Supporting Information

Simulating Aqueous-Phase Isoprene-Epoxydiol (IEPOX) Secondary Organic Aerosol Production During the 2013 Southern Oxidant and Aerosol Study (SOAS)

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This supporting information contains 13 pages: 5 tables, 9 figures

Table S1. Variables used in ISORROPIA-II, CMAQ-box and simpleGAMMA models.

Model Quantity	Units	Source of Estimate
SO_4^{2-}	μmol m^{-3}	ACSM
NO_3^-	μmol m^{-3}	ACSM
Cl^-	μmol m^{-3}	ACSM
NH_4^+	μmol m^{-3}	ACSM
NH_3	μmol m^{-3}	Ammonia Monitoring Network (AMoN)
IEPOX+ISOPOOH	mol cm^{-3}	HR-ToF-CIMS
Aerosol surface area[a]	cm^2 cm^{-3}	SEMS-MCPC
RH	fraction	NPS
Temperature	°C	NPS
LWC[b]	mol L^{-1}	ISORROPIA-II
SO_4^{2-}[b]	mol L^{-1}	ISORROPIA-II
HSO_4^-[b]	mol L^{-1}	ISORROPIA-II
NH_4^+[b]	mol L^{-1}	ISORROPIA-II
H^+[b]	mol L^{-1}	ISORROPIA-II
pH		Calculated from ISORROPIA-II outputs
wL[c]	cm^3 cm^{-3}	Calculated from ISORROPIA-II outputs and observed organic aerosol
2-methyltetrols	μg m^{-3}	GC/EI-MS
IEPOX-OS	μg m^{-3}	UPLC/DAD-ESI-HR-QTOFMS

[a]measured dry surface area was adjusted for the presence of water using aerosol water predicted by ISORROPIA-II: $A = A_{dry} * \left[\left(\frac{M_{inorganic}}{\rho_{inorganic}} + \frac{M_{org}}{\rho_{org}} + \frac{M_{water}}{\rho_{water}}\right) / \left(\frac{M_{inorganic}}{\rho_{inorganic}} + \frac{M_{org}}{org}\right)\right]^{2/3}$, where M_i is the mass of i per volume of air and ρ_i is the density of the species.
[b]aqueous-aerosol phase concentrations (C_i) obtained from ISORROPIA-II in mol L^{-1} were adjusted for the inclusion of organic aerosol (from the ACSM) prior to use in CMAQ and simpleGAMMA box model calculations: $C_i = C_{i,ISORROPIA}\, wL_{ISORROPIA}/wL$
[c]total liquid aerosol volume per volume of air including ISORROPIA-II predicted aqueous aerosol (sulfate, water, etc) and organic aerosol: $wL = wL_{ISORROPIA} + M_{org}/\rho_{org}$

Table S2. Correlation values (r^2) between the SOA tracers formed over 12 hours processing time and model variables. Measured SOA tracers are also correlated with the model variables.

	Tetrol (μg m^{-3})						IEPOXOS (μg m^{-3})					
	CMAQ		**simpleGAMMA**		**Measured**		**CMAQ**		**simpleGAMMA**		**Measured**	
	w/o corr.	*w/ corr.*	*w/o corr.*	*w/ corr.*	*w/o corr.*	*w/ corr.*	*w/o corr.*	*w/ corr.*	*w/o corr.*	*w/ corr.*	*w/o corr.*	*w/ corr.*
$k_{particle}$ (s^{-1})	0.26	0.68	0.16	0.69	0.07	0.39	0.36	0.68	0.30	0.71	0.23	0.46
$IEPOX_{(g)}$ (mol cm^{-3})	0.53	0.30	0.40	0.31	0.15	0.15	0.55	0.30	0.47	0.37	0.35	0.35
SA (cm^2 cm^{-3})	0.63	0.55	0.69	0.72	0.46	0.59	0.50	0.55	0.61	0.61	0.48	0.48
LWC (mol L^{-1})	0.06	0.11	0.01	0.19	0.01	0.16	0.12	0.11	0.07	0.12	0.08	0.05
a_{H^+} (mol L +)	0.30	0.50	0.20	0.53	0.09	0.32	0.40	0.55	0.34	0.64	0.26	0.50
RH	0.05	0.00	0.01	0.00	0.00	0.00	0.12	0.01	0.06	0.02	0.07	0.07
Volume (cm^3 cm^{-3})	0.17	0.13	0.41	0.23	0.33	0.18	0.08	0.10	0.24	0.12	0.14	0.06

w/ corr. and *w/o corr*. respectively refer to variables with and without liquid water added to the measured dry-size distribution to get the atmospherically relevant size distribution particles and organics added to the predicted particle volume by ISORROPIA.

Table S3. CMAQ predicted IEPOX and ISOPOOH for the Look Rock, TN site averaged by hour of day for July 2013. CMAQ simulations for this time period are the same as those in Pye et al. (2015).

Hour	Predicted ISOPOOH	Predicted IEPOX	Predicted IEPOX/ISOPOOH	Predicted ISOPOOH/IEPOX (*b*)
EST=GMT-5	ppt	ppt	ratio	ratio
0	42	152	3.24	0.28
1	39	142	3.41	0.28
2	40	139	3.77	0.29
3	43	142	4.24	0.30
4	42	146	4.52	0.29
5	35	133	4.08	0.26
6	29	105	3.11	0.27
7	40	116	2.44	0.34
8	70	162	2.25	0.43
9	103	187	1.65	0.55
10	131	198	1.36	0.66
11	154	216	1.33	0.71
12	173	248	1.40	0.70
13	187	282	1.53	0.66
14	199	324	1.67	0.61
15	187	345	1.83	0.54
16	183	336	1.84	0.54
17	164	278	1.78	0.59
18	134	207	1.70	0.65
19	109	167	1.66	0.65
20	86	153	1.91	0.56

Hour	Predicted ISOPOOH	Predicted IEPOX	Predicted IEPOX/ISOPOOH	Predicted ISOPOOH/IEPOX (*b*)
21	65	143	2.25	0.46
22	55	151	2.59	0.36
23	48	163	3.01	0.29

Table S4. Correlations of estimated and measured IEPOXOS and tetrols.

Estimated tracer	**simpleGAMMA**			**CMAQ-box**		
	r^2	**Slope**		**r^2**	**Slope**	
		t = 12 h	**t = 6 h**		**t = 12 h**	**t = 6 h**
IEPOXOS	0.60	1.04 ± 0.09	0.52 ± 0.04	0.57	0.74 ± 0.08	0.37 ± 0.04
Tetrols	0.53	3.25 ± 0.30	1.51 ± 0.14	0.50	2.27 ± 0.25	1.14 ± 0.12

Table S5. Multivariate regression analysis of relationships between $k_{particle}$ and SA to SOA tracers prediction (IEPOXOS and tetrols) as well as between a_{H^+} and SO_4^{2-} to $k_{particle}$.

	r^2	**p-value**
Equation S1: IEPOXOS	0.70	
Intercept		6.27×10^{-6}
$k_{particle}$		8.51×10^{-7}
SA		4.66×10^{-2}
Equation S2: Tetrol	0.73	
Intercept		1.25×10^{-7}

	r^2	p-value
$k_{particle}$		1.99×10^{-5}
SA		5.19×10^{-4}
Equation S3: $k_{particle}$	0.89	
Intercept		2.11×10^{-4}
a_{H^+}		6.25×10^{-19}
SO_4		2.82×10^{-5}

Multivariate regression models are:

$$IEPOXOS = a + b \cdot k_{particle} + c \cdot SA \quad \text{(S1)}$$

$$tetrol = a + b \cdot k_{particle} + c \cdot SA \quad \text{(S2)}$$

$$k_{particle} = a + b \cdot a_H^+ + c \cdot SO_4 \quad \text{(S3)}$$

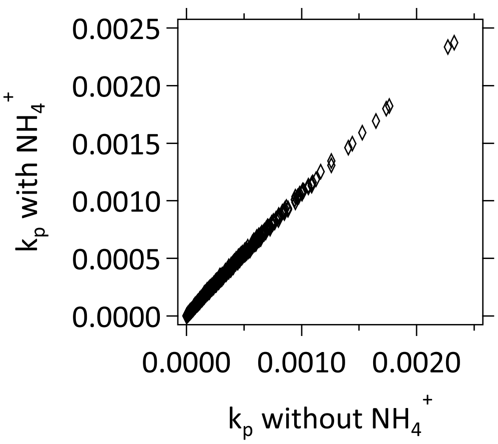

Figure S1. Effect of adding NH_4^+ protonation reaction with IEPOX in $k_{particle}$ (s^{-1}) is negligible as showed by slope of 1.05 for both CMAQ and simpleGAMMA.

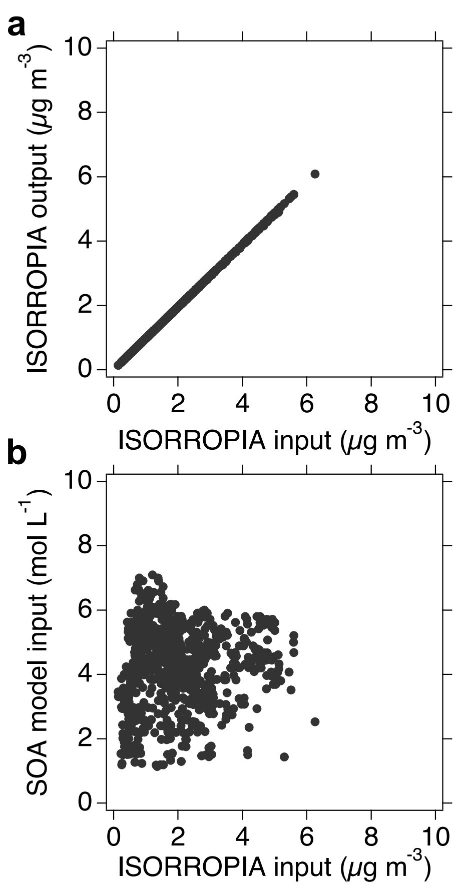

Figure S2. Scatterplots of [SO_4^{2-}] measured by the ACSM at LRK site (x-axis) versus (a) output of the ISORROPIA-II, and (b) input used in the SOA model (CMAQ and simpleGAMMA). Nucleophile concentration, for instance SO_4^{2-}, used as input in the SOA model considers contribution of other inorganic ions and organics, as described in the footnote of Table S1. Thus, the values are different from SO_4^{2-} measured by ACSM.

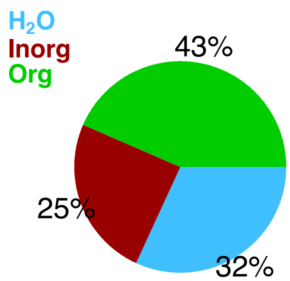

Figure S3. Fraction of inorganic (red), organic (green) and liquid water (blue) in the aerosol.

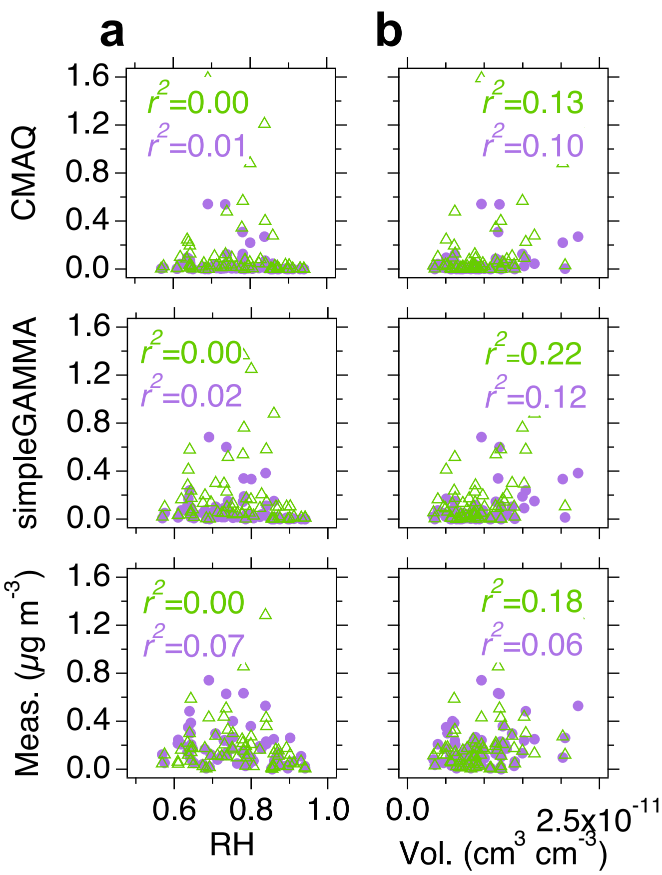

Figure S4. Correlation between estimated IEPOXOS (solid purple circle) and tetrols (open green triangle) by CMAQ and simpleGAMMA in µg m^{-3} as well as measured tracers during 2013 SOAS at LRK with model variables: (a) relative humidity (RH) and (b) aerosol volume (Vol., cm^3 cm^{-3}). RH is on average 0.77 ± 0.10 during the entire SOAS campaign.

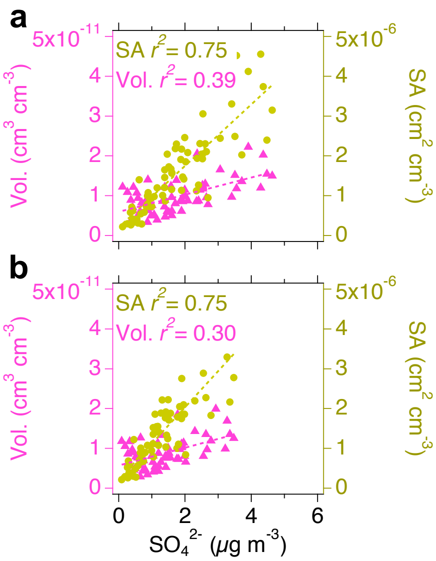

Figure S5. Correlation between aerosol surface area (SA) and liquid volume with sulfate mass concentration from ACSM measurements for (a) base case and (b) sulfate reduction scenarios. Reduction of sulfate does not impact correlation between sulfate, SA and volume.

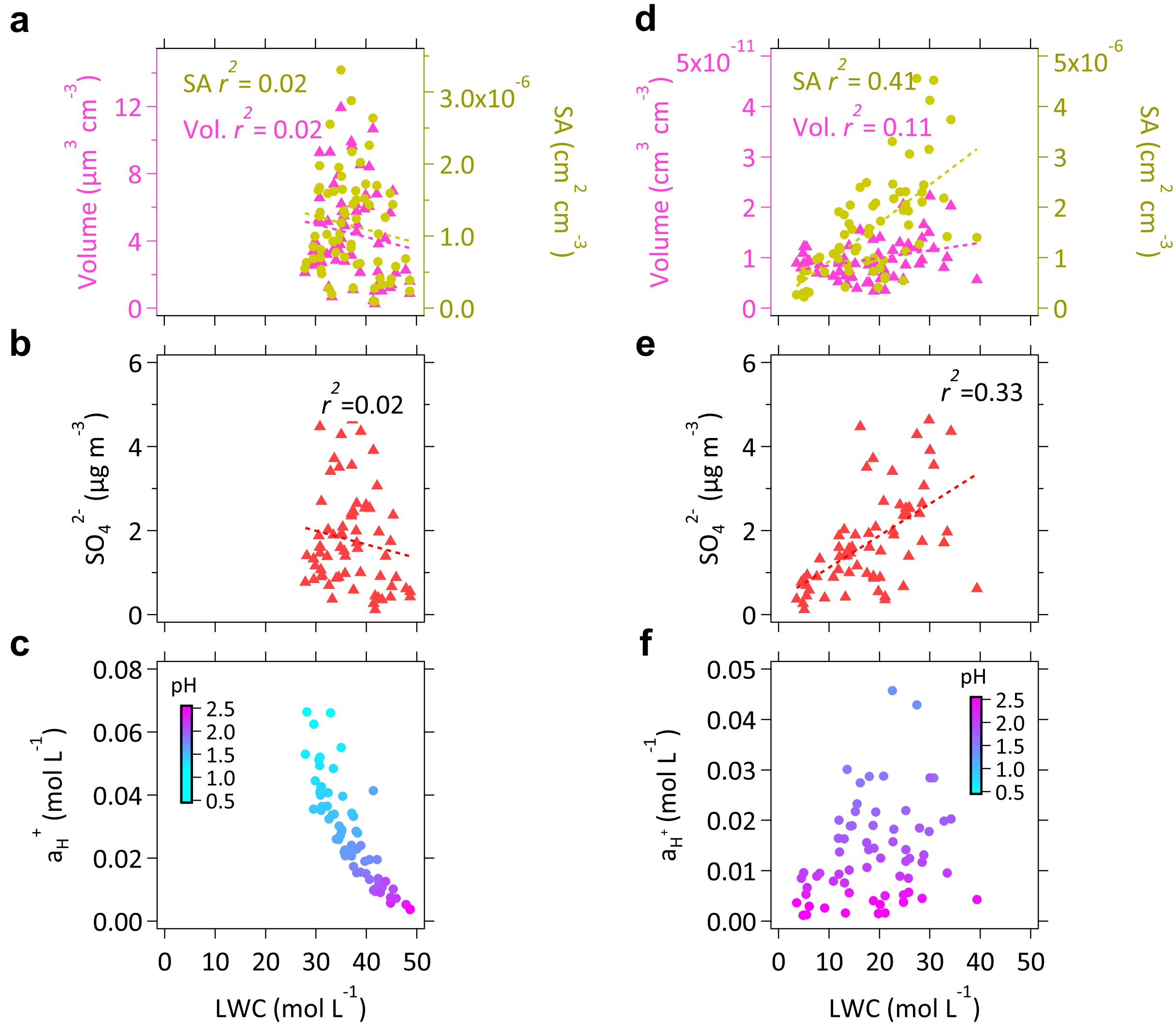

Figure S6. Dry aerosol surface area (SA) and volume measured by SEMS-MCPC (a), and sulfate aerosol measured by ACSM (b) show no relationship with estimated aerosol liquid water directly from ISORROPIA-II (excluding organic aerosol), whereas estimated proton activity (a_{H^+}) has a negative relationship (c). Aerosol SA and volume determined by SEMS-MCPC, ISORROPIA-II, and observed organic aerosol information (d), sulfate aerosol measured by ACSM (e), and estimated a_{H^+} (f) show a relationship with estimated aerosol liquid water when water, organic aerosol, and inorganic aerosol are properly included.

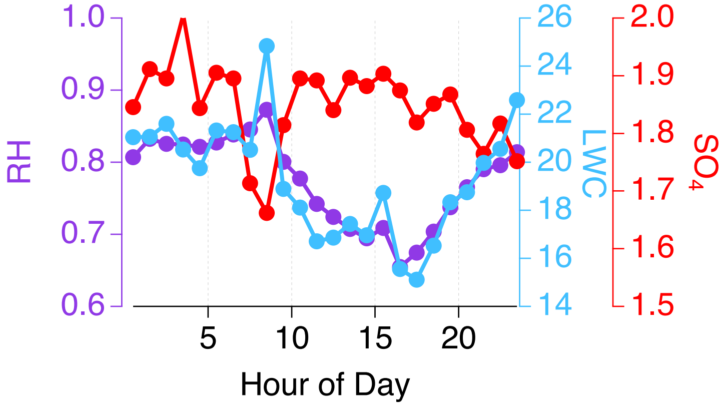

Figure S7. Diurnal trends of RH, LWC and sulfate at LRK site.

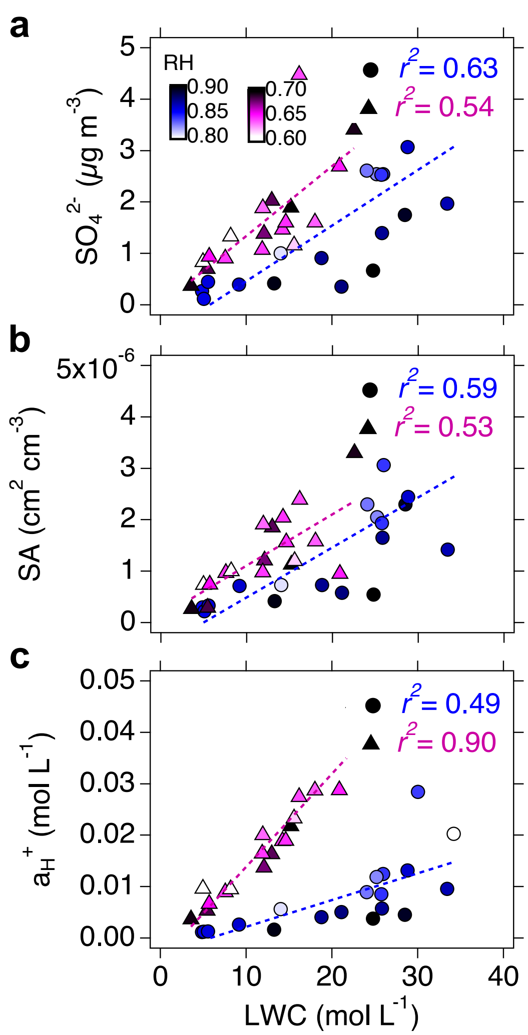

Figure S8. Scatterplots of (a) sulfate (SO_4^{2-}), (b) aerosol surface area (SA), and (c) acidity (a_H^+) versus LWC classified for RH ranges of 0.6 – 0.7 and 0.8 – 0.9.

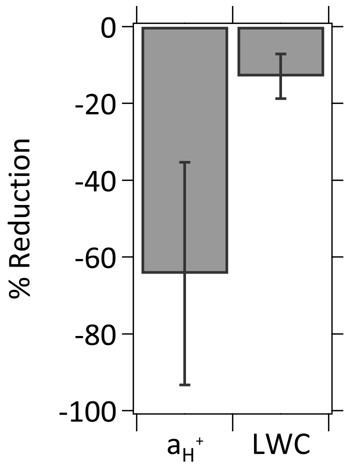

Figure S9. Effects of SO_4^{2-} reduction to proton activity (a_{H^+}) and aerosol liquid water content (LWC) variables are presented as average percentage of changes. Vertical bar shows one standard deviation of the average change percentage. Large changes are found in a_{H^+} variable; however, the variability is large as well. On the other hand, LWC variable does not change significantly.