

Supplement of Atmos. Chem. Phys. Discuss., 14, 27143–27193, 2014
<http://www.atmos-chem-phys-discuss.net/14/27143/2014/>
doi:10.5194/acpd-14-27143-2014-supplement
© Author(s) 2014. CC Attribution 3.0 License.



Supplement of

Particle water and pH in the southeastern United States

H. Guo et al.

Correspondence to: R. Weber (rodney.weber@eas.gatech.edu) and A. Nenes (athanasios.nenes@gatech.edu)

Supplementary materials

1. Ion balance vs H_{air}^+

An ion balance (or charge balance) of an aerosol is usually calculated as follows, for a $\text{NH}_4\text{-SO}_4\text{-NO}_3\text{-Cl-Na}$ -water inorganic aerosol.

$$\text{Charge Balance} = \frac{[\text{SO}_4^{2-}]}{48} + \frac{[\text{NO}_3^-]}{62} + \frac{[\text{Cl}^-]}{35.5} - \frac{[\text{NH}_4^+]}{18} - \frac{[\text{Na}^+]}{23} \quad (1)$$

where $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$, $[\text{Cl}^-]$, $[\text{NH}_4^+]$, and $[\text{Na}^+]$ are concentrations of these ions in the aerosol in units of g m^{-3} . An ion balance cannot be used as a proxy for the aerosol concentration of H^+ in air (i.e., moles H^+ per volume of air, denoted hereafter as H_{air}^+). For one reason, an ion balance assumes all ions are completely dissociated, but multiple forms are possible, depending on pH (e.g., sulfate can be in the form, of H_2SO_4 , HSO_4^- , or SO_4^{2-}). For example, if sulfate stays in the free form of H_2SO_4 , it doesn't add protons, but a charge balance simply assumes complete dissociation. Ammonium to sulfate molar ratios are also often used to assess particle acidity. In this study the $\text{NH}_4^+/\text{SO}_4^{2-}$ mole ratio is 1.4 ± 0.5 (mean \pm STD).

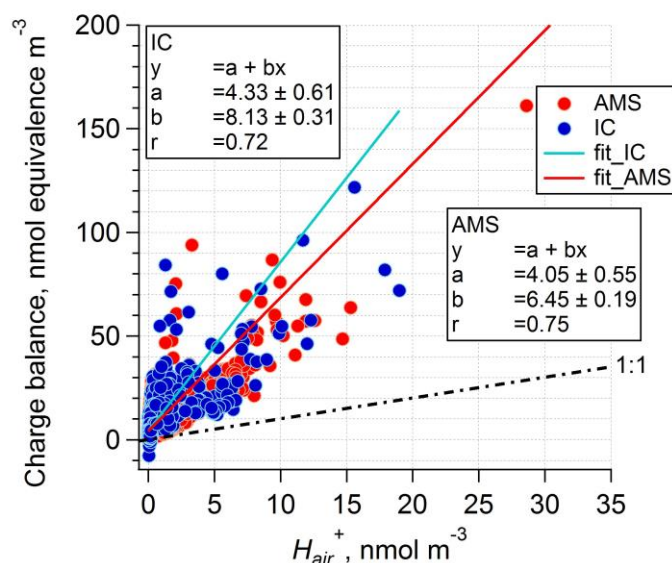


Fig. S1. Charge balances of particles are compared with ISORROPIA-II predicted concentration of protons in the particle, per volume of air, H_{air}^+ . Comparisons are based on IC and AMS data sets from CTR. Orthogonal distance regression (ODR) fits were applied.

2. Nephelometer RH sensor calibration

The nephelometer RH sensors were calibrated by placing the sensors in a properly sealed container above aqueous saturated salt solutions at known temperatures allowing accurate prediction of equilibrium RH (Greenspan, 1977). More than 3hours were allowed for each salt solution to reach water vapor saturation.

Table. S1. Theoretical and measured RH for saturated salt solution at 20°C

Compound	Equilibrium RH, %	Measured RH, %
K ₂ CO ₃	43.16 ± 0.33	40.39 ± 0.47
NaCl	75.47 ± 0.14	71.00 ± 0.00
KCl	85.11 ± 0.29	80.21 ± 0.38
KNO ₃	94.62 ± 0.66	88.60 ± 0.47

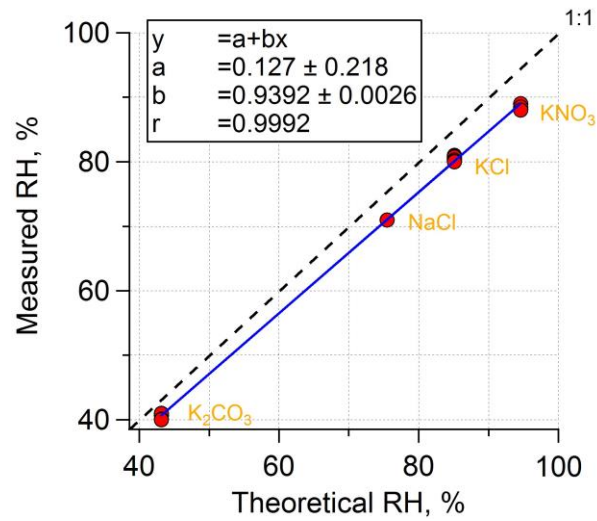


Fig. S2. A linear regression fit of measured RH.

3. LWC measurement principle by nephelometers

Particle water was indirectly measured by two nephelometers. The difference between ambient and dry scattering coefficients (σ_{sp}) is assumed to be caused by the loss of water. The ratio between wet or ambient scattering coefficient and dry scattering coefficient is referred to as $f(RH)$.

$$f(RH) = \frac{\sigma_{sp}(wet)}{\sigma_{sp}(dry)} = \frac{\int \frac{\pi}{4} Q_{wet} D_{p,wet}^2 N(D_p) dD_p}{\int \frac{\pi}{4} Q_{dry} D_{p,dry}^2 N(D_p) dD_p} \quad (2)$$

where Q is scattering efficiency, $N(D_p)$ is particle number size distribution, and N is the total number concentration. Assuming that $\overline{D_p}$ is the diameter of average surface,

$$\frac{\sigma_{sp}(wet)}{\sigma_{sp}(dry)} = \frac{\frac{\pi}{4} Q_{wet} \overline{D_{p,wet}}^2 N}{\frac{\pi}{4} Q_{dry} \overline{D_{p,dry}}^2 N} = \frac{Q_{wet} \overline{D_{p,wet}}^2}{Q_{dry} \overline{D_{p,dry}}^2} \quad (3)$$

$$\overline{D_{p,wet}} = \overline{D_{p,dry}} \sqrt{f(RH) Q_{wet}/Q_{dry}} \quad (3)$$

Based on Mie Theory calculations, Q over fine particle ($PM_{2.5}$) size range is plotted in the Figure 2. It shows the optimal scattering size range (570-680 nm) with highest scattering efficiencies for accumulation mode particles. The optimal scattering size range is supposed to be covered by both wet and dry particles. Assuming Q_{wet} and Q_{dry} are of similar magnitude,

$$\frac{Q_{wet}}{Q_{dry}} \approx 1 \quad (4)$$

Take Equation 4 into Equation 3. We get,

$$\overline{D_{p,wet}} = \overline{D_{p,dry}} \sqrt{f(RH)} \quad (5)$$

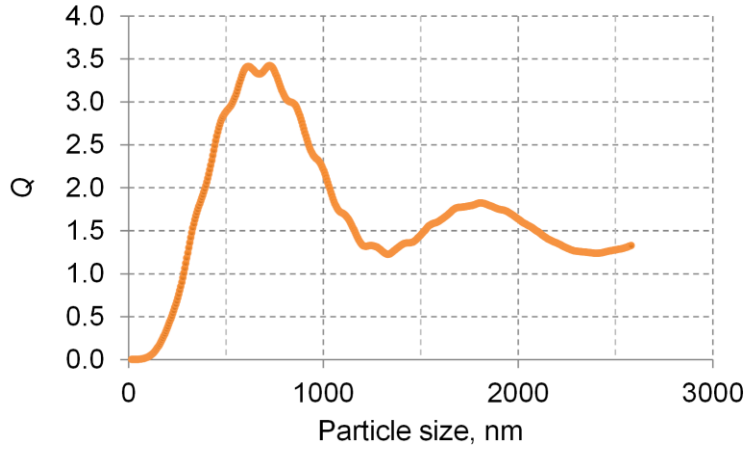


Fig. S3. Scattering efficiency (Q) over $PM_{2.5}$ size range at $\lambda = 530$ nm.

LWC is equal to the differences between wet particle volume and dry particle volume.

$$LWC = \frac{\pi}{6} \overline{D_{p,wet}}^3 N - \frac{\pi}{6} \overline{D_{p,dry}}^3 N \quad (6)$$

Since

$$\overline{D_{p,dry}}^3 = \frac{m}{\frac{\pi}{6} \rho_p N} \quad (7)$$

where m is dry $PM_{2.5}$ mass concentration and ρ_p is the density of dry aerosol. Take Equation 5 and 7 into Equation 6. Finally we get,

$$LWC = \frac{m}{\rho_p} [f(RH)^{1.5} - 1] \quad (8)$$

m measured by a TEOM was used. ρ_p was estimated from the particle composition including AMS total organics, ammonium, and sulfate, which accounted for 90% of the measure $PM_{2.5}$ dry mass (TEOM) on the SOAS study average. A typical organic density 1.4 g cm^{-3} is assumed (Turpin and Lim, 2001; King et al., 2007; Engelhart et al., 2008; Kuwata et al., 2012; Cerully et al., 2014), and the density of ammonium sulfate is assumed to be 1.77 g cm^{-3} (Sloane et al., 1991; Stein et al., 1994). ρ_p is calculated to be $1.49 \pm 0.04 \text{ g/cm}^3$ ($n = 4,393$) using mass fractions (ϵ) by Equation 9. The diurnal variation of aerosol density is shown in Figure 3.

$$\rho_p = \frac{1}{\epsilon(NH_4 + SO_4)/1.77 + \epsilon(Organics)/1.4} \text{ (g cm}^{-3}\text{)} \quad (9)$$

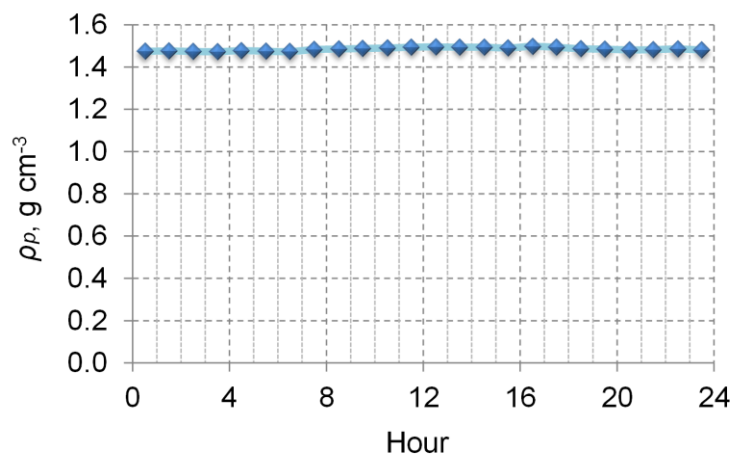


Fig. S4. Predicted $PM_{2.5}$ density diurnal profile. Median hourly density averages and standard error plotted as error bars (too small to be seen) at local hour are plotted.

4. Particulate organic hygroscopic parameter, κ_{org}

Overall κ_{org} has a study mean (\pm STD) as 0.126 ± 0.059 (Cerully et al., 2014). However, κ_{org} data is only available after June 20th, and were not measured during the first 20 days of SOAS field study. Diurnal hourly average κ_{org} was calculated and median values are plotted in Figure 4. Because κ_{org} median averages were scattered, three hours running averages were obtained.

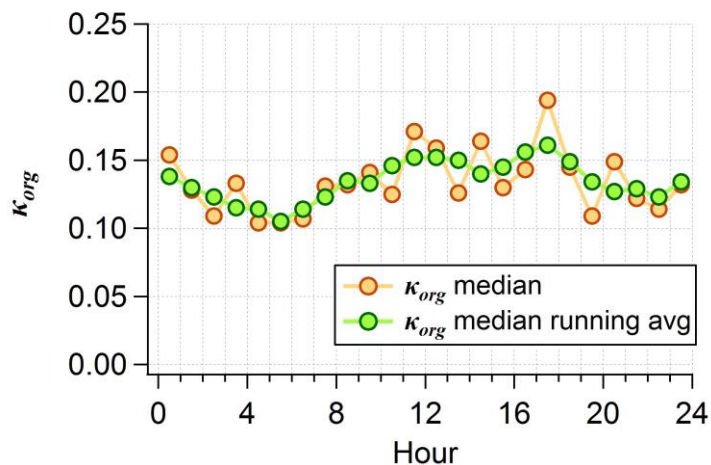


Fig. S5. κ_{org} diurnal variation. Median averages are plotted at local hours.

5. Filter based IC analysis at all sites

High-volume $PM_{2.5}$ filters, sampled parallel to AMS measurement, were analyzed by a DIONEX IC (UTAC-ULP1 concentrator column, AG11 guard column and AS11 anion column) to provide chemical information of the refractory ions (Na, K, Mg, Ca, PO_4). Filter-based nitrate is excluded due to artifacts (Hering and Cass, 1999; Chang et al., 2000). The ion compositions at various sites are similar, all dominated by SO_4 (64-74%) and then NH_4 (22-31%). We found the refractory ions usually accounted for < 5% (RS is the highest at 9%) of the sum of all ion inorganic ion mass for $PM_{2.5}$.

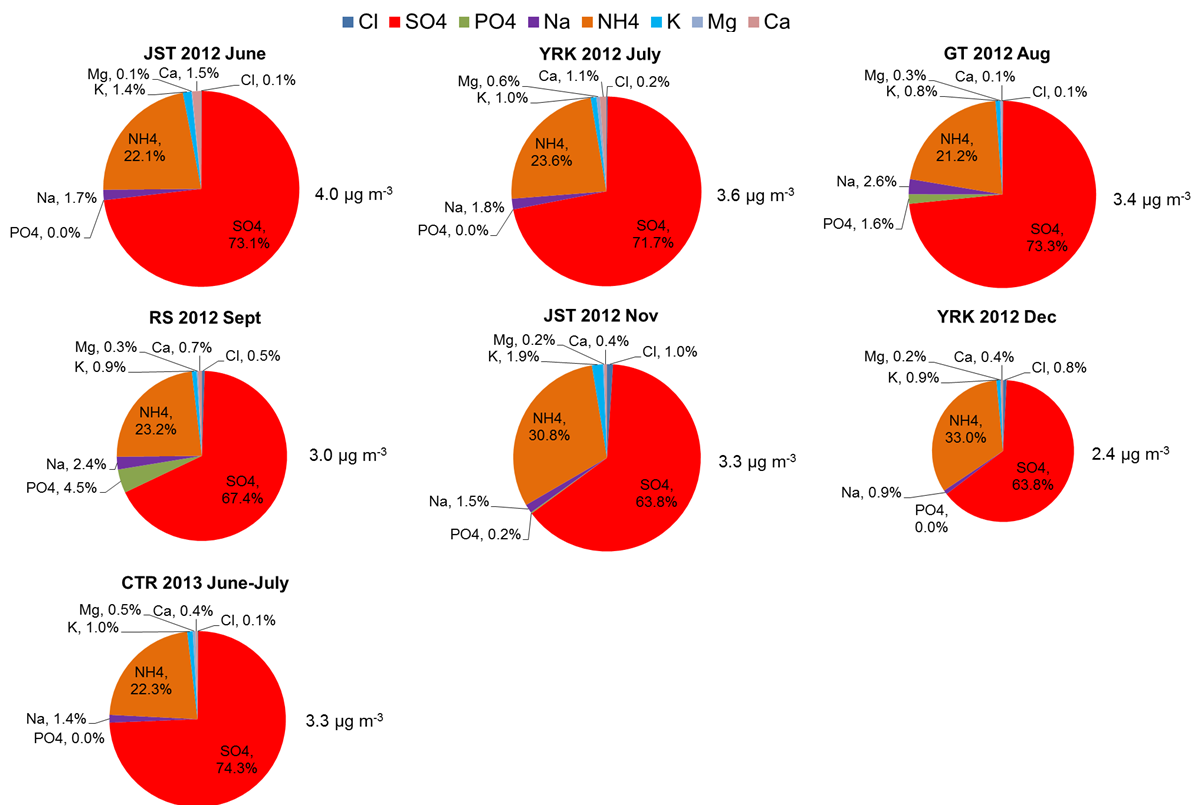


Fig. S6. Filter-based campaign averaged ion composition in PM_{2.5} at all sites. The mean concentrations of all the listed ions are labeled to the right of PI charts. Filter sampling, each 23 hrs, was parallel to AMS measurement. JST 2012 June is plotted rather than 2012 May due to no filter data available in 2012 May.

References:

Cerully, K., Bougiatioti, A., Guo, H., Xu, L., Hite, J., Ng, N. L., Weber, R., and Nenes, A.: On the link between hygroscopicity, volatility and aerosol oxidation state of ambient and water-soluble aerosol in the southeastern United States, *Atm. Chem. Phys. Disc.*, 2014.

Chang, M. C., Sioutas, C., Kim, S., Gong, H., and Linn, W. S.: Reduction of nitrate losses from filter and impactor samplers by means of concentration enrichment, *Atmospheric Environment*, 34, 85-98, Doi 10.1016/S1352-2310(99)00308-8, 2000.

Engelhart, G. J., Asa-Awuku, A., Nenes, A., and Pandis, S. N.: CCN activity and droplet growth kinetics of fresh and aged monoterpene secondary organic aerosol, *Atmospheric Chemistry and Physics*, 8, 3937-3949, 2008.

Greenspan, L.: Humidity Fixed Points of Binary Saturated Aqueous Solutions, *Journal of Research of the National Bureau of Standards*, 81A, 8, 1977.

Hering, S., and Cass, G.: The Magnitude of Bias in the Measurement of PM_{2.5} Arising from Volatilization of Particulate Nitrate from Teflon Filters, *Journal of the Air & Waste Management Association*, 49, 725-733, 10.1080/10473289.1999.10463843, 1999.

- King, S. M., Rosenoern, T., Shilling, J. E., Chen, Q., and Martin, S. T.: Cloud condensation nucleus activity of secondary organic aerosol particles mixed with sulfate, *Geophysical Research Letters*, 34, 10.1029/2007gl030390, 2007.
- Kuwata, M., Zorn, S. R., and Martin, S. T.: Using elemental ratios to predict the density of organic material composed of carbon, hydrogen, and oxygen, *Environmental science & technology*, 46, 787-794, 10.1021/es202525q, 2012.
- Sloane, C. S., Watson, J., Chow, J., Pritchett, L., and Richards, L. W.: Size-Segregated Fine Particle Measurements by Chemical-Species and Their Impact on Visibility Impairment in Denver, *Atmospheric Environment. Part A. General Topics*, 25, 1013-1024, Doi 10.1016/0960-1686(91)90143-U, 1991.
- Stein, S. W., Turpin, B. J., Cai, X. P., Huang, C. P. F., and Mcmurry, P. H.: Measurements of Relative Humidity-Dependent Bounce and Density for Atmospheric Particles Using the DMA-Impactor Technique, *Atmospheric Environment*, 28, 1739-1746, Doi 10.1016/1352-2310(94)90136-8, 1994.
- Turpin, B. J., and Lim, H.-J.: Species Contributions to PM_{2.5} Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass, *Aerosol Science and Technology*, 35, 602-610, 10.1080/02786820119445, 2001.