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Hygroscopic growth of water soluble organic carbon isolated from atmospheric aerosol collected at U.S. national parks and Storm Peak Laboratory

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Abstract. Due to the atmospheric abundance and chemical complexity of Water Soluble Organic Carbon (WSOC), its contribution to the hydration behavior of atmospheric aerosol is both significant and difficult to assess. For the present study, the hygroscopicity and CCN activity of isolated atmospheric WSOC particulate matter was measured without the compounding effects of common, soluble inorganic aerosol constituents. WSOC was extracted with high purity water from daily high-volume PM2.5 filter samples and separated from water soluble inorganic constituents using solid phase extraction. The WSOC filter extracts were concentrated and combined to provide sufficient mass for continuous generation of the WSOC-only aerosol over the combined measurement time of the tandem differential mobility analyzer and coupled scanning mobility particle sizer / CCN counter used for the analysis. Aerosol samples were taken at Great Smoky Mountains National Park during the summer of 2006 and fall-winter of 2007–08; Mount Rainier National Park during the summer of 2009; Storm Peak Laboratory (SPL) near Steamboat Springs, Colorado, during the summer of 2010; and Acadia National Park during the summer of 2011. Across all sampling locations and seasons, the hygroscopic growth of WSOC samples at 90% RH, expressed in terms of the hygroscopicity parameter, "kappa," ranged from 0.05 – 0.15. Comparisons between the hygroscopicity of WSOC and that of samples containing all soluble materials extracted from the filters implied a significant modification of the hydration behavior of inorganic components, including decreased hysteresis separating efflorescence and deliquescence and enhanced dissolution between 40 and 80% RH.

Keywords: aerosol, organic aerosol, ambient aerosol, hygroscopic growth, hygroscopicity, cloud condensation nuclei, visibility, aerosol hydration, TDMA, WSOC, CCN

1 Introduction

Interactions with atmospheric water are central to the major impacts of aerosols on human health (Vu et al., 2015), climate (IPCC, 2014) and visibility (Malm and Pitchford, 1997). The tendency of an aerosol to take up water in sub-saturated conditions—its hygroscopicity—directly affects its impact on climate and visibility by modifying the efficiency with which it scatters and absorbs radiation (Tang, 1996). Moreover, the presence of an aqueous phase in an aerosol affects its aging in the atmosphere, generally increasing the uptake of reactive and soluble trace gases and enhancing aerosol growth (Herrmann et al., 2015; Carlton and Turpin, 2013), significantly impacting all of its atmospheric roles. Likewise, atmospheric aerosols play a critical role in earth's climate as cloud condensation nuclei (CCN) (IPCC, 2014), while cloud processing, in turn, may dramatically modify the size distribution and chemical composition of aerosols (Herrmann et al., 2015).

Water soluble organic carbon (WSOC) is well-known to constitute a major fraction of atmospheric aerosols. Measurements at various locations and seasons, including the measurements associated with this report, have shown WSOC to constitute 20-90% of the total aerosol organic carbon (OC) (Du et al., 2014; Lowenthal et al., 2014; Anderson et al., 2008; Sullivan et al., 2004; Saxena and Hildemann, 1996). Atmospheric WSOC correlates strongly with secondary organic aerosol (SOA), but also has sources in primary biogenic aerosol such as pollen (Miyazaki et al., 2012) and that from biomass burning

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(Timonen et al., 2013). Sun et al. (2011) found that biogenic SOA (characterized by mass spectra) constituted ~75% of WSOC during the summer at rural sites in the eastern U.S., while biomass burning-like aerosol dominated during winter months. Finally, studies applying dual-isotope, radiocarbon analysis to WSOC indicate that modern carbon predominates in WSOC, but that fossil-carbon in aerosols can also contribute significantly (~20% of WSOC) in polluted air masses (Kirillova

5   et al., 2014; Kirillova et al., 2013; Miyazaki et al., 2012; Kirillova et al., 2010).

The atmospheric prevalence of WSOC anticipates a significant WSOC contribution to global, water-modulated aerosol impacts; yet assessing its impact is similarly challenging to modeling global SOA (Hallquist et al., 2009). Moreover, far fewer measurements of WSOC properties have been made to support such assessments and validate models than to support

10   the efforts to assess global SOA. This report of ambient WSOC hygroscopicity and CCN activity, from a series of five, month-long studies at remote continental sites in the U.S., helps bridge the gap between WSOC prevalence and the impact of WSOC on ambient aerosol properties.

Most methods of analyzing atmospheric aerosol-phase WSOC begin with the collection of a bulk sample of soluble aerosol

15   material either using a Particle-into-Liquid Sampler (PILS) or by extracting the soluble material from aerosol collected on filters (Psichoudaki and Pandis, 2013). Thus, the designation of organic material as water soluble has been called 'operational', defined by the method of dissolving the material (Psichoudaki and Pandis, 2013). These samples of Water Soluble aerosol Material (WSM) are frequently dominated by common inorganic compounds such as sulfate, nitrate, and ammonium.

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Extensive analysis of WSOC can be conducted on such mixtures. Total Organic Carbon (TOC) instruments can retrieve WSOC mass concentration (Chow et al., 2004) and chemical speciation can be determined using a wide range of analytical instruments. The hygroscopicity and CCN activity of WSOC can then be inferred by measuring those properties for WSM and estimating the contribution of WSOC from chemical composition and the well-known behavior of soluble inorganic

25   components (Cerully et al., 2015; Kristensen et al., 2012). This final modeling step introduces some uncertainty due to the complexity of WSOC composition, limitations of chemical analysis, non-ideal mixtures, and multiplicity of aerosol phases (Hodas et al., 2015). Alternatively, the physical characteristics of purely organic, laboratory-generated aerosols are frequently measured (Frosch et al., 2013; Engelhart et al., 2011; Frosch et al., 2011; Cruz and Pandis, 1997) to inform estimates of ambient WSOC properties and the mechanisms by which WSOC is formed. However, these also rely on

30   modeling in their application to ambient WSOC.

The measurements of WSOC hygroscopicity and CCN reported here rely on a third approach—isolating WSOC from the inorganic compounds in the WSM sample. Various methods of isolating WSOC exist, as reviewed by Duarte and Duarte (2011) and Sullivan and Weber (2006), capable of retaining from 50%−90% of sample WSOC with less than 5% retention of

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inorganic compounds. To the authors' knowledge, this approach to WSOC hydration properties has not been widely employed; notable exceptions were by Gysel et al. (2004) and Suda et al. (2012). The earlier work, by Gysel et al., carried out a bulk separation of organic matter from WSM extracts of filter-collected ambient aerosol. This isolated organic matter was then re-aerosolized and its hygroscopicity analyzed with a Tandem Differential Mobility Analyzer (TDMA). They

5   reported hygroscopic growth factors, GF, from 1.08−1.17 at 90% relative humidity, RH, corresponding to a hygroscopic parameter, κ (Petters and Kreidenweis, 2008), from ~0.03−0.08. The approach of Suda et al. (2012) is quite dissimilar, with extracts from filter samples of smog chamber-produced aerosol fractionated by reversed-phase high-performance liquid chromatography. The HPLC eluate was continuously atomized and analyzed using a Droplet Measurement Technologies CCN counter (CCNc). The approach described here bears many similarities to that of Gysel et al. (2004), but captured a

10   larger fraction of the WSOC.

1.1 Study details

This paper reports measurements of the hygroscopicity and CCN activity of WSOC samples isolated from aerosol samples collected during a series of five, month-long field campaigns as detailed in Table 1. The first four campaigns were part of a larger project focused on sources of visibility degradation in U.S. national parks. The measurements were designed to assess

15   the contribution of WSOC to aerosol water content and the resulting impact on visibility. These studies took place at Great Smoky Mountains (GRSM) National Park in eastern Tennessee, during the summer of 2006 and fall-winter of 2007−08 and at Mount Rainier (MORA) and Acadia (ACAD) national parks during the summers of 2009 and 2011, respectively. The results from these studies were reported by Lowenthal et al. (2009, 2015) and Taylor et al. (2011). A similar study took place at Storm Peak Laboratory (SPL) near Steamboat Springs, Colorado, in the summer of 2010. The measurements of

20   WSOC at SPL were part of a closure experiment attempting to estimate WSOC hygroscopicity from highly detailed chemical speciation and were variously reported by Hallar et al. (2013), Samburova et al. (2013), and Mazzoleni et al. (2012). This paper goes beyond those prior manuscripts to highlight the hydration behavior of ambient WSOC, especially the complementary enhancement of aerosol water uptake in internal mixtures of WSOC and common inorganic aerosol components.

25   ## 2 Methodology

The analysis of WSOC during the five projects reported here had three major steps: collection of daily, high volume, PM2.5 filter samples; laboratory-based isolation of WSM and WSOC; and analysis of the hygroscopicity and CCN activity of aerosol generated from those isolated fractions. We provide a brief synopsis of the steps but direct the reader elsewhere for detailed descriptions.

2.1 PM 2.5 filter samples

Four high-volume (~1100 L/min) PM2.5 filter samplers were operated during each project as described by Lowenthal et al. (2009). The filters were Teflon-impregnated glass fiber (TIGF) except during the first 12 days of the summer GRSM study, when Zefluor Teflon membrane filters were used. The filters were pre-cleaned by sonication in methanol and

5   dichloromethane. The sample period was 24 hours and filters were collected daily during each project and kept refrigerated during storage and shipping after sampling and prior to analysis.

2.2 WSOC sample production

High molecular weight WSOC, referred to as Humic Acid-Like Substances (HULIS), was isolated from the filters as described in Lowenthal et al. (2009), following the method of Duarte and Duarte (2005). WSM was extracted from the

10   filters by sonication in 250 mL of ultrapure water. The WSM solution was concentrated to 15−20 mL using a rotovap under gentle vacuum. WSOC was then isolated from the WSM using XAD-8 and XAD-4 macro-porous resins/chromatography columns: the WSOC was acidified and applied to the XAD-8 and XAD-4 columns in series, the columns were rinsed with ultrapure water to remove inorganic material, and the WSOC was eluted from the columns using a mixture of water and methanol. The WSOC eluate was then concentrated by drying and combined with filter extracts from other days to produce

15   sufficient samples for hygroscopicity and CCN activity analysis. After concentration and combination of consecutive daily samples, 5−8 samples of isolated WSOC sample material remained for each study.

Extraction with two resins, rather than one, increased the molecular weight range of retained WSOC components. XAD-8 material is traditionally used to isolate humic-like, high molecular weight substances while the XAD-4 column has been

20   demonstrated to retain lower molecular weight, hydrophilic organic compounds. The use of XAD-4 likely resulted in more complete and representative WSOC extracts when compared with single column approaches. However, a significant fraction of lower molecular weight organic acids, sugars, and alcohols—likely more hygroscopic than HULIS—were not retained by either XAD column (Samburova et al., 2013). The performance of the extraction technique is given in Table 1.

2.3 WSOC hygroscopicity and CCN activity analysis

25   WSOC hygroscopicity analysis was conducted using a TDMA largely identical to that described by Gasparini et al. (2006), configured as depicted in Fig. 1. CCN activity was measured using the same TDMA, operating as a Scanning Mobility Particle Sizer (SMPS), paired with a DMT CCN-100 counter (CCNc) in the configuration described by Frank et al. (2006).

2.4 Sample aerosol production

The isolated WSOC samples were aerosolized using a TSI 3076 atomizer configured to recirculate overspray. Several

30   precautions were necessary due to the limited sample material available (~5 mg dissolved in ~15 mL of water). First,

because the atomizer consumed ~45 mL of sample solution over the course of the RH-scanning TDMA measurements (~3 h) and the SMPS-CCNc measurements (~1.5 h), it was necessary to dilute the ~15 mL samples with ~40 mL of ultrapure water.

These very dilute samples were susceptible to contamination from residues in the atomizer assembly and soluble gases in the
5 compressed air stream. To prevent contamination, the atomizer assembly and reservoir were thoroughly purged with ultrapure water between measurements and with particular care following its use with ammonium sulfate for instrument calibration. Further, the compressed air stream was scrubbed using a HEPA filter and canisters containing silica desiccant and activated carbon.

10 Contamination was assessed by contrasting the size distribution produced by the atomizer with and without the extracts. Under consistent conditions, the atomizer will produce a consistent droplet size distribution. The resultant dry size distribution reflects the concentration of solute in those droplets; a thousand-fold increase in the dissolved concentration of the atomizer solution translates to a ten-fold shift in the diameter of particles produced. Before each sample was placed into the atomizer, the particle size distribution produced from atomizing ultrapure water was checked to ensure it was roughly
15 1000 times less concentrated than the sample solution and remained consistent for ~30 minutes. The atomizer was re-cleaned if it failed this test.

2.5 TDMA and SMPS-CCNc operation

Aerosol hygroscopic growth was analyzed through two series of measurements at RH spanning from 30% to 90%; a series to detect the deliquescence of an initially desiccated (~15% RH) aerosol and a series to detect the efflorescence of an initially
20 hydrated (RH ~90%) aerosol. For both, the initial dry diameter was 0.07 μm. CCN activity of aerosol samples from MORA, ACAD, and SPL was analyzed using the CCNc operated at 4 fixed supersaturations (nominally 0.2, 0.4, 0.6 and 0.8%) in parallel with the condensation particle counter (CPC) of the TDMA while operating the TDMA as an SMPS.

Both instruments were calibrated periodically during the studies. The critical sizing parameters of the TDMA,the flow
25 meters and high voltage sources,were calibrated directly using a Sensidyne Gilibrator and Fluke multimeter. The RH sensors and CCNc performance were calibrated using the instruments' response to an atomized, ammonium sulfate aerosol.

2.6 Result format

Each series of TDMA measurements resulted in a series of size distributions in which the location (representing particle size) of a single, narrow mode reflected the hygroscopic growth of the sample. For these experiments, the only parameter of
30 interest is the peak diameter of the mode. We report each measurement in terms of GF and RH, where GF is the ratio of the particle size at the peak of that mode to the dry particle diameter selected in the first DMA column (here 0.07 μm).

SMPS-CCNc measurements produce two particle size distributions: a conventional distribution based on the response from the CPC and a distribution of the particles that activate in the CCNc. For an internally mixed aerosol, the ratio of the size-dependent concentrations from these two distributions appears as a sigmoidal function that steps from 0 to 1 with increasing particle size. The mid-point of the transition (Dp50%) corresponds to the critical activation diameter for particles of that composition at the CCNc supersaturation.

3 Results and discussion

WSOC contribution comprised 22–93% of the PM2.5 organic carbon during these studies, with 46–100% recovered in the WSOC isolation process. Isolated WSOC was characterized by hygroscopicity parameters (κ) ranging from ~0.05–0.15 calculated from the GF at 90% RH. In addition to direct contribution to particle water uptake, WSOC appeared to complement the water uptake of inorganic compounds in WSM samples. Finally, measurements of samples from the GRSM winter and SPL studies implied that atomizer generated WSOC aerosol may assume complex morphologies.

3.1 Filter samples and WSOC extracts

As depicted in Table 1, WSOC concentration ranged from 0.22 to 1.41 µg/m^3. The lowest concentration, unsurprisingly, was during the sole winter study; otherwise, WSOC varied much more narrowly than reconstructed PM2.5. (PM2.5 was not measured, but Lowenthal et al. (2011) found the sum of measured constituents (SO$_4$, NO$_3$, etc.) reasonably duplicated PM2.5 measurements by co-located IMPROVE network samplers.)

For all studies, the WSOC isolation procedure effectively removed SO$_4^{2-}$. During the four national park studies, the cleaning efficiency was slightly higher, reflecting a slightly different methodology. For those projects, the samples were reprocessed until the reduction in sulfate reached 99%, likely reducing the fraction of WSOC retained. The Storm Peak Lab samples were only processed once, to maximize WSOC retention.

3.2 Seasonal and locational variation in WSOC hygroscopicity

Figure 2 shows the results of measurements of the samples collected during the five projects. The initially desiccated hygroscopic growth curves for each measurement are omitted for clarity. As reported by Lowenthal et al. (2015) these measurements indicate significant hygroscopic growth of the WSOC aerosol, and a sizable contribution to particulate water.

The measured hygroscopic growth varied little among the samples from each study, but contrasts were apparent between studies. The least hygroscopic samples were taken during the only winter study, likely indicating a smaller relative contribution from highly oxidized, lower molecular weight WSOC. This is consistent with the seasonal cycle of WSOC

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characteristics measured by Miyazaki et al. (2012) in a deciduous forest in Japan, which indicated low molecular weight, isoprene-derived WSOC only during summer months.

The differences in hygroscopicity between the samples collected during the summer studies could have various causes. GRSM samples were most hygroscopic. That site is characterized by being more polluted with much higher particulate mass loading, by deciduous (rather than coniferous) forest, and by being the southernmost site. From these characteristics, higher levels of isoprene, a more oxidative environment, and greater availability of aqueous aerosol for WSOC partitioning could be expected, all of which could contribute to WSOC dominated by lower molecular weight, highly oxidized species. Recent studies, e.g., Carlton and Turpin (2013), have emphasized the role of 'anthropogenic' particle water in biogenic SOA formation, especially in the eastern United States.

In Fig. 3, the hygroscopic growth and CCN activity measurements from each study have been recast in terms of κ, to illustrate the consistency between hydration behavior at high RH and for supersaturated conditions. The lines are study averages; the error bars indicate the standard deviation of those averaged measurements. In general, there is close agreement between hygroscopic growth at high RH and CCN activity estimates of κ.

The shape of these $\kappa(RH)$ curves indicates that WSOC behaves somewhat differently than an ideal, aqueous aerosol. Neglecting the influence of surface tension, $\kappa(RH)$ for an ideal, fully aqueous aerosol is constant and determined by relative molecular weights and densities of the solute and solvent (water). We rationalize minor deviations in the shapes of these $\kappa(RH)$ curves as non-ideal solution behavior and large deviations as changes in aerosol phase. In particular, an abrupt decrease in $\kappa(RH)$ with decreasing RH in measurements of an initially hydrated aerosol (shown here) can indicate efflorescence. One caveat to $\kappa(RH)$ inferred from hygroscopic growth, especially at low RH, is sensitivity to aerosol shape. When the shape is known, a corrective term—shape factor—is used to adjust the measured mobility diameter to a volume-equivalent diameter (e.g., cube-shaped, crystalline sodium chloride has the mobility of a spherical particle with 1.08 times its volume) (Wang et al., 2010; Zelenyuk et al., 2006). Here, aerosols are assumed to be spherical, having a shape factor of 1, with the notable exception discussed in the final section below.

Thus, as $\kappa(RH)$ for most WSOC samples is fairly constant from 40% RH through CCN activation, it is assumed that the soluble components in these particles are entirely dissolved in that range. However, at low RH, the $\kappa(RH)$ for the SPL and GRSM summer WSOC samples climbs from near zero to ~0.1. This suggests that these samples are insoluble below ~30% RH, *i.e.*, when the activity of the aerosol-phase water is less than ~0.3. For WSOC collected during the GRSM winter project, $\kappa(RH)$ also increases with increasing RH, but the change is less abrupt. With the remaining WSOC samples there is little change in $\kappa(RH)$ over the full RH range, suggesting high solubility. The $\kappa(RH)$ of WSM samples tends to increase with RH, especially for samples taken at SPL. Because Fig. 3 shows the behavior of initially hydrated particles, these $\kappa(RH)$

curves indicate that some species that make up the WSM leave the aqueous solution as RH decreases. Together with the WSOC measurements, this implies a complementary effect between WSOC and inorganic aerosol material—discussed in the next section.

3.3 Complementary enhancement of WSOC and inorganic dissolution

5   During two projects, the summers at GRSM and SPL, samples of both ambient WSOC and ambient WSM were isolated and analyzed. In addition to the compounds retained in the WSOC sample, WSM contains all water soluble inorganic and organic material not retained by the WSOC extraction. The contrasting hygroscopic growth curves of these materials suggests a significant complementary enhancement of water uptake by mixtures of WSOC and soluble, inorganic compounds. This result is not unanticipated; it is well known that the efflorescence/deliquescence behavior of inorganic

10   salts is modified by the presence of WSOC (Smith et al., 2012; Brooks et al., 2002; Hansson et al., 1998) and that inorganic salts will gradually dissolve with increasing RH *below* their deliquescence point if internally mixed with more-soluble compounds (Zardini et al., 2008; Ansari and Pandis, 1999). However, the isolation and analysis of ambient WSOC and WSM in the present study provides a unique perspective on these effects in complex, atmospherically representative mixtures.

15

The aerosol samples from GRSM and SPL were consistently distinct. GRSM samples were dominated by highly soluble, acidic sulfate, while SPL samples contained a less soluble mixture of sulfate, nitrate, and ammonium. Further, though the prevalence of WSOC at SPL and GRSM during the summers were similar (0.72 and 0.64 µg/m^3, respectively) the total loading of soluble material was several times greater at GRSM. For both studies, the more soluble fraction (whether WSOC

20   or inorganic) appears to enhance the contribution of the less soluble fraction to aerosol water uptake. The simplest likely mechanism for this enhancement is the availability of particle water associated with more soluble aerosol components to dissolve fractions of the less soluble aerosol components. Excess water becomes available as the initial, saturated solution associated with the more soluble component is diluted with hygroscopic growth (Tang, 1997).

3.4 Enhanced WSOC water uptake at low RH in mixtures with highly soluble, acidic sulfate

25   Samples collected at GRSM during the summer of 2006 were analyzed for common inorganic components. These measurements indicated aerosol consistently dominated by acidic sulfate (Lowenthal et al., 2009), which is highly soluble. The efflorescence point of ammonium bisulfate is below the RH readily achievable with the TDMA used in this study and also well below the minimum RH common at GRSM during the summer. Thus, the inorganic component was expected to be aqueous in all measurements.

30

In Fig. 4, the κ(RH) curves measured for both WSM and WSOC samples from GRSM summer are shown. The κ(RH) of both WSM and WSOC derived from sample 4 are mostly constant above 40% RH, suggesting that both the WSOC and the

WSM are fully dissolved at that point. The separation between the two WSM curves at low RH is likely an artifact of shape factor as discussed in Sect. 3.6. Though separation between pre-hydrated and pre-desiccated measurements can be indicative of hysteresis, it is only implied when the pre-desiccated κ(RH) curve falls below the pre-hydrated κ(RH) curve as appears in the results for WSM taken from sample 6.

5

The κ(RH) of WSOC sample 6 increases from near zero to 0.1 at ~62% RH, implying that the WSOC is insoluble at water activities below ~0.6. There is no hysteresis associated with this phase change—which suggests that the solid phase is not strongly ordered (i.e., crystalline) (Martin, 2000). The WSM κ(RH) shows a similar step, but at lower RH and with hysteresis. First, this implies that the WSOC dissolves at lower RH when mixed with highly soluble inorganic material than when in isolation. As described above, this is likely due to water associated with the inorganic aerosol fraction—a solution that becomes more dilute with increasing RH (and thus more water becomes available to dissolve a portion of the WSOC). There may be other rationalizations for this appearance, but this result parallels earlier studies that found soluble organics to lower the onset of the dissolution of ammonium sulfate and sodium chloride (Smith et al., 2012; Wu et al., 2011; Brooks et al., 2002; Choi and Chan, 2002; Cruz and Pandis, 2000; Hansson et al., 1998). Second, the appearance of hysteresis and phase transitions in the WSM measurements is not anticipated from the highly acidic and soluble inorganic WSM fraction, implying that WSOC is influencing the hygroscopic growth and dissolution of the inorganic WSM as well. Finally, WSOC is a minor fraction of WSM in these samples from GRSM (<25%), making its apparent contribution to WSM behavior more striking.

3.5 Enhanced water uptake by ammonium sulfate at low RH in mixtures with WSOC

The hydration behavior of WSM and WSOC samples from SPL suggests that highly soluble WSOC may enhance water uptake by inorganic aerosol components below their deliquescence point. WSM samples from SPL typically contained ammonium, sulfate, and substantial nitrate (an 'SNA' aerosol) (Hallar et al., 2013). This indicates that the sulfate was fully neutralized by ammonium, as nitrate formation is limited on acidic sulfate aerosol (Seinfeld and Pandis, 2006). In isolation this mixture of inorganic compounds should exhibit hysteresis and a deliquescence point above 70% RH if ammonium sulfate is the dominant species as at SPL (Martin, 2000). However, the presence of WSOC in the WSM mixtures from SPL greatly modifies this behavior, as is indicated by the WSM κ(RH) curves. The κ(RH) curves for an SNA aerosol dominated by ammonium sulfate would have abrupt steps at the deliquescence and efflorescence transitions. SNA aerosol exhibits hysteresis and these steps would occur separately in the two sets of measurements. However, hysteresis is not evident in Fig. 5. Moreover, WSM appears to gradually and reversibly dissolve (*i.e.*, the κ(RH) vs. RH curve is smooth and its slope is positive) as RH increases, rather than abruptly deliquesce.

This finding suggests that the hydration behavior of SNA aerosol in the atmosphere at these sites may deviate significantly from that expected for unmixed SNA. In all SPL WSM samples, hysteresis was limited, despite the general expectation that

SNA aerosol has distinct crystalline and metastable states. The gradual dissolution of the pre-desiccated aerosol is rationalized by the mechanism previously discussed. But the minor collapse of the metastable phase at high RH, rather than at the lower efflorescence RH typical of pure SNA solutions is less easily explained. Some studies have suggested that mixtures of WSOC and inorganic salts form amorphous, rather than crystalline, phases as they are dried (Mikhailov et al.,
5 2009); the data from our studies are insufficient to do more than speculate. What is clear is that SNA hysteresis is much less consequential in these mixtures with WSOC and that SNA can be expected to contribute more to aerosol water in the presence of highly soluble WSOC. The atmospheric impact of this behavior could be significant in dry climates where crystalline aerosol would otherwise form.

3.6 Variability in generated aerosol shape

10 Analysis of samples taken during the GRSM winter and SPL studies indicates separation between the pre-desiccated and pre-hydrated growth curves at low RH. In addition, the measured GF from these projects was consistently below unity at low RH (as illustrated in Fig. 6, showing the results from GRSM winter). Similar behavior was observed in the measurements of WSOC conducted by Gysel et al. (2004). These results suggest that the atomizer-generated aerosol is irregularly shaped such that the particles selected by the first DMA are less dense and, consequently, would be described by
15 an enhanced shape factor.

This hypothesis explains the lower-than-unity growth factor as the result of the irregularly shaped aerosol collapsing. In the pre-desiccated measurements this collapse occurs gradually as more of the WSOC dissolves as the controlled RH increases. In pre-hydrated measurements the irregular, atomizer generated aerosol collapses in the humidifying Nafion tube bundle
20 (shown in Fig. 1), regardless of the controlled RH.

The hypothesis relies on the desiccated shape produced by drying the atomized aerosol being different than the desiccated shape of the aerosol at low RH in the pre-hydrated measurements. Two factors contributing to this behavior have been put forward. First, the atomized aerosol is likely dried at a different rate than the pre-hydrated aerosol, though it is unclear
25 which is quicker in this configuration (for the impact of drying rate, see Wang et al. (2010)). Second, the charge state of the atomized aerosol is likely much higher than the pre-hydrated aerosol (which is primarily singly charged after exposure to a Po 210 source) (Berkland et al., 2004). Two details from these measurements lend support to the shape factor hypothesis. First, the pre-hydrated and pre-desiccated measurements eventually overlap, suggesting that there is no loss of mass through the drying and rehydrating process. Second, the WSOC $\kappa(RH)$ curves from SPL, above, indicate that the pre-hydrated
30 aerosol gradually comes into solution with increasing RH over the same RH range in which the pre-desiccated aerosol collapses. It should be noted that solute volume, necessary to infer κ, is derived from what appears to be the most dense desiccated particle size (i.e., the minimum size detected in the pre-hydrated measurements). Similarly, because this phenomenon (irregular shape) is hypothesized to be a laboratory artifact, hygroscopic growth is most accurately reported

with reference to the most dense aerosol configuration, i.e., as the ratio of hydrated particle diameter to the diameter of the most dense, approximately dry aerosol. Earlier reports of these data, such as Lowenthal et al. (2009), reflect this assumption.

4 Conclusions

The WSOC in ambient aerosol has been shown to contribute to water uptake through hygroscopic growth and likely through complementary effects with other soluble aerosol components. Samples of ambient WSOC gathered during five month-long studies at various sites were characterized by hygroscopic growth parameters (κ) ranging from 0.05 to 0.15. Measured hygroscopic growth over a range in RH indicated that κ(RH) was roughly constant from 40% RH to supersaturated conditions, implying that WSOC was fully dissolved at water activities above ~0.4. Most samples exhibited a gradual transition from κ(RH) ~0 at low RH to that constant, characteristic κ(RH) at some point below 40% RH. No hysteresis was indicated for that transition.

Contrasts between the hygroscopic growth of WSOC and total WSM samples from two of the studies suggest that soluble components in ambient aerosol can interact to enhance water uptake at atmospherically relevant RH. In particular, highly soluble WSOC can facilitate the gradual dissolution of sulfate-nitrate-ammonium (SNA) at RH below the typical deliquescence point for those substances. The hysteresis behavior of SNA-WSOC mixtures appears to be greatly truncated with mixed SNA-WSOC aerosol hydration instead characterized by gradual, reversible dissolution of SNA as RH increased from 40% to 80%.

Given the atmospheric abundance of internally mixed SNA and WSOC, this study not only indicates that WSOC contributes significantly to aerosol hygroscopicity but that a compartmentalized approach to WSOC and SNA hydration is flawed. The collection, isolation and analysis of WSOC from ambient aerosol provided a new perspective into the hydration behaviors of atmospherically complex mixtures of WSOC, but it is also a broad-brush and imprecise technique. We suggest that its primary value is in highlighting the complementary effects of WSOC and SNA hydration as a first-order impact on ambient aerosol hydration.

5 Data availability

Hygroscopicity and CCN activity data for each sample are included in the article supplement. Data related to the chemical analysis of aerosol samples are reported in Lowenthal et al. (2009, 2015), Hallar et al. (2013), Samburova et al. (2013), and Mazzoleni et al. (2012).

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Tables

Table 1: WSOC prevalence and extraction efficiency.

	GRSM Summer	GRSM Winter	MORA	ACAD	SPL
Sample period	7/19/2006 −8/17/2006	1/11/2008 −2/9/2008	8/1/2009 −8/30/2009	8/1/2011 −8/30/2011	6/24/2010 −7/28/2010
WSOC/OC	22%	21%	77%	93%	89%
SO4 cleaning efficiency	99.7%	99.2%	99.8%	99.8%	97.7%
Std. Dev.	0.3%	0.2%	0.2%	0.2%	2.2%
WSOC Recovery	46%	100%	90%	60%	73%
Std. Dev.	22%	17%	13%	70%	17%
WSOC (μg/m^3)	0.64	0.22	1.41	0.78	0.72
PM2.5 Reconstructed (μg/m^3)	16.2	5.3	5.0	3.1	2.3

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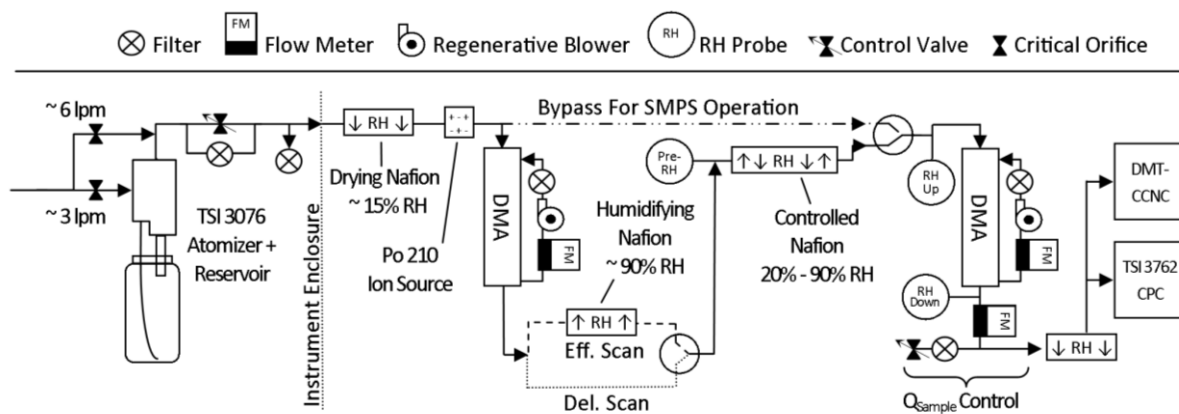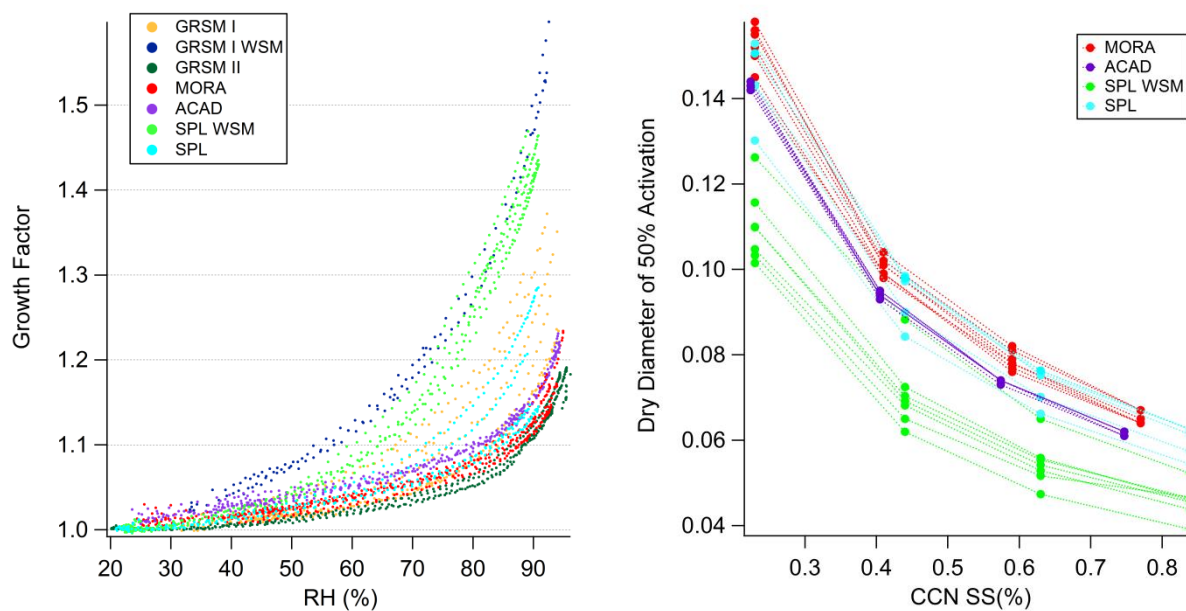and Physics
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Figures

Figure 1: **TDMA and SMPS-CCNc configuration.**

Figure 2: Hygroscopic growth curves for initially hydrated aerosol samples (designed to detect efflorescence) and CCN activity results. Hygroscopic growth was measured for all samples: From Great Smoky Mountains Summer (GRSM I), both total Water Soluble aerosol Material (WSM) and isolated WSOC; from GRSM winter (GRSM II) only WSOC; from Mount Rainier (MORA) only WSOC; from Acadia (ACAD) only WSOC; and from Storm Peak Lab (SPL), both WSM and WSOC. CCN measurements were conducted only on samples from MORA, ACAD, and SPL (both WSM and WSOC).

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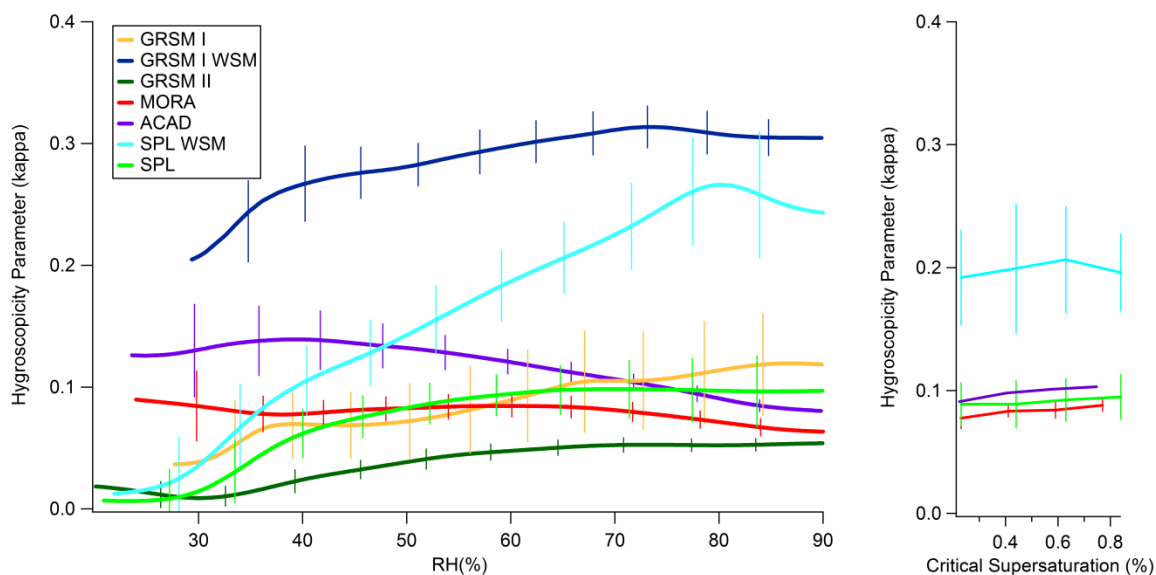
Figure 3: Average κ(RH) and κ(SS$_c$) from all initially hydrated hygroscopicity measurements for all WSOC and total Water Soluble aerosol Material (WSM) samples from Great Smoky Mountains Summer and Winter (GRSM I and II), Mount Rainier (MORA), Acadia (ACAD), and Storm Peak Lab (SPL).

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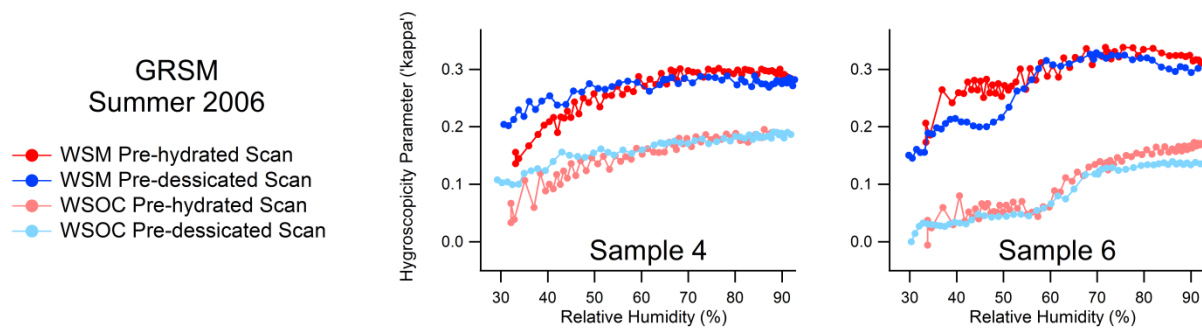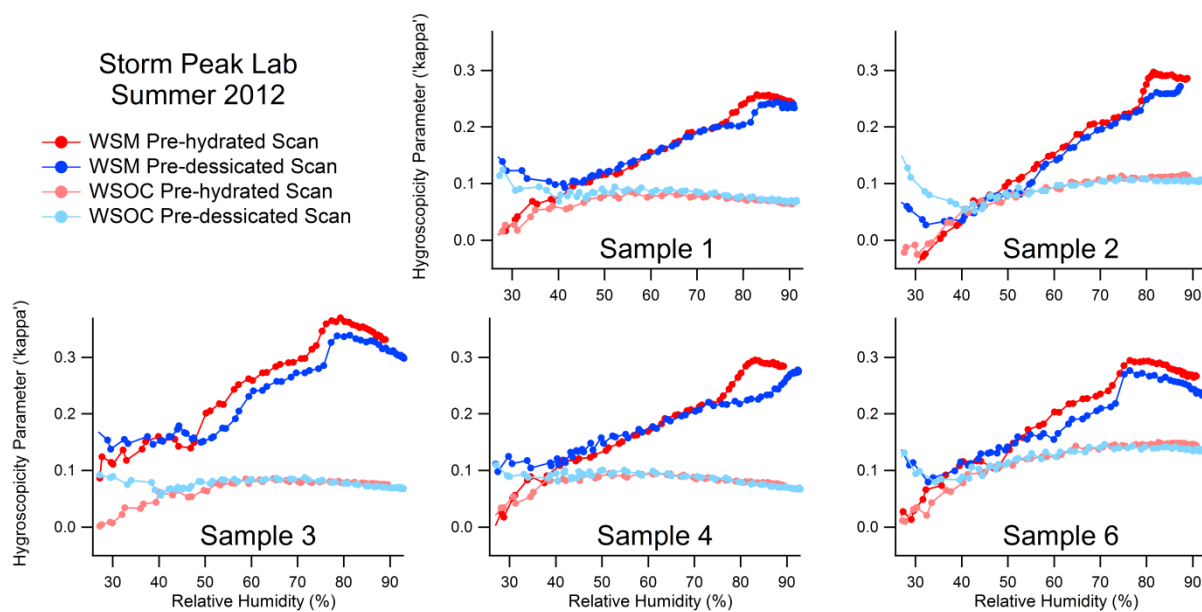
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Figure 4: Contrasting hygroscopic growth of WSOC and total Water Soluble aerosol Material (WSM) of samples from Great Smoky Mountains National Park in summer. For Sample 6, WSOC appears to dissolve at lower RH when associated with the WSM mixture.

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Figure 5: Contrasting hygroscopic growth of WSOC and total Water Soluble aerosol Material (WSM) samples from Storm Peak Lab. All WSM samples exhibit continuous, increasing dissolution with increasing RH.

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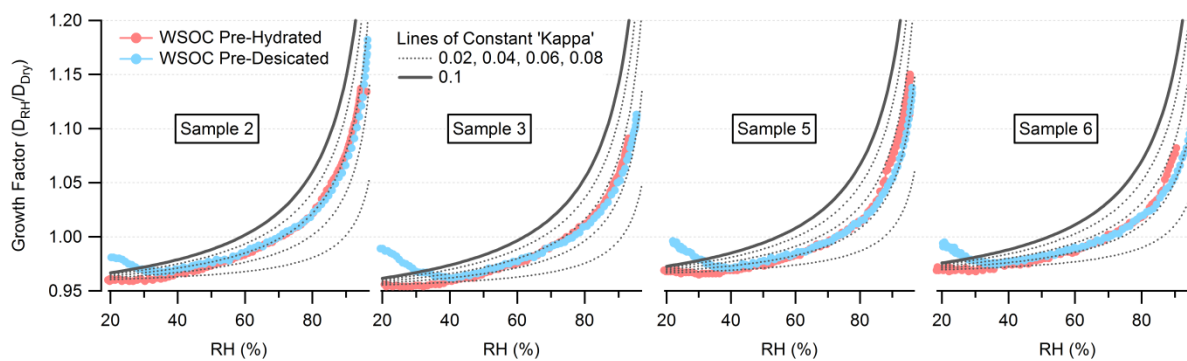
Figure 6: **Hygroscopic growth measurements of WSOC samples from Great Smoky Mountains National Park in winter.**