Supplemental Information for “Effect of Relative Humidity on SOA Formation from Isoprene/NO Photooxidation: Enhancement of 2-Methylglyceric Acid and Its Corresponding Oligoesters under Dry Conditions”

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1. Figures for the other set of experiments

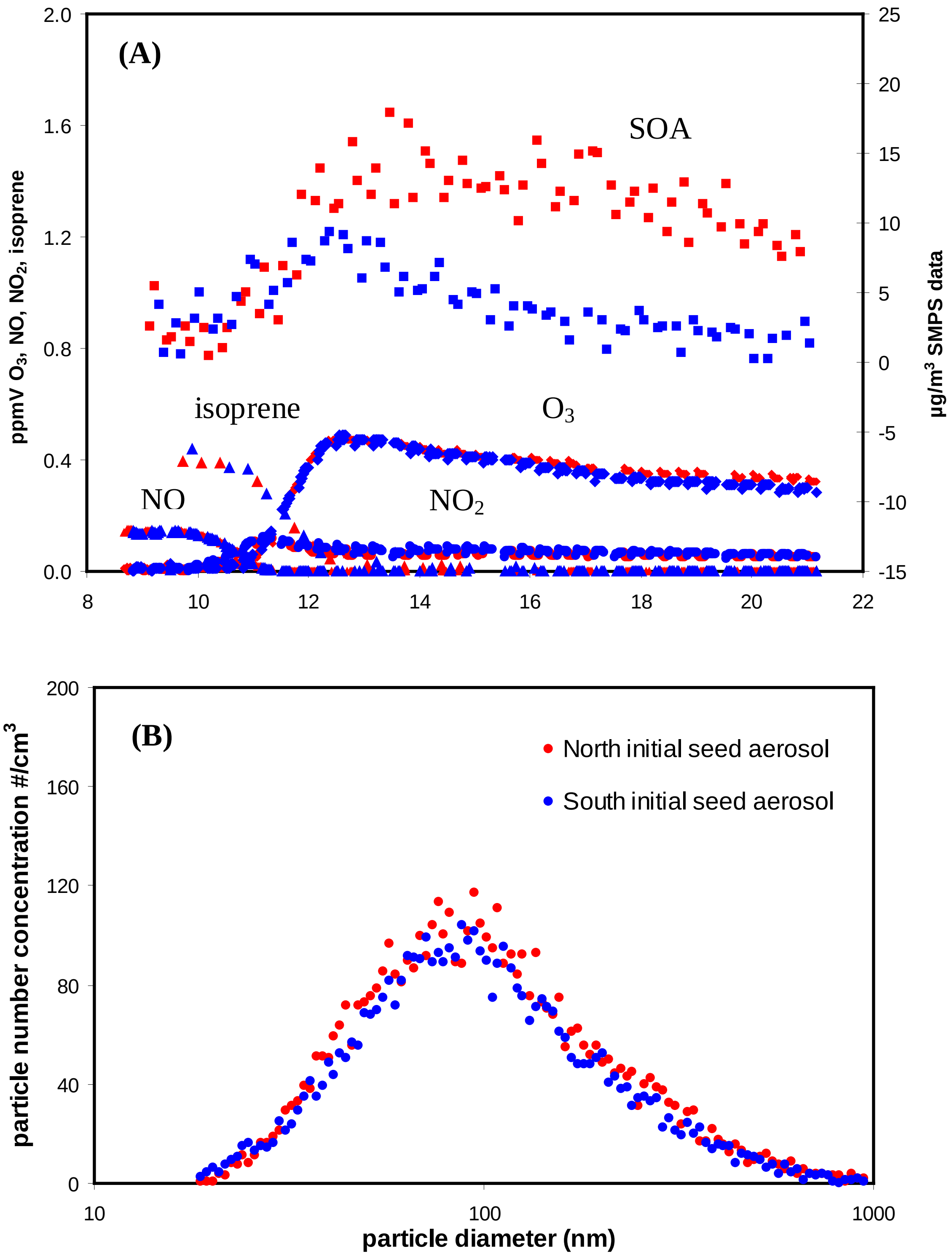

Fig. 1S. (A) Gas-phase measurement of O_3, NO_x, and isoprene and wall-loss uncorrected SOA data. (B) Particle size distributions under low- and high-RH conditions when the experiments began. The red dots are data from the North chamber (2010OCT15N, low-RH condition); the blue dots are data from South chamber (2010OCT15S, high-RH condition).

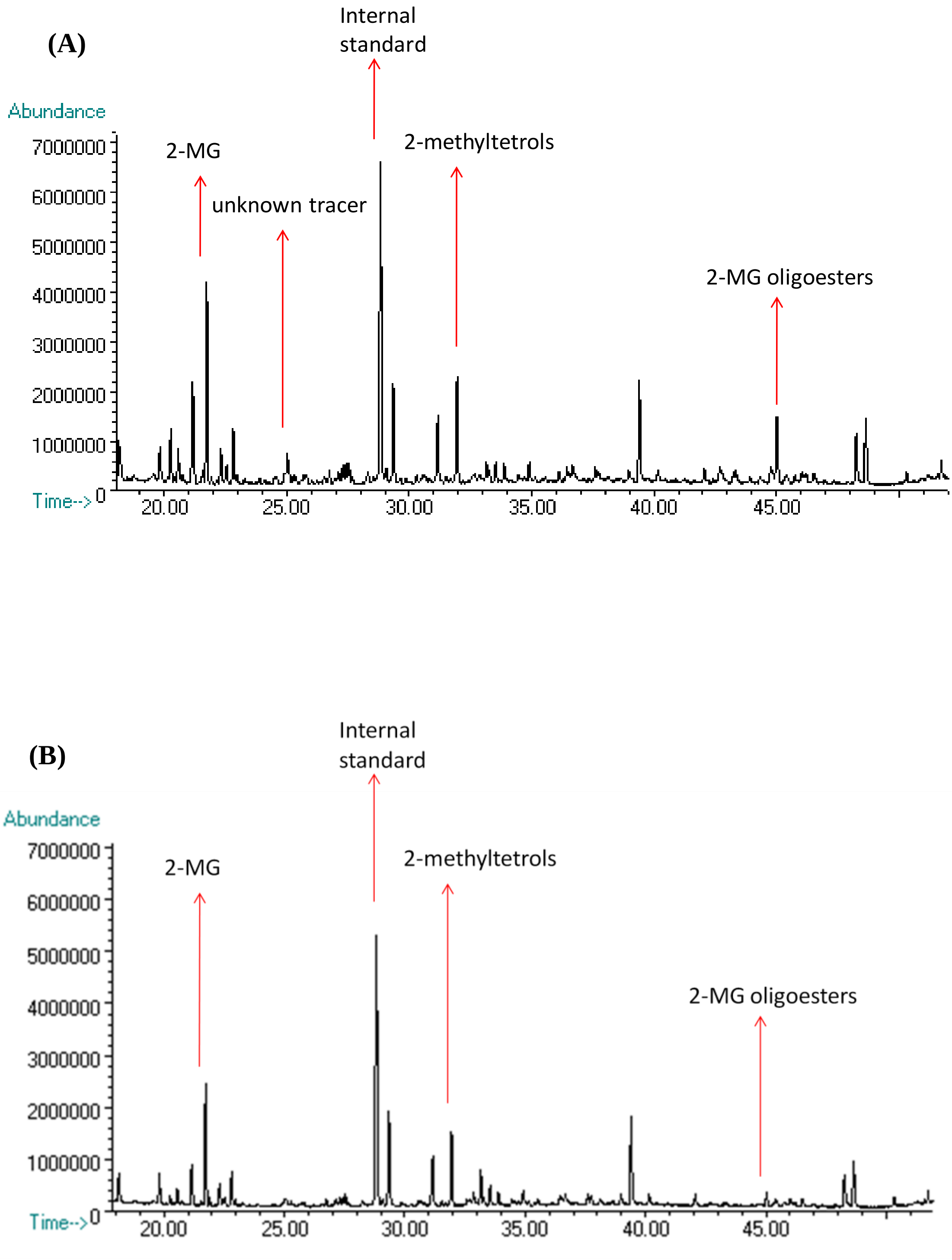

Fig. 2S. (A) GC/MS TIC of the filter extract of 2010OCT15N (low-RH experiment). (B) GC/MS TIC of the filter extract of 2010OCT15S (high-RH experiment).

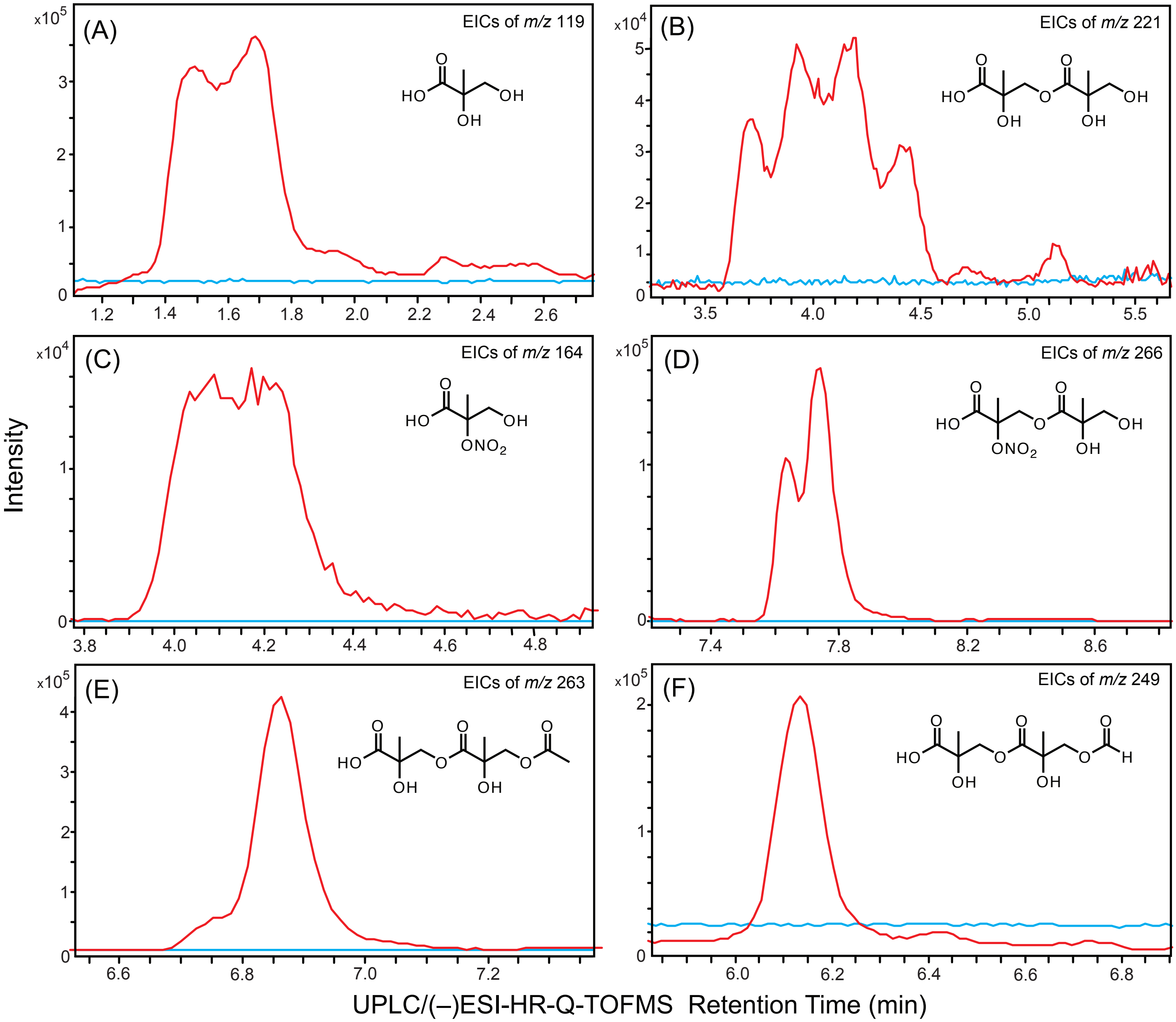

Fig. 3S. Comparison of known isoprene SOA constituents produced from low concentration isoprene oxidation experiments (2010OCT15) under initially high-NO and high-RH (blue lines) and low-RH (red lines) conditions in the presence of neutral ammonium sulfate seed aerosol. For simplicity, only one structural 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

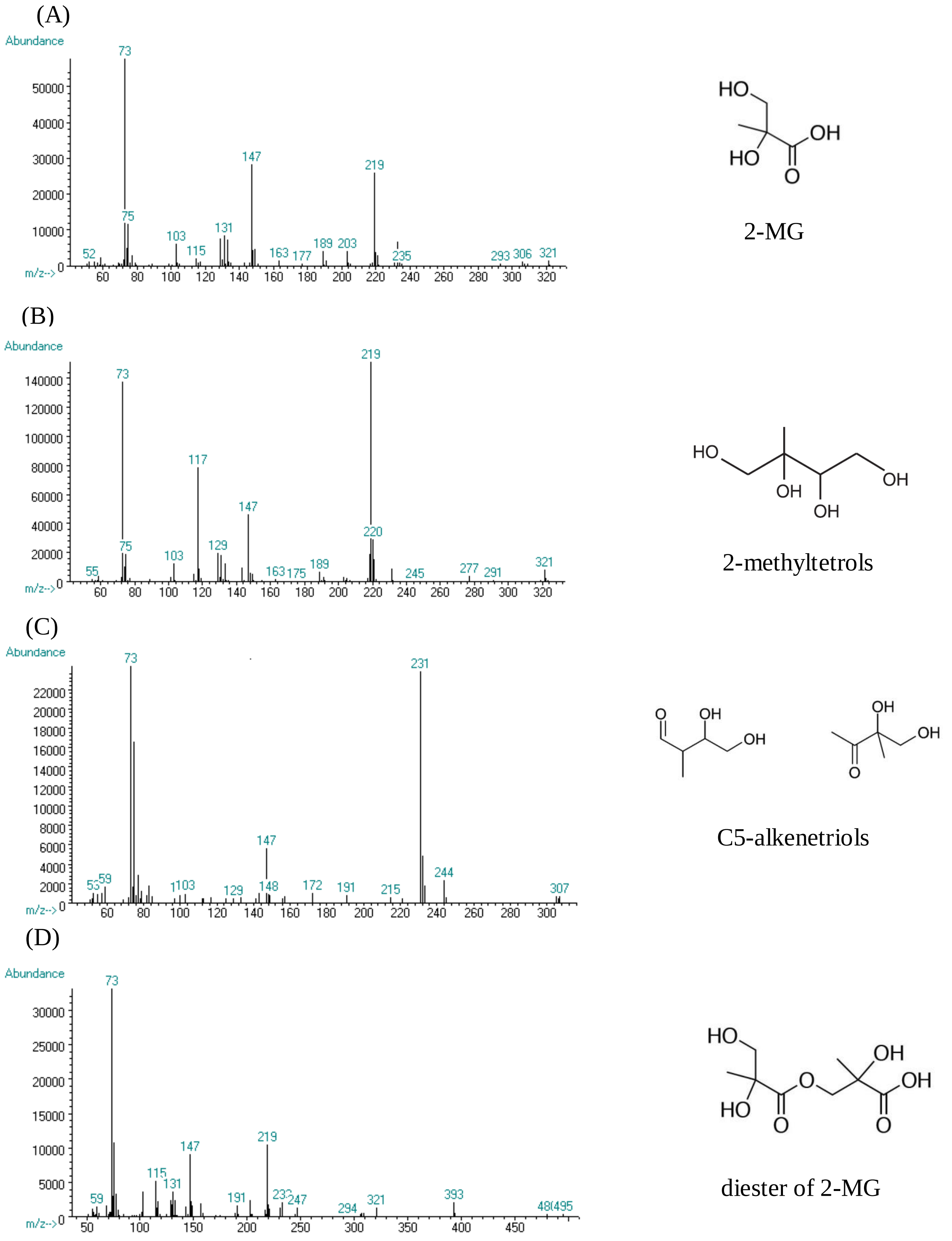

Fig. 4S. EI mass spectrums of detected SOA compounds on GC/MS. (A) 2-MG; (B) 2-methyltetrols; (C) C5-alkenetriols; (D) diester of 2-MG.

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

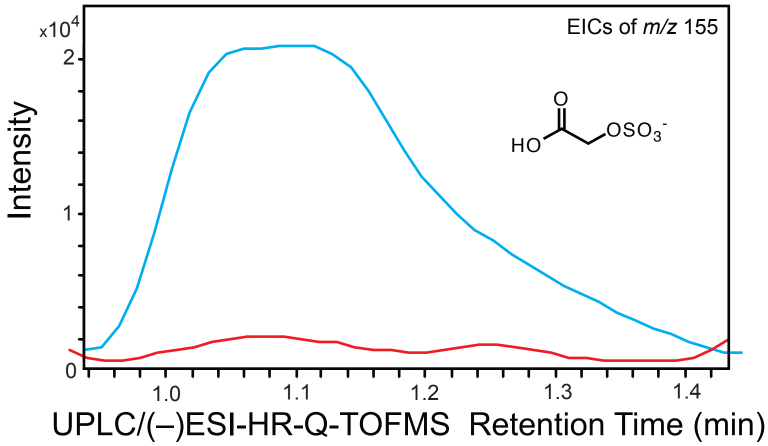

Fig. 5S. Comparison of the glyoxal-derived organosulfate (i.e., glycolic acid sulfate) (Galloway et al., 2009) produced from isoprene oxidation under initially high-NO and high-RH (blue lines) and low-RH (red lines) conditions in the presence of neutral ammonium sulfate seed aerosol. Consistent with 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)

4. Error Analysis

The system studied in this work includes both high-NO_x SOA constituents and low-NO_x SOA constituents. From the existing literature, the density for low-NO_x isoprene SOA is 1.25 g cm^{-3}, and for high-NO_x isoprene SOA is 1.35-1.4 g cm^{-3}. From our chemical analysis result, the SOA in the low-RH experiments tend to be heavier than that in the high-RH experiments. Thus the assumed density could give us an error of (-7% ~ 0%) for the low-RH experiments, and (-10% ~ 0%) for the high-RH experiments.

In addition, for the SMPS measurements, our prior analysis compared with filter sample mass (i.e., gravimetric analyses) indicates an approximate error of ±20% for both cases measuring TSP and ammonium sulfate seed aerosol. The temperature sensor and the dew point instrument may likely give a total error of ±5%. The LWC calculation based on the polynomial equation (Chan et al., 1992; Kleindienst et al., 1999) tends to have a higher error for the high-RH experiments than the low-RH experiments because the sensitivity of water uptake for ammonium sulfate is much higher at high RH. The error of this whole measurement and calculation is estimated to be ±10% for low-RH experiments and ±15% for high-RH experiments. Assuming the above errors are standard deviations, then the overall error calculated based on Equation (1) will be (-23% ~ +22%) for the low-RH experiments and (-27% ~ +25%) for the high-RH experiments.

$$\text{Overall Error} = \sqrt[2]{error_1{}^2 + error_2{}^2 + error_3{}^2} \qquad (1)$$

References

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