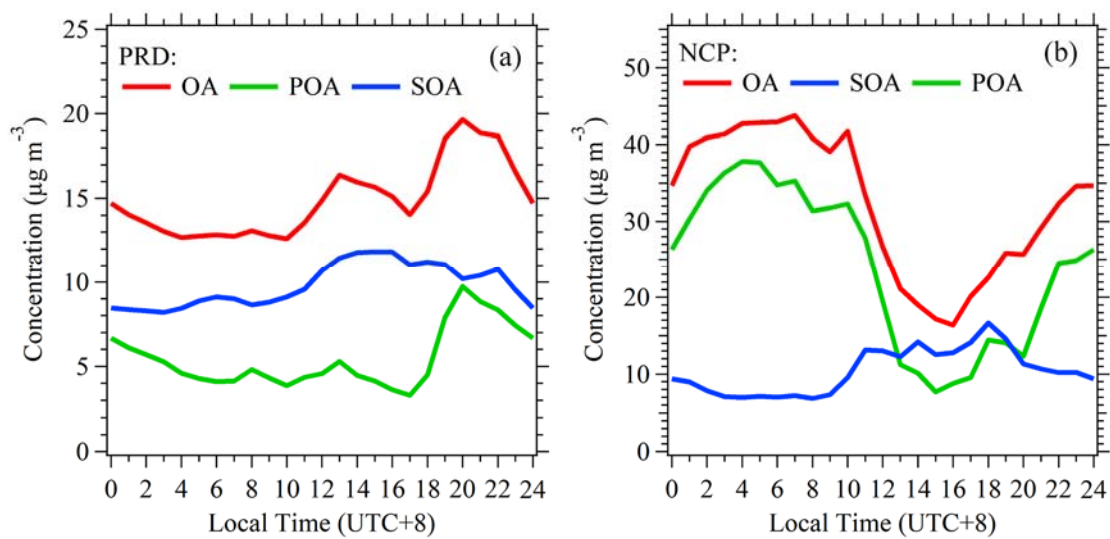
Figure S21. Diurnal variations of concentrations of organic aerosols (OA), secondary organic

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.

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Figure S22. The reported SOA yields as a function of OA concentrations for higher alkanes (C8-C21 alkanes) **(a-k)** under high-NO$_x$ condition from chamber studies(Lim and Ziemann, 2009;Presto et al., 2010a;Tkacik et al., 2012;Loza et al., 2014;Lamkaddam et al., 2017b).

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Figure S23. The reported SOA yields as a function of OA concentrations for monoaromatics (benzene, toluene, m-xylene, 1,2,3-TMB/1,2,4-TMB/1,3,5-TMB, styrene)(Ng et al., 2007;Li et al., 2016;Tajuelo et al., 2019) **(a-e)**, naphthalenes (naphthalene, methylnaphthalene, dimethylnaphthalenes)(Chan et al., 2009) **(f-h)** and isoprenoids (isoprene and α-pinene)(Carlton et al., 2009;Edney et al., 2005;Kleindienst et al., 2006;Pandis et al., 1991;Ahlberg et al., 2017) **(i-j)** under high-NO$_x$ condition from chamber studies.

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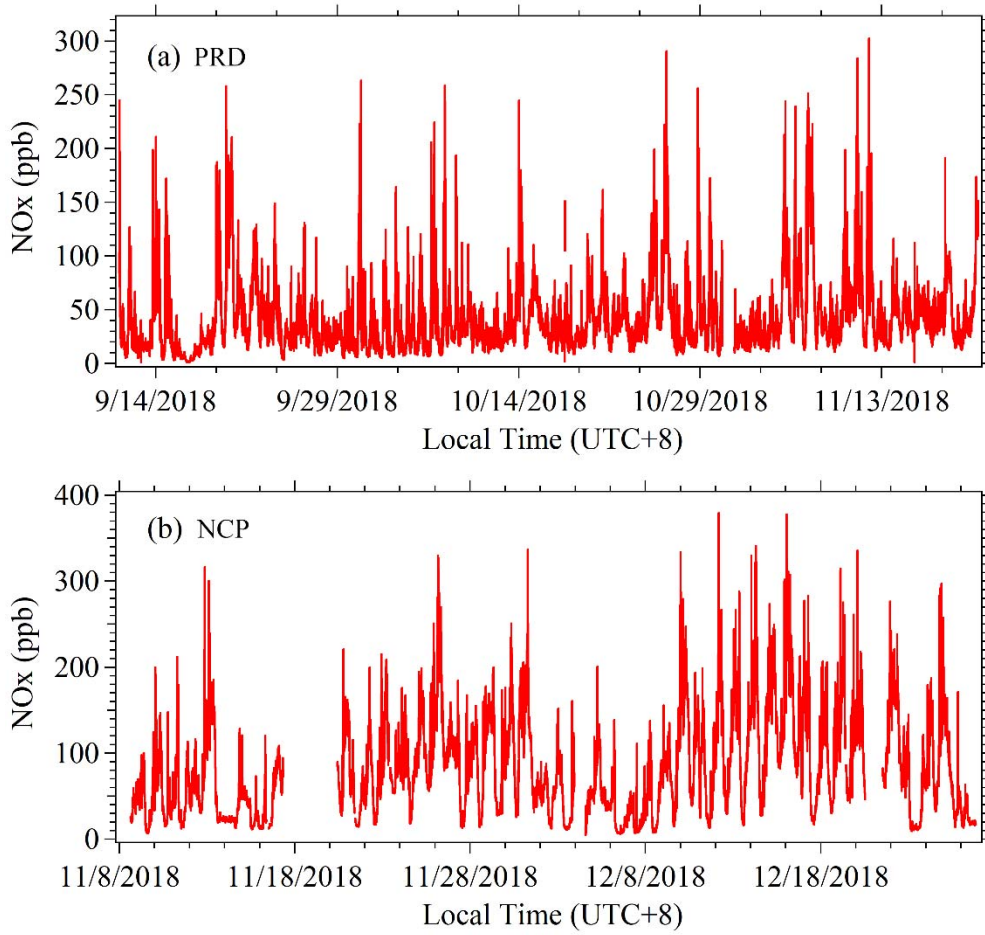
Figure S24. Time series of NO$_x$ during the PRD **(a)** and the NCP **(b)** campaigns, respectively.

Figure S25. Time series of SOA produced from higher alkanes (C8-C21 alkanes), monoaromatics (benzene, toluene, C8 aromatics, C9 aromatics and styrene), naphthalenes (naphthalene, methylnaphthalenes, dimethylnaphthalenes) and isoprenoids (isoprene and monoterpenes) as well as the measured SOA concentrations in PRD **(a)** and NCP **(b)**, respectively.

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Figure S26. Scatter plots of total SOA production from higher alkanes (C8-C21 alkanes), monoaromatics (benzene, toluene, C8 aromatics, C9 aromatics and styrene), naphthalenes (naphthalene, methylnaphthalenes, dimethylnaphthalenes) and isoprenoids (isoprene and monoterpenes) versus measured SOA concentrations during the PRD campaign **(a)** and NCP campaign **(b)**.

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Figure S27. The relative contributions to measured SOA concentrations from higher alkanes (C8-C21 alkanes), monoaromatics (benzene, toluene, C8 aromatics, C9 aromatics and styrene), naphthalenes (naphthalene, methylnaphthalenes, dimethylnaphthalenes) and isoprenoids (isoprene and monoterpenes) in PRD **(a)** and NCP **(b)**.

Figure S28. The average concentrations from higher alkanes (C8-C21 alkanes), monoaromatics (benzene, toluene, C8 aromatics, C9 aromatics and styrene), naphthalenes (naphthalene, methylnaphthalenes, dimethylnaphthalenes) and isoprenoids (isoprene and monoterpenes) in PRD **(a)** and NCP **(b)**, respectively.

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Figure S29. Diurnal variations of SOA yields of *n*-C15 alkane, benzene, naphthalene and *α*-pinene in PRD **(a)** and NCP **(b)**.

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Figure S30. The mean SOA production rates of higher alkanes (C8-C20 alkanes),
monoaromatics (benzene, toluene, C8 aromatics, C9 aromatics and styrene), naphthalenes
(naphthalene, methylnaphthalenes, dimethylnaphthalenes) and isoprenoids (isoprene and
monoterpenes) and their hourly diurnal variations in PRD **(a)** and NCP **(b)**. Diurnal variations
of alkanes, monoaromatics, naphthalenes and isoprenoids in PRD **(c)** and NCP **(d)**.

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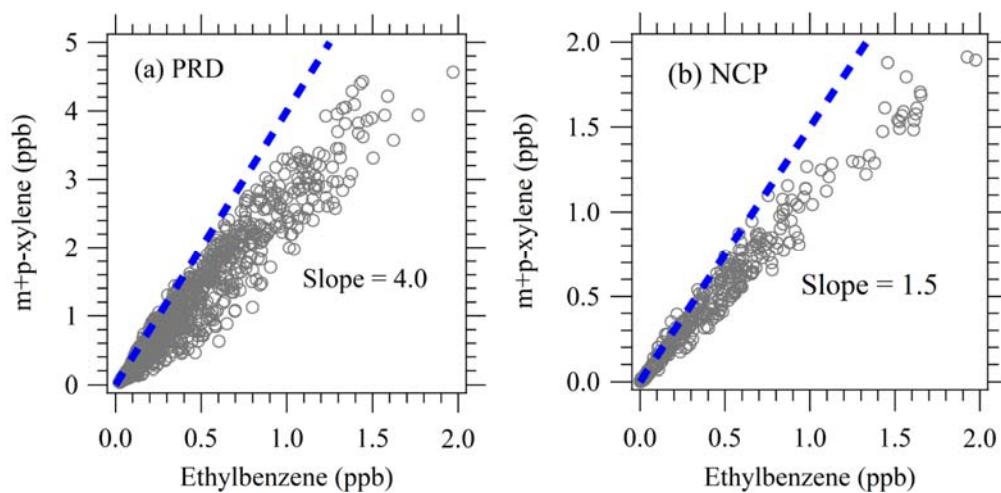
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Figure S31. Correlation of m+p-xylene with ethylbenzene in PRD **(a)** and NCP **(b)**. The dashed lines in both graphs indicate the estimated initial mission ratio of m+p-xylene/ethylbenzene.

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387   **Table S1**. The settings of the voltages of ion source voltages (Us, Uso), drift tube (Udrift, Udx)

388   and pressure of drift tube (pDrift) during automatical switching between NO^+ mode and H_3O^+

389   mode, respectively.

Setting	NO^+ mode	H_3O^+ mode
Us	40 V	150 V
Uso	100 V	80 V
Udrift	470 V	920 V
Udx	23.5 V	46 V
pDrift	3.8 mbar	3.8 mbar

390

391 **Table S2**. Fractions of *n*-alkanes in higher alkanes with same formulas derived from this study,

392 ambient air in Los Angeles, Bakersfield, Caldecott Tunnel and in vehicle exhausts.

Carbon Number	Fraction of *n*-alkanes in higher alkanes with same formulas					
	PRD[a]	Los Angeles[b]	Bakersfield[b]	Caldecott Tunnel[c]	Diese exhaust[d]	Liquid gasoline exhaust[d]
8	10.82	/	/	/	37.04	5.39
9	21.48	/	/	/	51.22	7.71
10	17.56	/	/	/	23.81	8.81
11	17.81	/	/	/	20.91	10.88
12	/	/	/	/	22.54	29.82
13	/	/	/	/	21.98	/
14	/	/	/	/	19.84	5.41
15	/	/	/	/	22.86	40
16	/	/	/	/	25.44	/
17	/	/	/	/	32.16	/
18	/	/	/	/	28.57	/
19	/	/	/	/	20.83	/
20	/	34.78	24.85	/	20.87	/
21	/	53.16	12.47	/	24.82	/
22	/	42.85	9.11	/	25.51	/
23	/	40.24	8.14	58.82	21.05	/
24	/	21.85	6.92	34.62	24.44	/
25	/	27.17	27.87	32.35	60	/
26	/	/	/	25	/	/
27	/	/	/	27.03	/	/
28	/	/	/	38.64	/	/
29	/	/	/	29.63	/	/
30	/	/	/	23.53	/	/

393 [a]:This work; [b]: Chan et al. (2013); [c]: Worton et al. (2014); [d]: Gentner et al. (2012)

394

395   **Table S3.** The calculated average SOA yields of higher alkanes in PRD and NCP.

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Compounds	Formula	Average SOA	Average SOA
Octane	C_8H_{18}	0.003±0.002	0.006±0.004
Nonane	C_9H_{20}	0.010±0.005	0.017±0.010
Decane	$C_{10}H_{22}$	0.026±0.012	0.040±0.021
Undecane	$C_{11}H_{24}$	0.058±0.020	0.080±0.036
Dodecane	$C_{12}H_{26}$	0.106±0.032	0.142±0.059
Tridecane	$C_{13}H_{28}$	0.249±0.061	0.305±0.103
Tetradecane	$C_{14}H_{30}$	0.329±0.070	0.388±0.118
Pentadecane	$C_{15}H_{32}$	0.386±0.081	0.450±0.135
Hexadecane	$C_{16}H_{34}$	0.428±0.086	0.492±0.141
Heptadecane	$C_{17}H_{36}$	0.488±0.096	0.556±0.156
Octadecane	$C_{18}H_{38}$	0.664±0.079	0.704±0.139
Nonadecane	$C_{19}H_{40}$	0.773±0.056	0.792±0.105
Eicosane	$C_{20}H_{42}$	0.860±0.025	0.863±0.054
Heneicosane	$C_{21}H_{44}$	0.877±0.025	0.870±0.046

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398   **Table S4.** Average biases in SOA yields due to vapour wall losses for various VOCs under

399   high-NO_x conditions from Zhang et al. (2014).

VOC	R_{wall}
Benzene	1.25±0.1
Toluene	1.13±0.06
m-xylene	1.2±0.1
Naphthalene	1.2±0.1
Isoprene	2.2±0.5
α-pinene	1.3±0.1
n-dodecane	1.16±0.08
2-methylundecane	1.4±0.2

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