Supplemental Information for "Effect of Relative Humidity on SOA Formation from Isoprene/NO Photooxidation: Role of Particle-Phase Esterification under Dry Conditions"

H. Zhang, J. D. Surratt, Y. H. Lin, J. Bapat, R. M. Kamens

Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, the University of North Carolina, Chapel Hill, NC 27599

Correspondence Author: J. D. Surratt (surratt@unc.edu)

1. Figures for the other set of experiments

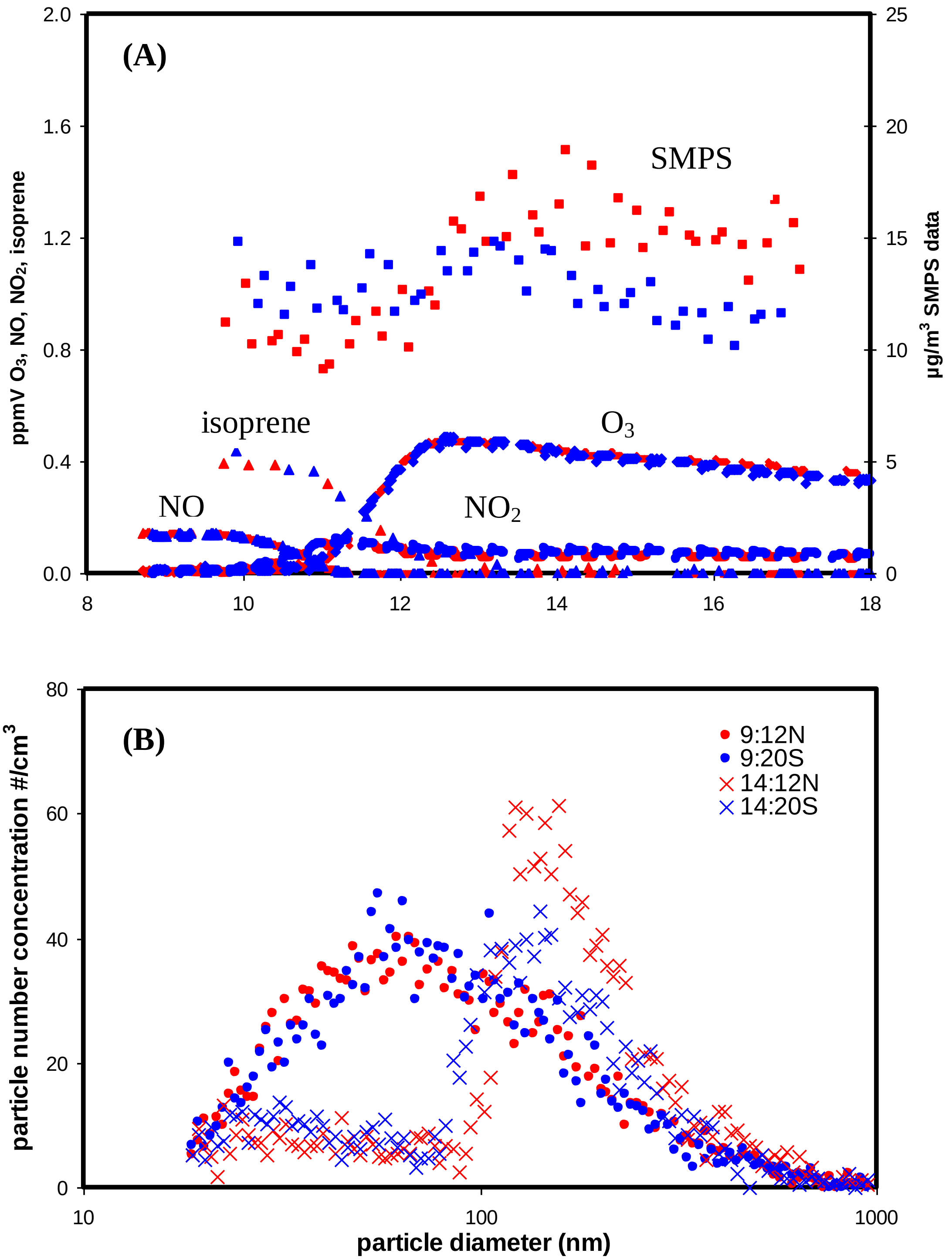

Fig. 1S. (A) Gas-phase measurement of O_3, NO_x, and isoprene and wall loss corrected SMPS data. (B) Particle size distributions under low- and high-RH conditions when the experiments began (9:12N and 9:20S) and reached the maximum mass concentrations (14:12N and 14:20S). The red dots are data from North chamber (2010OCT15N, low-RH); the blue dots are data from South chamber (2010OCT15S, high-RH). The circle dots in (B) represent particle size distributions at the beginning of experiments; the cross dots represent particle size distributions after the mass concentrations peaked.

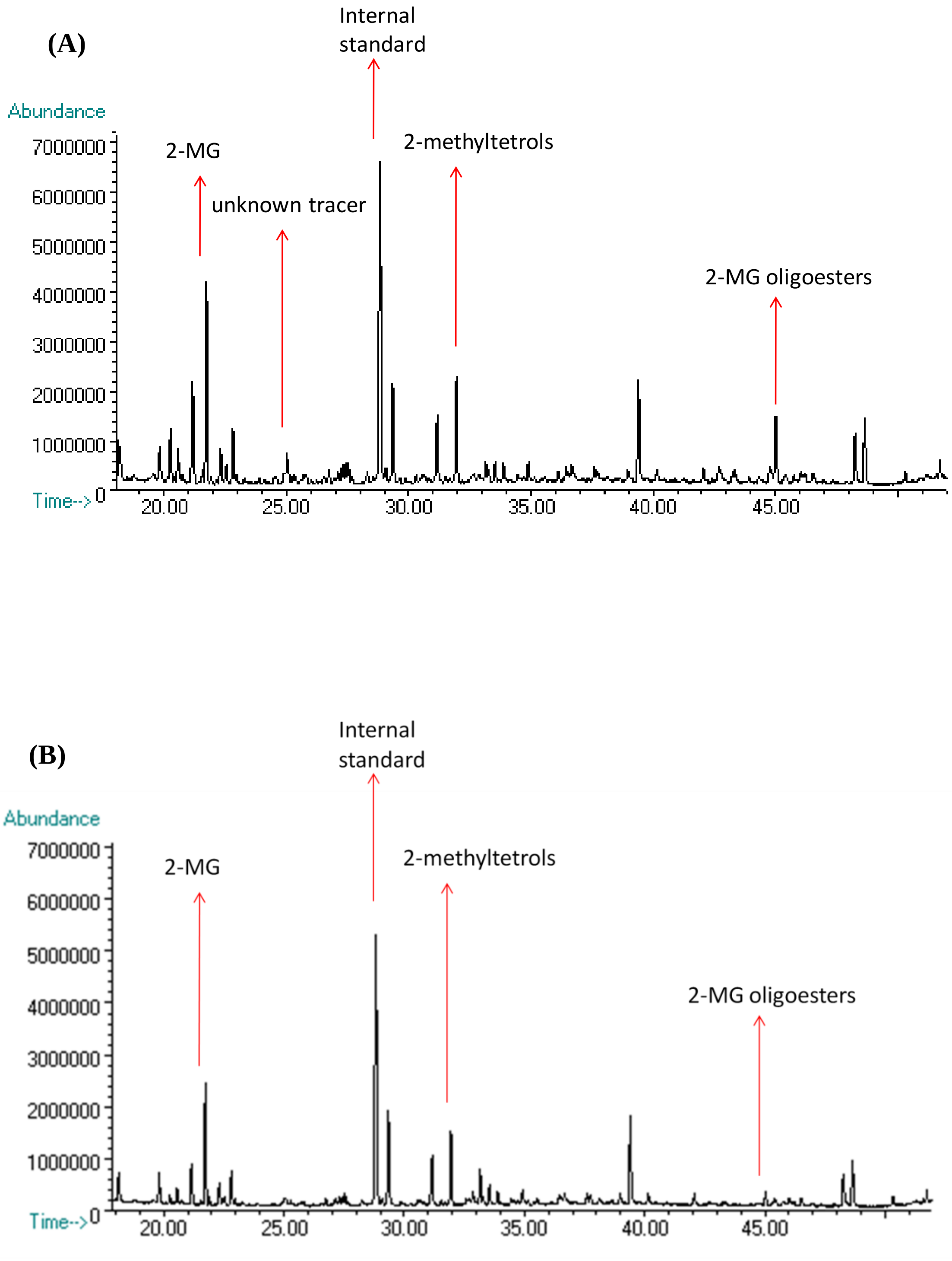

Fig. 2S. (A) GC/MS TIC of the filter extract of 2010OCT15N (low-RH experiment). (B) GC/MS TIC of the filter extract of 2010OCT15S (high-RH experiment).

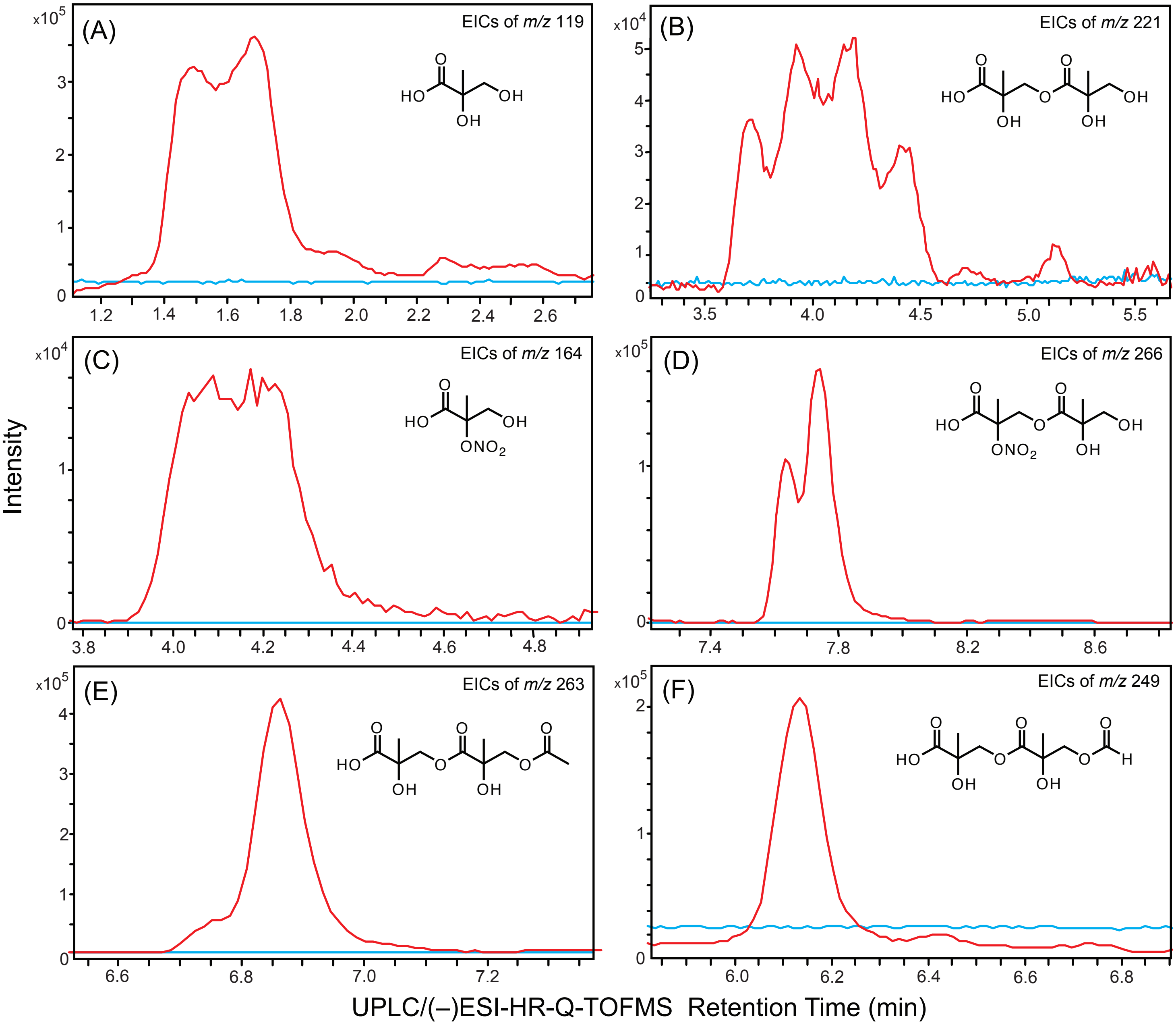

Fig. 3S. Comparison of known isoprene SOA constituents produced from low concentration isoprene oxidation experiments (2010OCT15) under initially high-NO and high-RH (blue lines) and low-RH (red lines) conditions in the presence of neutral ammonium sulfate seed aerosol. For simplicity, only one structural isomer is shown. All of the MPAN-derived SOA products (A-F), are found to increase in abundance under low-RH conditions. ESI-HR-Q-TOFMS accurate measurements show that the elemental compositions of these compounds are consistent with the proposed structures (see supplemental information, Table 1S).

2. EI mass spectrums of detected SOA compounds on GC/MS

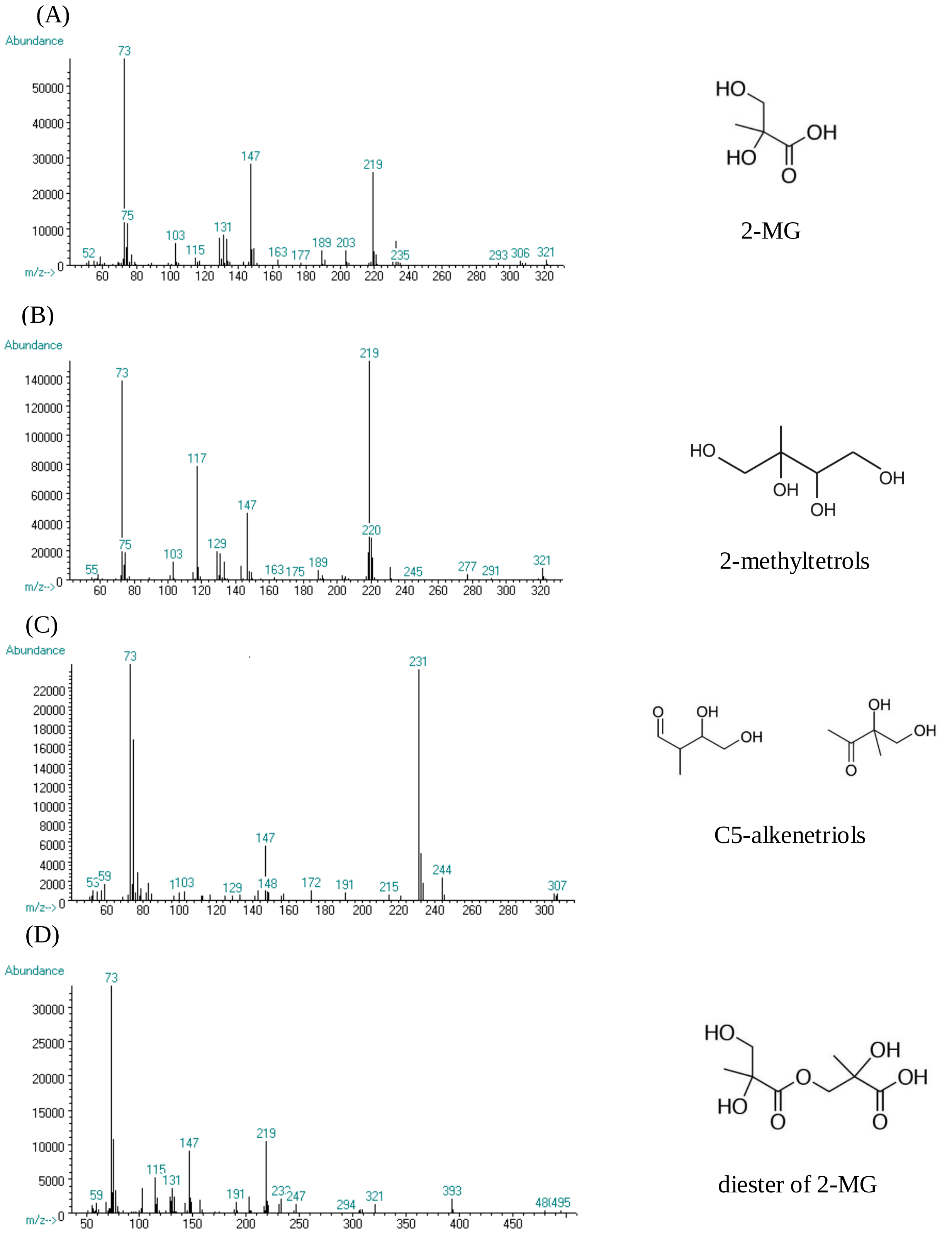

Fig. 4S. EI mass spectrums of detected SOA compounds on GC/MS. (A) 2-MG; (B) 2-methyltetrols; (C) C5-alkenetriols; (D) diester of 2-MG.

3. Other Information from UPLC/ESI-HR-Q-TOFMS

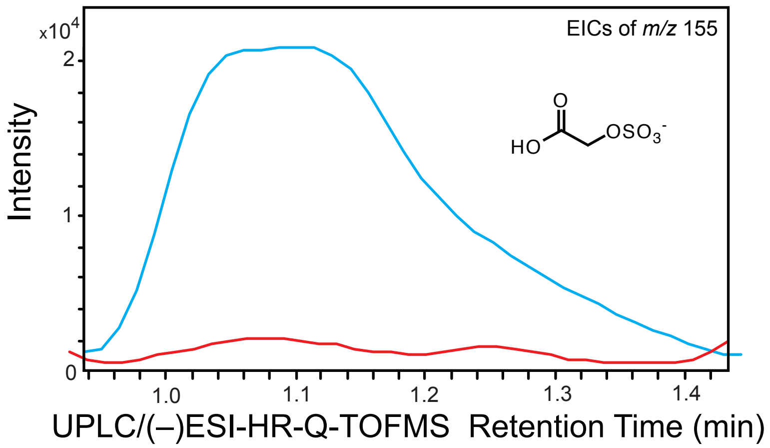

Fig. 5S. Comparison of the glyoxal-derived organosulfate (i.e., glycolic acid sulfate) (Galloway et al., 2009) produced from isoprene oxidation under initially high-NO and high-RH (blue lines) and low-RH (red lines) conditions in the presence of neutral ammonium sulfate seed aerosol. Consistent with the other isoprene-derived organosulfates shown in Fig. 3, this organosulfate was found to increase in abundance with increasing RH. ESI-HR-Q-TOFMS accurate measurements show that the elemental composition of this compound is consistent with the proposed structures (Table 1S).

Table 1S. Summary of accurate mass measurements obtained for isoprene SOA constituents produced from the dry experiment on 2010OCT21N.[a]

Measured Mass	TOFMS Suggested Ion Formula	Calculated Mass	Difference (mDa)
119.0337	$C_4H_7O_4^-$	119.0350	-1.3
154.9672	$C_2H_3O_6S^-$	154.9650	2.2
164.0192	$C_4H_6NO_6^-$	164.0201	-0.9
168.9797	$C_3H_6O_6S^-$	169.9812	-1.5
198.9904	$C_4H_7O_7S^-$	198.9918	-1.4
215.0251	$C_5H_{11}O_7S^-$	215.0225	2.6
221.0659	$C_8H_{13}O_7^-$	221.0667	-0.8
249.0602	$C_9H_{13}O_8^-$	249.0616	-1.4
263.0753	$C_{10}H_{15}O_8^-$	263.0772	-1.9
266.0494	$C_8H_{12}NO_9^-$	266.0518	-2.4

[a] Larger oligosters of 2-MG, such as *m/z* 323, 351, 365, and 370, were also observed to elute from the UPLC column at much later RTs but are not reported here. These data are consistent with previous work (Surratt et al., 2006, 2010; Chan et al., 2010)

References

Edney, E. O., Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Wang, W., and Claeys, M: Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO_x/SO_2/air mixtures and their detection in ambient $PM_{2.5}$ samples collected in the eastern United States, Atmos. Environ., 39, 5281–5289, 2005.

Galloway, M., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Flagan, R. C., Seinfeld, J. H., and Keutsch, F. N: Glyoxal uptake on ammonium sulphate seed aerosol: Reaction and reversibility of uptake under dark and irradiated conditions, Atmos. Chem. Phys., 9, 3331–3345, 2009.

Surratt, J.D., Murphy, S.M., Kroll, J.H., Ng, N.L., Hildebrabdt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R.C., Seinfeld, J.H., 2006. Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. The Journal of Physical Chemistry A. 110, 9665-9690.

Surratt, J.D., Chan, A.W.H., Eddingsaas, N.C., Chan, M., Loza, C.L., Kwan, A.J., Hersey, S.P., Flagan, R.C., Wennberg, P.O., Seinfeld, J.H., 2010. Reactive intermediates revealed in secondary organic aerosol formation from isoprene. PNAS. 107, 6640-6645.

Szmigielski, R., Surratt, J.D., Vermeylen, R., Szmigielska, K., Kroll, J.H., Ng, N.L., Murphy, S.M., Sorooshian, A., Seinfeld, J.H., Claeys, M., 2007. Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formation from the photooxidation of isoprene using trimethylsilylation and gas chromatography/ion trap mass spectrometry. Journal of Mass Spectrometry. 42, 101 – 116.