Supplement of Atmos. Chem. Phys., 18, 1611–1628, 2018
https://doi.org/10.5194/acp-18-1611-2018-supplement

Atmospheric Chemistry and Physics
Open Access
EGU

Supplement of

Effects of NO_x and SO_2 on the secondary organic aerosol formation from photooxidation of α-pinene and limonene

Defeng Zhao et al.

Correspondence to: Thomas F. Mentel (t.mentel@fz-juelich.de)

Table S1. Detailed conditions of the experiments in this study

Experiment No.	VOC (ppb)	SO_2 added (ppb)	NO added (ppb)	T (K)[a]	RH (%)[b]	Scheme
#1	α-pinene (20.2)	0	0	304-311-314	32	Low NO_x low SO_2
#2	α-pinene (21.4)	0	19	307-314-317	29	Low NO_x high SO_2
#3	α-pinene (17.5)	15	0	291-298-302	34	High NO_x low SO_2
#4	α-pinene (18.7)	15	17	300-303-305	42	High NO_x how SO_2
#5	Limonene (7.4)	0	0	294-303-307	31	Low NO_x low SO_2
#6	Limonene (7.5)	0	25	303-310-313	28	Low NO_x high SO_2
#7	Limonene (7.8)	15	0	293-301-305	29	High NO_x low SO_2
#8	Limonene (7.4)	15	17	296-305-309	28	High NO_x high SO_2
#9	Limonene (6.0)	2	17	296-306-310	28	High NO_x moderate SO_2

[a]: The minimum, average and maximum temperature are shown.

[b]: The average RHs of the period of monoterpenes photooxidation are shown.

Table S2. Summary of the effect of NO_x on monoterpene SOA yield in the literature

VOC	Oxidation	NO_x (ppb)	Seed aerosol	OH source/OH centration (molecules cm^{-3})	RH (%)	Literature
α-pinene 15-30 ppb; 150-200 ppb[a]	Ozonolysis	4.6 - 2000 ppb $[VOC]_0/[NOx]_0$: 0.65-391	No seed[b]	Low OH[c]	Dry[d]	(Presto et al., 2005)
α-pinene 15 ppb	Photooxidation	≤2-1000 ppb	$(NH_4)_2SO_4$ as seed	Low NO_x: 3×10^6; high NO_x: initial 2×10^7	3.7-6.4	(Ng et al., 2007)
α-pinene 19.8-52.4 ppb	Photooxidation	Low NO_x: not reported. High NO_x: 800 ppb	No seed, $(NH_4)_2SO_4$ or $(NH_4)_2SO_4$ +H_2SO_4	Low NO_x: H_2O_2/initial OH 2×10^6; high NO_x: HONO and CH_3NO_2/initial OH 6-20×10^6	<10	(Eddingsaas et al., 2012)
α-pinene 12 ppb	Photooxidation	0.5 ppb-60 ppb (steady state)	No seed, $(NH_4)_2SO_4$	O_3 (78 ppb)/~4-7×10^7	63	(Sarrafzadeh et al., 2016)
α-pinene 13.6-20.4 ppb	Photooxidation	Low NO_x: <0.3 ppb High NO_x: 66-82 ppb	$(NH_4)_2SO_4$ or $(NH_4)_2SO_4$ +H_2SO_4	H_2O_2/ low NO_x: OH 0.8-1.1×10^6; high NO_x: OH 4.3-5.9×10^6	29-68	(Han et al., 2016)
α-pinene 16.1-31.7 ppb	Photooxidation	Low NO_x: <1.9 ppb High NO_x: 19.675.1 ppb	$(NH_4)_2SO_4$ +H_2SO_4 or H_2SO_4+NH_4HSO_4	HONO/N.A.[e]	23-75	(Stirnweis et al., 2017)
α-pinene ~20 ppb	Photooxidation	Low NO_x: ~0.05-0.2 ppb High NO_x: 20 ppb	No seed or SO_2 was added.	HONO/ OH: (1-15)$\times10^6$	28-42	This study

[a]: Two levels of α-pinene concentration were used.
[b]: In one high NOx, experiment $(NH_4)_2SO_4$ was used as seed aerosol.
[c]: OH scavenger was added.
[d]: RH was not specified.
[e]: OH concentrations were not specified.

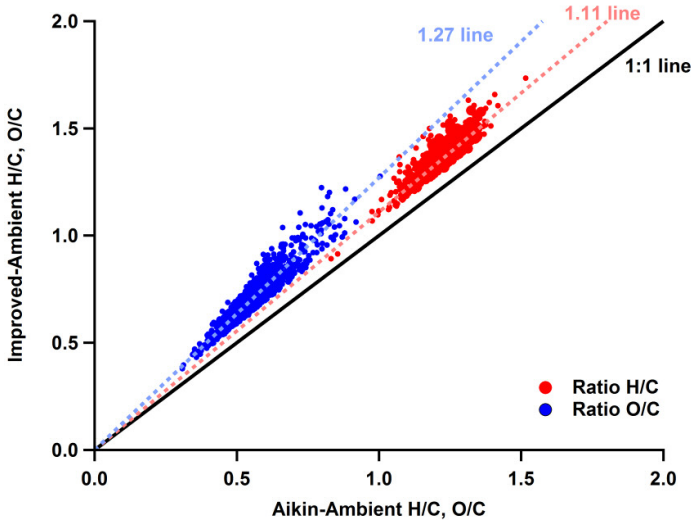


Figure S1. Comparison of the H/C and O/C obtained using the method of Canagaratna et al. (2015) with that obtained using the method of Aiken et al. (2007).

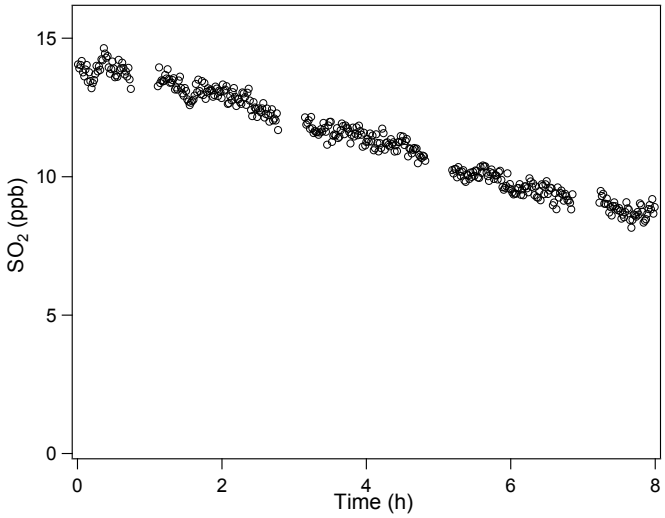


Figure S2. Time series of SO_2 concentration in an experiment with SO_2 added.

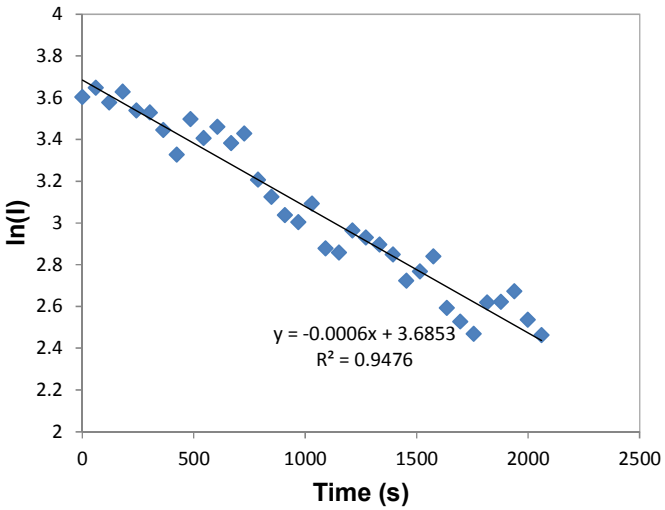
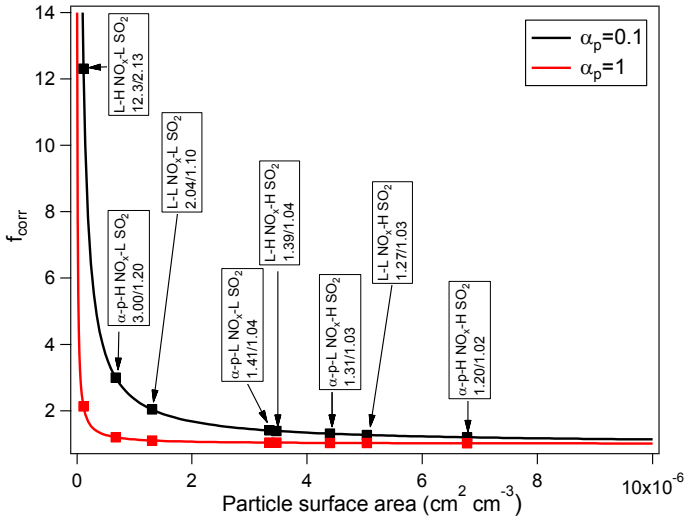
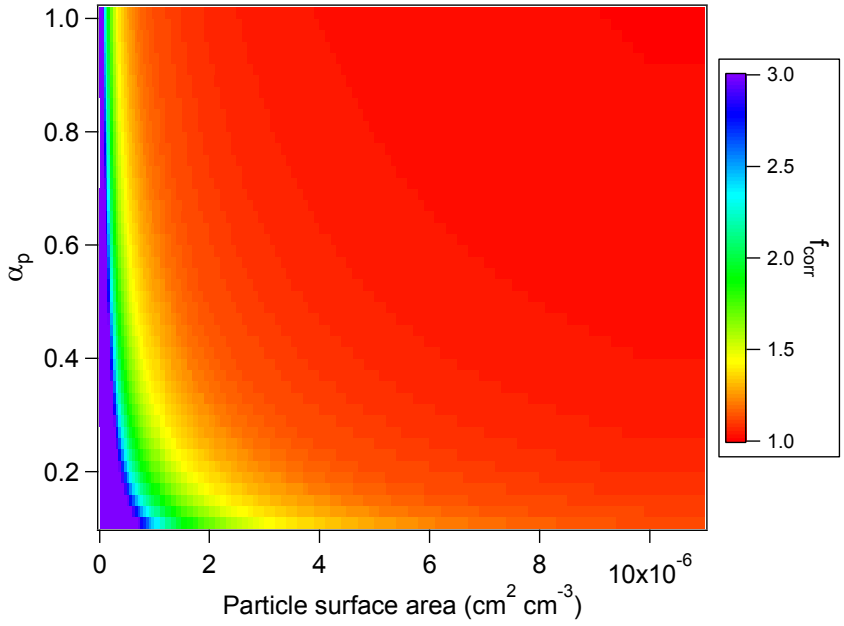


Figure S3. Decay of $C_{10}H_{15}NO_8$ (MW 277 g/mol) in the dark chamber. Y-axis shows the natural logarithm of the peak intensity obtained from CIMS. The raw data were averaged to 1 min.



(a)



(b)

Figure S4. (a) Correction factor (f_{corr}) to account for the influence of vapor wall loss on SOA yield. The curves were derived using an average molecular weight of 200 g/mol and an accommodation coefficient (α_p) on particles of 0.1 and 1, respectively. The lines show the f_{corr} as a function of aerosol surface area concentration and solid squares show the peak aerosol surface area concentration in each experiment. The experiments corresponding to each points are shown. "α-p" and "L" denote α-pinene and limonene, respectively. "L" and "H" denote low and high, respectively. For example, "α-p-H NO_x-L SO_2" denote the experiment of α-pinene oxidation under high NO_x and low SO_2. And the two numbers in each label box show the correction factors (f_{corr}) derived using α_p of 0.1 and 1, respectively. (b). Correction factor (f_{corr}) as a function of particle surface area and accommodation coefficient of organic vapors.

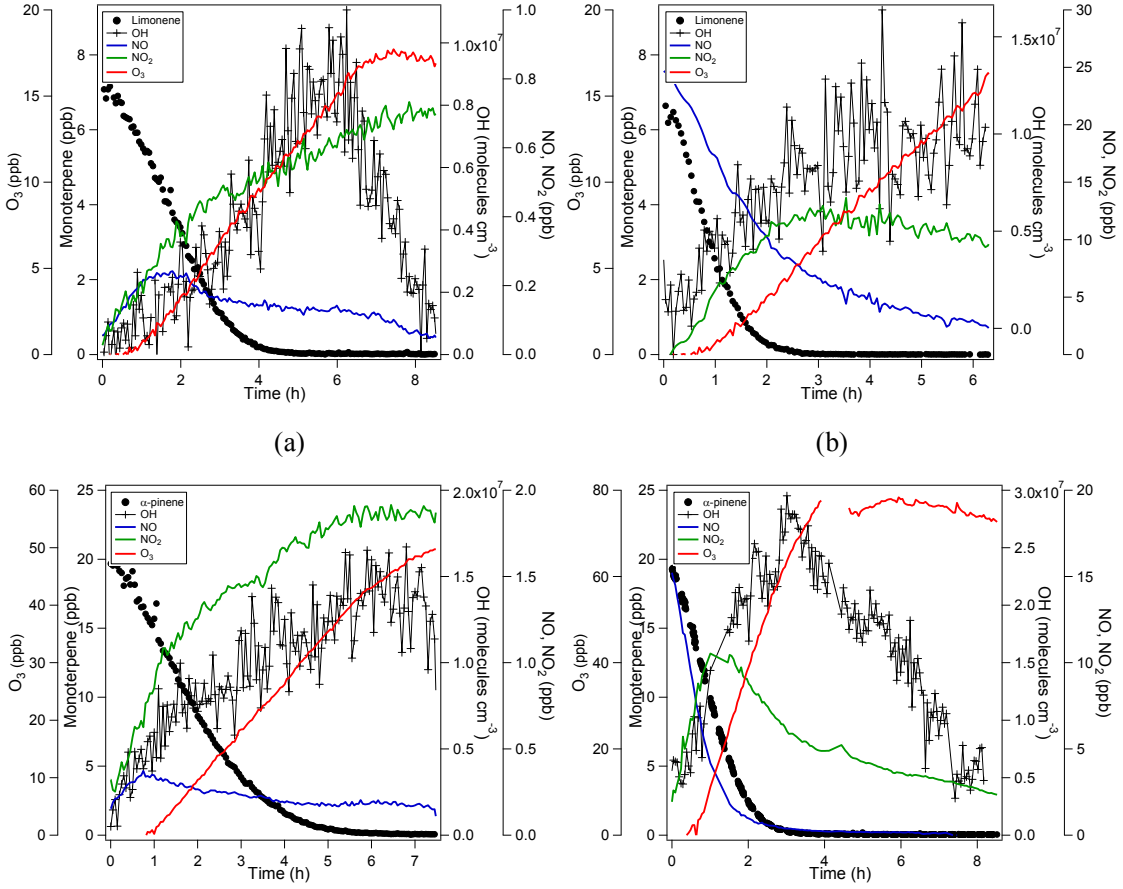


Figure S5. Time series of VOC, OH, NO, NO_2, and O_3 concentrations at low SO_2 for low NO_x (a, c) and high NO_x (b, d). (a, b) and (c, d) are for limonene and α-pinene photooxidation, respectively. Similar trends were observed under high SO_2.

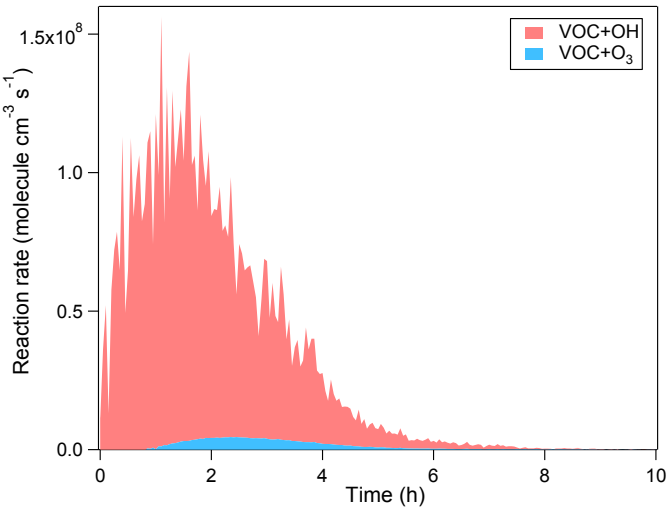


Figure S6. Comparison of the reaction rates of monoterpene with OH and with O_3 in a typical experiment of this study. The reaction rate of VOC+OH is stacked on that of VOC+O_3. Monoterpene oxidation was dominated by OH oxidation. Here the data in α-pinene photooxidation at low NO_x are shown. The scattering of the reaction rate of monoterpene with OH is due to the variations in the OH concentrations and OH measurement.

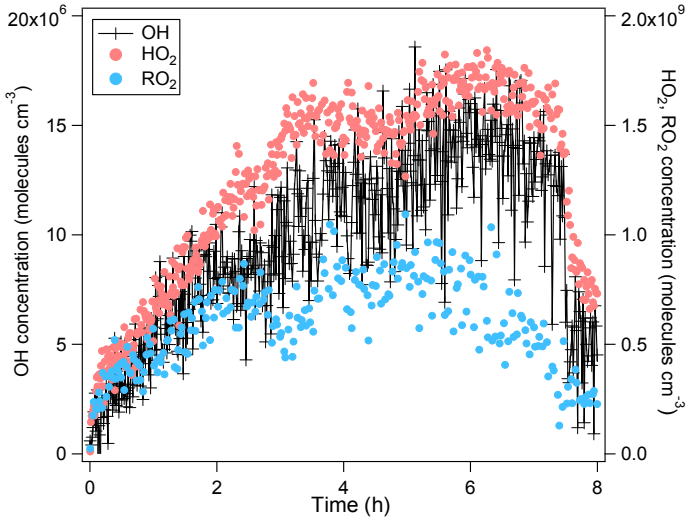
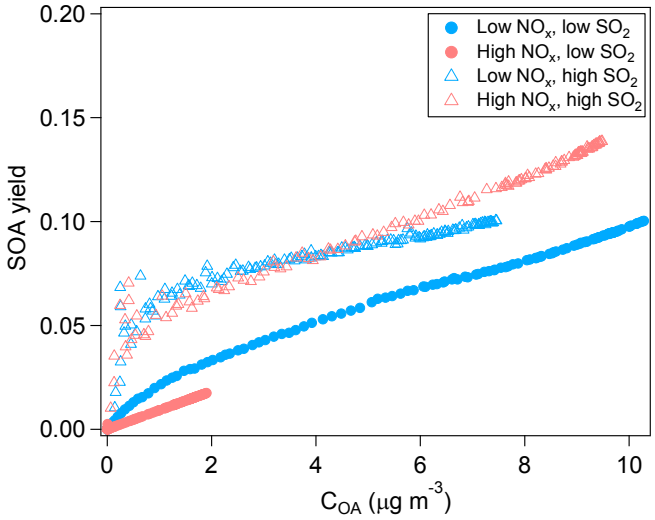
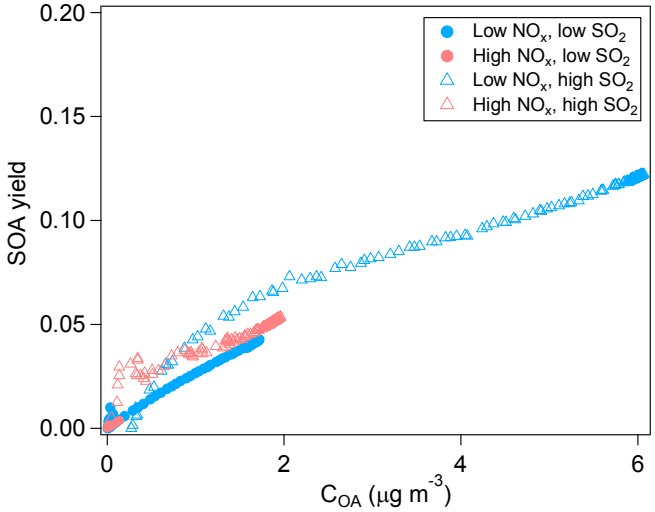


Figure S7. The concentrations of OH, HO_2 and RO_2 radicals in a typical experiment of this study. Here the data in α-pinene photooxidation at low NO_x are shown.



(a)



(b)

Figure S8. SOA yield from the photooxidation of α-pinene (a) and limonene (b) as a function of organic aerosol concentration (C_{OA}) in different NO_x and SO_2 conditions. Both SOA yield and organic aerosol concentration were corrected for particle wall loss and dilution.

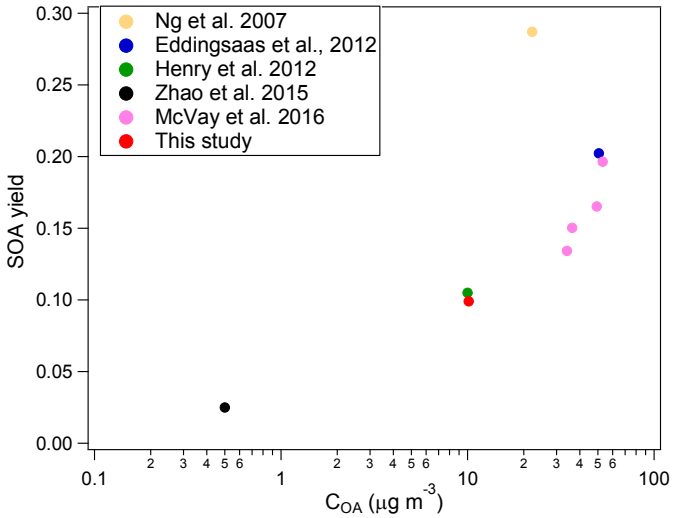


Figure S9. Comparison of the SOA yield as a function of organic aerosol concentration from α-pinene photooxidation at low NO_x with literature data. SOA yield and organic aerosol concentration in this study were corrected for particle wall loss and dilution. SOA particle density in all studies was adjusted to 1 g cm^{-3}. The data for Henry et al. (2012) was extracted from Figure 2, experiment 1 in their study. The data for McVay et al. (2016) were extracted from Figure 2-4 in their study. The data extracted from figures in the literature may be subject to uncertainties.

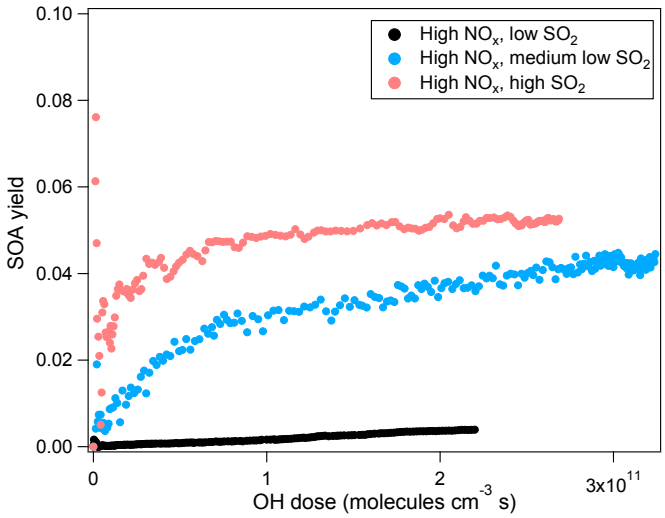


Figure S10. SOA yield at varying SO_2 concentrations for SOA from limonene oxidation at high NO_x. The SO_2 concentrations for low SO_2, moderate SO_2 and high SO_2 are <0.05 ppb, 2 ppb and 15 ppb, respectively.

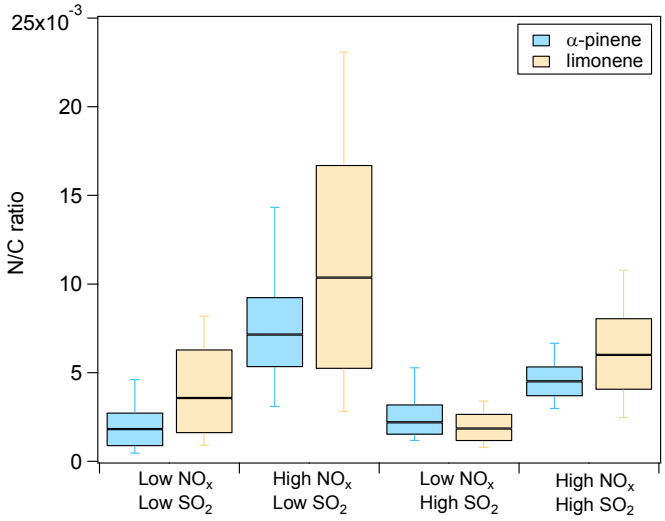


Figure S11. The nitrogen to carbon ratio (N/C) in the SOA formed in different conditions for α-pinene and limonene oxidation. The black line, box, and whiskers show the median, 25th and 75th percentile, and 10th and 90th percentile, respectively.

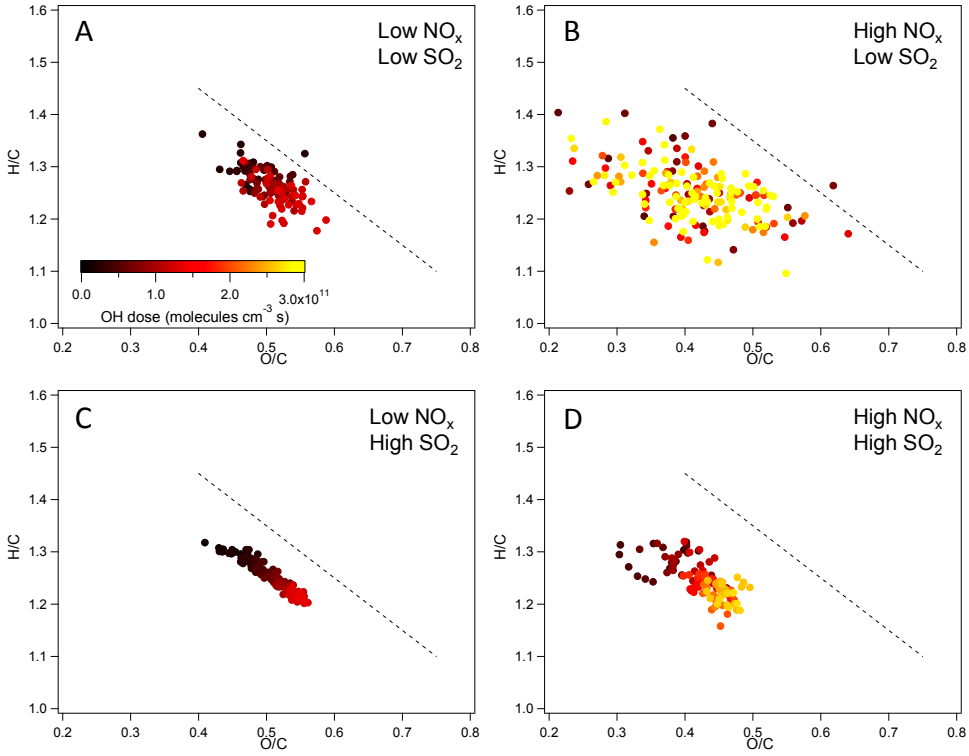


Figure S12. H/C and O/C ratios of SOA from photooxidation of limonene in different NO_x and SO_2 conditions. A: low NO_x, low SO_2, B: high NO_x, low SO_2, C: low NO_x, high SO_2, D: high NO_x, high SO_2. Note that in the high NO_x, low SO_2 condition (panel B), the AMS signal was too low to derive reliable H/C and O/C due to the low particle mass concentration and small particle size. Therefore, the data from an experiment with high NO_x (20 ppb NO) and moderate SO_2 (2 ppb) is shown instead in panel B. The black dashed line corresponds to the slope of -1.

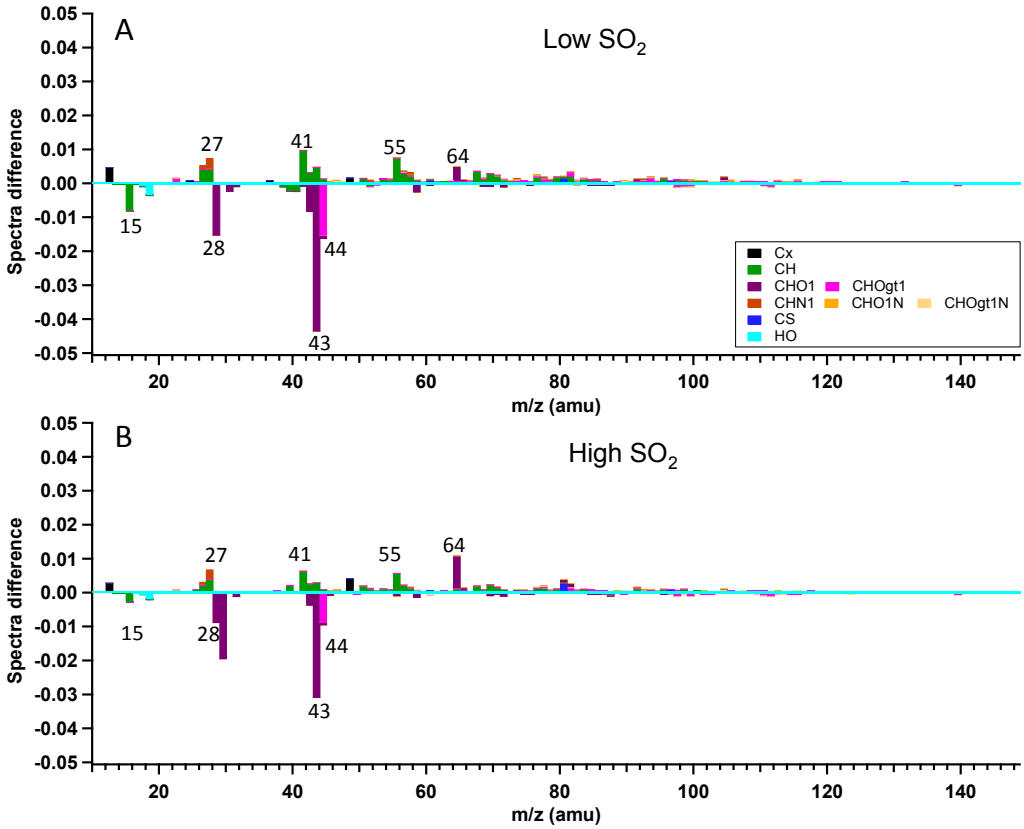


Figure S13. The difference in the mass spectra of organics of the SOA from limonene photooxidation between high NO_x and low NO_x conditions (high NO_x-low NO_x). SOA was formed at low SO_2 (a) and high SO_2 (b). The different chemical family of high resolution mass peaks are stacked at each unit mass *m/z* ("gt1" means greater than 1). The mass spectra were normalized to the total organic signals. Note that in the high NO_x, low SO_2 condition (panel A), the signal of AMS was too low. Therefore, the data in panel A show an experiment with high NO_x (20 ppb NO) and moderate SO_2 (2 ppb) instead.

References

Aiken, A. C., DeCarlo, P. F., and Jimenez, J. L.: Elemental analysis of organic species with electron ionization high-resolution mass spectrometry, Anal. Chem., 79, 8350-8358, 10.1021/ac071150w, 2007.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, 10.5194/acp-15-253-2015, 2015.

Eddingsaas, N. C., Loza, C. L., Yee, L. D., Chan, M., Schilling, K. A., Chhabra, P. S., Seinfeld, J. H., and Wennberg, P. O.: alpha-pinene photooxidation under controlled chemical conditions - Part 2: SOA yield and composition in low- and high-NOx environments, Atmos. Chem. Phys., 12, 7413-7427, 10.5194/acp-12-7413-2012, 2012.

Han, Y. M., Stroud, C. A., Liggio, J., and Li, S. M.: The effect of particle acidity on secondary organic aerosol formation from alpha-pinene photooxidation under atmospherically relevant conditions, Atmos. Chem. Phys., 16, 13929-13944, 10.5194/acp-16-13929-2016, 2016.

Henry, K. M., Lohaus, T., and Donahue, N. M.: Organic Aerosol Yields from alpha-Pinene Oxidation: Bridging the Gap between First-Generation Yields and Aging Chemistry, Environ. Sci. Technol., 46, 12347-12354, 10.1021/es302060y, 2012.

McVay, R. C., Zhang, X., Aumont, B., Valorso, R., Camredon, M., La, Y. S., Wennberg, P. O., and Seinfeld, J. H.: SOA formation from the photooxidation of alpha-pinene: systematic exploration of the simulation of chamber data, Atmos. Chem. Phys., 16, 2785-2802, 10.5194/acp-16-2785-2016, 2016.

Ng, N. L., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Kroll, J. H., Kwan, A. J., McCabe, D. C., Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C., and Seinfeld, J. H.: Effect of NO(x) level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, Atmos. Chem. Phys., 7, 5159-5174, 2007.

Presto, A. A., Hartz, K. E. H., and Donahue, N. M.: Secondary organic aerosol production from terpene ozonolysis. 2. Effect of NOx concentration, Environ. Sci. Technol., 39, 7046-7054, 10.1021/es050400s, 2005.

Sarrafzadeh, M., Wildt, J., Pullinen, I., Springer, M., Kleist, E., Tillmann, R., Schmitt, S. H., Wu, C., Mentel, T. F., Zhao, D. F., Hastie, D. R., and Kiendler-Scharr, A.: Impact of NOx and OH on secondary organic aerosol formation from beta-pinene photooxidation, Atmos. Chem. Phys., 16, 11237-11248, 10.5194/acp-16-11237-2016, 2016.

Stirnweis, L., Marcolli, C., Dommen, J., Barmet, P., Frege, C., Platt, S. M., Bruns, E. A., Krapf, M., Slowik, J. G., Wolf, R., Prevot, A. S. H., Baltensperger, U., and El-Haddad, I.: Assessing the influence of NOx concentrations and relative humidity on secondary organic aerosol yields from alpha-pinene photo-oxidation through smog chamber experiments and modelling calculations, Atmos. Chem. Phys., 17, 5035-5061, 10.5194/acp-17-5035-2017, 2017.