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Supplement of

Trends in particle-phase liquid water during the Southern Oxidant and Aerosol Study

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1. SMPS Volume Validation

The SMPS was co-located with PM 2.5 aerosol loadings determined by a tapered element oscillating microbalance (TEOM) (Patashnick and Rupprecht, 1991). The TEOM instrument was operated by Atmospheric Administration, Atmospheric Research & Analysis, Inc. as a part of the SEARCH network. SEARCH operations, sampling, and measurement procedures can be found in Hansen et al. (2003) and Edgerton et al. (2005, 2006). The TEOM (R&P Model 1400 a/b) uses oscillating microbalance to provide continuous measurements of PM_{2.5} dry mass concentration at 5-minute intervals. Briefly, particles with aerodynamic particle diameter $D > 2.5 \mu\text{m}$ are removed using a cyclone impactor and particles are dried to $\text{RH} < 20\%$ using a Nafion drier. To compare the TEOM mass with the SMPS volume concentrations SMPS dry volume timestamps were consequently rounded to the nearest fifth minute.

Figure S1 shows the SMPS volume concentration and TEOM mass concentration time series. Note that a mass concentration of $1 \mu\text{g m}^{-3}$ equals $1 \mu\text{m}^3 \text{cm}^{-3}$ assuming spherical particles with unit density of 1g cm^{-3} . The time-series shows that the TEOM and SMPS fluctuate in tandem. The scatterplot of the two time-series is shown in Fig. S2, which shows that the average offset between the two measurements is ~ 1.5 , corresponding to an effective aerosol density of 1.5g cm^{-3} . Sulfate salts and organics composed $\sim 50\%$ of particles during SOAS. The density of ammonium sulfate and organics are $\rho = 1.77 \text{g cm}^{-3}$ and $0.8 < \rho < 1.5$, respectively. Notably, the density of the organic fraction is most uncertain since it depends on the number and quality of functional groups associated with the carbon chain (e.g. Girolami et al., 1994). We point out that this closure between TEOM mass and SMPS volume is approximate since the two techniques have different size cutoffs ($2.5 \mu\text{m}$ vs $1 \mu\text{m}$), the SMPS volume may be biased due to particle shape effects, and residual water present at $\text{RH} < 20\%$ and the presence of volatile compounds may differentially affect the two measurements (Moya et al., 2011). Nevertheless, the correlation between TEOM mass and SMPS volume, combined with the observed effective density of 1.5g cm^{-3} is reasonable to suggest that the SMPS volume measurements were not significantly biased.

2. Analysis without modal fit

The mean and quartiles of parameters without resorting to log-normal parameter fitting are reported in Table S1. Particles with $D > 700 \text{nm}$ were excluded to screen for arcing artifacts.

Water volume, semi-volatile volume, κ_{vol} , and gf_{vol} were calculated using the unfitted data and Eqs. 6, 7, 1, and 4 respectively.

3. Relative humidity dependence of kappa

Thermodynamic model calculations were performed to test the potential influence of relative humidity on the diel cycle of kappa. Model III of the online version of the Extended Aerosol Inorganic Model (<http://www.aim.env.uea.ac.uk/aim/model3/mod3rhw.php>, Clegg et al., 1998, Clegg et al., 2001) was initialized with fixed amounts of NH_4^+ , H^+ , SO_4^{2-} , NO_3^- , and a single organic species defined in Table S2. Molar amounts were estimated to approximately represent the PILS measured mass concentrations of sulfate, nitrate, ammonia, and WSOM. H^+ concentrations were obtained by forcing charge balance. Metastable solutions were expected to be present during the dry-humidified cycle. Therefore the formation of solids was suppressed in the model. Since speciation of the organic fraction was not available, we assumed that the average carbon chain length was C_{10} and that the functional group composition consists of one acid, three hydroxyl, and one carbonyl group. The molecular mass of the organic compound corresponds to 232 g mol^{-1} . The assumed ratio of hydroxyl to carboxyl groups is 3:1 and similar to measurements of ambient monoterpene SOA ($\sim 2.7:1$) (Russell et al., 2011). Activity coefficients were estimated using the semi-empirical UNIFAC group contribution method (Fredenslund et al., 1975) and tabulated interaction parameters of Hansen et al. (1991). The E-AIM model computes the water content $[\text{H}_2\text{O}]_{(\text{aq})}$ of the solution and the molarity of dissolved species: $[\text{NH}_4^+]_{\text{aq}}$, $[\text{HSO}_4^-]_{\text{aq}}$, $[\text{NO}_3^-]_{\text{aq}}$, $[\text{OH}^-]_{\text{aq}}$, $[\text{NH}_3]_{(\text{aq})}$, and $[\text{WSOM}]_{(\text{aq})}$, for a specified water activity. The sum of these parameters corresponds to the number of moles in solution. The osmotic coefficient is obtained from the well-known relationship

$$a_w^{-1} = 1 + \Phi \frac{n_s}{n_w} \quad (\text{S1})$$

where n_s is the number of moles of dissolved species in solution, n_w is the number of moles of water, a_w is the water activity, and Φ is the apparent osmotic coefficient. Variations in the osmotic coefficient with relative humidity are responsible for the humidity dependence of κ (Petters and Kreidenweis, 2007). Note that the dissociation of molecules and potential removal of molecules from solution via solubility would be captured in this definition of Φ since the

number of moles of solution, n_s , is directly obtained from the output of the thermodynamic model. Figure S3 shows the variation of Φ with a_w for the illustrative test solution. The model Φ increases with decreasing a_w . A change in a_w from 0.9 to 0.4 results in a $\sim 60\%$ increase in Φ and a concomitant increase in κ . Thus the increase in κ_{vol} during daytime (Fig. 8 and 10) is partly driven by changes in aerosol hygroscopicity with RH. Precise deconvolution of the relative importance of changing RH and chemical composition in determining the aerosol hygroscopicity will require a better description of the organic fraction, a description of the aerosol mixing state, estimation of organic aerosol molecular weight and density, and inclusion of unresolved non-hygroscopic species (dust, black carbon) to relate Φ to κ .

Figures

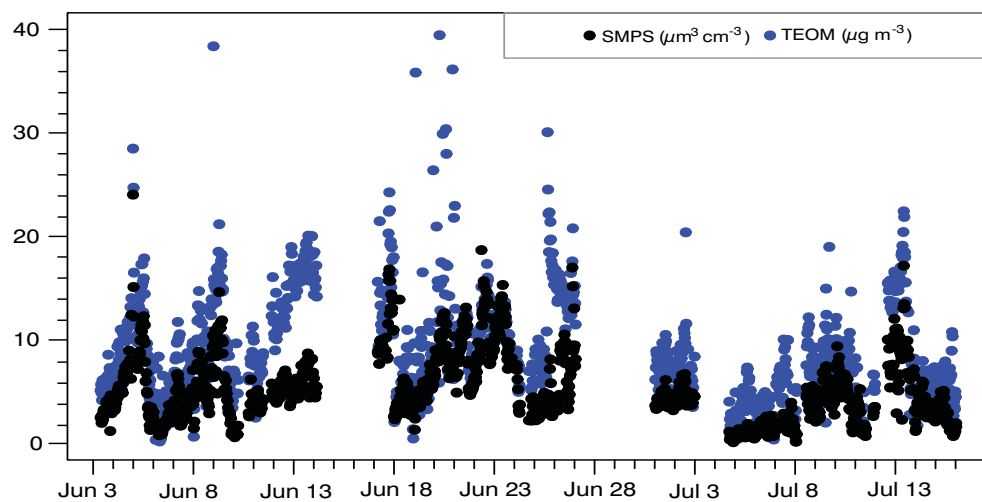


Fig. S1. Time series of TEOM mass (blue) and SMPS dry volume (black).

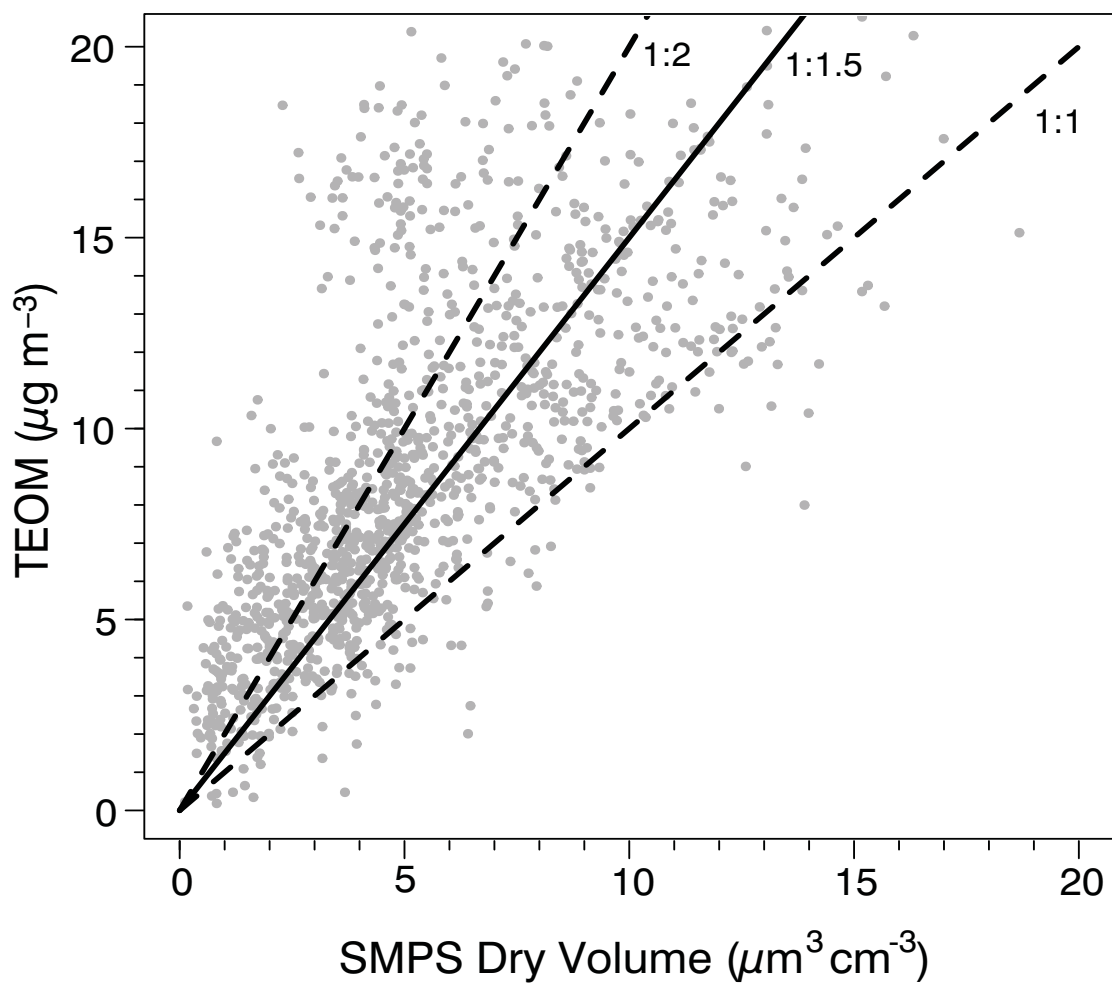


Fig. S2. Scatterplot of TEOM particulate matter mass ($\mu\text{g m}^{-3}$) and SMPS dry volume ($\mu\text{m}^3 \text{cm}^{-3}$) with 1:1 and 1:2 line. The 1:1.5 line indicates the best-fit line calculated from the data.

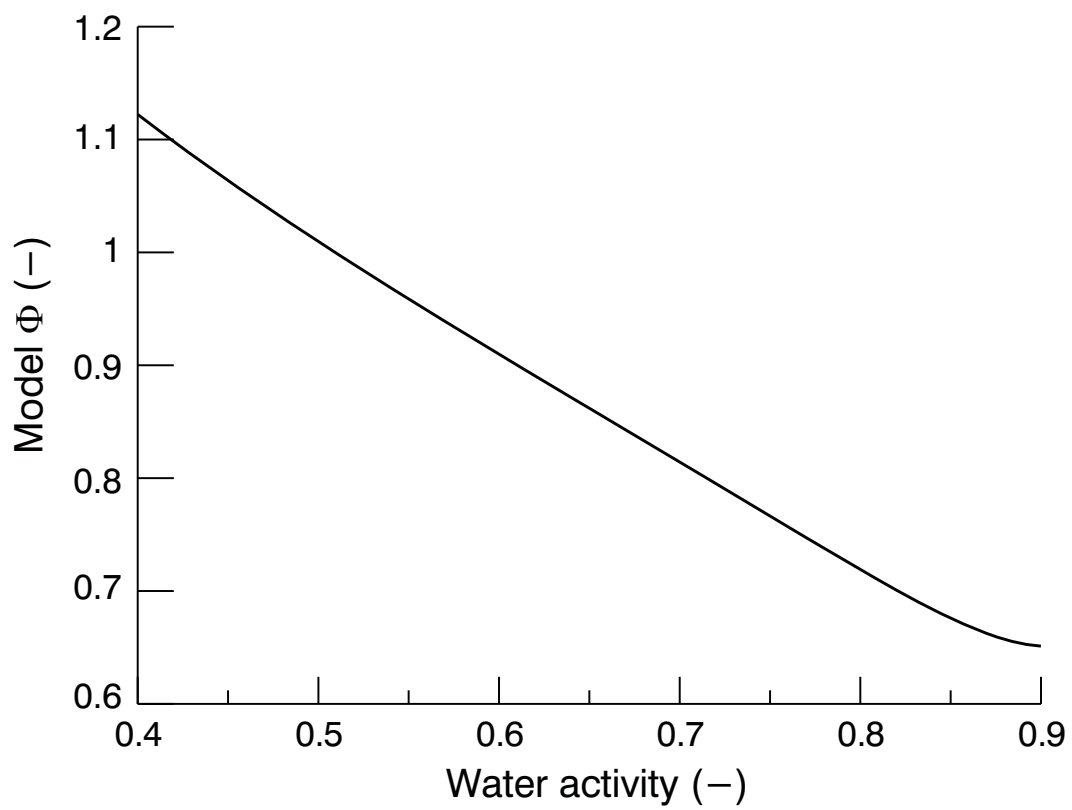


Fig. S3: Variation of the E-AIM Model III derived osmotic coefficient with water activity.

Tables

Table S1. Mean and quartiles of number concentration N_{conc} , particle phase water volume V_w , semi-volatile volume V_{sv} , volume of solutes V_d , and gf_{vol} for unfitted data.

Parameter	Units	Mean	25% Quartile	50% Quartile	75% Quartile
N_{conc}	cm^{-3}	2732	1541	2185	3249
V_w	$\mu\text{m}^3 \text{cm}^{-3}$	3.91	1.14	2.7	4.97
V_{sv}	$\mu\text{m}^3 \text{cm}^{-3}$	0.0099	-0.85	0.19	1.31
V_d	$\mu\text{m}^3 \text{cm}^{-3}$	5.748	3.3	5.0	7.793
K_{vol}	dimensionless	0.31	0.12	0.24	0.41
gf_{vol}	dimensionless	1.72	1.31	1.57	1.95

Table S2. Solute concentrations for E-AIM model initialization. The UNIFAC functional groups representation of the organic molecule is 1*COOH 3*OH 1*CH₂CO 3*CH₂ 3*CH 1*CH₃.

	Cations		Anions		Organic
	NH ₄ ⁺	H ⁺	SO ₄ ²⁻	NO ₃ ⁻	C ₁₀ O ₆ H ₁₆
Molecular Mass (g mol ⁻¹)	18.03851	1.008	96.07	62.0049	232.23
Mass concentration (μg m ⁻³)	0.46	0.01	1.71	0.06	3.15
Molar concentration (nmol m ⁻³)	25.4	11.3	17.8	1.17	13.6

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