

Hygroscopic Organic Aerosols during BRAVO?

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ABSTRACT

The hygroscopic properties of the organic fraction of aerosols are poorly understood. The ability of organic aerosols to absorb water as a function of relative humidity (RH) was examined using data collected during the 1999 Big Bend Regional Aerosol and Visibility Observational Study (BRAVO). (On average, organics accounted for 22% of fine particulate matter with an aerodynamic diameter less than 2.5 μm ($\text{PM}_{2.5}$) mass). Hourly RH exceeded 80% only 3.5% of the time and averaged 44%. BRAVO aerosol chemical composition and dry particle size distributions were used to estimate $\text{PM}_{2.5}$ light scattering (Bsp) at low and high ambient RH. Liquid water growth associated with inorganic species was sufficient to account for measured Bsp for RH between 70 and 95%.

IMPLICATIONS

Atmospheric aerosols reduce visibility and affect climate through their radiative and cloud nucleating properties. The ability of organic aerosols to absorb water as a function of RH (hygroscopicity) would enhance all of these effects. The results of analysis of the BRAVO data suggest that organic aerosols during the study period were not hygroscopic. Some previous studies support this result, while others do not. BRAVO may not be representative because conditions during the study were very dry and organics accounted for only ~20% of the $\text{PM}_{2.5}$ aerosol during BRAVO. All of this implies that organic aerosol hygroscopicity remains an active area of research.

INTRODUCTION

Organic carbon (OC) is a significant fraction of the aerosol in urban and remote locations.¹⁻³ However, only 20% or less of the total and water-soluble organic fraction has been specifically identified.⁴⁻⁶ New analytical approaches reduce the scope of the problem by classifying a myriad of unidentified water-soluble organic compounds into smaller groups of characteristic functionality (e.g., neutral, mono- and di-acids, and polyacids) or molecular weight.⁷⁻⁹ This may provide a more manageable framework for characterizing the physical and chemical properties of organics in mixed aerosols.

Theoretical and laboratory analysis suggests that organics could affect the hygroscopic behavior of mixed inorganic and organic aerosols. Ansari and Pandis¹⁰ used integrated inorganic and organic water growth models to estimate the effects of secondary organic aerosols (SOA) on water uptake by sodium chloride (NaCl) and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) particles. They concluded that at low relative humidity (RH) (~50%) and high SOA mass fractions (~30%), SOA accounted for 20% of the aerosol water. In this case, they assumed that inorganic and organic constituents behaved independently. Ming and Russell¹¹ combined thermodynamic models for inorganic and organic species to estimate the effects of organics on water uptake by sea salt aerosols. Their approach considered interactions between organic and inorganic solutes and water. They concluded that sea salt comprising 30% organic species would absorb 15% less water under equilibrium conditions at RH >50% than would purely inorganic sea salt. Cruz and Pandis¹² performed laboratory

experiments on mixtures of NaCl, $(\text{NH}_4)_2\text{SO}_4$, and glutaric and pinonic acids. They found that the deliquescence RHs of the inorganic salts were unaffected by the presence of organics at any organic mass fraction. They concluded that within the uncertainty of their analysis, water uptake by inorganic-organic mixtures can be predicted from the growth characteristics of the pure compounds and their respective mass fractions. However, their results also suggest that water uptake by the inorganic salts is diminished or enhanced at low and high organic mass fractions, respectively.

Prezzi et al.¹³ examined the sub- and supersaturated hygroscopic properties of dicarboxylic acids (oxalic, malonic, succinic, glutaric, and adipic) in the laboratory. Malonic and glutaric acid particles exhibited strong hygroscopic growth at high subsaturated RH, and all compounds except adipic acid were efficient cloud condensation nuclei (CCN). Hansson et al.¹⁴ found that mixtures of NaCl and tetracosane, octanoic, and lauric acids exhibited slightly lower deliquescence RH and smaller growth factors at 85% RH than did pure NaCl particles. Facchini et al.¹⁵ measured large decreases in aerosol droplet surface tension as a function of dissolved OC concentration. They concluded that this effect could increase the number of droplets activated in clouds, leading to a potentially significant increase in stratus cloud albedo.

Empirical evidence for the role of organics in water uptake by ambient aerosols is mixed. While dicarboxylic acids may affect the hygroscopic properties of laboratory aerosols, they generally represent a very small fraction of soluble material in ambient aerosols and cloud water.^{4,16} Novakov and Penner¹⁷ could not account for the observed cloud droplet number concentration in the marine environment without considering both inorganic and organic aerosol mass. Organics inhibited aerosol liquid water growth in urban Los Angeles by 25–35% but contributed significantly (25–40%) to water growth at a remote location in the Grand Canyon.¹⁸

Dick et al.¹⁹ measured water uptake as a function of RH using a TDMA (tandem differential mobility analyzer) and reported significant water uptake by organics during the Southeastern Aerosol and Visibility Study (SEAVS). Conversely, Hand et al.²⁰ estimated aerosol water content from dry and ambient size distribution measurements and concluded that sulfate (SO_4^{2-}) compounds could account for all of the observed water growth during SEAVS. Malm et al.^{21,22} concluded that the difference between dried and humidified fine particles with aerodynamic diameters less than $2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) light scattering (Bsp) measurements as a function of RH could be accounted for by inorganic water growth during SEAVS.

Speer et al.²³ measured water uptake by $\text{PM}_{2.5}$ on Teflon filters from Research Triangle Park, NC, by beta

attenuation in a humidity-controlled chamber. RH was increased from 4 to 94% in 5% increments and then decreased similarly to 12%. Hysteresis was observed in most cases. Water associated with inorganic SO_4^{2-} and nitrate (NO_3^-) estimated with the Aerosol Inorganics Model (AIM)²⁴ accounted for ~80%, on average, of the measured water mass. Speer et al. concluded that the “residual water” was associated with organics. The amount of water per unit mass of organics was approximately half of that associated with $(\text{NH}_4)_2\text{SO}_4$ (at unit mass) at 60 and 80% RH.

The Big Bend Regional Aerosol and Visibility Observational Study (BRAVO) was conducted during the summer and fall of 1999 under the sponsorship of the U.S. Environmental Protection Agency (EPA), the National Park Service, the Texas Natural Resources Conservation Commission, and EPRI to elucidate the sources of haze in Big Bend National Park (BBNP) in southwest Texas.²⁵ The study included monitoring of aerosols, sulfur dioxide (SO_2), and haze at sites throughout Texas, and tracer releases, modeling, and intensive sampling in BBNP.^{26,27} Using methods similar to those of Malm et al.,^{21,22} Malm et al.²⁸ concluded that water uptake by organic aerosols during BRAVO was not significant. While there is reason to believe that organics alter the hygroscopic behavior of ambient aerosols, such effects must be demonstrated in the field and reconciled with theory and laboratory studies. In this paper, aerosol size distribution, chemical composition, and light scattering measurements are used to examine the hygroscopic properties of the BRAVO aerosol.

METHODS

The BRAVO study was conducted between July 1 and October 31, 1999. The data used in this study were obtained at the K-Bar Ranch site in BBNP. The data, which are available on the BRAVO Web site maintained by the Desert Research Institute, have undergone Level 1 validation.²⁹ Hourly-averaged dry particle sizes were measured with a TSI differential mobility analyzer (DMA), a PMS LASAIR optical particle counter (OPC), and a TSI aerodynamic particle sizer (APS) in 21, 7, and 39 channels whose nominal midpoints ranged from 54 to 858, 100 to 2000, and 1241 to 20,535 nm, respectively, preceded by a diffusion or heating dryer. The BRAVO particle size measurements are described in detail elsewhere.^{30–32}

$\text{PM}_{2.5}$, ion (SO_4^{2-} , NO_3^- , chloride [Cl^-], ammonium [NH_4^+]), element, and organic and elemental carbon (OC and EC) concentrations were measured on a daily basis with IMPROVE samplers.^{2,33} Size-resolved ion (calcium [Ca^{2+}], Cl^- , potassium [K^+], magnesium [Mg^{2+}], sodium [Na^+], NH_4^+ , NO_3^- , SO_4^{2-}) concentrations were also measured daily with MOUDI (Micro Orifice Uniform

Deposit Impactor) samplers. Ambient Bsp for the fine fraction was measured with an Optec NGN-2 nephelometer preceded by a Bendix-240 PM_{2.5} size-selective inlet. Temperature and RH were measured continuously.

Our approach for evaluating organic hygroscopicity is analogous to those used previously.^{20–22,28} In this case, measured Bsp is used as an index and Bsp is estimated from the dry particle size distributions with Mie theory, allowing for water uptake by inorganic compounds only. A systematic underestimation of Bsp at elevated humidity would provide evidence for water uptake by organics.

To estimate Bsp from the dry particle size distributions, assumptions about the chemical composition of the particles as a function of size must be made to derive the particle refractive index (RI) and its water content at ambient RH. These parameters were estimated assuming that all hourly particle size distributions during a 24-hr period were characterized by the IMPROVE sample concentrations and corresponding MOUDI size distributions on that day. Because EC and OC size distributions were not measured, it was assumed that their size distributions were the same as that of SO₄²⁻. This assumption may not be realistic for OC, whose size distribution has been found to be multimodal in rural locations.^{34,35} To evaluate the impact of the OC size distribution, we also assumed that the OC size distribution was bimodal lognormal with the OC mass distributed equally between two modes, with geometric mean diameters of 0.3 and 0.8 μm and geometric standard deviations of 1.5.

Concentrations of (NH₄)₂SO₄, ammonium bisulfate (NH₄HSO₄), and sulfuric acid (H₂SO₄) were estimated by balancing the IMPROVE NH₄⁺ and SO₄²⁻ molar abundances, segregated by size according to their corresponding MOUDI size distributions. For simplicity, we have not considered letovicite ((NH₄)₃H(SO₄)₂), which is less acidic than NH₄HSO₄.

The nominal OPC channel diameters represent the manufacturer's calibration with polystyrene latex spheres with an RI of 1.59. Hand and Kreidenweis³¹ presented data for calibrating the OPC as a function of RI. The OPC channel diameters were adjusted using these data along with volume-averaged indices of refraction calculated from the average IMPROVE and MOUDI chemical composition over the OPC size range. The APS channel diameters were converted from aerodynamic to Stokes (geometric) diameters using the volume-averaged densities calculated from the average IMPROVE and MOUDI chemical composition over the APS size range.

Water was added to the dry particles as a function of RH using experimentally derived water activity data for (NH₄)₂SO₄, NH₄HSO₄, H₂SO₄, and sodium nitrate (NaNO₃).^{36,37} The water activity values for these inorganic compounds were taken directly from the SCAPE2

gas-aerosol equilibrium model code.³⁸ These data represent the hysteresis branches of the growth curves for (NH₄)₂SO₄ and NH₄HSO₄. It was assumed that these salt solutions were supersaturated below their deliquescence RHs (80 and 40%, respectively). Day et al.³⁹ and Malm et al.²⁸ found little evidence for deliquescence during SEAVS or BRAVO, respectively.

To evaluate the potential effects of organic water uptake, we used water activity data for hygroscopic organic acids determined experimentally by Peng et al.⁴⁰ They presented a generalized relationship between aerosol growth ($D_{rh(i)}/D_{dry}$, the ratio of particle diameter (D) at $rh(i)$ to the dry diameter) for several compounds of atmospheric interest, malonic, citric, malic, and tartaric acids, which behaved similarly.

$$D_{rh(i)}/D_{dry} = (1 - RH/100)^{-0.163} \quad (1)$$

Water was added to the dry components as a function of RH according to the ZSR (Zdanovskii-Stokes-Robinson) assumption, where the water associated with a component in a mixture at a given RH is assumed to be the same as it would be in a binary water solution at the same RH.⁴¹

The liquid water content of the aerosol is thus

$$W = \sum M_i/m_{i0}(a_w) \quad (2)$$

where M_i is the molar concentration of species i in a multicomponent aerosol (mol/m³), W is the mass concentration of aerosol liquid water (kg/m³), and $m_{i0}(a_w)$ is the molality of a water solution of species i at the water activity a_w (equivalent to the RH) of the multicomponent solution.³⁸ This simple mixing model assumes additivity and does not attempt to account for solute (inorganic or organic) interactions. It has been used in numerous applications and thermodynamic equilibrium models.^{19,23,42,43}

Bsp was calculated with Mie theory using code developed by Barber and Hill⁴⁴ for homogeneous spheres. Data from all three sizing instruments were combined as follows: (1) DMA: 54–290 nm (14 channels); (2) OPC: 326–1120 nm (4 channels); and (3) APS: 1148–1725 nm (6 channels). All chemical components were assumed to be internally mixed. Volume-averaged indices of refraction were calculated by channel for each hourly particle size distribution based on the chemical composition of the corresponding 24-hr IMPROVE and MOUDI samples. The refractive indices and densities of the individual chemical components are listed in Table 1. Estimated Bsp is the sum over all size bins of the product of the scattering cross section calculated at 550 nm (the wavelength used in the

Table 1. RI and density of components used for Bsp estimation.

Species	RI	Density (g/cm ⁻³)
(NH ₄) ₂ SO ₄	1.521 ⁴⁶	1.77 ⁴⁹
NH ₄ HSO ₄	1.473 ⁴⁶	1.78 ⁴⁹
H ₂ SO ₄	1.426 ⁴⁶	1.84 ⁴⁹
NaNO ₃	1.59 ⁴⁷	2.261 ⁴⁹
OCM	1.55 ⁴⁸	1.2 ⁴⁸
EC	1.96, i0.66 ⁴⁶	1.7 ⁴⁸
Soil dust	1.56, i0.005 ⁴⁶	2.3 ⁴⁸
Water	1.33 ⁴⁶	1 ⁴⁹

NGN-2 nephelometer) of particles with diameters equal to the bin midpoints and the number of particles in the bin.

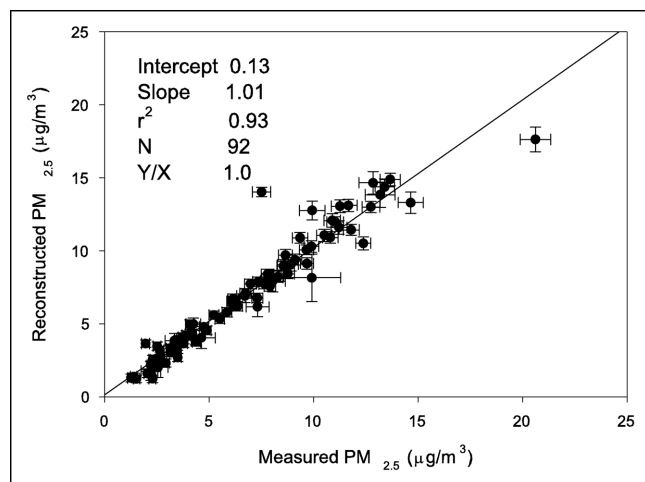
RESULTS AND DISCUSSION

Chemical Composition

Figure 1 compares measured and reconstructed PM_{2.5} mass. The reconstructed mass is estimated as the sum of the major chemical components: NH₄⁺, SO₄²⁻, NO₃⁻, organic compound mass (OCM), EC, and soil dust. The ratio of OCM to OC is assumed to be 1.4, and the mass of soil dust is estimated from the sum of the oxides of the major crustal elements:^{2,33}

$$\begin{aligned} \text{Soil} = & 2.2 \times \text{Al} + 2.49 \times \text{Si} + 1.63 \times \text{Ca} \\ & + 2.42 \times \text{Fe} + 1.94 \times \text{Ti} \end{aligned} \quad (3)$$

Figure 1 demonstrates that the chemical measurements were consistent with PM_{2.5} mass during BRAVO. Table 2 gives the average IMPROVE chemical concentrations and composition as a percent of measured mass. The BRAVO aerosol was dominated by ammoniated SO₄²⁻, OCM, and

**Figure 1.** Reconstructed vs. 24-hr average IMPROVE PM_{2.5} mass with measurement errors shown.**Table 2.** Average BRAVO concentrations and composition as percentage of PM_{2.5} mass (± standard deviation).

Species	Concentration (ng/m ³)	Composition (%)
SO ₄ ²⁻	2919 ± 2049 ^a	43 ± 11
NH ₄ ⁺	948 ± 631	14.1 ± 3.6
NO ₃ ⁻	191 ± 108	3.6 ± 2.6
OCM ^a	1267 ± 798	22 ± 11
EC	160 ± 112	2.8 ± 1.7
Na ⁺	77 ± 57	1.44 ± 1.5
Cl ⁻	6.6 ± 15.6	0.18 ± 0.45
Soil dust	999 ± 1358	14.6 ± 12.7

^aOCM = 1.4 × OC concentration.^{2,33}

soil dust, and the percentage of SO₄²⁻ and NH₄⁺ was relatively constant over time.

On average, 60, 39, and 1% of the IMPROVE SO₄²⁻ were present as (NH₄)₂SO₄, NH₄HSO₄, and H₂SO₄, respectively. Chloride (Cl⁻) concentrations were very low (Table 2) and it was depleted with respect to its seawater ratio to Na⁺ (1.8) by factors of 8–21 based on the respective average MOUDI and IMPROVE concentrations. Because Na⁺ and NO₃⁻ were nearly equimolar (see Table 2, molar ratio = 0.92), we assumed that all of the NO₃⁻ was present as NaNO₃ and ignored small amounts of NaCl and sodium sulfate (Na₂SO₄) that may have been associated with excess Na⁺.

The MOUDI species concentrations were each normalized to their totals over all stages, converted to percentages, and inverted using Twomey's iterative least-squares algorithm.⁴⁵ Average size distributions for SO₄²⁻, NH₄⁺, NO₃⁻, Na⁺, Cl⁻, and Ca²⁺ calculated from 41 daily MOUDI samples collected from July 2 to October 29, 1999, are presented in Figure 2. Note that the SO₄²⁻ and NH₄⁺ distributions are nearly identical and very narrow, indicating that they were relatively constant over time. The averages of the geometric mean diameters and geometric standard deviations of the SO₄²⁻ mass distributions are 0.53 ± 0.08 and 2 ± 0.4, respectively. The NO₃⁻, Na⁺, Cl⁻, and Ca²⁺ distributions were bimodal with most of the mass in the coarse mode. It was assumed that the soil size distribution was the same as that of Ca²⁺. As described previously, Figure 2 also displays a bimodal lognormal OC distribution with geometric means of 0.3 and 0.8 µm and geometric standard deviations of 1.5.

Estimated Light Scattering

To evaluate the chemical contributions to water growth at elevated humidity using Bsp as an index, we must be able to precisely estimate Bsp under relatively dry conditions, where little liquid water is present. During BRAVO, the average hourly RH was 44%. The RH was less than 50% for

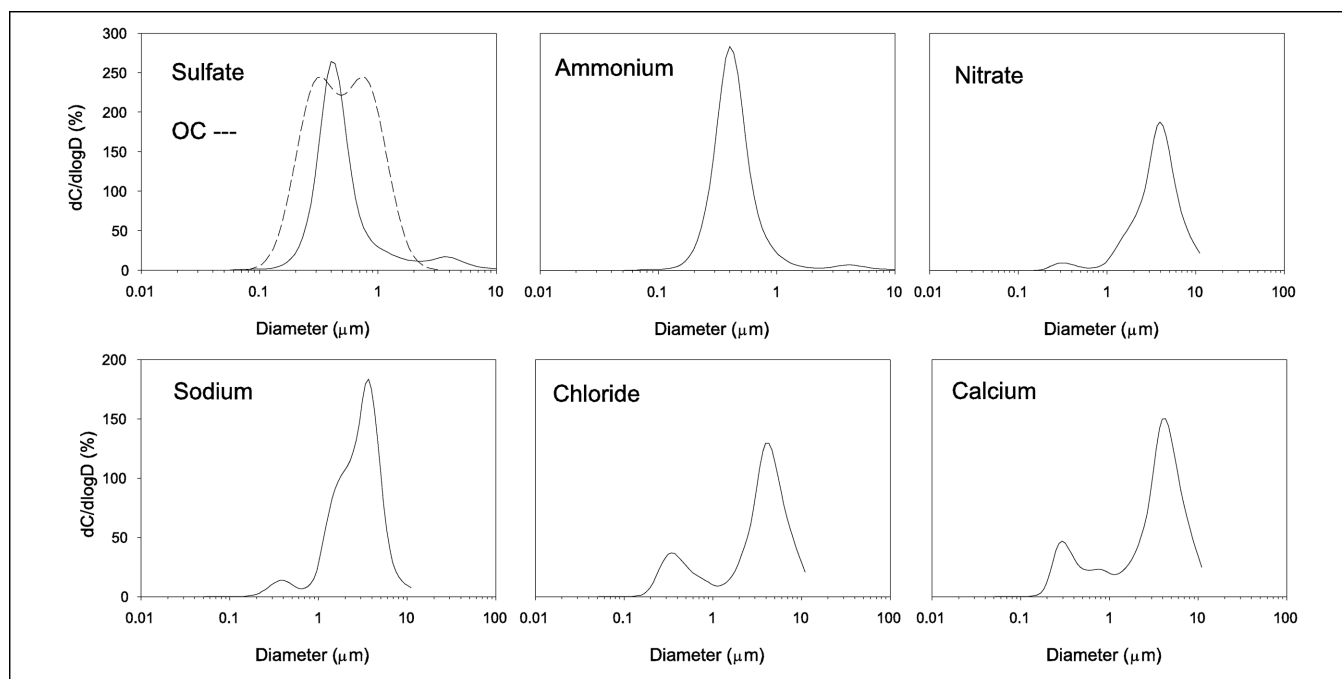


Figure 2. Average (%) MOUDI size distributions during BRAVO, where C is species concentration and D is particle diameter.

two-thirds of the study period and greater than 80% only 3% of the time. Figure 3a compares measured fine Bsp and Bsp estimated for 145 hourly particle size distributions with $RH < 30\%$. Liquid water was added to the particles according to eq 2. While there was a systematic overprediction of $\sim 13\%$, the precision was very high ($r^2 = 0.98$), suggesting that the “dry” case can be used as a baseline from which to evaluate OC water uptake at higher RH.

Bsp was then estimated for 42 cases where the average hourly RH was greater than 70 but less than 95%. The results, shown in Figure 3b as solid circles, are similar to those for the dry case. Excluding six consecutive hourly data points (September 14, 1999, 1:00–7:00 a.m., circled in Figure 3b), the slopes in Figures 3a (1.13) and 3b (1.15) are nearly identical. Including these points raises the “wet” slope to 1.34. Overestimation in these cases may be related to the presence of relatively more insoluble material during this period than in the 24-hr average composition used to model their hygroscopic behavior. In any case, these results suggest that water uptake by inorganic compounds was sufficient to account for Bsp at $RH > 70\%$.

Given that OC accounted for only 22% of $PM_{2.5}$ mass, on average, would OC water uptake be discernable even if it occurred? To address this, we assumed that all of the OC was hygroscopic and followed the growth curve determined by Peng et al.⁴⁰ for several hygroscopic organic acids, as described previously. This function of RH is not as steep as those of the inorganic compounds considered here. Eq 1 suggests a D_{90}/D_0 of 1.46 for OC compared with 1.74 for ammonium sulfate.³⁶ The enhancement of

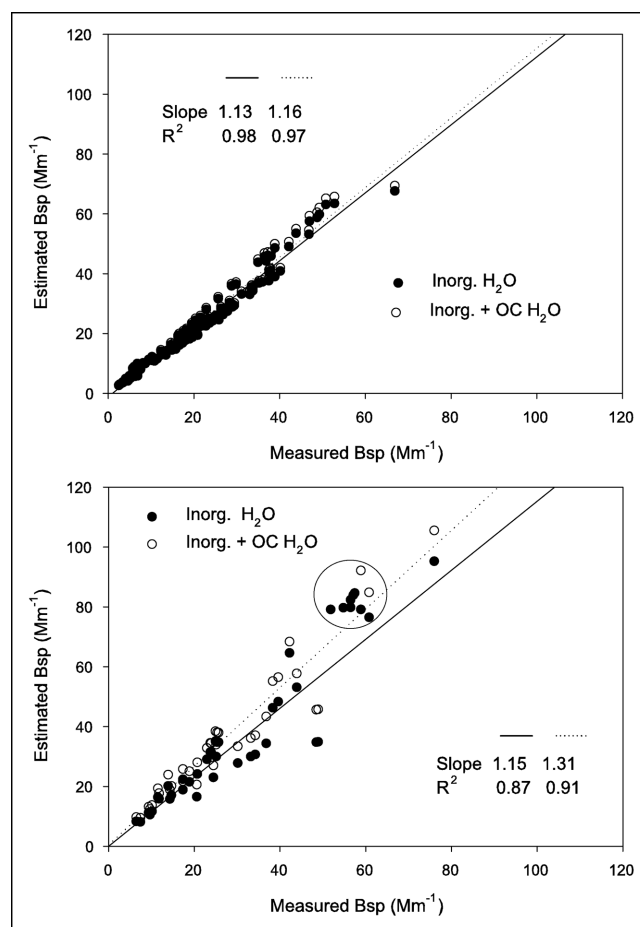


Figure 3. Measured and estimated Bsp: (a) for 145 hourly size distributions with $RH < 30\%$ and (b) for 42 hourly size distributions with $70 \leq RH \leq 95\%$. The open circles in (b) represent Bsp estimated assuming water growth by organics as described in the text.

Bsp caused by OC water uptake is shown as open circles in Figures 3a and 3b. Under near-dry conditions, the effect is negligible (Figure 3a). However, for RH >70% (Figure 3b), the effect is clearly larger as the slope of estimated on measured Bsp increases from 1.15 to 1.31. Including the six circled points raises the slope with OC water from 1.31 to 1.45. The simplest interpretation of these results is that organics during BRAVO were not very hygroscopic. It is possible that the estimation of inorganic water uptake using the ZSR relationship and literature-based water activities was high-biased. An alternative explanation, that organics absorbed some water but suppressed inorganic water uptake, is plausible but not provable with these data.

By assuming that the OC and SO_4^{2-} size distributions were the same, the contribution of OC to scattering under dry and wet conditions is maximized with respect to sulfate. To evaluate the sensitivity of the results to the assumption that OC and SO_4^{2-} shared the same size distribution, Bsp was recalculated assuming the bimodal log-normal OC size distribution described previously and shown in Figure 2. The results are virtually indistinguishable from those shown in Figure 3. For example, the dry and wet slopes changed from 1.13 and 1.15 (Figures 3a and 3b, respectively) to 1.12 and 1.15, respectively, when the bimodal lognormal distribution was used for OC.

CONCLUSIONS

Water uptake by organic aerosols was examined using aerosol chemical composition, particle size distribution, and $\text{PM}_{2.5}$ light scattering measurements measured during the BRAVO study. OC comprised ~20% of $\text{PM}_{2.5}$ mass during BRAVO. Bsp under dry conditions (RH <30%) was estimated precisely from the measured particle size distributions, providing a "baseline" for evaluating water uptake by organic aerosols under more humid conditions. Based on a simple mixing model (ZSR), water growth associated with inorganic salts was sufficient to account for measured $\text{PM}_{2.5}$ Bsp at an RH between 70 and 95%. Assuming that BRAVO OC behaved similarly to hygroscopic organic acids in the laboratory resulted in a relative overprediction of 15% in Bsp. While these results support those of Malm et al.²⁸ for BRAVO, the hygroscopic behavior of organics in mixed aerosols is a complex issue that must be evaluated with additional theoretical, laboratory, and field studies.

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