Supplement.

Variation and Trend of Nitrate radical reactivity towards volatile organic compounds in Beijing, China

Hejun Hu et al.,

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Content:

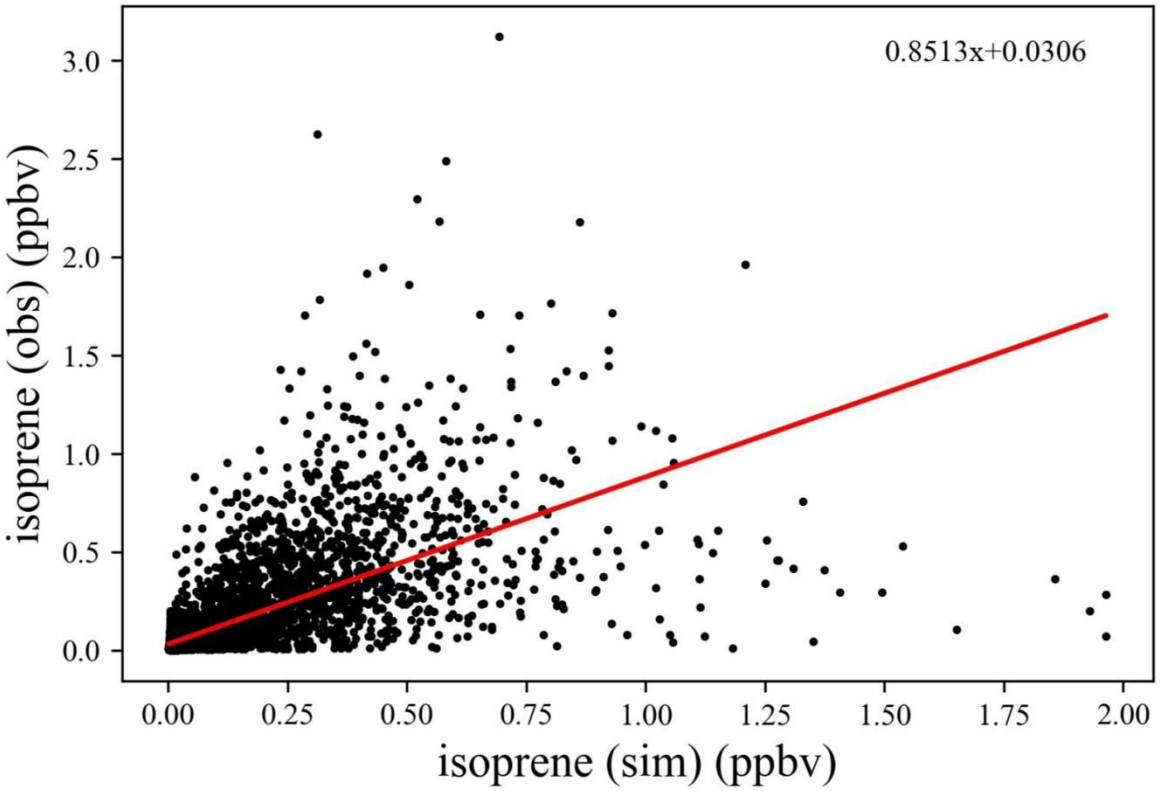

Figure S1. The intercomparing of measured and simulated isoprene in year 2019 in urban Beijing, which shows the overall overestimation of the modelling result compared with the observation.

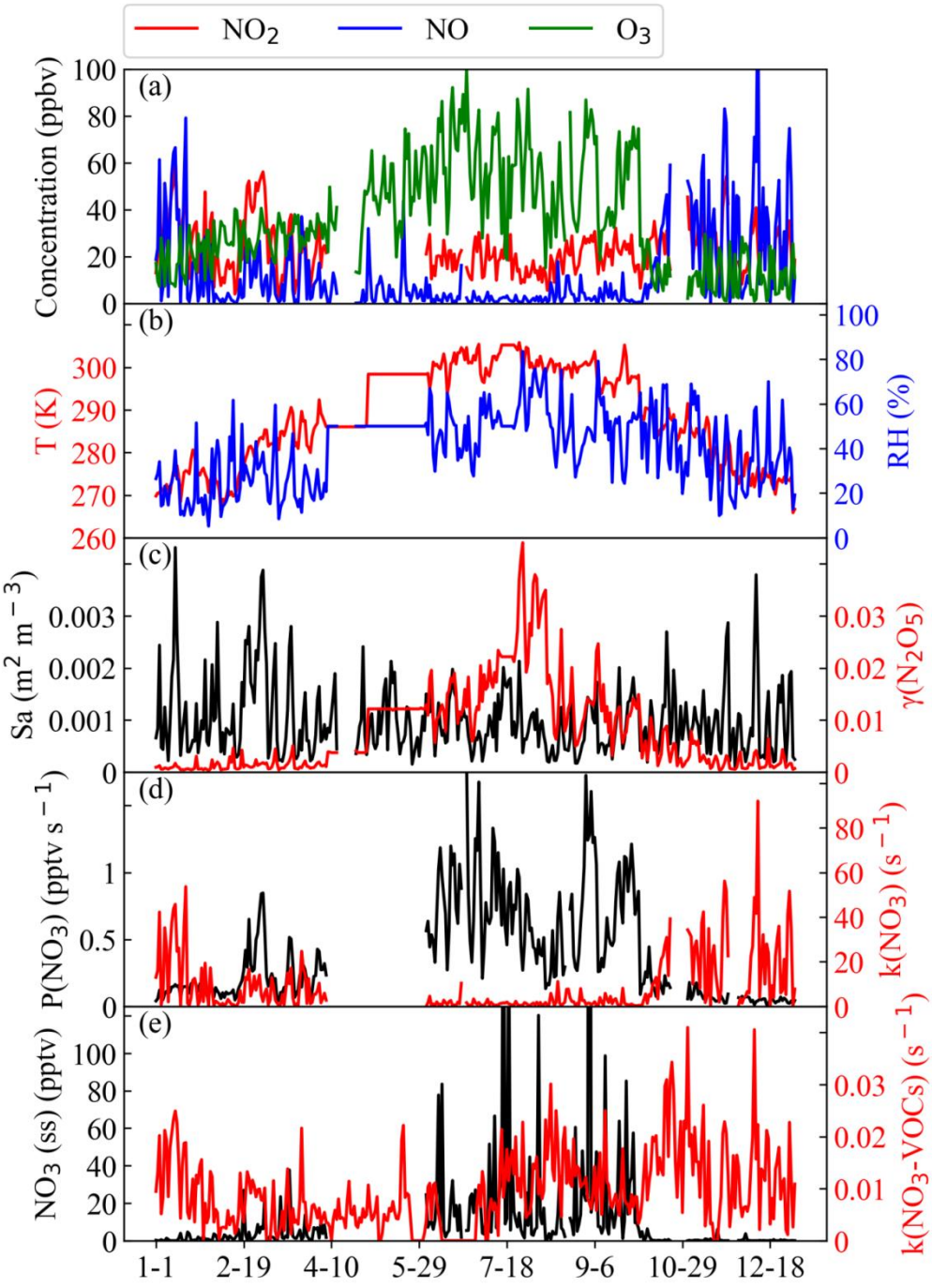

Figure S2. (a) Time series of concentrations of NO, NO_2 and O_3. (b) Time series of thermodynamic temperature and relative humidity. (c) Time series of the aerosol surface area densities and dimensionless uptake coefficients of N_2O_5, (d) Time series of NO_3 production rate and NO_3 loss term. (e) Time series of NO_3 stationary-state concentrations and the NO_3 loss term through the reaction with VOC (actual NO_3 reactivity towards VOC). All the date were averaged with the time resolution of 1 day.

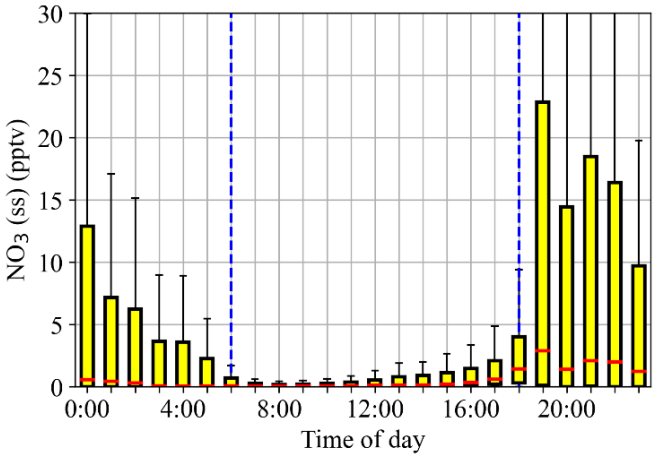

Figure S3. Median diel profile of the estimated NO_3 concentrations. The yellow boxes, the red lines and the black lines represent the box diagrams (25-75 percentiles), the median values and the error bars (+standard deviation) of NO_3 concentrations, respectively. Daytime and nighttime data are divided by the blue dotted lines.

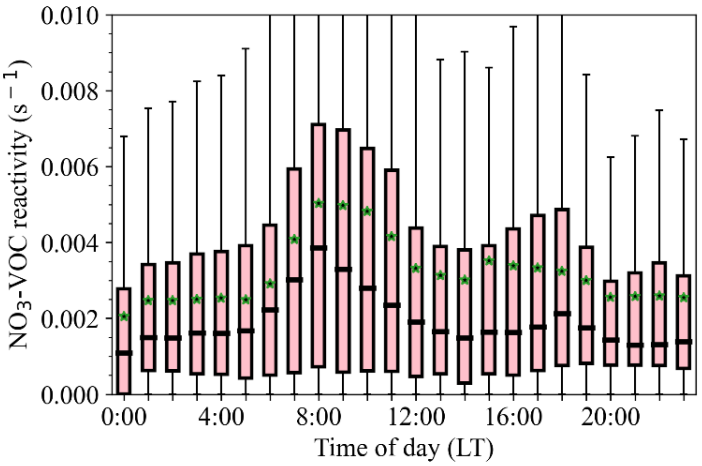

Figure S4. The box whisker plot of NO_3 reactivity towards VOC on annual average. The pink parts represent the variation range from 25 to 75 quantiles; The black bars represent error bars (± standard deviations) of the NO_3 reactivity towards VOC; The green asterisks and the black lines represent the average and the median value, respectively.

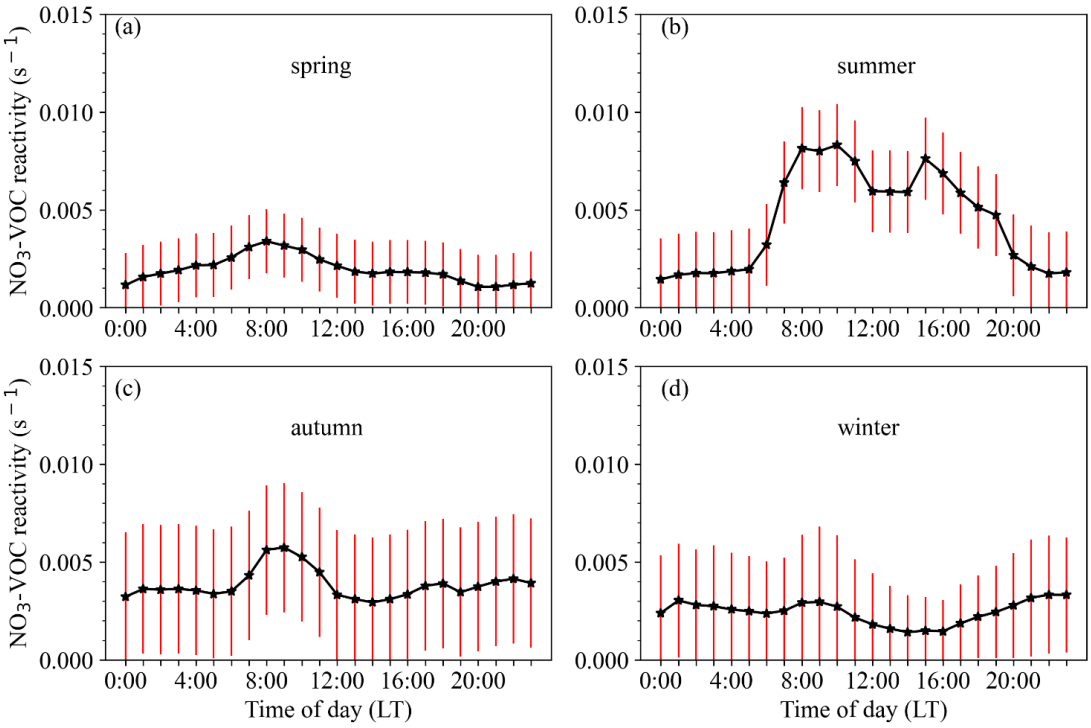

Figure S5. The season-averaged diel profiles of k_{NO3}. (a) - (d) respectively represent the mean diurnal profiles of k_{NO3} in four seasons. The red lines represent the error bars (± standard deviations) of the reactivity.

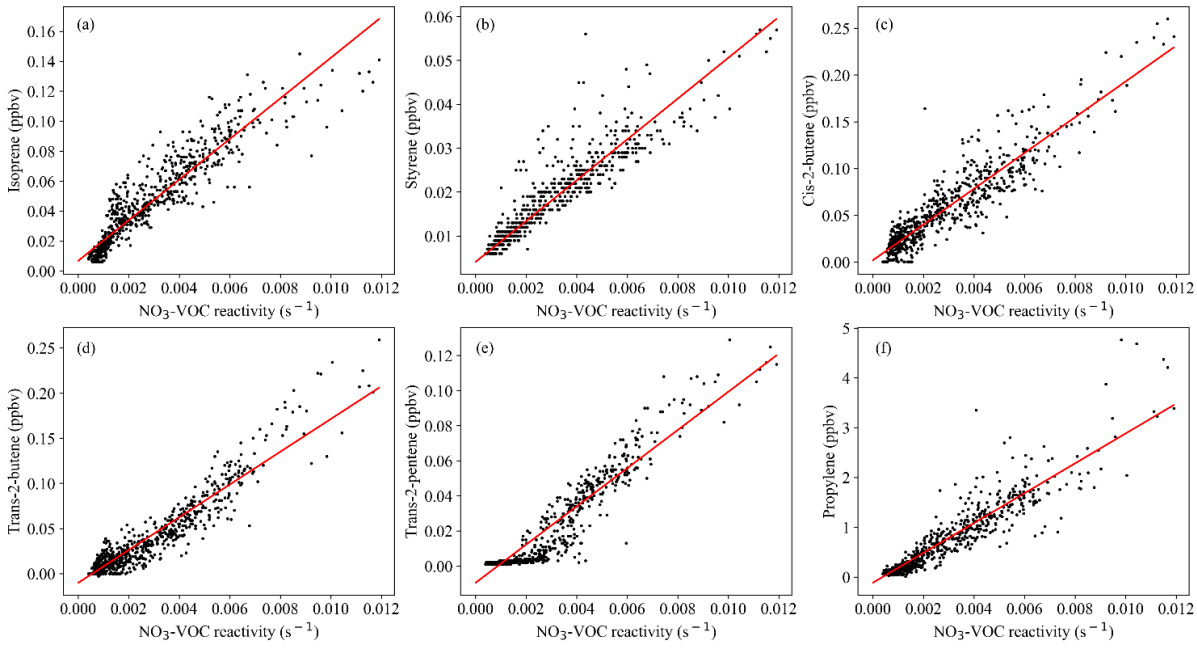

Figure S6. The correlation between the concentrations of isoprene, styrene, cis-2-butene, trans-2-butene, trans-2-pentene, propylene and NO_3 reactivity towards VOC. The black dots are the scattered points and the red lines are the fitting lines, the detailed correlation coefficients are summarized in Table S2.

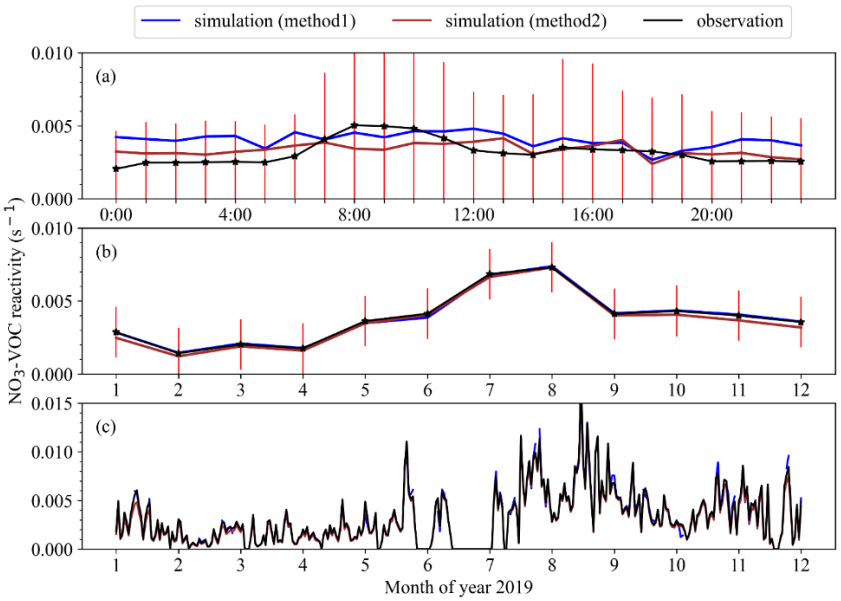

Figure S7. (a) is a campaign-averaged diel profile (time resolution = 1 hour) of measured NO_3 reactivity toward VOC and the reactivity estimated by the two parameterization methods. (b) is a mean monthly profile of measured NO_3 reactivity toward VOC and the reactivity estimated by the two parameterization methods. The red lines are error bars of measured NO_3 reactivity towards VOC. (c) depicts the time series of measured daily NO_3 reactivity toward VOC and the reactivity estimated by the two parameterization methods. The red lines are error bars of measured NO_3 reactivity towards VOC.

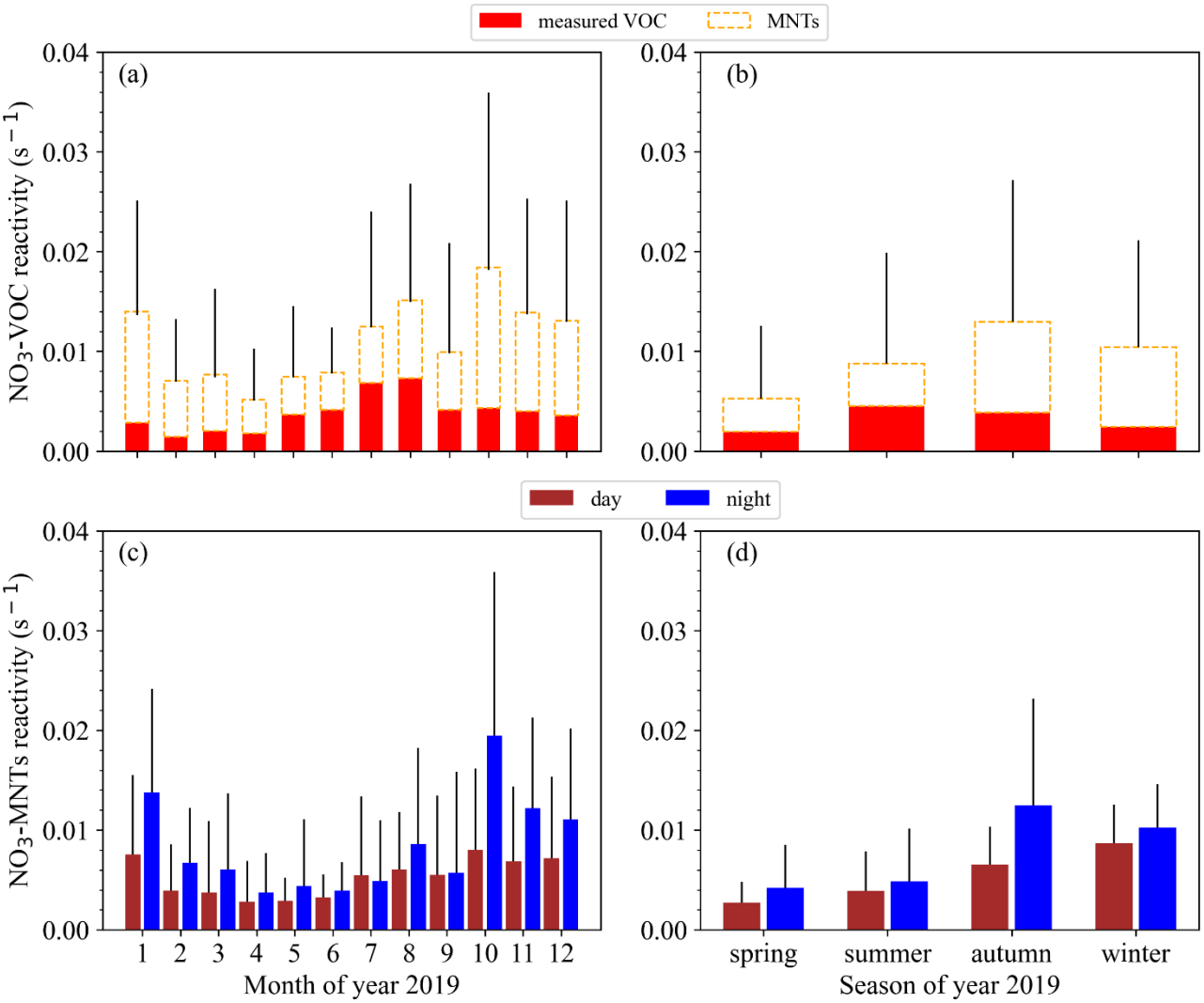

Figure S8. The histograms of monthly (a) and seasonal-averaged (b) NO_3 reactivity towards estimated MNTs. The black lines are the error lines (+ standard deviation) of NO_3 reactivity towards MNTs (thick lines). The histograms of monthly (c) and seasonal-averaged (d) NO_3 reactivity towards MNTs divided into daytime and nighttime data. The black lines are the error lines (+ standard deviation) of NO_3 reactivity towards MNTs.

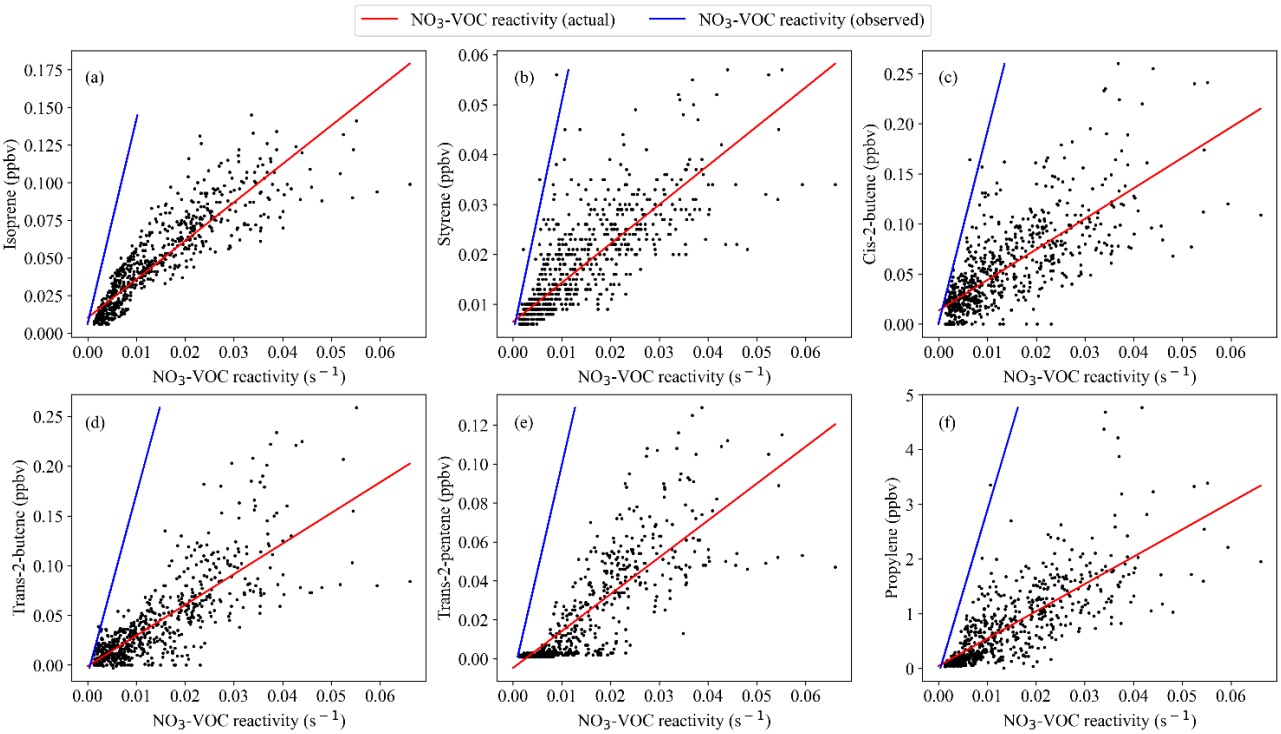

Figure S9. (a) - (f) respectively depict the correlation plots of key VOC concentrations and the actual NO_3 reactivity (w/ MTs) towards VOC in January. The black dots are the scattered points the red lines are the fitting lines. To aid comparison, the fitting lines of the observed reactivity (w/o MTs) are also plotted (blue).

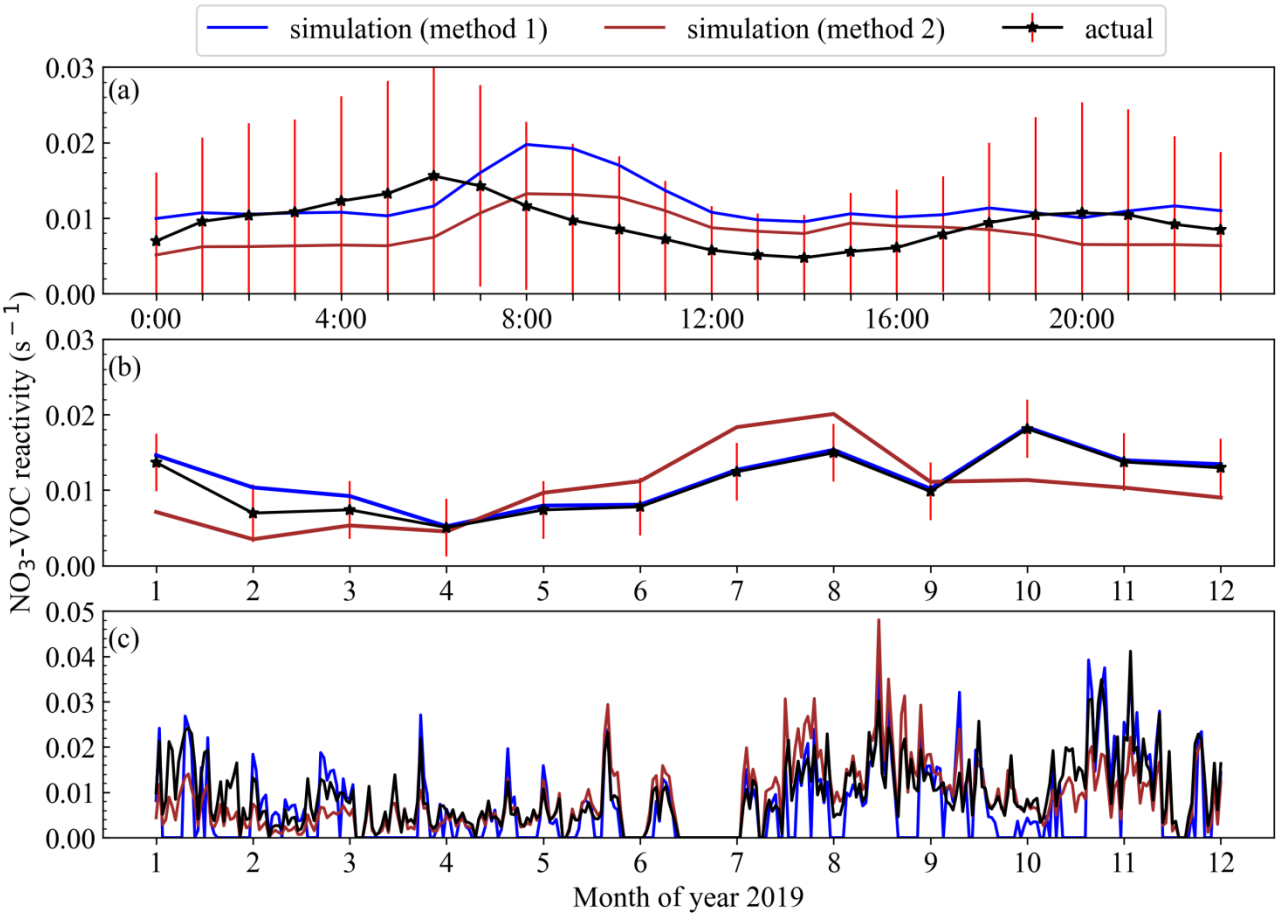

Figure S10. (a) is a campaign-averaged diel profile (time resolution = 1 hour) of actual NO_3 reactivity toward VOC (including monoterpenes) and the actual reactivity estimated by the two parameterization methods. (b) is a mean monthly profile of actual NO_3 reactivity toward VOC and the reactivity estimated by the two parameterization methods. The red lines are error bars of actual NO_3 reactivity towards VOC. (c) depicts the time series with time resolution of one day of actual NO_3 reactivity toward VOC and the reactivity estimated by the two parameterization methods. The red lines are error bars of actual NO_3 reactivity toward VOC.

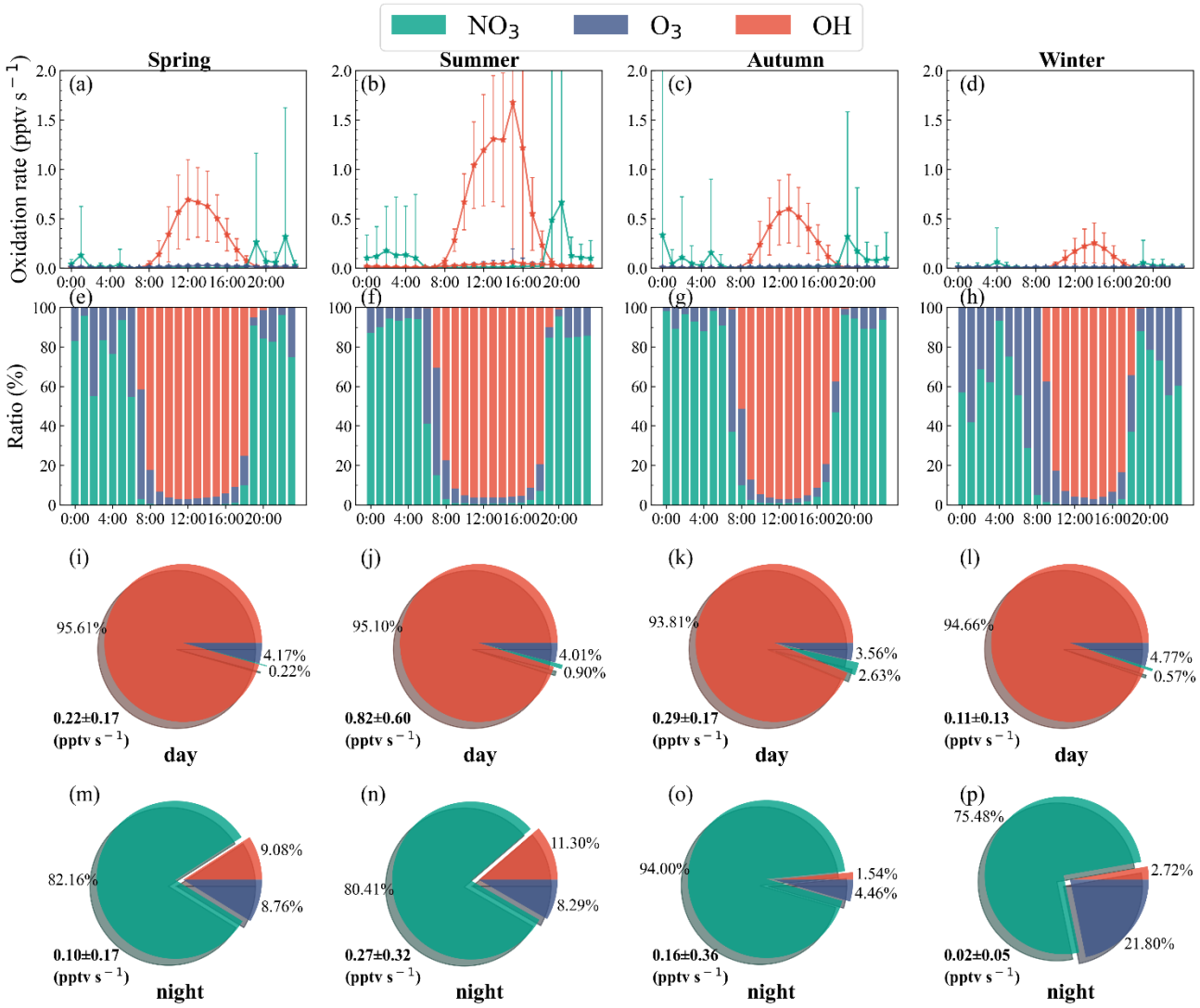

Figure S11. (a-d) Median diurnal profiles of VOC oxidation rate by atmospheric oxidants in different seasons. The error bars (±standard deviation) are plotted. (e-h) Fractions of VOC oxidation rate by atmospheric oxidants in different seasons. The oxidation fraction by different oxidants is differentiated by colors. (i-p) Pie charts representing the daytime and the nighttime VOC oxidation rate by OH, NO_3 and O_3 during different seasons, with the averaged values and standard deviations.

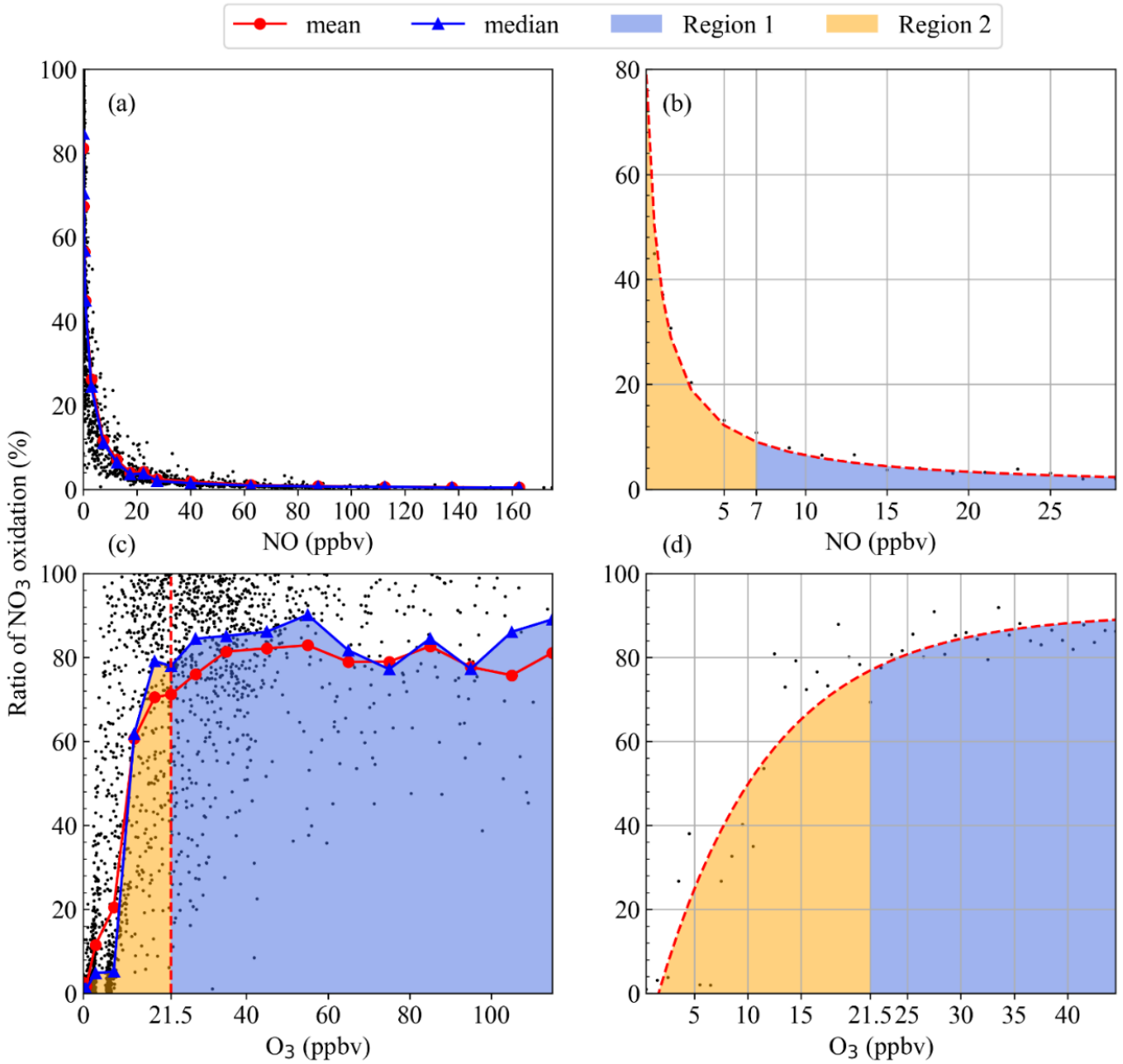

Figure S12. Fitting diagrams between ratios of nighttime VOC oxidized by NO_3 and concentrations of NO (a and b) and O_3 (c and d). The colored regions indicate the different effects of NO or O_3 concentrations on the ratios. Region 1 and region 2 respectively represent "strong effect" and the "weak effect" of NO or O_3 concentrations.

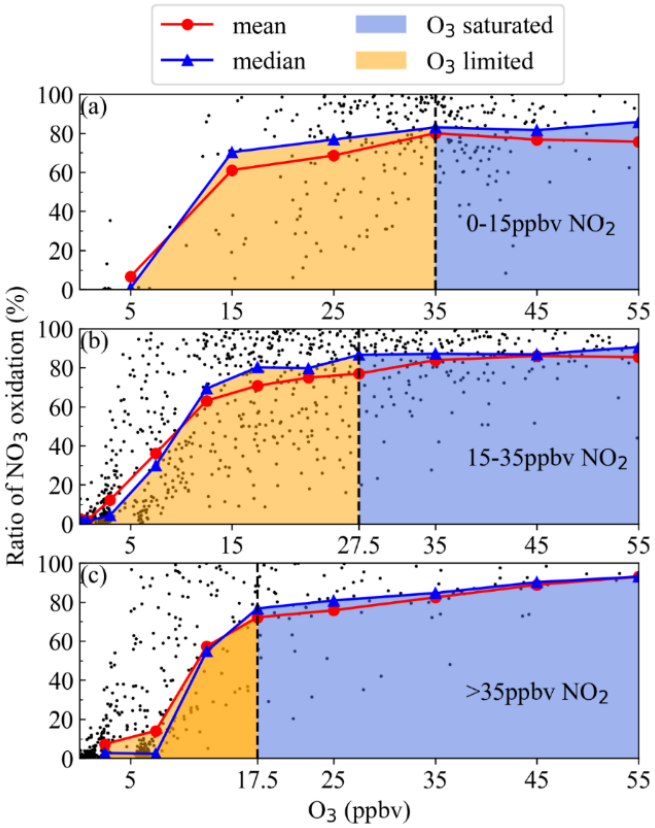

Figure S13. (a) (b) (c) respectively depict the fitting diagrams between the ratio of nighttime VOC oxidized by NO_3 and O_3 concentrations existing in different NO_2 concentrations. To aid comparison, the NO_2 concentrations and the threshold values of O_3 are marked in the figures. Colored regions represent different effects of O_3 concentrations donated in the legend.

Table S1. Reaction rate coefficients of VOC with NO_3 used in our study

VOC	k (298K) (10^{15} cm^3 molecule^{-1} s^{-1})	A Factor (10^{12} cm^3 molecule^{-1} s^{-1})	Ea/R (K)	Ref
ethane	0.005	/	/	1
ethylene	0.210	3.3	2880	2
propane	0.035	/	/	1
propylene	9.490	0.459	1156	1
isobutane	0.106	3.05	3060	2
n-butane	0.046	2.76	3279	1
acetylene	0.210	/	/	4
trans-2-butene	390	0.390	0	2
1-butene	13.5	0.314	938	1
cis-2-butene	352	/	/	1
cyclopentane	0.140	0.00014	0	2
isopentane	0.162	2.99	2927	2
n-pentane	0.087	/	/	1
1-pentene	15	/	/	1
trans-2-pentene	390	0.390	0	2
Isoprene	700	3.15	450	1
cis-2-pentene	350	0.350	0	2
2,2-dimethylbutane	0.440	0.00044	0	2
2,3-dimethylbutane	0.440	/	/	1
2-methylpentane	0.180	/	/	1
3-methylpentane	0.220	/	/	1
1-hexene	0.180	/	/	1
n-hexane	0.110	0.00011	0	2
2,4-dimethylpentane	0.150	/	/	1
methylcyclopentane	0.320	/	/	3
2-methylhexane	0.180	0.00018	0	2
cyclohexane	0.140	/	/	1
2,3-dimethylpentane	0.330	/	/	3
3-methylhexane	0.180	0.00018	0	2
Benzene	0.015	/	/	1
2,2,4-trimethylpentane	0.090	/	/	1
n-heptane	0.150	/	/	1
methylcyclohexane	0.420	/	/	5
2,3,4-trimethylpentane	0.440	/	/	3
2-methylheptane	0.130	/	/	5
3-methylheptane	0.160	/	/	5
toluene	0.070	/	/	1
n-octane	0.190	/	/	1
ethylbenzene	0.300	/	/	1
n-nonane	0.230	/	/	1
m,p-xylene	0.380	/	/	1

o-xylene	0.410	/	/	1
styrene	1500	/	/	1
iso-propylbenzene	1	0.001	0	2
n-propylbenzene	1	0.001	0	2
m-ethyltoluene	0.900	0.00090	0	2
p-ethyltoluene	0.860	0.00086	0	2
n-decane	0.280	/	/	1
1,3,5-trimethylbenzene	0.880	/	/	1
o-ethyltoluene	0.900	0.00090	0	2
1,2,4-trimethylbenzene	1.8	/	/	1
1,2,3-trimethylbenzene	1.9	/	/	1
m-diethylbenzene	7	/	/	5
p-diethylbenzene	8.6	/	/	5
n-undecane	0.330	/	/	5
n-dodecane	0.380	/	/	5
limonene	12200	/	/	1
α-pinene	6160	1.19	-490	1
β-pinene	2510	/	/	1
sabinene	10000	/	/	1
myrcene	11100	/	/	1
3-carene	9100	/	/	1
ocimene	22000	/	/	1
2-carene	19000	/	/	1
acetone	0.015	/	/	1

ref1:(Atkinson and Arey, 2003)

ref2: (Brown et al., 2011)

ref3: (Ambrose et al., 2007)

ref4: IUPAC

ref5: Estimated

Table S2. Species contributions to NO_3 reactivity towards top six VOC in different seasons.

	Spring		Summer		Autumn		Winter	
	VOC	Fraction	VOC	Fraction	VOC	Fraction	VOC	Fraction
1	isoprene	40.04%	isoprene	77.16%	isoprene	43.21%	styrene	39.77%
2	styrene	37.86%	styrene	11.95%	styrene	36.09%	isoprene	20.42%
3	trans-2-butene	7.76%	cis-2-butene	4.20%	cis-2-butene	6.00%	cis-2-butene	11.95%
4	cis-2-butene	4.27%	trans-2-butene	3.51%	trans-2-butene	4.85%	trans-2-butene	4.85%
5	propylene	2.05%	propylene	0.67%	trans-2-pentene	2.81%	trans-2-pentene	2.81%
6	trans-2-pentene	1.75%	trans-2-pentene	0.39%	propylene	1.72%	propylene	1.72%

Table S3. Correlation coefficients and fitting equations between VOC concentrations and k_{NO3} in each month (where y represents VOC concentrations (ppbv), x represents the reactivity (s^{-1})). We selected the indicators with the best correlation coefficients.

VOC	Jan		Feb		Mar		Apr	
	R	equation	R	equation	R	equation	R	equation
isoprene	0.92	y=13.56x+0.0068	0.92	y=15.74x+0.0017	0.83	y=10.09x+0.0035	0.66	y=7.02x+0.011
styrene	0.92	y=4.65x+0.0041	0.88	y=5.41x+0.002	0.96	y=15.69x-0.0011	0.98	y=18.79x-0.008
cis-2-butene	0.92	y=19.13x+0.0017	0.82	y=22.56x-0.0004	0.87	y=7.44x-0.0018	0.74	y=5.50x+0.0011
trans-2-butene	0.94	y=18.15x-0.010	0.88	y=14.69x-0.005	0.83	y=8.58x-0.0014	0.58	y=5.89x+0.0065
trans-2-pentene	0.95	y=10.89x-0.0096	0.82	y=7.21x-0.004	0.77	y=4.42x-0.0019	0.78	y=3.29x-0.0021
propylene	0.92	y=299.85x-0.12	0.86	y=284.25x-0.004	0.76	y=119.19x+0.027	0.51	y=85.13x+0.099
VOC	May		Jun		Jul		Aug	
	R	equation	R		R		R	
isoprene	0.94	y=45.46x-0.024	0.96	y=45.51x-0.0063	0.96	y=45.36x-0.012	0.98	y=55.49x-0.062
styrene	0.44	y=3.46x+0.0061	0.20	y=3.49x+0.0018	0.59	y=3.33x-0.0006	0.13	y=0.68x+0.016
cis-2-butene	0.48	y=2.32x+0.0034	0.18	y=2.29x+0.0012	0.58	y=2.63x+0.018	0.12	y=0.75x+0.025
trans-2-butene	0.53	y=4.53x+0.0081	0.35	y=4.44x+0.0016	0.62	y=3.27x+0.0087	0.12	y=0.53x+0.013
trans-2-pentene	0.34	y=1.06x-0.0001	0.27	y=0.51x+0.0	0.38	y=0.87x-0.0033	0.088	y=0.155x+0.0024
propylene	0.15	y=18.69x+0.1026	0.0133	y=26.40x+0.0207	0.0849	y=6.32x+0.1298	0.0062	y=2.33x+0.1432
VOC	Sep		Oct		Nov		Dec	
	R	equation	R	equation	R	equation	R	equation
isoprene	0.98	y=55.87x-0.049	0.72	y=14.47x+0.025	0.90	y=9.66x+0.0064	0.93	y=7.28x+0.011
styrene	0.17	y=0.70x+0.014	0.93	y=13.18x-0.0076	0.97	y=14.88x-0.0	0.98	y=16.49x-0.0012
cis-2-butene	0.096	y=0.42x+0.016	0.89	y=8.24x+0.0007	0.94	y=9.15x-0.0022	0.93	y=7.56x-0.0042
trans-2-butene	0.16	y=0.49x+0.0039	0.90	y=9.81x-0.010	0.90	y=8.69x-0.0067	0.88	y=7.08x-0.0086
trans-2-pentene	0.068	y=0.10x+0.0019	0.88	y=5.42x-0.0067	0.94	y=6.03x-0.0042	0.91	y=5.82x-0.0038
propylene	-0.055	y=-0.23x+0.17	0.78	y=86.00x+0.018	0.86	y=123.56x+0.058	0.78	y=184.23x+0.0045

Table S4. Correlation coefficients and fitting equations between VOC concentrations and the actual NO_3 reactivity towards VOC (including monoterpenes) in each month (where y represents VOC concentrations (ppbv), x represents the actual reactivity (s^{-1})). The indicators and corresponding parameterization equations are colored.

VOC	Jan		Feb		Mar		Apr	
	R	equation	R	equation	R	equation	R	equation
isoprene	0.88	y=2.55x+0.010	0.89	y=2.79x+0.0044	0.84	y=2.05x+0.0074	0.5431	y=1.71x+0.014
styrene	0.76	y=0.78x+0.0064	0.68	y=0.79x+0.0041	0.68	y=2.47x+0.0089	0.7515	y=4.35x+0.0025
cis-2-butene	0.71	y=3.0469x0.014	0.61	y=3.17x+0.0089	0.72	y=1.33x+0.0021	0.7151	y=1.55x+0.0028
trans-2-butene	0.80	y=3.08x-0.0012	0.79	y=2.43x-0.0014	0.67	y=1.50x+0.0033	0.4244	y=1.31x+0.010
trans-2-pentene	0.83	y=1.89x-0.0048	0.82	y=1.33x-0.0031	0.81	y=0.97x-0.0006	0.7981	y=0.99x-0.0013
propylene	0.76	y=49.88x+0.044	0.73	y=45.10x+0.079	0.54	y=18.81x+0.10	0.4047	y=20.16x+0.14
VOC	May		Jun		Jul		Aug	
	R	equation	R	equation	R	equation	R	equation
isoprene	0.56	y=14.57x+0.019	0.66	y=20.88x+0.001	0.74	y=22.32x+0.014	0.68	y=22.10x+0.0086
styrene	0.70	y=2.27x+0.0029	0.45	y=2.221x+0.001	0.49	y=1.77x+0.0001	0.50	y=0.97x+0.0071
cis-2-butene	0.62	y=1.33x+0.0024	0.27	y=1.34x+0.0009	0.50	y=1.50x+0.017	0.38	y=0.82x+0.019
trans-2-butene	0.45	y=1.97x+0.0095	0.24	y=2.24x+0.0019	0.50	y=1.72x+0.0094	0.41	y=0.71x+0.0066
trans-2-pentene	0.61	y=0.84x-0.0019	0.45	y=0.34x-0.0001	0.27	y=0.38x-0.0023	0.37	y=0.28x-0.0004
propylene	0.21	y=10.16x+0.097	0.069	y=15.08x+0.018	0.19	y=5.20x+0.11	0.19	y=3.46x+0.11
VOC	Sep		Oct		Nov		Dec	
		equation	R	equation	R	equation	R	equation
isoprene	0.51	y=11.88x+0.063	0.57	y=2.31x+0.045	0.89	y=2.69x+0.0078	0.93	y=2.31x+0.0075
styrene	0.52	y=0.76x+0.0097	0.82	y=2.28x+0.007	0.83	y=3.69x+0.0076	0.88	y=4.71x-0.0035
cis-2-butene	0.43	y=0.57x+0.012	0.81	y=1.48x+0.009	0.90	y=2.50x-0.0003	0.85	y=2.19x-0.0056
trans-2-butene	0.62	y=0.72x-0.001	0.83	y=1.78x-0.0007	0.88	y=2.42x-0.0054	0.79	y=2.02x-0.0096
trans-2-pentene	0.59	y=0.30x-0.0007	0.84	y=1.01x-0.0019	0.89	y=1.63x-0.0027	0.88	y=1.78x-0.006
propylene	0.18	y=2.37x+0.15	0.68	y=14.70x+0.12	0.71	y=29.93x+0.13	0.62	y=47.06x+0.045

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