Supplement of

Low-level isoprene observed during summertime at a forested mountaintop site in southern China: implications for strong regional atmospheric oxidative capacity

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Text S1. Calculation of the atmospheric reaction time of isoprene

The atmospheric reaction time of isoprene was estimated from the parameterization method through the empirical relationship between isoprene and its oxidation products MVK and MACR, based on the assumption that the processing time of the air mass was identical for MACR and MVK and there were no additional sources of MACR and MVK apart from the oxidation of isoprene. A chemical kinetic calculation is simplified to the following analytical expression for the MVK/isoprene and MACR/isoprene ratio. In this "back-of-the-envelope" approach, we have assumed that the rates of turbulent mixing and horizontal convection are similar for all three compounds, *i.e.*, the difference in the rate does not play a significant role during the time of transport from the nearby forest canopy to the altitude of the observation (Kuhn et al., 2007).

The chemical loss of isoprene (ISO) by reaction with OH during the day, and with NO_3 during the night, can be described by the following reactions:

$$ISO + OH \rightarrow y_{MACR,OH}\, MACR + y_{MVK,OH}\, MVK \qquad k_{ISO,OH} = 2.7 \times 10^{-11}\, e^{390/T} \qquad \text{(S1)}$$

$$MVK + OH \rightarrow \text{products} \qquad k_{MVK,OH} = 2.6 \times 10^{-12}\, e^{610/T} \qquad \text{(S2)}$$

$$MACR + OH \rightarrow \text{products} \qquad k_{MACR,OH} = 8.0 \times 10^{-12}\, e^{380/T} \qquad \text{(S3)}$$

$$ISO + NO_3 \rightarrow y_{MACR,NO_3}\, MACR + y_{MVK,NO_3}\, MVK \qquad k_{ISO,NO_3} = 2.95 \times 10^{-12}\, e^{-450/T} \qquad \text{(S4)}$$

$$MVK + NO_3 \rightarrow \text{products} \qquad k_{MVK,NO_3} < 6.0 \times 10^{-16} \qquad \text{(S5)}$$

$$MACR + NO_3 \rightarrow \text{products} \qquad k_{MACR,NO_3} = 3.4 \times 10^{-15} \qquad \text{(S6)}$$

Where *k* are the temperature dependent reaction rate coefficients taken from the IUPAC database (http://iupac.pole-ether.fr/) (Atkinson et al., 2006). *y* are yields of MVK and MACR from isoprene reaction with OH and NO_3. *T* is temperature (unit in K).

The yields from OH-initiated isoprene oxidation are a nonlinear function of nitrogen oxide (NO). Previous applications of this method (de Gouw, 2005; Karl et al., 2007; Kuhn et al., 2007; Roberts et al., 2006; Stroud et al., 2001) have assumed lab-derived high-NO yields of 0.33 and 0.23 for MVK and MACR, respectively (Atkinson and Arey, 2003b), but this may not be appropriate in the present case. In this study, we chose the results in Master Chemical Mechanism (MCM) v3.3.1 (Jenkin et al., 2015). The resulting yield curves are interpolated to observed NO mixing ratios (**Fig. S1**).

The yields from NO_3-initiated isoprene oxidation are constants (**Table S1**).

Integration of the kinetic equations for this system shows that the product/parent ratios are a function of the rate constants (*k*), yield (y), reaction time (Δt) and radical concentration. In the case of daytime MACR, for example,

$$\frac{[MACR]}{[ISO]} = \frac{y_{MACR,OH}\, k_{ISO,OH}}{(k_{MACR,OH} - k_{ISO,OH})} \times \left[1 - \mathrm{e}^{(k_{ISO,OH} - k_{MACR,OH})\,[OH]\,\Delta t}\right] \qquad \text{(S1)}$$

Where the [ISO], [MACR] and [OH] are the reactant concentrations (number densities, in molecules cm^{-3}).

The reaction time (Δt) implied by any observed daughter/parent ratio depends on the concentration of radical (*i.e.*, OH and NO_3), which was not measured and varies as an air mass ages. Rather than assume a single "typical" value for OH, we express reaction time in terms of "exposure", defined here as the product of radical concentration and reaction time. Then, exposures can be calculated from observed daughter/parent ratios by inverting Eq. (S1), In the case of daytime MACR, for example,

$$[OH]\,\Delta t = \frac{\ln\left(1 - \frac{[\mathrm{MACR}]}{[\mathrm{ISO}]} \times \frac{k_{MACR,OH} - k_{ISO,OH}}{y_{MACR,OH}\, k_{ISO,OH}}\right)}{(k_{ISO,OH} - k_{MACR,OH})} \qquad \text{(S2)}$$

Also, the atmospheric reaction time of isoprene can be calculated based on the modeled OH and NO_3 concentrations in this study.

Text S2. Photochemical age of the air mass

Similar to the above exposure calculation methods, we chose three pairs of VOC species: toluene/benzene, ethylbenzene/benzene and m,p-xylene/benzene to calculate the photochemical age of the air mass.

$$Benzene + OH \rightarrow \text{products} \qquad k_{benzene,OH} = 2.3 \times 10^{-12}\, e^{-190/T} \qquad \text{(S7)}$$

$$Toluene + OH \rightarrow \text{products} \qquad k_{Toluene,OH} = 1.8 \times 10^{-12}\, e^{340/T} \qquad \text{(S8)}$$

$$Ethylbenzene + OH \rightarrow \text{products} \qquad k_{Ethylbenzene,OH} = 7.0 \times 10^{-12} \qquad \text{(S9)}$$

$$m,p - Xylene + OH \rightarrow \text{products} \qquad k_{m,p-Xylene,OH} = 1.89 \times 10^{-11} \qquad \text{(S10)}$$

Toluene, ethylbenzene and m,p-xylene react faster with hydroxyl radicals (OH) than benzene. Then photochemical age is determined by the following equation:

$$PA_{T/B} = \frac{1}{[OH]\,(k_{T,OH}-k_{B,OH})} \times \left[\ln\left(\frac{[T]}{[\mathrm{B}]}\right)_0 - \ln\left(\frac{[T]}{[\mathrm{B}]}\right)\right] \qquad \text{(S3)}$$

$$PA_{X/B} = \frac{1}{[OH]\,(k_{X,OH}-k_{B,OH})} \times \left[\ln\left(\frac{[X]}{[\mathrm{B}]}\right)_0 - \ln\left(\frac{[X]}{[\mathrm{B}]}\right)\right] \qquad \text{(S4)}$$

$$PA_{E/B} = \frac{1}{[OH]\,(k_{E,OH}-k_{B,OH})} \times \left[\ln\left(\frac{[E]}{[\mathrm{B}]}\right)_0 - \ln\left(\frac{[\mathrm{E}]}{[\mathrm{B}]}\right)\right] \qquad \text{(S5)}$$

Here, $PA_{T/B}$, $PA_{X/B}$ and $PA_{E/B}$ denote the calculated photochemical age by three methods. [*B*], [*T*], [*X*] and [*E*] represent the mixing ratios of benzene, toluene, m,p-xylene and ethylbenzene, respectively. $k_{B,OH}$, $k_{T,OH}$, $k_{X,OH}$ and $k_{E,OH}$ indicate the OH reaction rate coefficient of benzene, toluene, m,p-xylene and ethylbenzene, respectively. [*OH*] represents the modeled concentrations of OH radical. $([T]/[B])_0$, $([X]/[B])_0$ and $([E]/[B])_0$ is the initial concentration ratio of toluene/benzene, ethylbenzene/benzene and m,p-xylene/benzene in fresh emissions, *i.e.*, the initial emission ratio before aging begins. [*T*]/[*B*], [*X*]/[*B*] and [*E*]/[*B*] is the measured concentration ratio. As presented in **Fig. S2**, we chose 6, 1.5 and 1.4 molecules cm^{-3} / molecules cm^{-3} as the initial emission ratios of toluene to benzene, ethylbenzene to benzene and m,p-xylene to benzene, as they were the largest ratios in diurnal variations for the study.

Text S3. Data analysis and graph plotting by R

Data analysis and graph plotting were performed using the open source R package "openair" (Carslaw, 2015; Carslaw and Ropkins, 2012). Specifically, for those dedicated functions for data analysis and plots generated in openair, the "transform", "selectByDate", "merge" and "subset" functions were used to calculate and filter the data; the "quantile", "summary" and "t.test" functions were used to do statistical analysis. The "timePlot" function was used to plot time series of measured species. The "plot" function was used to plot scatter and diagram diurnal variations.

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Tables

Table S1: Rate constants and lifetime for isoprene, MVK and MACR, and yields of MVK and MACR from the isoprene reactions.

Compound	Rate constants [a] with			Yield [b] from isoprene reaction with / (lifetime [b] for reaction with)		
	OH	NO_3	O_3	OH	NO_3	O_3
Isoprene	1.0×10^{-10}	7.0×10^{-13}	1.3×10^{-17}	-/ 0.4 h	-/ 0.8 h	-/ 24 h
MVK	2.0×10^{-11}	3.2×10^{-16}	5.2×10^{-18}	0.33 / 1.9 h	0.035 / 0.5 yr	0.16 / 61 h
MACR	2.9×10^{-11}	3.7×10^{-15}	1.2×10^{-18}	0.23 / 1.0 h	0.035 / 72 h	0.41 / 10 d

[a] (Atkinson et al., 2006) and references therein, unit in cm^3 molecule^{-1} s^{-1}, temperature in 298 K.

[b] (Atkinson and Arey, 2003a, b) and references therein. Lifetime calculated using the following: for OH radical reactions, a 12-h daytime average of 8.0×10^6 molecules cm^{-3}; for NO_3 radical reactions, a 12-h nighttime average of 5.0×10^8 molecules cm^{-3}; and for O_3, a 24-h average of 1.0×10^{12} molecules cm^{-3}.

Figures

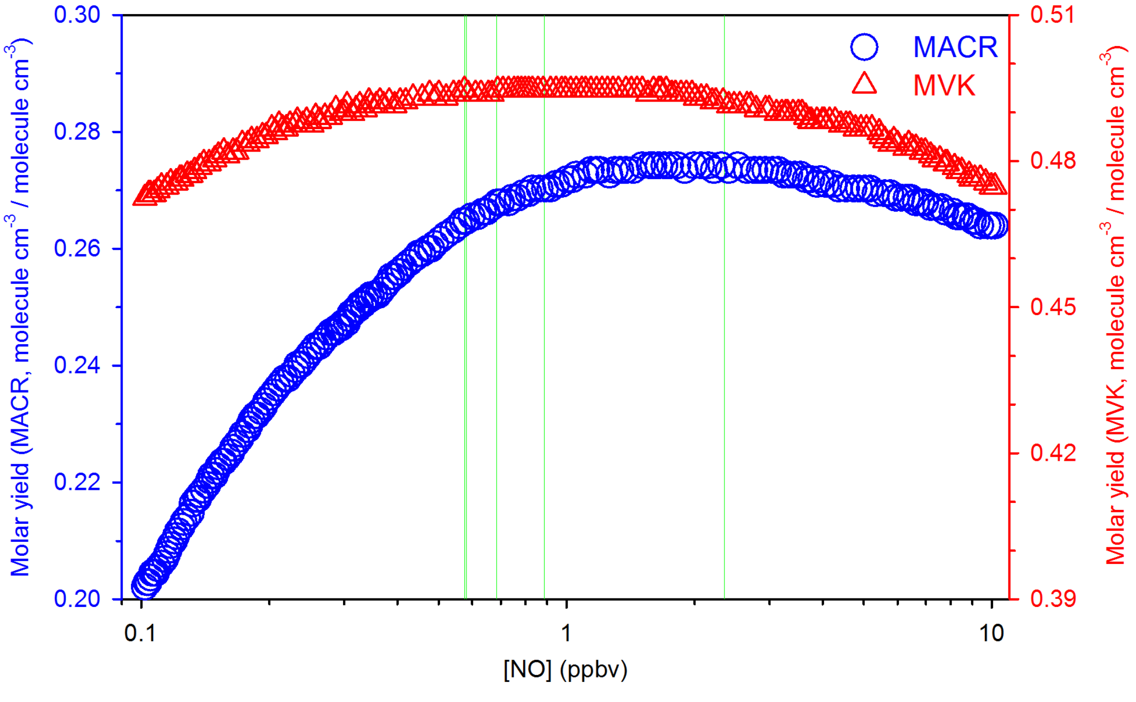

Fig. S1: Molar yields of the main first-generation products (MVK and MACR) of the OH-initiated oxidation of isoprene as a function of NO mixing ratio, at 298 K, as represented in MCM v3.3.1 (Jenkin et al., 2015). Thin green vertical lines denote, from left to right, the 1st, 5th, 50th, 95th and 99th percentiles of hourly NO observed during the present study.

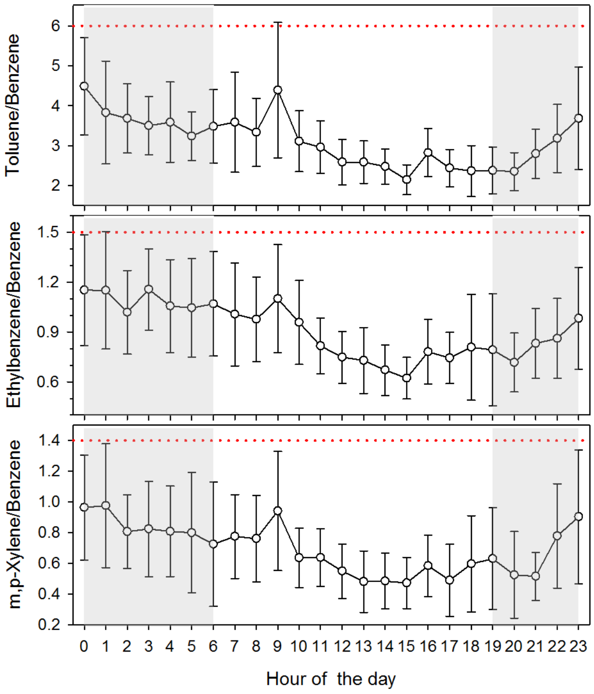

Fig. S2. **Ratios of toluene to benzene, ethylbenzene to benzene and m,p-xylene to benzene in Nanling site in Jul.-Aug. 2016. Red dotted line denotes the highest ratio, assumed as the initial emission ratios of 6, 1.5 and 1.4 molecules cm^{-3} / molecules cm^{-3}, respectively. Shaded regions denote the nighttime periods. Error bars indicate the 95% confidence interval.**