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Enhanced secondary organic aerosol formation due to water uptake by fine particles

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Enhanced secondary organic aerosol formation due to water uptake by fine particles

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[1]   This study characterizes the partitioning behavior of a significant fraction of the ambient organic aerosol through simultaneous measurements of gas and particle water-soluble organic carbon (WSOC). During the summer in Atlanta, WSOC gas/particle partitioning showed a strong RH dependence that was attributed to particulate liquid water. At elevated RH levels ($>\sim70\%$), a significant increase in WSOC partitioning to the particle phase was observed and followed the predicted water uptake by fine particles. The enhancement in particle-phase partitioning translated to increased median particle WSOC concentrations ranging from $0.3-0.9$ μg C m^{-3}. The results provide a detailed overview of the WSOC partitioning behavior in the summertime in an urban region dominated by biogenic emissions, and indicate that secondary organic aerosol formation involving partitioning to liquid water may be a significant aerosol formation route that is generally not considered. **Citation:** Hennigan, C. J., M. H. Bergin, J. E. Dibb, and R. J. Weber (2008), Enhanced secondary organic aerosol formation due to water uptake by fine particles, *Geophys. Res. Lett.*, *35*, L18801, doi:10.1029/2008GL035046.

1.   Introduction

[2]   Current models tend to under-predict secondary organic aerosol (SOA) concentrations by a significant degree [*de Gouw et al.*, 2005]. The source of this negative model bias is unknown. Explanations include unidentified SOA-producing VOCs [*Goldstein and Galbally*, 2007] and differing SOA formation mechanisms such as heterogeneous chemical reaction in clouds [*Lim et al.*, 2005] or smaller haze particles [*Volkamer et al.*, 2007].

[3]   The gas/particle partitioning of organic compounds is central to the understanding of SOA formation. A major pathway for SOA formation is through the oxidation of hydrocarbons in the gas phase to form less volatile products. These semi-volatile products can condense and establish equilibrium (i.e., partition) between the gas and particle phase, even at levels below their saturation vapor pressures [*Pankow*, 1994].

[4]   The effects of particulate water and relative humidity (RH) on SOA formation and yields have been investigated through both modeling and smog chamber studies. In smog chamber studies, *Cocker et al.* [2001a] found no difference in SOA yields from the photooxidation of m-xylene or 1, 3, 5-trimethylbenzene with the addition of aqueous inorganic seed particles, compared to yields in the presence of dry inorganic seed, or in the absence of seed particles. *Cocker et al.* [2001b] also found a decrease in the SOA yields of α−pinene/O$_3$ systems when wet inorganic seed particles were present, compared to either dry inorganic seed or no seed particles present. Additionally, *Edney et al.* [2000] found no enhancement in SOA yields from toluene due to the presence of liquid water in smog chamber experiments.

[5]   In predictions of SOA formation from five different hydrocarbons, *Seinfeld et al.* [2001] found, for all five systems modeled, increasing SOA mass with increasing RH (for $0 \leq RH \leq 80\%$). This was attributed to the effect of water on the average molecular weight of the absorbing organic phase (MW_{om}) and on the particle-phase activity coefficient (ζ), two parameters which influence gas/particle partitioning. *Pun and Seigneur* [2007] predict that certain SOA systems are sensitive to liquid water content. For example, modeled SOA yields from benzene were a factor of $3-4$ higher when liquid water concentrations were 10 μg m^{-3} compared to 1 μg m^{-3}. *Chang and Pankow* [2008] propose a modified equilibrium gas/particle partitioning model that accounts for the RH effect on MW_{om} and ζ. Their results indicate that neglecting the RH effect can lead to predicted SOA concentrations that are a factor of two lower than model predictions that include the effect. Due to this potentially substantial shortcoming in predicted SOA concentrations, a number of recent studies suggest that this RH effect should be incorporated into model predictions of SOA [*Chang and Pankow*, 2008; *Pun and Seigneur*, 2007; and *Seinfeld et al.*, 2001].

[6]   Water uptake by particles could also affect partitioning through other SOA formation mechanisms, such as reactions of organic compounds in the aqueous phase. Recent studies [e.g., *Lim et al.*, 2005] suggest that heterogeneous chemical reactions could result in significant SOA formation beyond that predicted by models that neglect this process. If aqueous-phase reactions, like hydration, metal catalysis, or reaction with hydroxyl radical, were a significant source of SOA, then under equilibrium conditions adding liquid water could enhance particle-phase partitioning by increasing the capacity for these reactions to take place.

[7]   Particulate organic compounds that are water-soluble (WSOC$_p$) have been established as a relevant and significant component in the atmosphere [e.g., *Decesari et al.*, 2002; *Miyazaki et al.*, 2006; *Kondo et al.*, 2007; *Weber et al.*, 2007]. The use of a single bulk measurement like WSOC to quantify the wide range of chemical complexities comprising the organic aerosol has disadvantages and

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advantages. The disadvantage is that all information on properties and processes relating to specific compounds is lost. The advantage, however, is that a single (and relatively simple) measurement can be used to comprehensively quantify an important component of the ambient aerosol. In contrast, comprehensive characterization of the organic aerosol by single component analysis has not been possible. Studies have shown that in the absence of significant biomass burning contributions, $WSOC_p$ is mainly from SOA formation and typically represents approximately 75 to 80% (gC/gC) of the SOA mass concentration [*Miyazaki et al.*, 2006; *Kondo et al.*, 2007]. $WSOC_p$ often accounts for more than 50% of total particulate organic carbon (OC) in urban regions [*Sullivan et al.*, 2004] with higher fractions in rural environments [*Weber et al.*, 2007].

[8] This study extends the use of $WSOC_p$ to include measurement of bulk water-soluble organic gases ($WSOC_g$) and examines the impact of RH (and hence particulate liquid water) on the partitioning of ambient WSOC. There are limitations with this non-chemically specific approach. In particular, if the chemical compositions of $WSOC_p$ and $WSOC_g$ were largely dissimilar and unrelated, then it is unlikely that any processes would be revealed and no visible trends in WSOC partitioning observed. However, clear trends in WSOC partitioning were observed throughout the summertime and these findings not only help characterize the formation of SOA in Atlanta, but provide a means for simple parameterization of a complex process. Previous studies into the partitioning behavior of ambient organic compounds have looked at individual compounds or groups of compounds that comprise a very small fraction of OC mass. In this new approach to characterize the partitioning of organic aerosol, the trends we observe represent the behavior of a significant fraction of the ambient OC budget.

2. Methods

[9] Measurements were made from the roof-top of the Environmental Science and Technology Building on the Georgia Institute of Technology campus from 11 May–20 September, 2007. The roof top is ~20 m above ground level and the air sample inlet ~3 m above roof level. Located near the center of Atlanta, the measurements included $WSOC_g$, $WSOC_p$, and OC, as well as meteorological parameters.

[10] Hourly-averaged measurements of $PM_{2.5}$ OC were made with a Sunset Labs OCEC field analyzer (Sunset Laboratory Inc., Tigard, OR, see *Weber et al.* [2007] for operational details). To measure fine ($PM_{2.5}$ via a sharp-cut impactor [*Marple et al.*, 1991]) $WSOC_p$, the PILS-WSOC method was used [*Sullivan et al.*, 2004]. The $WSOC_p$ sample integration time was six minutes and the measurement uncertainty was approximately 10% [*Sullivan et al.*, 2004]. Similar to the method described by *Anderson et al.* [2008], a mist chamber was used to measure $WSOC_g$. This mist chamber has been shown to efficiently sample gases with an effective Henry's Law constant, K_H, greater than ~10^3 [*Spaulding et al.*, 2002]. Sample air was pulled at approximately 21 L min^{-1} through a Teflon filter for complete removal of particles. The sample then entered a

glass mist chamber initially filled with 10 mL deionized (DI) water and fitted with a hydrophobic Teflon filter at the chamber exit. The instrument was automated to collect a five-minute batch sample once every ten minutes and the six-minute $WSOC_p$ measurements were merged onto these sample times. An overall uncertainty for the $WSOC_g$ measurement was estimated at 7%.

3. Results and Discussion

[11] For the entire study, mean and median $WSOC_p$ concentrations were 3.3 μg C m^{-3} and 2.9 μg C m^{-3}, respectively. Study mean and median concentrations of $WSOC_g$ were 13.7 μg C m^{-3} and 11.8 μg C m^{-3}, respectively. To investigate the partitioning of WSOC, we examine the parameter, F_p

$$F_p = \frac{WSOC_p}{WSOC_p + WSOC_g} \tag{1}$$

which represents the fraction of total WSOC in the particle phase. Note that F_p is related to the particle/gas WSOC concentration ratio by

$$\frac{WSOC_p}{WSOC_g} = \frac{F_p}{1 - F_p} \tag{2}$$

It is apparent from overall study concentrations that gasphase components accounted for a significantly larger fraction of total WSOC than particulate components; for the entire study, the mean F_p was 0.207 while the median was 0.203.

[12] A box plot of F_p vs. RH (Figure 1a) was generated by sorting the entire summer data set (n = 10994) into eight RH bins. This analysis is useful because it gives a clear view of data trends for a large data set, and the number of data points within each bin (average n = 1374) provide high statistical strength to the analysis.

[13] The relationship between F_p and RH (Figure 1a) shows compelling evidence for a strong RH effect on WSOC partitioning. The data showed increased particlephase partitioning when the ambient RH was at or above 70% and, as will be discussed, suggests the uptake of water by particles was responsible for this enhancement. Below 70% RH, F_p showed little variation, with a mean value of 0.190 ± 0.005 (mean ± 1σ for the five median values). At RH greater than or equal to 70%, F_p rose sharply with RH and reached a maximum of 0.305 at RH greater than or equal to 90%. This indicates that the fraction of WSOC in the particle phase increased by more than 50% at the highest RH levels, compared with that below 70%. To quantify this impact on increased SOA mass concentration, ΔF_p was calculated for each of the three bins above 70% RH. ΔF_p was defined as the difference between the bin median F_p and 0.190, the mean F_p below 70% RH. ΔF_p was multiplied by the median total WSOC concentration for each bin to provide the additional SOA concentration relative to dryer conditions. Shown in Table 1, the partitioning shift resulted in a substantial increase in SOA mass concentrations. For the RH range of 70–79%, the SOA enhancement was 0.3 μg C m^{-3}. For 80–89% RH, the SOA enhancement
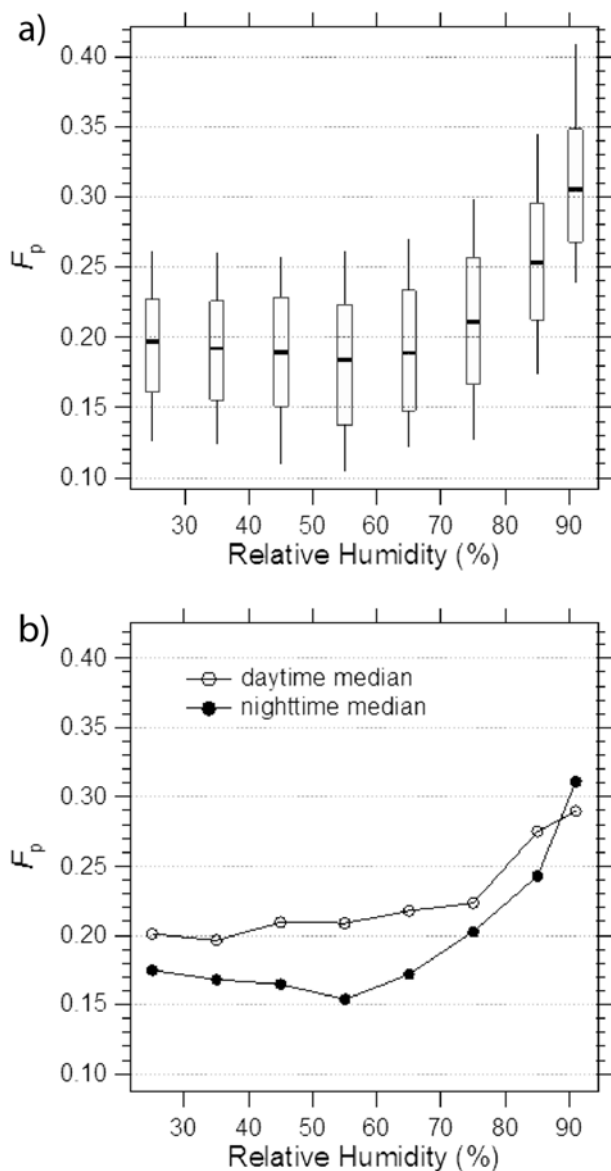
Figure 1. (a) Particulate WSOC fraction, F_p, as a function of RH. The data were binned according to RH, and median (thick horizontal line), 25th and 75th percentiles (lower and upper box), and 10th and 90th percentiles (lower and upper whiskers) are shown for each bin. (b) Also shown are median daytime and nighttime F_p values as a function of RH.

was 0.6 μg C m^{-3}, and for values above 89% RH, the SOA enhancement was 0.9 μg C m^{-3}.

[14] Table 1 also illustrates that the median total WSOC concentration decreased as RH increased. This behavior was caused by WSOC$_p$ and WSOC$_g$ concentrations both increasing linearly with increasing temperature, possibly due to the role of photochemistry in WSOC formation and/or increased emissions of biogenic precursors with warmer conditions. This likely obscured the expected effect of temperature on partitioning (C. J. Hennigan et al., manuscript in preparation, 2008). Because temperature and RH are inversely related, the positive correlations between temperature and both WSOC species translated into nega-

tive correlations with RH. Despite decreasing total WSOC concentrations with RH, the enhanced SOA concentrations at high RH were significant. The SOA increases at high RH levels represent values on the order of 10–25% of the mean summer WSOC$_p$ concentration. WSOC$_p$ accounted for, on average, 70% of OC, so the added SOA signifies a meaningful contribution to OC as well.

[15] Figure 1b shows the difference in the partitioning effect between night and day. Generally, more WSOC was partitioned in the particle phase during the day than at night and may result in part from diurnal variability in oxidant or other pertinent species (e.g., NO$_x$) concentrations. Despite a higher mean total WSOC concentration at night (17.1 μg C m^{-3}) than during the day (16.8 μg C m^{-3}), this phenomenon resulted in a mean daytime WSOC$_p$ concentration (3.5 μg C m^{-3}) that was approximately 10% higher than the mean nighttime concentration (3.2 μg C m^{-3}). Although there were differences in the day/night F_p levels, it is noteworthy that the F_p dependences on RH were similar and that the enhancement of particle-phase partitioning was not limited to one period, but was observed at elevated RH, regardless of the time of day.

[16] The distinct relationship between F_p and RH implicates aerosol water uptake as the likely cause for the observed enhancement in particle-phase partitioning. Figure 2, which shows the RH dependence of median F_p values, modeled aerosol liquid water concentrations, and an indirect measure of water uptake by ambient aerosol, supports this assertion. The liquid water concentration was predicted with the ISORROPIA-II thermodynamic equilibrium model [*Fountoukis and Nenes*, 2007], using mean sulfate, nitrate, and ammonium concentrations from the August 1999 Atlanta Supersite data [*Solomon et al.*, 2003]. Though the model does not consider the effect of organics on water uptake, the high inorganic concentrations (sum = 14.7 μg m^{-3}) and large mass fraction of PM$_{2.5}$ suggest that the model results provide a reasonable estimate of the hygroscopic behavior of typical aerosol for the Atlanta summertime. The *Malm and Day* [2001] data represent a measure of f(RH), the enhancement in light scattering as a function of RH that is attributed to water uptake. These particular data had an inorganic/organic mass ratio of ~1, and thus in a relative sense, were compositionally similar to Atlanta aerosol as well. Their data show a flatter region below ~50% RH, compared to the model results, and are in better qualitative agreement with our observations. The similarities in the RH dependences of F_p, modeled aerosol water, and ambient aerosol water uptake above 55% RH in Figure 2 are striking. These similarities suggest that the increase in particulate condensed water with increasing RH was re-

Table 1. Increases in F_p for RH > = 70% Compared to Lower RH (ΔF_p), Median Total WSOC (WSOC$_p$ + WSOC$_g$), and the Resulting Estimated SOA Enhancement

Bin Mid-point RH	ΔF_p	Total WSOC[a]	SOA Enhancement[a]
75%	0.021	13.4	0.3
85%	0.063	10.3	0.6
92%	0.115	7.8	0.9

[a]Units are μg C m^{-3}.
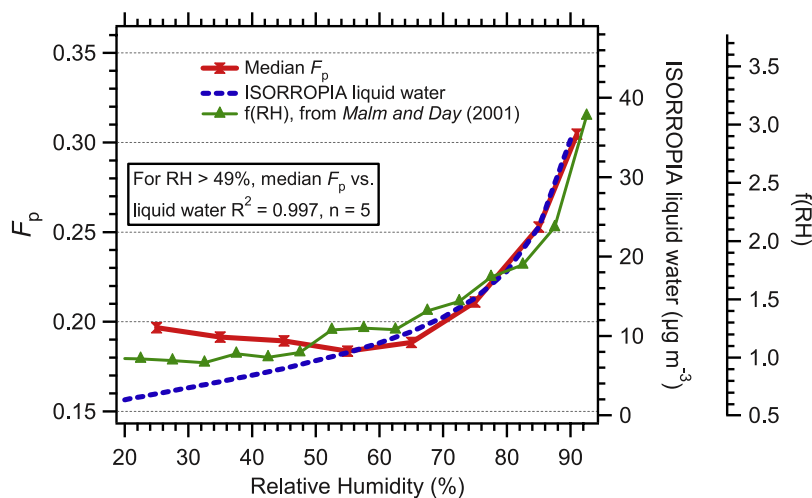
Figure 2. RH dependence of median particulate WSOC fraction, as well as modeled (from ISORROPIA-II) and observed (using scattering enhancement, f(RH), from *Malm and Day* [2001]) water uptake for aerosol with composition representative of that for the Atlanta summertime.

sponsible for the observed increase in F_p. It is possible, however, that the F_p-RH relationship was actually a byproduct of a relationship between F_p and some other variable related to RH, although this seems unlikely. For example, the production of semi-volatile organic compounds (SVOCs) that partition to the aerosol phase often involves the hydroxyl radical (OH) concentration, which depends on water vapor concentrations. Consistencies in the day/night partitioning behavior of WSOC (Figure 1b) and the strong similarities between F_p and modeled and observed water uptake (Figure 2) suggest that the F_p-RH relationship of Figure 1 is most directly explained by partitioning of $WSOC_g$ into particulate water. Because water uptake is largely determined by inorganic salts [*Malm and Day*, 2001], these findings suggest that inorganic aerosol have an indirect role in SOA formation. This does not, however, suggest a correlation between major inorganic components and SOA. Rather, because of persistent and appreciable inorganic salt concentrations typically present in Atlanta [*Weber et al.*, 2003], the seeds for water uptake exist nearly all of the time.

[17] These results are consistent with our previous findings that suggest a link between aerosol water and both $WSOC_p$ and secondary nitrate production [*Hennigan et al.*, 2008]. In that study, the formation of relatively fresh (∼2−3 hours) $WSOC_p$ in a region of predominantly anthropogenic emissions was also likely related to aerosol water, as was nitrate, in agreement with known nitrate thermodynamic properties. In Mexico City, we found $WSOC_p$ and nitrate production in the morning during periods of high aerosol liquid water concentrations (∼20 μg m^{-3}). However, changes in ambient conditions, which led to the sudden evaporation of most particle-bound water, were shortly followed by the volatilization of some fraction (∼10−20%) of $WSOC_p$ and a more significant fraction of the nitrate (∼30%). Though *Hennigan et al.* [2008] and the present study both suggest a link between $WSOC_p$ and aerosol water, this present study does not assess the reversibility of the observed partitioning enhancement. The question of reversible partitioning is a significant one and will be explored in future studies.

[18] Our results also qualitatively agree with the findings of *Seinfeld et al.* [2001] and *Pun and Seigneur* [2007], which predict a positive impact of particle water on SOA formation. In general, the present results disagree with the findings of *Cocker et al.* [2001a, 2001b] and *Edney et al.* [2000], who found no SOA enhancements due to particle water in smog chamber experiments. One explanation for this difference is that heterogeneous chemical reactions could have contributed to the partitioning effect observed in ambient measurements. It is possible that the enhanced particle-phase partitioning associated with water uptake in the current study was a product of additional organic reactions in the particle phase. It is likewise possible that experimental conditions (i.e., high chemical and water purity, scavenging of gas-phase OH, high aerosol loadings, O_3 concentrations, etc.) used in the smog chamber studies were not conducive to heterogeneous reactions.

[19] The strong evidence for a WSOC partitioning dependence on liquid-water suggests a process more consistent with Henry's law-type partitioning of SVOCs to particle-water. Because $WSOC_g$ is expected to be composed mostly of low carbon number oxygenated compounds (e.g., formaldehyde, dicarbonyls, formic and acetic acid, and other small SVOCs), it is possible that most of the increased $WSOC_p$ with RH is due to partitioning of these highly-soluble small compounds. This alone, however, also fails to describe the observations since the liquid water concentrations associated with fine particles are likely too small to simply dissolve the observed WSOC mass partitioned to fine particles. For example, the increased dissolved aerosol mass of a highly soluble and relatively abundant compound (e.g., formic acid at 5 μg m^{-3}) at an RH of 90% (∼35 μg m^{-3} liquid water) compared to that at 40% (∼7 μg m^{-3} liquid water) is ∼10^{-5} μg m^{-3}. Subsequent aqueous phase conversion of dissolved SVOCs leading to further Henry's law partitioning to the particle phase may better account for the observed $WSOC_p$/$WSOC_g$ enhancements. Alternatively, larger $WSOC_g$ species may partition far more than currently thought.

[20] In summary, this study presents a new approach to examine the gas/particle partitioning of ambient SOA where, instead of analyzing individual compounds, the bulk WSOC was examined. Particulate WSOC accounted for, on average, 70% of OC for the entire summer. Thus, in a general sense these results describe the partitioning behavior of a major fraction of total OC. At elevated RH levels, median SOA enhancements ($0.3-0.9$ μg C m^{-3}) were significant in the context of ambient concentrations. The results are also intriguing given that the overall partitioning behavior represents the mass-averaged property of a chemically complex system. The present findings clearly show that aerosol water associated with fine particles significantly impacts the partitioning behavior of organic compounds and may be a major SOA formation route in summertime Atlanta. This mechanism may also be an effective means for producing SOA in other environments and may partly explain the under-prediction of SOA by current models.

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