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Water Absorption by Secondary Organic Aerosol and Its Effect on Inorganic Aerosol Behavior

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The hygroscopic nature of atmospheric aerosol has generally been associated with its inorganic fraction. In this study, a group contribution method is used to predict the water absorption of secondary organic aerosol (SOA). Compared against growth measurements of mixed inorganic−organic particles, this method appears to provide a first-order approximation in predicting SOA water absorption. The growth of common SOA species is predicted to be significantly less than common atmospheric inorganic salts such as $(NH_4)_2SO_4$ and NaCl. Using this group contribution method as a tool in predicting SOA water absorption, an integrated modeling approach is developed combining available SOA and inorganic aerosol models to predict overall aerosol behavior. The effect of SOA on water absorption and nitrate partitioning between the gas and aerosol phases is determined. On average, it appears that SOA accounts for approximately 7% of total aerosol water and increases aerosol nitrate concentrations by approximately 10%. At high relative humidity (≥85%) and low SOA mass fractions (<20% of total $PM_{2.5}$), the role of SOA in nitrate partitioning and its contribution to total aerosol water is negligible. However, the water absorption of SOA appears to be less sensitive to changes in relative humidity than that of inorganic species, and thus at low relative humidity (∼50%) and high SOA mass fraction concentrations (∼30% of total $PM_{2.5}$), SOA is predicted to account for approximately 20% of total aerosol water and a 50% increase in aerosol nitrate concentrations. These findings could improve the results of modeling studies where aerosol nitrate has often been underpredicted.

Introduction

Organic aerosol generally comprises 30−60% of total fine particulate matter (PM) (*1, 2*), and as such has a significant role in the overall behavior of atmospheric aerosols. The hygroscopic nature of atmospheric aerosols, resulting in their growth with increasing relative humidity (rh), is important for the study of visibility, growth, cloud activation, reactivity, and atmospheric lifetime of aerosols. However, the water absorption of atmospheric particles has conventionally been associated with their inorganic fraction; the contribution of organic aerosols has generally been neglected.

The organic fraction of PM in both rural and urban areas is a complex mixture of hundreds of compounds. In analyzing primary and secondary organic aerosol (SOA) products, typically only 15−30% of the product mass can be identified (*3−12*). For these reasons and a lack of direct chemical analyses to differentiate between primary and secondary aerosols, it is difficult to separate contributions of primary versus secondary organic components. However, several indirect methods have been developed to estimate concentrations of both of these components (*13−16*). These studies have shown that SOA concentrations can be as high as 80% of total fine organic mass for periods of high photochemical activity. As such, the contributions of SOA components has received increased attention. Many researchers have examined the gas-aerosol partitioning of SOA and have developed models for its mathematical description (*17−23*). Others have investigated the hygroscopic properties of some organic and mixed inorganic−organic particles. Na et al. (*24*) measured the water activity of supersaturated aqueous organic solutions. Andrews and Larson (*25*) proposed that the deliquescence relative humidity (DRH) of NaCl decreased from 75% to 70−73% when coated with an organic surfactant film. Xiong et al. (*26*) showed that organic monolayer films could retard the growth of H_2SO_4 droplets depending on film thickness. Hameri et al. (*27−28*) measured the growth of mixed inorganic and slightly soluble organic particles and suggested that these organic compounds behaved as totally insoluble compounds. Cruz and Pandis (*29*) measured the growth of mixed inorganic−organic particles and found no detectable differences between the DRH of the mixed particles versus that of the pure inorganic particle. In addition, they determined that in some cases, the organic compound appeared to enhance water absorption of the mixed particles, whereas in other cases, a diminishing effect was observed. Saxena et al. (*30*) also found that organic aerosols appeared to diminish the water uptake of inorganic aerosols at urban locations and enhance inorganic aerosol water absorption at nonurban locations. Finally, Vartiainen et al. (*31, 32*) measured a 2% increase in mass for diesel exhaust particles as rh was increased from 45 to 90% and also found that these particles became more hygroscopic after aging for 9−10 h.

In light of these findings, questions still remain concerning the hygroscopic properties of organic aerosols. The overall contribution of SOA to total aerosol water and its possible effect on the partitioning of semivolatile inorganics between the gas and aerosol phases is still uncertain. In the present study, the water absorption of SOA is estimated based on a group contribution method. With this method, hygroscopic properties of mixed inorganic−organic particles are estimated and compared to measurements by Cruz and Pandis (*29*). In addition, representative SOA species are identified from ambient measurements and smog chamber experiments and are used in formulating an integrated modeling approach. The integrated approach is used to determine the effect of ambient SOA on total water absorption and nitrate partitioning. The possible effect of SOA water absorption on nitrate partitioning is an addition to previous work (*33−35*) where the general underprediction of aerosol nitrate in highly polluted areas by aerosol equilibrium models was investigated. In this analysis, the possible water absorption of primary organic aerosols is not considered as it appears that these species absorb trace amounts of water (*31, 32, 36, 37*) even at high rh (∼90%).

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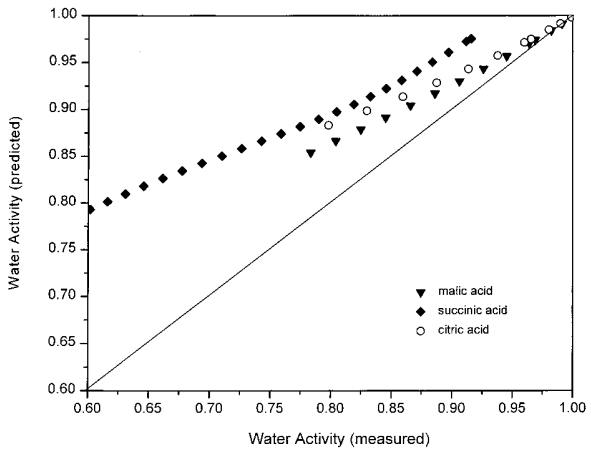

FIGURE 1. Predicted (UNIFAC) versus measured water activity for succinic acid (*24*), malic acid (*48*), and citric acid (*48*).

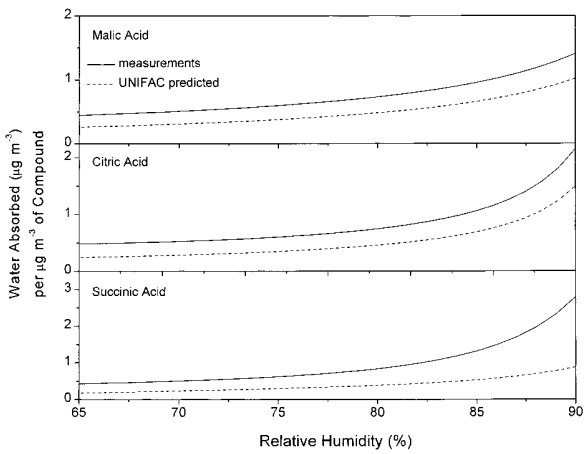

FIGURE 2. Predictions (UNIFAC) for water absorbed (μg m^{-3}) versus those based on measurements for 1 μg m^{-3} of succinic, malic, and citric acids.

Group Contribution Methods

To predict the water absorption by a multicomponent organic solution, water activity data for each component is required. Although the water absorption of common atmospheric inorganic salts (i.e. NH_4NO_3, NaCl, $(NH_4)_2SO_4$) has been characterized and water activity measurements are available (*38*−*40*), similar measurements are scarce for organic compounds; alternate methods must be used to estimate their water activities. This problem has been encountered frequently in industrial applications (process synthesis, biochemical, pharmaceutical) and has motivated the development of group contribution methods. Group contribution methods treat organic compounds as aggregates of different functional groups (i.e. OH, COOH, CH_3) which reduces the complexity in estimating their properties. UNIFAC (UNIquac Functional-group Activity Coefficient), perhaps the most widely used method in industrial applications, was developed by Fredenslund et al. (*41*), and can be used to estimate activity coefficients for components in multicomponent organic mixtures. To use UNIFAC, several parameters are needed for individual functional groups including surface area and volume parameters (Q and R, respectively) and a parameter for the interaction of groups, a_{mn}. These parameters can be obtained from Gmehling et al. (*42*) and undergo continued development and evaluation. A more detailed discussion of UNIFAC can be found in Reid et al. (*43*).

Saxena and Hildemann (*44*) evaluated the performance of UNIFAC against measurements for organic compounds and found that water activities can be estimated to within approximately 15%. In their evaluation of UNIFAC, Saxena included compounds whose presence in the atmospheric particulate phase is unlikely, and therefore, a more atmospherically relevant performance measure of UNIFAC is desired. Although the availability of water activity measurements for organic compounds is limited, measurements are available for three compounds that have been identified as organic aerosols in smog chamber and ambient measurement studies. These include succinic, malic, and citric acids. Na et al. (*24*) measured the water activity of succinic acid which has a structure similar to glutaric and adipic acids; these latter two acids have been identified as SOA by Grosjean and Friedlander (*45*). Malic acid has been identified as a SOA component by Khwaja (*46*) and Sempere et al. (*47*); citric acid was selected since its structure is similar to malic acid. Water activities for malic and citric acids were measured by Carlo (*48*).

Figure 1 shows the performance of UNIFAC (5th revision, *49*) for the aforementioned organic species against measurements for water activity. As seen, a positive bias appears in the predictions of UNIFAC; it overpredicts measurements by as much as 30% in some cases. These results can be used to determine the concentration of water absorbed for each compound (Figure 2). The overprediction of the water activity in Figure 1 results in an overall underprediction of aerosol water as shown in Figure 2. Based on these results, UNIFAC predicts approximately 40% lower concentrations of aerosol water than that based on measurements. Thus, in the following analysis, an uncertainty of 40% in UNIFAC predicted water concentrations for organic compounds will be used throughout all calculations. Although this result is based on an analysis of only three compounds, it nonetheless provides a reasonable estimate of likely uncertainties in using UNIFAC for our purposes.

Predicting Hygroscopic Properties of Mixed Inorganic−Organic Aerosols

The hygroscopic growth of aerosols is often expressed by a growth factor at a specific rh, $G_f(rh)$

$$G_f(rh) = \frac{d_f(rh)}{d_i} \tag{1}$$

where d_i and $d_f(rh)$ are dry and wet (at the given rh) diameters, respectively. d_i is normally measured at a low enough rh (<10%) to minimize the amount of water present in the system so that a virtually dry particle exists. Since the predictive methods here involve mass concentrations and not particle size, $G_f(rh)$ can be calculated by

$$G_f(rh) = \left(\frac{\rho_o W_f}{\rho_f W_o}\right)^{1/3} \tag{2}$$

where ρ_o and ρ_f are dry (rh < 10%) and wet densities, and W_o and W_f are dry (rh < 10%) and wet particle mass, respectively. For predicting $G_f(rh)$ for a mixed inorganic−organic particle, the total water absorbed by the particle at a given rh is required. To estimate the total water absorbed, an additive approach is used where UNIFAC is used to predict the water absorbed by the organic fraction and an inorganic aerosol equilibrium model is used for the inorganic fraction. SEQUILIB (*50*), SCAPE2 (*51*), EQUISOLV II (*52*), GFEMN (*53*), and ISORROPIA (*54*) are available inorganic aerosol equilibrium models which partition semivolatile inorganic components (i.e. NH_4NO_3) between the gas and aerosol phases based on thermodynamic principles; each model also allows calculation of the aerosol water content. Based on its

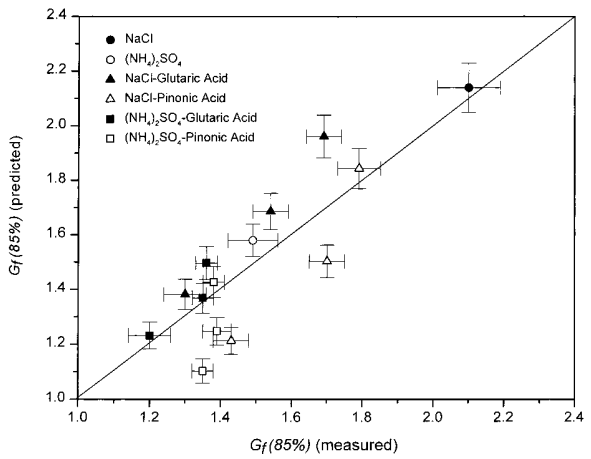

FIGURE 3. Predicted versus measured (29) G_f (*85%*) for mixed inorganic−organic particles.

simplicity and computational structure, SCAPE2 is used in the following analyses. Furthermore, for simulating the water uptake of wet particles, significant differences will not be introduced in using one model versus another (*33*). Ansari and Pandis (*33, 34*) present a detailed comparison of the aforementioned models for the deliquescence and efflorescence branch behavior of inorganic aerosols. ρ_o and ρ_f are estimated based on the volume fraction of each component in the mixed particle and using the inorganic solution density measurements of Tang (*55*).

Figure 3 shows a comparison of $G_f(85\%)$ predicted theoretically versus measurements by Cruz and Pandis (*29*) for mixed particles of different mass fractions of NaCl, $(NH_4)_2SO_4$, glutaric acid, and pinonic acid. For the uncertainty estimates for the predictions, we assume a 5% uncertainty in ρ_o and ρ_f and a 40% uncertainty resulting from using UNIFAC to predict the organic compound water absorption. The water absorption of the inorganic compounds predicted by SCAPE2 is based on fits to binary water activity data of Chan et al. (*39*) and Tang and Munkelwitz (*40*) and is assumed to contribute at most a 5% uncertainty in calculating $G_f(rh)$. Propagating this uncertainty through eq 2 the total uncertainty in $G_f(rh)$ is approximately 5%. This low uncertainty is the result of the cube root in eq 2 and since the UNIFAC predicted organic water absorption (which has the highest uncertainty) is significantly less than the initial particle mass and the inorganic water absorption predicted by SCAPE2. On average, predictions are within 10% of measurements for $G_f(85\%)$. Thus, based on this initial analysis using UNIFAC with eq 2 to predict $G_f(rh)$ for mixed particles, it appears that UNIFAC is a reasonable first approximation for estimating organic water absorption. However, to fully test UNIFAC in this capacity, $G_f(rh)$ and water activities for other atmospherically important organic particles must be measured in future studies.

Hygroscopic Properties of Representative SOA Species

SOA is generally formed via the photooxidation of reactive organic gases (i.e. α-pinene, xylene, ethylbenzene). Given that dozens of different SOA compounds may be produced from the reaction of one reactive organic gas, it is difficult to identify these products and thus model overall SOA behavior. The complexity of understanding this behavior can be reduced if the SOA behavior is approximated by that of "representative" species. For example, in the photooxidation of ethylbenzene, Forstner et al. (*3*) identified 20 different SOA products. If only a few of these products (those having the highest mass concentrations) are used to represent the properties of SOA formed from ethylbenzene, the task of predicting SOA properties is simplified. This approach is used in identifying representative SOA products of common reactive organic gases.

TABLE 1. Identified SOA Products from the Photooxidation of Organic Gases

organic gas precursor	selected major identified SOA compounds	ref
ethylbenzene	methyl maleic anhydride maleic anhydride acetophenone	*(3)*
xylene	methyl maleic anhydride tolualdehyde	*(3)*
1,2,4-trimethylbenzene	methyl maleic anhydride methyl acetophenone	*(3)*
naphthalene	2 formyl cinnamaldehyde nitronaphthalene	*(56)*
methylnaphthalene	methylnitronaphthalene	*(57)*
alkyl phenol	dinitrocresol	*(58)*
phenol	nitrophenol	*(59)*
toluene	methyl maleic anhydride succinic anhydride	*(3)*
cyclohexane	cyclohexanone cyclohexyl nitrate	*(60)*
α- and β-pinene	pinonic acid nopinone pinic acid organonitrate	*(61−63)*
cyclic olefins	adipic acid glutaric acid glutaraldehyde	*(45)*

Table 1 presents the results of selected smog chamber experiments where the photooxidation products of organic gases have been identified. For most of the precursor gases shown in Table 1, the SOA species listed are those having the highest concentrations. It should be noted that in most cases, only 15−30% of the total SOA mass generated in a photooxidation experiment could be identified. The precursor gases shown in Table 1 are assumed to be the primary contributors to SOA formation (*15*). Hence, we assume that the SOA products listed in Table 1 are a representation of the total SOA. Since compounds have been identified to represent total SOA concentrations, UNIFAC and eq 2 can be used to estimate their hygroscopic growth. Table 2 shows predicted $G_f(85\%)$ for the representative SOA species in Table 1. Most of the species have $G_f(85\%) < 1.1$, whereas by comparison, $G_f(85\%)$ of $(NH_4)_2SO_4$ and NaCl are 1.5 and 2.1, respectively. Hence, based on the results presented in Table 2, SOA appear to absorb significantly less water than atmospherically important inorganic components such as $(NH_4)_2SO_4$ and NaCl at high rh (∼85%).

Coupling the Partitioning of Semivolatile Inorganic Aerosols with SOA Formation

With UNIFAC as a tool to predict the water absorption of SOA, a model can be developed to simulate overall aerosol behavior by combining available SOA and inorganic aerosol models. Some of these available models include SOAM (*64*), SOAM2 (*15*) for SOA and GFEMN, SCAPE2, and ISORROPIA for inorganic aerosols. SOAM and SOAM2 simulate the formation, transport, and deposition of SOA and are based on the atmospheric diffusion equation (*65, 66*) and include the SAPRC gas-phase chemical mechanism by Carter (*67*). In addition, SOAM2 assumes that each lumped organic precursor may produce two condensable species (*18, 22*) and uses a pseudoideal solution theory to partition these species between the gas and aerosol phases based on available effective saturation concentrations. Our approach in coupling these two models to predict overall aerosol behavior is (1) use SOAM2 to predict SOA concentration levels, (2) predict the water absorption of the total SOA with UNIFAC, and (3)

TABLE 2. UNIFAC Predicted $G_f(85\%)$ for SOA Species

compound	$G_f(85\%)$	compound	$G_f(85\%)$
methylnitronaphthalene	1.00 ± 0.10	dinitrocresol	1.02 ± 0.10
nitronaphthalene	1.00 ± 0.10	glutaraldehyde	1.03 ± 0.10
methyl acetophenone	1.00 ± 0.10	pinic acid	1.04 ± 0.10
tolaldehyde	1.00 ± 0.10	succinic anydride	1.06 ± 0.11
nopinone	1.00 ± 0.10	dinitrophenol	1.07 ± 0.11
2-formyl cinnamaldehyde	1.00 ± 0.10	methyl maleic anhydride	1.09 ± 0.11
acetophenone	1.00 ± 0.10	adipic acid	1.10 ± 0.11
cyclohexanone	1.00 ± 0.10	glutaric acid	1.13 ± 0.11
cyclohexyl nitrate	1.01 ± 0.10	maleic anydride	1.14 ± 0.11
pinonic acid	1.02 ± 0.10	malic acid	1.23 ± 0.12

TABLE 3. Predicted SOA Product Concentrations and Their Assigned Representative Compounds for Fresno, CA, January 4–6, 1995 (*15*)

reactive organic gases	lumped precursor in SOAM2	SOA product	representative SOA compound	predicted aerosol concn (μg m^{-3})	% of SOA
ethyl-, butyl-, propylbenzenes	AAR5	AEA5	methyl maleic anhydride	0.17	2.8
		AEX5	acetophenone	0.33	
xylenes, 1,2,3- and 1,2,4-TMB[1], naphthalene	AAR6	AEA6	methyl maleic anhydride	1.77	39.7
		AEX6	2-formyl cinnamaldehyde	5.13	
methylnaphthalenes, 1,3,5-TMB[1], tetralin	AAR7	AEA7	methylnitronaphthalene	0.91	16.7
		AEX7	methyl maleic anhydride	2.00	
toluene	TOLU	AETL	methyl maleic anhydride	1.42	24
		AETM	succinic anhydride	2.75	
C5–C7 normal and cycloalkanes	AAR3	AEA3	cyclohexanone	0.37	2.1
C8–C15 normal and cycloalkanes	AAR4	AEA4	N/A	0.85	4.9
α-pinene	APIN	AEAP	pinonic acid	1.26	7.2
β-pinene	BPIN	AEBP	nopinone	0.20	1.1
alkyl phenols	CRES	AECR	dinitrocresol	0.41	2.4
nitrophenols	NPHE	AENP	nitrophenol	0.20	1.1

[1] TMB = trimethylbenzene.

use SCAPE2 with the SOA water absorption as an additional input to simulate inorganic aerosol behavior. For this approach however, all particles are assumed to be liquid; the deliquescence of ambient SOA species and their possible effect on the deliquescence of ambient inorganic components remains uncertain because of limited available experimental data.

Table 3 shows SOAM2 results of Strader et al. (*15*) for SOA speciation for conditions closely matching those occurring during the winter in urban areas in Central California. As seen, maximum concentrations of SOA in this area were predicted to be approximately 18 μg m^{-3}, and the aromatic precursors (AAR5, AAR6, AAR7, TOLU) contributed approximately 75% of the total SOA formation. Since SOAM2 does not explicitly identify the SOA products, the SOA compounds shown in Table 1 are used for the calculation of the properties of the SOA products from SOAM2. For example, for the reaction of lumped precursor AAR7, which includes organic gases methylnaphthalenes, 1,3,5-trimethylbenzene, and tetralin, we assume the SOA products to be methylnitronaphthalene (from methylnaphthalene) and methyl maleic anhydride (from the photooxidation of 1,3,5-trimethylbenzene, Table 1). These SOA products have the highest concentrations based on available smog chamber experiments.

SOA formation is simulated with SOAM2 with the composition distribution shown in Table 3 for conditions based on the IMS95 measurements at Fresno in 1995 (*68*). Since the modeling approach is an additive one with regards to aerosol water, total aerosol water (SOA + inorganics) is always greater than the aerosol water absorbed by the inorganic fraction. Figure 4 shows the resulting aerosol water and aerosol nitrate behavior with the coupled modeling approach with and without SOA water absorption. In Figure 4a, the

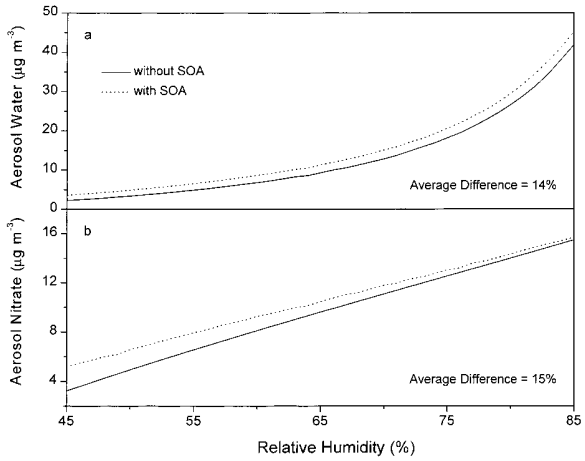

FIGURE 4. Predicted aerosol water and nitrate concentrations (μg m^{-3}) with and without SOA concentrations. Input: temperature = 298 K, total SOA = 15 μg m^{-3}, NH_3^T = 10 μg m^{-3}, HNO_3^T = 20 μg m^{-3}, SO_4 = 2.5 μg m^{-3}.

average increase in aerosol water because of the SOA is approximately 14% over the rh region shown. The SOA contribution (8%) decreases at high rh (85%) as the hygroscopic inorganic fraction absorbs significantly more water than the organic fraction. Conversely, at low rh (45%), the SOA contribution to total aerosol water is higher (22%); the inorganic fraction absorbs significantly less water at low rh than high rh, where for SOA, its water absorption is not as sensitive to changes in rh. At even lower rh (<45%, not shown), the SOA contribution to aerosol water increases significantly. For example, at rh = 25%, the predicted SOA contribution to aerosol water is approximately 42%.

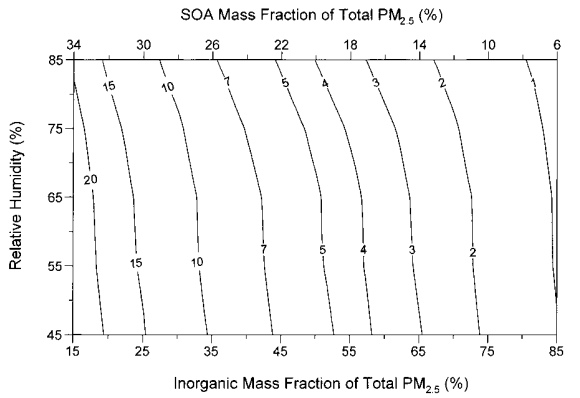

FIGURE 5. Average SOA contribution to total aerosol water (percent by mass) as a function of inorganic mass fraction of $PM_{2.5}$.

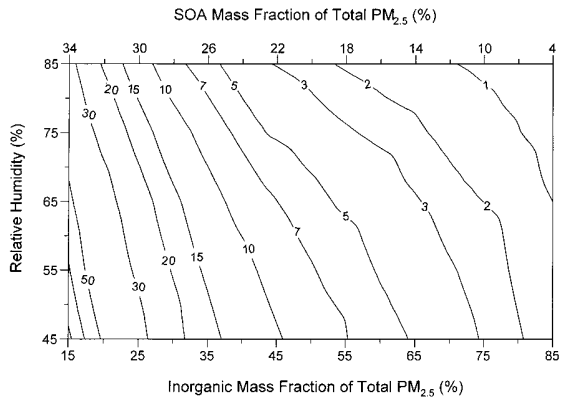

FIGURE 6. Average increase in predicted aerosol nitrate concentration (percent by mass) by including SOA concentrations as a function of inorganic mass fraction of $PM_{2.5}$.

Figure 4b shows the predicted aerosol nitrate concentration as a function of rh with and without the SOA contribution to aerosol water. Since there is more water present in the system because of the SOA contribution, more nitrate is transferred from the gas to the aerosol phase compared to when the SOA contribution to total aerosol water is excluded. The average difference in aerosol nitrate concentrations is approximately 15% with the effect being greater at low rh. The differences are larger at low rh, because in this region, the SOA contribution to aerosol water is 15% higher as shown in the previous paragraph. For rh < 45% (not shown), the SOA contribution to aerosol water results in a significantly higher aerosol nitrate concentration. At rh = 25%, a 50% increase in aerosol nitrate is predicted as a result of the SOA contribution to aerosol water. Since the average SOA contribution to aerosol water is higher in this case, a higher percentage of nitrate will transfer to the aerosol phase. At high rh, the contribution of SOA to aerosol water is significantly less than the inorganic fraction, and therefore the SOA has a smaller effect in transferring nitrate to the aerosol phase.

Average Effect of SOA on Water Absorption and Nitrate Partitioning

The above analysis shows that the water absorbed by SOA can have a significant effect on overall aerosol behavior depending on rh and composition. Therefore, the integrated modeling approach is applied to investigate the average contribution of SOA to the total aerosol water and its effect on nitrate partitioning between the gas and aerosol phases. To perform this analysis, aerosol behavior was simulated for a broad range of $PM_{2.5}$ component (inorganic and primary and secondary organic aerosols, dust) concentrations and for a broad rh range. For this extended analysis, aerosol behavior is simulated with the integrated approach for varying concentrations for H_2SO_4, NH_3, HNO_3, and a remaining particulate matter (RPM) component (1−10, 1−10, 1−20, and 1−20 $\mu g\ m^{-3}$, respectively). This RPM component is assumed to exist as 40% primary organic aerosol, 40% SOA, and the remaining 20% as dust (2, 13). The primary organics and dust are assumed not to absorb water and thus not to have any effect on inorganic aerosol behavior; these components serve as contributors to total $PM_{2.5}$. SOA composition for RPM was kept constant for all simulations (see Table 3), temperature was kept constant at 298 K, and 45−85% was used for the rh range. The concentration ranges mentioned span a large composition space, including a wide inorganic aerosol space of varying NH_4NO_3 and $(NH_4)_2SO_4$ concentrations, and hence can provide valuable information for areas with differing concentrations of $PM_{2.5}$. Figure 5 shows the average SOA contribution to aerosol water for the resulting simulations as a function of rh and inorganic and SOA mass fractions of total $PM_{2.5}$. For these simulations, total $PM_{2.5}$ includes ammonium, nitrate, sulfate, and RPM components. As expected, the contribution of SOA to aerosol water is highest at high SOA mass fractions (low inorganic mass fractions). In these regions, there are low concentrations of inorganic components and high concentrations of SOA. Thus, despite being less hygroscopic than inorganic components, the SOA contribution to aerosol water can be as high as 15−20% for areas where the aerosol mass is dominated by SOA. Conversely, at high inorganic mass fractions, the SOA contribution to aerosol water is significantly less (<5%). In these cases, since the inorganic components are dominant and significantly more hygroscopic than the SOA, there is little SOA contribution to total aerosol water. As rh decreases, the SOA contribution increases as described in the previous section. For typical U.S. conditions, where 40−45% of the total $PM_{2.5}$ concentration consists of inorganics (2), the SOA contribution to aerosol water is approximately 7% based on Figure 5. Although not shown, for cases where SOA and inorganics are the dominant components of $PM_{2.5}$, the SOA contribution to aerosol water is higher, approximately 10−15% assuming a 50:50 wt % mixture of SOA and inorganics.

Figure 6 shows the average difference in predicted aerosol nitrate concentrations when coupling SOA and inorganic aerosol behavior. At low inorganic mass fractions (high SOA concentrations), SOA may account for as much as a 30−50% increase in aerosol nitrate. In this region, SOA increases the aerosol water concentrations by 15−20% based on Figure 5. This increase in aerosol water causes a significant amount of nitric acid in the gas phase to transfer to the aerosol phase. At high inorganic mass fractions, there is a minor SOA contribution to aerosol water (<5%), and, therefore, this additional water does not cause the transfer of a significant amount of nitrate to the aerosol phase. As rh increases at a given concentration, the net effect of SOA on nitrate partitioning decreases. At higher rh (>65%), the inorganic fraction absorbs more water than the organic fraction, and thus the effect of SOA in transferring nitrate to the aerosol phase decreases. For typical U.S. conditions as describe above (40−45% inorganic mass fraction of $PM_{2.5}$), there is approximately a 10% increase in aerosol nitrate predicted with the coupled model. For a 50:50 (percent by weight) mixture of SOA and inorganics, the increase in aerosol nitrate is higher, 15% (not shown).

Discussion

Based on the limited results presented here, it appears that the contribution of SOA to total aerosol water and its role in the transfer of nitrate from the gas to the aerosol phase is

negligible at high rh (≥85%) and low SOA mass fractions (<20% of total $PM_{2.5}$). However, at low rh (~50%) and high SOA mass fractions (>20% of total $PM_{2.5}$), the role of SOA in total aerosol water and in the transfer of nitrate to the aerosol phase is significant as shown in Figures 5 and 6; these results suggest that the water absorption of SOA species are not as sensitive to changes in rh as that of inorganic species.

Nonetheless, given the possible weaknesses of the integrated modeling method, the results presented here serve as a first-order approximation. In the analysis, it was assumed that the organic compounds do not change the thermodynamics (i.e. activity coefficients) of the inorganic components. With little information concerning the identity of SOA compounds and their subsequent properties, accurately predicting the thermodynamics of SOA and its possible effects on the thermodynamics of inorganic components is difficult.

The preceding analysis was based on an additive approach in predicting the total aerosol water concentrations of SOA and inorganic aerosols; total aerosol water (SOA and inorganics) will thus be higher than that from inorganic aerosols. However, Saxena et al. (30) observed that for an urban location, organic aerosols appeared to diminish inorganic water uptake. In this case, the organic material may act as a film retarding the transfer of water to the particle. Furthermore, the organic components may have altered the thermodynamics of the inorganic components thus causing a lower content of aerosol water. Cruz and Pandis (29) observed a similar effect in their growth studies of mixed inorganic−organic particles.

Moreover, in the preceding analysis, all particles were assumed to be wet (efflorescence branch of aerosol behavior). Without knowing the deliquescence behavior of SOA species and its possible effect on the deliquescence behavior of inorganic components, it is difficult to include the deliquescence branch behavior of aerosols in this analysis. For cases where models predict crystalline inorganic species at low rh, the predicted effect of SOA on total aerosol water content and nitrate partitioning would be more profound than the results presented here.

The effect of primary organic aerosols on total aerosol water uptake was not considered in this analysis. In the case of diesel trucks, Vartiainen et al. (31, 32) observed that weights of emitted diesel soot particles increased by less than 2% over rh of 45−90% and that these particles became slightly more hygroscopic after an aging period of 9−10 h; Weingartner et al. (36, 37) observed similar properties for carbon and diesel soot particles. Li et al. (69−71) and Dua et al. (72) studied the hygroscopic properties at rh > 99% for some indoor primary aerosols, but the rh ranges in their study are normally not encountered in the atmosphere, and most of the primary aerosols they analyzed are generally not present in significant atmospheric concentrations.

Much of the analysis in this study focused on the effect of SOA water absorption on the partitioning of nitrate for $PM_{2.5}$. In these cases, nitrate is generally present as volatile NH_4NO_3 (1). However, for PM_{10} which includes coarse nitrate, nitrate is also present in compounds with significantly less volatility than NH_4NO_3 (i.e. $NaNO_3$, $(CaNO_3)_2$, KNO_3). Because of the difficulty in separating volatile and nonvolatile nitrate in PM_{10}, the analysis presented here is for $PM_{2.5}$ where most of the nitrate is present as NH_4NO_3. Even so, in the coarse mode, the effect of the little coarse SOA water absorption on nitrate partitioning is most probably negligible.

Based on the modeling approach presented in this study, it appears that SOA enhances not only the water absorption of aerosols but also the transfer of nitrate from the gas to the aerosol phase. In previous studies (34, 35), aerosol equilibrium models tended to underpredict aerosol nitrate in polluted areas by approximately 30%. The dynamics of aerosol behavior may explain part of the general underprediction of aerosol nitrate concentrations. Given the results of this study, the inclusion of SOA species in modeling aerosol behavior may also explain a portion of the error in predicting aerosol nitrate. For downtown Los Angeles, where the inorganic mass fraction is approximately 40% of the total $PM_{2.5}$ (1), a 10% increase in aerosol nitrate concentration is predicted based on the results of this study. These results implicate the importance of including the water absorption of SOA and its effect on nitrate partitioning in modeling studies.

Finally, based on the results shown, it appears that UNIFAC provides a first-order approximation in estimating the hygroscopic properties of organic aerosols. Additional measurements of water activities of organic compounds are necessary to fully evaluate the utility of UNIFAC in predicting hygroscopic properties of atmospherically relevant organic components.

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