Dear Editor and Referees:

We would like to thank our reviewers for taking time to evaluate this manuscript and provide thoughtful comments. The primary criticism, that our paper lacked sufficient quantitative support for its claims, was well made and led to substantial improvement in our analysis and manuscript. We have addressed this criticism and all other comments in the attached supplement.

Our response addresses each reviewer in turn. Referee comments are in **bold,** followed by our response in plain text. Changes to the manuscript are given in *italics*. Specific changes are in red. Many of the comments are shared by each referee. For brevity, we only address these points fully when they are first raised, but provide brief summaries and references in response to subsequent similar comments.

Referee Comment 1:

This paper presents the results of laboratory experiments performed to characterize the hygroscopicity of water-soluble organic carbon isolated from ambient filter samples collected at several U.S. national parks. Overall, the authors show convincingly that the WSOC makes an important contribution to the hygroscopic properties of the aerosols, even if it is a relatively minor contributor to the PM mass. The findings are significant and certainly relevant for ACP. The paper is concise, well-organized, and the writing is polished. I highly recommend it for publication after the following items are addressed:

Thank you for taking time to review this work and for affirming the value of the results. We believe that we have answered each of the following comments leading to significant improvements of the manuscript.

Comment 1.1

The biggest weakness (or opportunity for improvement) is that the authors do not extend their analyses to estimate the contribution of WSOC (and inorganic salts) to water uptake as a function of RH for each of the locations/seasons. The major finding in the paper, from the conclusions: "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." But this is only qualitative, in line with the major discussion surrounding this point in the manuscript. It seems that the authors' current results would enable a more quantitative interpretation of the effects of the WSOC on the hygroscopicity of the ambient particles.

The criticism that the paper is too qualitative is well taken, and repeated by all referees. Each reviewer primarily criticized the lack of quantification of the tendency of WSOC to enhance the water uptake by the inorganic fraction. Our response and description of the steps taken to rectify this issue are given here and will be referenced in answers below.

Referee 1 makes two suggestions here: a) that the estimated contribution of WSOC and inorganic salts to water uptake be extended to all locations and seasons, and b) that the impact of WSOC on the hygroscopic growth of ambient particles be quantified.

In response to the first suggestion, we acknowledge that in isolation, WSOC hygroscopicity could be extrapolated based on atmospheric conditions to estimate seasonal contribution to particle water. However, the focus of this manuscript is on the enhanced uptake of water due to interactions between WSOC and inorganic ions. This effect is more difficult to extrapolate as there are unfortunate limitations in our dataset. Mainly, extracts containing all water soluble aerosol constituents (Water Soluble Materials or WSM) were not prepared for most seasons and locations. These studies were narrowly designed to demonstrate WSOC hygroscopicity; the findings presented here are somewhat incidental. Likewise, only the Storm Peak Lab study, part of a separate project, provided detailed chemical speciation. Thus, it is difficult to do much more than speculate about the broad contribution of WSOC to hygroscopic growth during all seasons and locations. But we have made significant changes to the manuscript attempting to quantify these effects and indicate why, based on our limited data, they might be widespread.

> The manuscript was significantly expanded to quantify of the enhancement of water uptake due to interactions between organics as discussed in the following response. Sections 3.3-3.5 were largely rewritten to address this point. The effect on particle water at SPL is described in Fig. 5 and discussed on page 15, lines 20-26. The potential to extrapolate these effects is based on the ubiquitous presence of low-DRH WSOC during these studies, which is emphasized frequently (e.g. p.15, line 26; p.18, line 15). However, extrapolating would require knowledge or estimation of WSM properties (only available for SPL) and is beyond the scope of this work.

The second suggestion by Referee 1—also made by Referees 2 and 3—requests that we quantify the impact of WSOC on aerosol water uptake by the full mixture of water soluble aerosol material (WSM). The point is well taken and we believe the changes made have improved the manuscript.

The referees' criticism focuses on our qualitative assertion that, because WSOC deliquesces at lower RH than many inorganic aerosol constituents (or is aqueous throughout the measure RH range), it likely allows inorganic components to enter solution at lower RH than they would in isolation. The referees' comments ask that we further quantify this enhancement and more precisely isolate the effect of WSOC.

In response, we have adopted the referees' suggested approach. To quantify and isolate the enhanced water uptake of WSOC and inorganics in mixtures, we have contrasted the measured WSM hygroscopic growth with a prediction of WSM growth that assumes no interaction between the organic and inorganic fraction—essentially a ZSR-like estimate. This allows us to attribute the contrast between observed and expected WSM hygroscopicity to the interaction of WSOM and inorganics.

> To address this comment, we have re-written Sections 3.3-3.5 (pages 12-16) to incorporate a more sophisticated treatment of this effect. The extended response provided here (below) is largely duplicative of the reworked portion of the manuscript.

Our approach is similar to that employed by Gysel et al. (2004). The 'expected' WSM hygroscopic growth is estimated from the hygroscopic properties of the inorganic (modeled) and organic (WSOM, measured) water soluble compounds, i.e., the two components of WSM. The inorganic contribution is estimated using the E-AIM model of Clegg and Wexler (see list of E-Aim publications below). WSOM hygroscopicity was directly measured using the methods described in the paper. The expected hygroscopic growth is predicted assuming no interaction—which is a straightforward volume (of the solutes) weighted average of the hygroscopicity parameter.

There are a number of key assumptions in each of these three steps: modeling inorganic hygroscopicity, applying the measured hygroscopicity of WSOM, and predicting their combined hygroscopicity.

Modeling Inorganic Hygroscopic Growth

We evaluated two hygroscopic growth models—E-AIM and ISORROPIA II—for this task and decided the E-AIM model was more appropriate. Though the inorganic composition was analyzed for the SPL study, there were several difficulties in producing what we believe to be supportable and reasonable estimates of hygroscopic growth. First, the composition data indicates both that there are insufficient cations to neutralize the sulfate *and* a sizable portion of nitrate. Second, several of the cations detected are not treated by the E-AIM model.

The first issue arises because the presence of nitrate requires that sulfate in the samples be neutralized. (Fountoukis, C. and A. Nenes, 2007). However, the cations measured do not adequately account for neutralized sulfate. We resolve this issue by assuming that the ammonium was under-measured and model the hygroscopic growth by balancing the measured anions with additional ammonium (rather than protons).

This approach—assuming that the sulfate was in fact neutralized by ammonium—is supported by two strong arguments and two weaker arguments. First, if the sulfate was not neutralized and following the approach of Gysel et al. (2004) we assumed that the missing cations were offset with H^+, the resulting estimation of WSM hygroscopicity is clearly unrealistic. Often this would imply a sizable fraction of ammonium bisulfate (k(50% RH) = ~0.8), drastically over predicting the WSM hygroscopicity. While our use of this model *is* intended to demonstrate a similar error (underestimation), underestimation is consistent with expected behavior: components with low deliquescence points are well known to enhance water uptake by less soluble aerosol components. Second is the consistent presence of nitrate, which does not partition to particles containing acidic sulfate. Third, it is supported by the difficulty of measuring ammonium. Finally, it is supported by the appearance of hysteresis and deliquescence at high RH (~80%) in each of the measurements, which is consistent with a major fraction of ammonium sulfate. Unfortunately, this all introduces some uncertainty about the actual characteristics of the inorganic fraction and undermines the ultimate conclusion that highly soluble organic matter enhances water uptake. In the end, we increased the amount of ammonium input to the model to fully neutralize the sulfate.

We deal with the second issue, the presence of cations not treated by E-AIM (Ca^{2+}, K^+, Mg^{2+}) by either substituting Na^+ (K^+, Mg^{2+}), or suppressing SO_4^{2-} (Ca^{2+}, reflecting the much lower solubility of gypsum). Though this is not an exact approach, these are minor constituents.

Finally, we translate the model results into k(RH). k(RH) is primarily a volume based property and we use the density calculator hosted on the E-AIM web site to translate the aqueous solutions into volumes.

> *Changes in the manuscript: We have included the estimated hygroscopic growth of the inorganic species in Figures 4 and 6, which depict the hygroscopic growth of the SPL and*

> *GRSM Summer samples. We have also added a similar discussion to the text, describing our approach to modeling these compounds.*

Applying the Measured Hygroscopicity of WSOC

The studies reported in this paper all involved measuring the hygroscopicity of samples of WSOM isolated from ambient aerosol using a TDMA. As we will return to in our response to later comments, there are two main gaps between these measurements and the hygroscopic properties of the WSOM in the full WSM (and in ambient aerosol).

First, TDMA measurements are reflective of mobility diameter of particles, which does not necessarily translate accurately to volume. The hygroscopic growth parameter, k(RH), is derived from changes in particle volume and is thus similarly uncertain. While we believe that there is good reason to suspect that these particles are nearly spherical (e.g., Gysel et al., 2004; Mikhailov et al., 2009; Boreddy and Kawamura, 2016) there is simply no definitive evidence to evaluate this contention. We expand on this limitation in the paper and below.

Second, while the WSOM extracts typically represented a large majority of the total WSOM in the WSOC, a significant fraction was not captured. It is known from analyses reported in other papers that the missing fraction is expected to include smaller organic molecules—and is therefore likely to enhance the hygroscopicity of the WSM to a greater degree than the WSOM extracts would indicate.

> *Changes in the manuscript: To attempt to capture the impact of this missing fraction we have added error bars to both the WSOM and WSOM+INORGANIC estimate indicating the impact if the missing fraction was characterized by k(RH) 50% higher than the WSOM extract. In addition, we have added a description of this impact to the text.*

Estimating WSM hygroscopic growth from modeled inorganic and measured WSOM hygroscopic growth

Once we have a k(RH) curve representative of the inorganic and organic fractions, it is straightforward to estimate $k(RH)_{mixed}$, assuming no interaction. It is simply the volume weighted average of k(RH)'s of the individual solutes. (Petters, M. D. and S. M. Kreidenweis, 2007) Because the chemical analysis of the WSM only provides component mass, it is necessary to assume the density of WSOM (the density of the inorganic compounds involved are well known). We assume a density of 1.5 g/cm^3 for WSOM, but include error bars to indicate the wide uncertainty this introduces.

> *Changes in the manuscript: Beyond the section describing our approach, we include the results of our modeling effort in Figures 4 and 6, to contrast that expected hygroscopic growth with the measured hygroscopic growth of WSM.*

Papers Cited in this response:

Gysel, M., E. Weingartner, et al. (2004). "Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol." Atmos. Chem. Phys. 4(1): 35-50.

Boreddy, S. K. R. and K. Kawamura (2016). "Hygroscopic growth of water-soluble matter extracted from remote marine aerosols over the western North Pacific: Influence of pollutants transported from East Asia." Science of The Total Environment 557–558: 285-295.

Mikhailov, E., S. Vlasenko, et al. (2009). "Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations." Atmos. Chem. Phys. 9(24): 9491-9522.

Petters, M. D. and S. M. Kreidenweis (2007). "A single parameter representation of hygroscopic growth and cloud condensation nucleus activity." Atmos. Chem. Phys. 7(8): 1961-1971.

Fountoukis, C. and A. Nenes (2007). "ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+–Ca^{2+}–Mg^{2+}–NH_4^+–Na^+–SO_4^{2-}–NO_3^-–Cl^-–H_2O aerosols." Atmos. Chem. Phys. 7(17): 4639-4659.

The E-Aim Papers

Carslaw, K. S., S. L. Clegg, et al. (1995). "null." The Journal of Physical Chemistry 99(29): 11557-11574.

Clegg, S. L. and P. Brimblecombe (2005). "Comment on the “Thermodynamic Dissociation Constant of the Bisulfate Ion from Raman and Ion Interaction Modeling Studies of Aqueous Sulfuric Acid at Low Temperatures”." The Journal of Physical Chemistry A 109(11): 2703-2706.

Clegg, S. L., P. Brimblecombe, et al. (1998). "Thermodynamic Model of the System H+−NH4+−Na+−SO42-−NO3-−Cl-−H2O at 298.15 K." The Journal of Physical Chemistry A 102(12): 2155-2171.

Clegg, S. L., P. Brimblecombe, et al. (1998). "Thermodynamic Model of the System H+−NH4+−SO42-−NO3-−H2O at Tropospheric Temperatures." The Journal of Physical Chemistry A 102(12): 2137-2154.

Massucci, M., S. L. Clegg, et al. (1999). "Equilibrium Partial Pressures, Thermodynamic Properties of Aqueous and Solid Phases, and Cl2 Production from Aqueous HCl and HNO3 and Their Mixtures." The Journal of Physical Chemistry A 103(21): 4209-4226.

Comment 1.2:

Two relevant studies are not included, but which should be: The introduction could include a brief discussion of Asa -Awuku et al. (2008), which characterized the CCN activity of WSOC isolated from biomass burning samples. Additionally, Guo et al. (2015)

analyzed the contribution of organics to aerosol water in the southeastern U.S. Although their methods were different, the results of Guo et al. (2015) can provide some important context and comparison for the present study, especially the samples from Great Smoky Mountains National Park.

Changes in manuscript: The Asa-Awuku et al. study is extremely relevant, relies on similar use of solid phase extraction, and will be included in the introduction. Similarly, we have added Guo et al. to our discussion of WSOC prevalence and contribution to particle water.

Asa-Awuku et al. (2008) is discussed on page 2, lines 2-8 and page 11, lines 9-11.

Guo et al. (2015) is discussed with on page 3, lines 24-25.

Comment 1.3:

Should the WSOC concentrations presented throughout the paper have units of µg -C m -3 ? If not, how have the authors converted from OC to OM?

Changes in manuscript: Referee 1 is correct, the units of WSOC would be most clearly conveyed as µg-C·m^{-3}. *We have revised the manuscript accordingly.*

This change has been incorporated and µgC/m^3 is used where possible for the sake of clarity.

Comment 1.4:

I question some of the WSOC concentrations presented in Table 1, especially the samples from GRSM. WSOC contributions of only 4% to the total reconstructed PM 2.5 mass appear to be unrealistically low.

This is a reasonable question, but these results are consistent with the co-located IMPROVE site measurements for the same period. Sulfate was typically reported in the 15 µg/m^3 range, and the total OC values were around ~3 µg-C/m^3. Our results indicated that WSOC was ~22% of OC, which is lower than typical.

Comment 1.5

I realize that prior papers have presented data from this same study, which the authors cite; however, I think the paper would benefit from added experimental details. Specifically, many of the results compare the pre-hydrated and pre-desiccated scans. Even if this information can be found in another paper, I recommend adding detail to the Methods section to clarify the sequence of the measurements so that the distinction between them is evident.

Changes in manuscript: In response to this comment and similar comments below, we have added more details to the methods section including descriptions of the pre-hydrated and pre-desiccated scans.

The methods section has been expanded significantly.

P.7, lines 21-32 describes the pre-hydrated and pre-desiccated scans in much greater detail, linking their operation to Fig. 1.

Comment 1.6

In what ways might the unrecovered WSOC alter the conclusions? The authors have some idea of which types of compounds are likely not recovered – there should be at least a brief discussion of how these compounds could alter the results.

In response to this (and similar comments), we have expanded our discussion and analysis of the contribution of un-recovered WSOC. The fraction of WSOC in the WSM that was not isolated is likely comprised of smaller organic molecules; k(RH) measured of the isolated WSOC will likely underestimate the actual contribution of WSOC to WSM (and ultimately ambient aerosol) hygroscopicity.

Changes in manuscript: To account for this effect, we have included error bars in Figures 4 and 5 that illustrate, given the amount of WSOC that was not recovered, how much enhancement in total WSOC hygroscopicity we might expect. We have also added a description of this source of error to the discussion.

The effect of unrecovered WSOC is now discussed on page 13, lines 24-31 and depicted in Fig. 4.

Comment 1.7

Finally, in Section 3.6 – what kind of irregular shape do the authors propose? "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." It is not clear how the rate of drying would contribute to this effect? The authors do not believe that they lose WSOC mass in the experimental setup (Section 3.6, line 28) . But this at least seems plausible, given recent ambient results (El- Sayed et al., 2016) and laboratory studies (see multiple papers from the De Haan and Turpin groups). Overall, the explanations put forth in this section are shaky, and need further development .

This point is well received—we do not have any measurements or data that would provide a definitive explanation for this behavior. The discussion was originally included because as earlier, similar studies have reported similar behavior (e.g., Gysel et al., 2004) we felt it was worthwhile to indicate that we had noticed the same—and give a few off-the-cuff rationalizations. We also included this section to explain how we selected a baseline for our growth factor measurements.

We have done further research on the topic. Several other groups have detected the same behavior and we have reworked our discussion to draw more heavily on those studies (rather than guesswork). In particular, Gysel et al. (2004) look more systematically at this behavior and described it as restructuring. They used SEM to look at the particle shapes, which were spherical. They also recreated the behavior with of well-known non-volatile compounds: with nordic reference humic and fulvic acids and salts. Boreddy and Kawamura (2016) report on a similar behavior, and mainly adopted the rationalization of Gysel et al.—which hinged on rates of evaporation leading to internal cracks and voids.

A similar behavior was also noticed by Mikhailov et al. (2009) for oxalic acid and levoglucosan. Their investigation found that spray drying could produce particles with high void fractions that collapse through humidification/drying cycles.

Still, it is possible that this is an artifact of evaporation, and we will note that in our discussion.

> Section 3.6 (pp.17,18) has been largely rewritten in response to this and similar comments, focusing on similar reports by Gysel et al. and others.

Papers cited in response

Gysel, M., E. Weingartner, et al. (2004). "Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol." Atmos. Chem. Phys. 4(1): 35-50.

Boreddy, S. K. R. and K. Kawamura (2016). "Hygroscopic growth of water-soluble matter extracted from remote marine aerosols over the western North Pacific: Influence of pollutants transported from East Asia." Science of The Total Environment 557–558: 285-295.

Mikhailov, E., S. Vlasenko, et al. (2009). "Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations." Atmos. Chem. Phys. 9(24): 9491-9522.

Technical Corrections

none

References

Asa -Awuku , et al.: Investigation of molar volume and surfactant characteristics of water -soluble organic compounds in biomass burning aerosol, Atmos. Chem. Phys. , 8, 799-812, 2008.

El-Sayed, et al.: Drying -Induced Evaporation of Secondary Organic Aerosol during Summer, Environ. Sci. Technol. , 50, 3626- 3633, 2016.

Guo , et al., Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys. , 15, 5211- 5228, 2015.

Referee Comment 2:

General comments

This paper presents hygroscopic properties of isolated WSOC and total water-soluble matter (WSM) extracted from PM 2.5 filter samples collected at several U.S. sites. The authors measured the hygroscopic parameters of both WSOC isolated and WSM in the laboratory under different RH conditions. They discuss the relative importance of the isolated WSOC and its interaction with inorganic components in terms of particle hygroscopicity. The present work may provide insights into our understanding on aerosol hydration/dehydration process by organics interacting with inorganics. Overall, however, the manuscript lacks quantitative discussion (see comments below), which makes conclusions rather weak throughout the paper. Moreover, most of the discussion are not convincing because supporting data are not shown in most parts of the paper. The discussion too much relies on the data shown in previous works already published, particularly regarding chemical characterization of the WSM. Although the data presented seems to be valuable, there are a number of important issues that need to be worked out before I recommend its publication in ACP.

We thank Referee 2 for thoughtfully evaluating this manuscript. We hope that we have addressed the major concern, the lack of quantitative evaluation. As we describe in our response to Referee Comment 1.1, we have expanded our analysis to isolate and quantify the contribution of WSOC to WSM hygroscopic growth. We have also sought to include more of the chemical analysis results (from earlier publications) on which we have based this quantification.

Specific comments

(1) My major concern is on the exact fraction of WSOC isolated from the WSM compared with "the exact total WSOC" that can be measured without using any XAD columns. In Table 1, although the "WSOC recovery" is shown, it is not clear how the authors calculated/estimated the numbers. It is expected that there might be WSOC components that are not retained either XAD-8 or XAD-4. What is the percentage of these components, and how do these WSOC affect the conclusions? This point should be closely linked to the major conclusion in which the author mentioned the contribution of WSOC to the hygroscopicity of WSM.

In response to Referee 2's methodological questions, we have expanded our description of the TOC analysis methods employed to determine the OC content of the WSM and WSOC, as well as the details of the "WSOC recovery calculation."

The second point made by Referee 2 is appreciated: we have expanded our analysis of the impact of the WSOC that was not retained in the resin-isolated WSOC samples. Our approach is covered in more detail in our response to a similar comment by Referee 1—in responses 1.1 and 1.6. As this comment notes, the discussion is tightly tied to our quantification of the contribution of WSOC to WSM hygroscopicity. In brief, we illustrate and discuss the sensitivity of our conclusions to the possibility that the missing WSOC has different characteristics than the WSOC analyzed by TDMA.

> *Changes in manuscript: We have elaborated on the underlying chemical analysis from earlier projects, providing more details and more data. We have also greatly expanded our evaluation of WSOC's contribution to WSM hygroscopicity, including the possible impact of WSOC not isolated and analyzed.*
>
> The methods section, at page 6, lines 11-25, has been expanded to include descriptions of the chemical analysis of the filters and extracts during these studies. In particular, the methods of analyzing WSOC are described in lines 15-23, including the determination of WSOC recovery.
>
> The effect of unrecovered WSOC is now discussed on page 13, lines 24-31 and depicted in Fig. 4.

(2) How did the authors quantify WSOC? More detailed description on the detection of WSOC is needed including if any syringe filters were used to remove any particulate OC in samples, an instrument used, lower limit of detection, measurement uncertainty, etc. In addition, is the unit of WSOC µg/m3, or µgC/m3? If the authors discuss WSOM in µg/m3, then how was the mass of WSOC converted to that of WSOM?

Beyond answering these reasonable questions, we have generally expanded the discussion of the production of WSOC extracts. We appreciate the criticism that we did not adequately incorporate findings reported in earlier studies and have attempted to include more details.

> *Changes in manuscript: The specific questions about WSOC extraction and chemical analysis are now answered in the methods section. The distinction between WSOM and WSOC is clarified by incorporating units of µgC/m^3. We have also indicated the conversion from OC to OM used for the National Park studies, 1.8, and for the Storm Peak Lab Study, 2.1.*
>
> A detailed discussion of WSOC chemical analysis was added on page 6, in lines 15-23, which describes the instrumentation and process of quantifying WSOC, including measurement uncertainty.
>
> The description of extract preparation has also been expanded, beginning on page 5, line 24, and reports the use of a PTFE membrane filter.
>
> In response to this and similar comments, WSOC is now consistently reported in µgC/m^3. The conversion between WSOC and WSOM is reported on page 6, line 21.

(3) Methodology of the hygroscopicity and CCN measurements: The authors should provide more detailed explanations for the settings and calculation with regard to the GF and CCN measurements. Several parameters are not defined in the text, such as water-activity, shape factor, etc. Also, the authors should provide how they derived several important parameters (e .g. κ values), together with some estimation of uncertainty for

the GF and CCN measurements. This is important to evaluate the quality of these measurements.

> *Changes in manuscript: In the methodology section, we have expanded our description of the hygroscopicity and CCN activity measurements. We provide a rough estimate of uncertainty for both the TDMA and CCNc instruments. Also, in keeping with our extended analysis of the relative contributions of WSOC and inorganic ions to WSM hygroscopicity, included more details of the calculations involved.*
>
> The description of hygroscopicity and CCN measurements has been greatly expanded in Section 2.5, beginning on page 7, in response to this and similar comments. The instrument settings (p.7, lines 19-32; p.8, line 28-32) and data processing routines (p.8, lines 1-8, 21-26) are discussed in greater depth, as are the measurement uncertainties (p.9, lines 12-28).
>
> Water activity has been largely eliminated from the manuscript, while shape factor has been elaborated on page 9, lines 21-28 and page 11, lines 15-18.
>
> The equations used for calculating κ are now included on page 8, line 10 and page 9, line 10.

(4) I understand that this study is linked with the previous works in terms of the chemical characterization of aerosols using the same/similar sample sets obtained at the same observational sites. However, almost none of the chemical component in the WSM (besides WSOC) is shown in the manuscript, only referring to the prior papers. The authors should show the amount of each inorganic component (at least SNA) relative to that of WSOC and should add more discussion on that data. Otherwise the discussion is very weak regarding the interaction between WSOC and inorganics, and their contribution to the hygroscopicity.

Detailed chemical characterizations are not available for every study, but we have added the available data. Fortunately, for the SPL study, the focus of our analysis, there is data. As the referee notes, this information is critical in our effort to isolate the effect of WSOC on hygroscopicity

> *Changes in manuscript: We have added tables describing the chemical composition, where it is available. These tables make table 2 redundant and it has been removed.*
>
> Available WSM composition data has been included in Table 2, including SNA.

(5) Table 1: It is not clear how the authors estimated "sulfate cleaning efficiency."

Cleaning efficiency is one minus the ratio of the concentrations of sulfate in the WSOC and WSM samples, given as a percentage. Sulfate concentration was measured using IC.

> *Changes in manuscript: We clarify this in our expanded description of the chemical analysis and extract preparation.*

> Page 6, lines 13-15, describe the basis for estimating sulfate cleaning efficiency*.*

(6) The authors have used the term "highly soluble WSOC" in several parts of the manuscript (e.g., P.10 L.20, P.11, L.7). What is the definition of this "highly soluble WSOC," and what is the difference between this term and "isolated WSOC" which the authors measured?

This point is well taken. We intend no particular category of "highly soluble WSOC," distinct from isolated WSOC. It is an imprecise way of reminding the reader that WSOC is more soluble than many inorganic WSM species.

> *Changes in manuscript: We have removed or reworded each instance of this usage.*
>
> Each use of 'highly soluble' has either been replaced or supplemented with "low-DRH."

(7) The authors should add more details on the site descriptions: characteristics of each site (rural, mountain, forest, relative influence of anthropogenic vs. biogenic sources, etc.) should be listed maybe in Table 1 or in an additional table. Also why were those sites selected or appropriate to study the hygroscopicity of WSOC? It is really difficult to understand the major difference among the sites for general readers.

> *Changes in manuscript: Basic site details have been added and more discussion of the sites added to Section 2.1.*
>
> P.5, lines 6-15: The sites have been described in greater detail, including location, general character, and basic influences.

(8) In figures 4-6, the authors Most of readers may not be interested in the sample number, but interested in the exact difference among the samples in terms of their chemical characteristics.

The numbers were originally intended to allow comparison with prior publications but are now useful for referencing tabulated chemical characteristics.

> Table 2 has been added and relies on the sample numbers. The numbers are also useful for correlation with earlier studies and with the data supplement.

(9) Section 3.6: Discussion on possible effects of aerosol shape is too speculative. Again, the authors only refer to the previous works and do not show any supporting data to convince readers of their hypothesis. For example, if the authors assume a shape factor other than 1, then how can this support the discussion here?

This criticism is well received. We have made changes as discussed in our response to comment 1.7 above.

In response to this criticism, we have largely rewritten Section 3.6 to emphasize the conclusions of other researchers who have detected similar behavior, and move away from speculation.

(10) In Table 1, “SO4” should be “SO 4 2 −” or “sulfate”

This change has been made to Table 1.

Referee Comment III:

The study reports hygroscopic growth factors, kappa and CCN activity of water-soluble aerosol components in the form of re-aerosolized liquid samples from filters originally collected in National Park locations in the US. The methods, in particular the separation of WSOC from WSM, and the separate analysis of WSOC hygroscopicity, are novel and very interesting to the community. The results show that WSOC has large effects on the hygroscopic behaviors of mixed organic/inorganic aerosols. The paper is well-written and the topic is very relevant.

We are grateful for Referee III's thoughtful review of this manuscript. We believe that we have answered each comment and improved the discussion paper significantly.

The following points should be addressed before publication:

General comments 1) The complex experimental setup and measurement program deserve a more detailed description, in particular concerning uncertainties and the exact measurement program. What were the ranges of uncertainty and stability of the various RH settings and flow rates? How were the TDMA data inverted and growth factors determined? What were the uncertainties in the determined activation diameters? The section on TDMA and SMPS-CCNC operation would also profit from a better links between the text and Figure 1: What were the setpoints of size and RH at which points in the setup and in time for which measurement series?

We have expanded the methodology section in response to this and similar comments above, with special attention to these questions.

> The description of the experimental setup given in Section 2 has been greatly expanded in response to this and similar comments. Measurement uncertainties for hygroscopicity and CCN analysis are given on page 9, lines 15-28; for the chemical analysis on page 6, lines 18-19. The program of chemical analysis is also described on page 6, lines 9-25. The TDMA and CCN-SMPS measurements are elaborated in Section 2.5.
>
> TDMA operation is described in more detail on page 7, lines 19-32, including links with Fig. 1 and the relevant size and RH setpoints.
>
> The processing of TDMA data is described on page 8, lines 19-26.

2) More detail should also be provided on the handling and chemical analysis of the filter samples. How many filters, and which days were combined for each re-aerosolized sample? How might aerosol properties have changed over the course of the days combined into each sample? Also, it appears that some of the filter samples were taken as long as ten years ago - when were they extracted, and when were the laboratory measurements done? Can it be ensured that there are no artefacts from storage due to evaporation or other processes? In the results, fractions of WSOC and OC are re- ported, as well as WSOC retention percentages. How was this assessed, was there an independent WSOC measurement? How (and when) was OC measured? It would also be

much more reader-friendly to present the inorganic composition of the combined samples in this paper, rather than (more or less explicitly) referring to earlier studies (do they feature the same combination of filters to larger samples?).

We have attempted to respond to each of these questions, but do not reach the variation in aerosol properties over the course of days. Adequate treatment of aerosol sources is beyond the scope of this (quickly lengthening) paper.

> *Changes in Manuscript: We have added more details on the capture and preparation of the WSOC extracts. The basic sample information (how many days were combined, etc.) are already included in the supplement. We have added some limited discussion of the preservation of the samples and the timeline of the laboratory studies. We also have expanded the description of the chemical analysis (OC and WSOC). Finally, as we note in response to Comment 4 of referee 2, we have included tables with the available composition data. This includes the detailed inorganic composition of the Storm Peak Lab samples, the focus of our analysis.*
>
> More detail on filter handling and chemical analysis is given now given in Section 2.2. Details of which daily filters are combined in each sample are included in the Data Supplement, which is now referenced on page 6, line 1.
>
> The timeline of analysis is given more attention (e.g. page 6, line 27, which describes the time between extraction and hygroscopicity analysis). The year-to-year stability of extracts is defended on page 6, line 28.
>
> The chemical analysis procedures and assessment WSOC concentration are described on page 6, line 15-23.

3) The discussion on the enhancement of hygroscopic growth through WSOC could, and should, be more quantitative. “Enhancements” would be more obvious if measured values were compared to reference values - either of measured hygroscopic properties of the inorganic components (not just the total WSM) or of theoretical values/theoretical growth curves of inorganic salts in the Figures. See more specific comments below.

This comment is shared by each referee and the point is well taken. Our approach is detailed above in the response to the first comment of referee 1. In sum, we have followed this suggestion fairly closely by incorporating theoretical growth curves or inorganic compounds drawn from the E-AIM model.

> This approach has been largely adopted, resulting in a reworking of Sections 3.3-3.5 in the manuscript. A detailed response is given above in response to the first comment, but it is mostly duplicative of the actual changes and discussion in the manuscript.

4) The discussion of impact of particle shape needs substantiation. It seems a stretch to invoke two different mechanisms of particle shape changes as an explanation for both the deliquescence and efflorescence branch of the growth curves. The collapse of particle structures upon hydration is a known effect for aerosol types such as fresh com-

bustion agglomerates, but it is a far less obvious thought for a re-aerosolized WSOC sample. How do the authors know that the atomized aerosol is "irregularly shaped"? A discussion of the growth factor uncertainties deriving from the experimental setup and from GF determination from the DMA2 size distribution should be given. Also, why are the GF<1 not showing in the GRSM GF curve in Figure 2?

This critique is well taken and is shared by each reviewer; a full response is given for comment 1.7. Briefly, we have reworked the shape-factor discussion to focus on prior examples in the literature and practical effects on our results. While we have no definitive basis in our measurements for this conclusion, there are several groups that have reported and investigated similar behavior. Most notably Mikhailov et al., 2009, claim that spray drying of oxalic acid can produce aerosol with void fractions approaching 40%.

> In response to this and similar comments, Section 3.6 has been reworked to focus on earlier examples reported in the literature.
>
> The uncertainties associated with growth factor are now discussed on page 9, lines 21-28 and page 11, lines 15-18.
>
> The growth curves in Fig. 2 are normalized to reflect the minimum size recorded, as discussed on page 17, lines 11-13 and page 10, lines 14-16.

Gysel, M., E. Weingartner, et al. (2004). "Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol." Atmos. Chem. Phys. 4(1): 35-50.

Boreddy, S. K. R. and K. Kawamura (2016). "Hygroscopic growth of water-soluble matter extracted from remote marine aerosols over the western North Pacific: Influence of pollutants transported from East Asia." Science of The Total Environment 557–558: 285-295.

Mikhailov, E., S. Vlasenko, et al. (2009). "Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations." Atmos. Chem. Phys. 9(24): 9491-9522.

Detailed comments:

p.4, Section 1.1: Please give more details on those locations and sampling sites.

> As we note in response to comment 2.7, we have added details to Section 2.1, page 5, lines 4-15.

p.6, line 20: Why was this exact dry diameter chosen?

The diameter was chosen to correspond to the peak of the size distribution generated by the atomizer; these were very dilute solutions.

> Page 7, lines 21-22 clarify this choice.

p.6, line 24: How often is "periodically"?

Changes to the manuscript: We specify that extensive calibrations were done at the outset of the laboratory portion of these measurements, while RH calibrations were conducted at the beginning and at least once more over the course of the measurements for each study (a period of ~10 days).

Page 9, lines 12-14, clarify calibration frequency.

p.7, lines 14-16: This should be described earlier, along with more details on the measurement methods and results of the inorganic compounds.

We have added this description to the methodologies section (p.6, lines 9-25) and added the inorganic composition in table 2.

p.7, line 23: Please specify here: which one is the winter study? It is not reader-friendly to have him/her leaf back to the study description, find the abbreviation that refers to the winter study, and then re-locate that abbreviation in Figure 2.

We have incorporated this suggestion.

GRSM Winter has been added in a parenthetical to make this clear. P.10, line 6.

Figure 2: a) dark blue and dark green, as well as light blue and light green are hard to distinguish. How about a different symbol but the same color for WSM and WSOC of the same location?

We have made these modifications to Figure 2.

We have modified the symbols in Fig. 2 and attempted to improve the clarity. We have kept the color scheme for the sake of matching other figures.

It would also be nice to call "GRSM I"/"GRSM II" "GRSM summer" and "GRSM winter", to spare the reader repeated leafing back for which one is which.

We have made this change to Figure 2 and throughout the manuscript.

b) This presentation of activation diameters should be commented on in more detail in the text. Alternatively, it could be dropped.

We have added some description to the methodology section (p.8, line 28) and dropped this from the caption.

p.8, line 19: what kind of change classifies as "minor", what as "large"? Please expand (or add a reference) on how a "large" change in kappa indicates a phase change.

We have rephrased this description to use the more familiar and descriptive word 'abrupt.'

p.8, line 30-31: In Figure 3, GRSM I starts at around 0.3 -I would not call this "near zero".

P.11, line 21: This was a mistake and has been corrected to reference SPL and MORA samples.

p.9, line 8: “complementary enhancement” as compared to what? The inorganic components alone? (Below or above efflorescence?) For this, a reference hygroscopicity value (measured or calculated) of the isolated inorganic components should be given.What is currently shown in Figure 3 is just that total WSM has a higher kappa than the WSOM, which is not surprising. The paper would improve substantially if this analysis could be more quantitative.

Sections 3.3-3.5, including this discussion, have been largely reworked in an attempt to quantify this analysis.

p.9, line 6-7: These chemical compositions should be shown in a figure.

We have incorporated this composition data into Table 2.

p.9, line 20: Where and how is this shown?

This claim is more strongly supported now, and more clearly and correctly stated in the reworked analysis of this section.

p.9, line 26: Where is this argument going?

We clarified this discussion to reflect the more quantitative approach adopted in response to these comments.

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 water uptake~~dissolution~~ between 30~~40~~ and 70~~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, t~~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

(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 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 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 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.

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 components (Cerully et al., 2015; Kristensen et al., 2012). Using this approach, Guo et al. (2015) reported an average contribution by WSOC of 35% to particulate water across several sites in the south-eastern U.S. ~~This final modeling~~However, the calculations required to subtract the inorganic contribution ~~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 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~~ a 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 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); Asa-Awuku et al. (2008); and ~~and~~ Suda et al. (2012). The earlier work, by Gysel et al.~~,~~ (2004) 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 reported hygroscopic growth factors, GF, from 1.08–1.17 at 90% relative humidity, RH, corresponding to a hygroscopic parameter, κ (Petters and Kreidenweis, 2007~~8~~), from ~0.03–0.08. Asa-Awuku et al. used similar methods not only to 'desalt' samples of biomass burning aerosol, but also to isolate hydrophilic and hydrophobic WSOC—all for the purpose of determining how each fraction impacted aerosol hygroscopic growth within a multi-parameter, Köhler-theory based framework. 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 larger fraction of the WSOC. Moreover, the present work is distinguished by its focus on solubility.

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 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 primary 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 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.

2 Methodology

The analysis of WSOC for~~during~~ the five field studies~~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

PM2.5 filter samples were taken during five month-long studies. The first two studies, during the summer of 2006 and winter of 2007-2008, were conducted at the Look Rock Air Quality Station (35.633°N, 83.941°W, 806 m asl). Look Rock is in eastern Tennessee, situated on a ridge (~480 m) overlooking Great Smoky Mountains National Park (GRSM) to the south-east and rural farmland of the Tennessee River valley to the north-west. The third study took place near the southeast border of Mount Rainier National Park (MORA) in the state of Washington (46.758°N, 122.124°W, 426 m asl) during the summer of 2009. The site was situated in a remote valley, surrounded by heavily-logged coniferous forest. The fourth study, during the summer of 2010, took place at Storm Peak Laboratory (SPL), situated on a high ridge in remote north-western Colorado (40.455°N, 106.744°W, 3214 m asl). Due to its elevation, SPL provides unique access to the free troposphere and is influenced by both local and distant sources (Hallar et al., 2013). The final study, during the summer of 2011, was conducted on the Schoodic Peninsula in Maine, which lies west of Acadia National Park (ACAD) (44.341°N, 68.060°W, 20 m asl), across Bar Harbor. The coast of Maine near Acadia National Park is mostly rural, while the interior is sparsely inhabited coniferous forest. These sites were primarily selected for their proximity to national parks.

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 dichloromethane. The sample period was 24 hours. ~~and f~~Filters were collected daily from each sampler during ~~each~~ all projects and were ~~and~~ kept refrigerated during storage and shipping after sampling and prior to analysis. Filters were typically processed within three months of the completion of the respective measurement campaign.

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, 2015), following the method of Duarte and Duarte (2005). First, WSM was extracted from each daily set of 4 high-volume ~~the~~ filters by sonication in 250 mL of ultrapure water, then removed through a PTFE membrane filter.~~.~~ 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 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 month-long study. The filter days associated with each sample are given in the data supplement. ~~.~~

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 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).

Chemical analyses of inorganic ions and OC were conducted at various stages of the extraction process. Filter captured sulfate, nitrate, and chloride were measured using ion chromatography (IC) (Dionex DX 3000); ammonium using automated colorimetry (Astoria 301A analyzer) (Lowenthal et al. 2009; Samburova et al., 2013). Similar IC and colorimetry measurements were conducted on the extracts (Lowenthal et. al 2009) and to determine the “Sulfate Cleaning Efficiency” reported in Table 1. Filter and extract OC and OM were determined using thermo-optical reflectance (TOR) (Chow et al., 2004) and/or total organic carbon (TOC) (OI Analytical Aurora 1030W TOC Analyzer) methods—which showed good agreement (Lowenthal et al., 2015). During the SPL study, dissolved WSOC was measured using only TOC (Shimadzu Model TOC-VCSH). During the four national park studies, measurement uncertainties for OC, sulfate, nitrate, and ammonium were 12, 5, 26, and 5% (Lowenthal et al., 2015). The OM to OC ratio was evaluated by depositing and drying isolated WSOC sample material on pre-fired quartz filter punches, and combining TOR carbon analysis with before-and-after measurements of the punch mass; a standard value of 1.8 was employed during all studies except SPL, for which 2.1 was assumed. The performance of the WSOC extraction, summarized as WSOC Recovery in Table 1, was evaluated by before-and-after measurements of dissolved OC (Lowenthal et al. 2009). More extensive chemical analysis was conducted on the extracts prepared during the SPL project, including detailed speciation of WSOC and IC measurements of crustal ions (using a Dionex CS16 column) in WSM samples (Samburova et al., 2013).

~~The performance of the extraction technique is given in Table 1.~~

2.3 WSOC hygroscopicity and CCN activity analysis

The hygroscopicity and CCN activity of the prepared samples from each study were evaluated within several months of their extraction. The samples were continuously refrigerated which effectively preserved their properties. A remnant of a GRSM Summer sample was re-analyzed alongside the GRSM Winter samples over a year after its first analysis and showed little change in hygroscopicity. 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~~generation

The isolated WSOC samples were aerosolized using a TSI 3076 atomizer configured to recirculate overspray. Several 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 compressed air stream. To ~~prevent~~minimize 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.

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 particle 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 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

The hygroscopicity of each sample was evaluated in two sets of TDMA measurements~~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 hydrated (RH ~90%) aerosol.

~~For~~In both, the first DMA column was operated to select~~the initial~~ dry particles with electrical mobility ~~-~~diameter ~~was~~of 0.07 μm, roughly corresponding to the peak in number concentration of the dried atomizer generated aerosol. The second DMA column was operated in conjunction with the condensation particle counter (CPC) as a traditional SMPS, capturing the response of this roughly monodisperse aerosol to the humidification and drying processes occurring between the two DMA columns at ~90s intervals. During the first series—the "pre-desiccated" or "deliquescence" scan~~. —~~—the dry, monodisperse aerosol bypassed the humidifying Perma Pure PD-Series Nafion tube bundle as depicted in Fig. 1. The aerosol was next directed through the RH controlled Nafion tube bundle, which was used to track a gradually descending RH setpoint from ~90% to ~25% RH over the course of ~90 minutes. Thus, this configuration mapped the hygroscopic growth response of an initially desiccated aerosol to capture deliquescence behavior. The second series—the "pre-hydrated" or "efflorescence" scan—mapped the hygroscopic growth of an initially hydrated aerosol to detect distinct efflorescence transitions and meta-stable hydration states. During the second series, the monodisperse aerosol passed through the humidifying Nafion tube bundle, while the controlled Nafion tracked an RH setpoint that gradually increased from ~25% to ~90% RH.

Each series of TDMA measurements resulted in a series of size distributions captured by the second DMA column and CPC operating as an SMPS, in which the location (representing particle size) of a single, narrow mode reflected the hygroscopic growth of the sample. Each distribution was condensed to a single parameter, growth factor, or GF(RH), which is the ratio of the particle size detected by the second DMA/CPC to the dry particle diameter selected in the first DMA column (here 0.07 μm). The basic GF(RH) curves for each sample from each study are included in the data supplement. Growth factor is an intuitive metric of hygroscopicity, but we primarily discuss these results using the 'kappa' hygroscopicity parameterization, κ(RH), of Petters and Kreidenweis (2007). GF(RH) translates directly into κ(RH).

(1)

$$\kappa(\mathrm{RH}) = (GF(RH)^3 - 1)\,\frac{\left(\exp\left(\frac{A}{GF(RH)\cdot D_p}\right) - RH\right)}{RH}$$

(2)

$$A = \frac{4\cdot\sigma_{s/a}\cdot MW_{water}}{R\cdot T\cdot\rho_{water}}$$

Here, $\sigma_{s/a}$ is assumed equal to 0.072 J m^{-2}, the surface tension of pure water. D_p, the dry diameter, is chosen to reflect the minimum particle size detected, rather than the size selected by the first DMA column (0.07 μm), to correct for a measurement artifact described in Section XZY below. These particles are assumed to be spherical. Among the advantages of κ(RH) is that it is more closely a bulk property of the material; for an ideal solution, κ(RH) is independent of RH and proportional to the molecular volume of the solute.

The CPC count array was inverted with respect to the second DMA only; the resulting distributions retained the natural breadth and multiply charged particles contribution from the aerosol population selected by the first DMA. Neither impacts the results. Multiply charged particles were expected to be relatively rare, as the generated aerosol distribution was quite narrow and the selected size near its peak. For these experiments, the only parameter of interest was the peak diameter of the resultant size distribution, not its breadth. But the distributions were narrow and well-resolved, driven by the TDMA's sheath-to-sample flow ratio of 10:1 (30 vs. 3 l/min).

CCN activity of aerosol samples from MORA, ACAD, and SPL was analyzed using a DMT~~-the~~ CCNc operated at ~~4~~four 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. 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, such as the atomizer generated aerosol measured here, 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. That is, at sizes below the critical activation diameter of the aerosol for the set supersaturation, the CCNc size distribution is zero; above the aerosol's activation diameter the CCN and CCNc distributions are identical. The mid-point of the transition between these regimes ($D_p50\%$) corresponds to the critical dry diameter for CCN activation at the set CCNc supersaturation. These results are typically reported as $D_p50\%(SS_C)$ as in Fig. 2, where SS_C is the aerosol critical supersaturation expressed as a percentage. $D_p50\%(SS_C)$ also translates into κ(SS_C), which is comparable to κ(RH) (Petters and Kreidenweis, 2013) , as in Fig. 3.

(3)

$$\kappa(SS_C) = \frac{4A^3}{27 \cdot D_p 50\%(SS_C)^3 \cdot ln(SS_C + 1)^2}$$

This equation is an approximation of κ(SS_C), slightly overestimating (~5%) where κ(SS_C) < 0.2. It is retained for its consistency with other studies. *A* is given in Eq. (2), above.

Both instruments were calibrated ~~periodically during the studies~~at the outset of each study and least once more over the course of measurements (~10 days).~~.~~ The critical sizing parameters of the TDMA, the flow 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. The uncertainty associated with TDMA and SMPS-CCNc measurements is primarily driven by uncertainty in RH and supersaturation. RH was measured using Vaisala HMM-22D RH probes, which have a manufacturer reported accuracy of ±2-3%. The precision of CCNc supersaturation has been reported to range from ±1-5% depending on the stability of ambient conditions and time period (Rose et al., 2008). The uncertainty associated with particle sizing by the TDMA/SMPS instrument, linked to the sheath flow rate measurement (±1%) and high voltage supply (±0.5% for the relevant voltage range), is lower, near ±0.001 μm at 0.070 μm. Additional uncertainty arises from the possibility of irregularly shaped aerosol. Shape factor, the ratio between

TDMA-relevant particle mobility diameter and particle volume-equivalent diameter, is used to correct for the depressed mobility of irregularly shaped particles and commonly ranges from 1.02 for ammonium sulfate to 1.08 for cubic sodium chloride to 1.24 for irregularly formed sodium chloride (Wang et al., 2010). Calculations of κ(RH) are very sensitive to shape factor at low RH: an uncertainty of ±0.03 in shape factor can easily translate to >50% uncertainty in κ(RH) at low RH but <5% at high RH. No independent recoveries of shape factor, such as SEM micrographs, were made during these studies to constrain this uncertainty. Some confidence can be gained from the continuity between measurements before and after the particles dissolve (and become spherical)—which is detected at low RH for all WSOC samples.

~~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 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~~ particles may assume complex morphologies.

3.1 Filter samples and WSOC extracts

As ~~depicted~~ presented in Table 1, WSOC concentration ranged from 0.22 to 1.41 µg·C/m^3. The lowest concentration, unsurprisingly, was during the sole winter study (GRSM Winter); otherwise, WSOC varied much more narrowly than reconstructed PM2.5. (PM2.5 was not measured, but Lowenthal et al. (~~2011~~2015) 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~~ analysis of the samples collected during the five projects. The pre-~~initially~~ desiccated hygroscopic growth curves for each measurement are omitted for clarity, and the scans are normalized with respect to their minimum GF according to the discussion of Section 3.6 below.~~.~~ 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 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 that 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. Somewhat surprisingly, the largest deviation is lower CCN-activity-derived κ for the SPL WSM samples: the potential for droplet surface tension depression (leading to *enhanced* CCN inferred κ) by surface active organics can be enhanced in mixtures with inorganic ions like WSM (Asa-Awuku et al., 2008).

The shape of these κ(RH) curves indicates that WSOC behaves somewhat differently than an ideal, aqueous aerosol. Neglecting the influence of surface tension, κ(RH) for an ideal, fully aqueous aerosol is relatively constant and determined by relative molecular weights and densities of the solute and solvent (water). We rationalize minor deviations in the shapes of these κ(RH) curves as non-ideal solution behavior, ~~and large~~and abrupt deviations as changes in aerosol phase. In particular, an abrupt decrease in κ(RH) with decreasing RH in measurements of an initially hydrated aerosol (shown here) can indicate efflorescence. One caveat to κ(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, particles~~aerosols~~ are assumed to be spherical, having a shape factor of 1, with the notable exception discussed in the ~~final section~~Section 3.6 below.

Thus, as κ(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~~ κ(RH) for the SPL and ~~GRSM summer~~MORA WSOC samples climbs from near zero to ~0.1, indicating a distinct deliquescence point (DRH). Neglecting curvature effects, DRH relates to solubility as it is the vapor pressure over a solute-saturated solution. This suggests that the solubility of these samples limits the existence of an aqueous phase to ~~are insoluble below ~~~RH >30%~~ RH~~, *i.e.*, ~~when the~~when the activity of the aerosol-phase water is greater~~less~~ than ~0.3. For WSOC collected during the GRSM winter project, κ(RH) also increases with increasing RH, but the change is less abrupt. With the remaining WSOC samples there is little change in κ(RH) over the full RH range, suggesting lower, undetected DRH and higher solubility. The κ(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 κ(RH) curves indicate that some species that make up the WSM gradually leave the aqueous solution as RH decreases. ~~—~~Together with the WSOC measurements, this implies a complementary effect between WSOC and inorganic aerosol material which is~~—~~ discussed in the next section.

3.3 Complementary enhancement of water uptake by mixtures of WSOC and inorganic ions ~~of WSOC and inorganic dissolution~~

During two projects, the summers at GRSM and SPL, samples of both ambient WSOC and ambient WSM were isolated and analyzed (only WSOC samples were analyzed for the remaining three projects). In addition to the compounds retained in the WSOC sample, the WSM samples contained~~s~~ all water soluble inorganic and organic material not retained by the WSOC extraction. The ~~The contrasting h~~hygroscopic growth ~~curves~~ of these materials indicates~~suggests a significant complementary enhancement of water uptake~~ that ~~by~~ mixtures of WSOC and soluble, inorganic compounds can uptake significantly more water than their individual ~~hygroscopici~~hygroscopicities~~ty~~ would predict. This result is not unanticipated ~~.; iIt~~as it is well known that the efflorescence/deliquescence behavior of inorganic salts is modified by the presence of

WSOC (Smith et al., 2012; Marcolli et al., 2004; Brooks et al., 2002; Hansson et al., 1998) and that deliquescence point of an internal mixture of inorganic salts ~~will gradually dissolve with increasing RH *below*~~is generally lower than the~~ir~~ deliquescence points ~~if internally mixed with more-soluble compounds~~of the individual compounds~~, reaching a minimum at some eutectic combination of the compoiunds~~ (Zardini et al., 2008; Ansari and Pandis, 1999). However, the isolation and analysis~~analysis~~ of ~~ambient~~ atmospheric WSOC and WSM in the present study provides a unique perspective on these effects in complex, atmospherically representative mixtures.

~~The aerosol samples from GRSM and SPL were veryconsistently 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 WSOMC 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 (typicallywhether WSOC or inorganic) appears to enhance the contribution of the less soluble fraction to aerosol water uptake. The simplest likely mechanismexplanation for this enhancement the depression of DRH in mixed solutions: solutes more readily dissolve into complex mixtures (Zardini et al., 2008).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 mostre soluble, more eutectic mixture dissolves component is diluted with hygroscopic growth (Tang, 1997).~~

To quantify and isolate this complementary effect, the measured WSM hygroscopicity for the SPL and GRSM Summer samples is contrasted with a modeled prediction of WSM hygroscopicity that assumes no interaction between the organic and inorganic fractions—a ZSR-like estimate. Particularly for samples from SPL, this prediction consistently underestimated water uptake by WSM at RH between 30 and 70%, as illustrated in Fig. 4, and suggests that interactions between the inorganic and organic fractions enhance water uptake. As is explored below, this enhancement is linked to the RH at which the inorganic PM dissolves. ~~The difference between the prediction and actual WSM hygroscopicity indicates that interaction between WSOM and inorganic aerosol material can enhance total water uptake. This approach is similar to that employed by Gysel et al (2004).~~

~~WSM hygroscopicity is predicted from the measured WSOM hygroscopicity and a modeled estimate of the inorganic hygroscopicity. The E-AIM model was chosen to predict~~

3.4~~5~~ Storm Peak Lab: Enhanced water uptake driven by low-DRH WSOC~~by ammonium sulfate at low RH in mixtures with WSOC~~

Enhanced water uptake is most clearly demonstrated in the results from Storm Peak Laboratory in remote norther Colorado. Primarily this is because the SPL study involved more detailed chemical analysis as well as a full set of complementary WSM and WSOC samples. As noted above, the enhancement of water uptake is shown by contrasting the measured WSM hygroscopic growth with a prediction of WSM hygroscopic growth based upon the independent contribution of WSOC and inorganic components assuming no interaction. This prediction is based on the measured WSOC hygroscopicity and the inorganic hygroscopicity estimated from composition.

Modeling the hygroscopic properties from the available SPL inorganic composition was done using the E-AIM thermodynamic model (Clegg and Brimblecombe, 2005;Clegg et al., 1998a, b) and presented several challenges. First, E-AIM does not treat K^+, Mg^{2+}, and Ca^{2+}. However, it does treat multiple solid phases, including hydrates. Critically, it appears to handle the addition of nitrate more realistically than other models. The untreated cations K^+ and Mg^{2+} were included in the model input as charge equivalent Na^+, while Ca^{2+} was assumed to remove one sulfate ion to form $CaSO_4$ or gypsum, both of which are relatively insoluble, only expected to dissolve at high RH, and not expected to impact the relevant deliquescence transitions.

A second issue is that that the inorganic anions and cations for these samples do not balance (Hallar et al., 2013). In very similar analysis of WSM and WSOC, Gysel et al. (2004) assumed that a negative ion balance was simply offset with protons. For various reasons, we more closely followed the approach of Hallar et al. (2013) and assumed that the missing cations are ammonium. This approach was chosen largely because the samples all contained significant nitrate which does not typically exist in the aerosol phase with acidic, un-neutralized sulfate (Fountoukis and Nenes, 2007). The cations in the available composition data are insufficient to neutralize the detected sulfate (the average ammonium to sulfate ratio is ~0.93). Next, assuming a more acidic aerosol would dramatically overestimate the hygroscopic growth. κ(RH) for ammonium bisulfate, with a molar ratio of ammonium to sulfate of one, is almost 0.8 at 50% RH, much higher than is indicated by the WSM samples. Similarly, each WSM sample exhibits an abrupt increase in κ(RH) near 80%, which appears to correspond to the deliquescence of the inorganic fraction, but is inconsistent with the acidic mixtures the ammonium to sulfate ratios indicate (DRH of ammonium bisulfate is ~40% RH). The E-AIM results, given as solute mass in- and out-of-solution, were translated into κ(RH) using the density model of Clegg and Wexler (2011a, b) and are depicted by the dashed lines in Fig 4.

WSM hygroscopicity as predicted from the independent hygroscopicity of the organic (measured) and inorganic (modeled) fraction of each sample by simply taking the dry-solute-volume weighted average of the independent κ(RH) (Petters and Kreidenweis, 2007) is shown in green in Fig. 4. While the dry solute volume of the inorganic fraction can be accurately calculated from the known mass and modeled density, no density information is available for the WSOC. We assume a value of 1.5 g/cm^3, relative to WSOM, but also show that the results are relatively insensitive to this assumption by including the results of assuming 1.3 and 1.7 g/cm^3 for contrast. A second minor assumption is that the WSOC properties measured are representative of all the WSOC present in the WSM samples. Other facets of the SPL project have reported that un-extracted WSOC was characterized by relatively lower molecular weight (Hallar et al., 2013; Samburova et al., 2013), which in an ideal mixture would cause greater hygroscopic growth. However, the impact here is expected to be limited; as shown in Table 2, unrecovered WSOC is a minor fraction. Figure 4 shows the result of assuming that the κ(RH) of the unanalyzed WSOC is 1.5 times that of the analyzed fraction, constraining the likely impact of WSOC not retained by the isolation process. The uncertainty in WSOC density and unanalyzed WSOC is minor and does not appear to account for the enhancement in water uptake by mixed aerosol.

A final note should be made concerning the composition data relied on for this analysis. For Samples 2 and 4, the reported concentrations of inorganic compounds derived from direct analysis of the samples were not consistent with concurrent daily filter-based PM2.5 composition measurements and produced unrealistic predicted WSM hygroscopicity. For this analysis, the relative prevalence of inorganic compounds for those samples was derived from the daily measurements. For Sample 2, the relative abundance of WSOC was also inferred. In inferring composition, no attempt was made to correct for the filter sampling artifacts, such as adsorption of OC, reported by Lowenthal et al. (2009). The potential underestimation is expected to be minor and not impact the overall conclusion.

The measured and predicted WSM, WSOC, and modeled inorganic hygroscopicity for each sample from SPL are shown in Fig. 4. As described in Tables 1 and 2, PM2.5 collected during the SPL was predominantly organic, and the average WSOC to OC ratio was 89%. Each WSOC sample fully deliquesced at RH from 25-35%, above which κ(RH) remains fairly constant near 0.1. The potential impact of the un-recovered WSOC, assuming it is 50% more hygroscopic than that recovered, is indicated by the smaller markers above each WSOC data point. Apart from Sample 6, for which the unrecovered fraction was large and κ(RH) relatively high, the impact is very minor. At low RH SPL samples exhibit a behavior shared by WSOC sample from the GRSM Winter study, as well as by the WSOC studied by Gysel et al. (2004): the pre-desiccated measurement-based κ(RH) climbs steeply with decreasing RH while that based on the pre-hydrated measurements converge to zero. Section 3.6, below, discusses this further, suggesting that it is a measurement artifact related to generated particle morphology. For the purposes of this discussion we assume that, at low RH, the pre-hydrated measurements are representative of the actual deliquescence properties of the samples.

The inorganic soluble material in SPL WSM samples was dominated by a mixture of sulfate (54% of inorganic mass averaged across samples), nitrate (18%), and ammonium (11%), with minor fractions of Cl^- (<1%), K^+ (8%), Na^+ (1%), Mg^{2+} (1%), and Ca^{2+} (6%) (Hallar et al., 2013). The hygroscopic growth of the inorganic fraction estimated using the E-AIM model was fairly consistent from sample to sample, characterized by gradual deliquescence from 45-75% RH. The gradual dissolution predicted by E-AIM is punctuated by the formation of several hydrates and minor salts, but dominated by ammonium sulfate. The model predicts that ammonium sulfate will dissolve gradually below its pure DRH as a solution containing other ions is a more effective solvent (Marcolli et al., 2004). In each sample, the inorganic components are predicted to fully dissolve at RH > 75%.

Measured WSM hygroscopicity of each sample indicates gradual dissolution from 30-80% RH, with a small abrupt increase around 80%. In Samples 1, 2, and 4, this transition is associated with a small hysteresis loop, which suggests the existence of an ordered, crystalline phase (Martin, 2000). Apart from this small hysteresis loop, there is little difference between the pre-desiccated and pre-hydrated measurements and dissolution and formation of solids appears reversible. Because the WSOC measurements indicate that it will be dissolved above 30% RH and because WSOC cannot account for κ(RH) above ~0.07 ($\kappa(\mathrm{RH})_{\mathrm{WSOC}}$ reduced in proportion to WSOC contribution to dry particle volume), the gradual dissolution can be attributed to the inorganic fraction. However, based on the expected deliquescence profile of the inorganic fraction predicted using E-AIM, this dissolution should not take place at all below 45% RH, and should not contribute significantly until ~60% RH.

The impact of this shift in the deliquescence RH of the inorganic fraction of the WSM samples is evident in the contrast between the predicted and measured WSM hygroscopicity. Near 90% RH, where both the predicted and measured WSM κ(RH) of most samples have plateaued indicating that all solutes are dissolved, there is reasonably good agreement between them, given the uncertainties involved. The observed difference is most likely due to error in the measured relative abundance of inorganic and organic compounds, which determines the relative weight of the inorganic and organic hygroscopicities. Errors in WSOC and inorganic hygroscopicity would need to be unrealistically large to close the gap; in Sample 3 for example, κ(RH) would need to peak above 0.85. More relevant to this discussion are the errors in the deliquescence profile at lower RH. First, there is some inconsistency in the point at which κ(RH) plateaus, and all solutes have dissolved. The model captures the profile of Samples 2 and 3, but predicts full dissolution at too low RH for the other three samples. For all samples, however, the model generally predicts the deliquescence at much higher RH than is evident from the measured WSM profiles. This behavior is consistent with the expectation that DRH is depressed in mixtures (e.g., Marcolli et al., 2004). This trend is even evident near the DRH of WSOC. Because no part of the inorganic fraction is expected to be dissolved below 45% RH, the expected WSM hygroscopicity profile is below even the WSOC curve. Yet κ(RH) of the measured WSM is consistently higher than WSOC at low RH. For Sample 2, the measured onset of dissolution of WSM is even lower than that of 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~~These results indicate that the hydration behavior of ~~SNA aerosol~~complex, internally mixed aerosol ~~in the atmosphere at these sites~~ may deviate significantly from that expected based on its major inorganic constituents~~for unmixed SNA~~. The average error of the expected vs. measured WSM hygroscopicity at SPL, shown in Fig. 5, indicates that at low RH the measured κ(RH) for WSM is on average twice that expected. This roughly corresponds to doubling of aerosol water. This behavior is rationalized by depressed DRH of compounds in mixtures (Smith et al., 2012; Wu et al., 2011; Marcolli et al., 2004; Brooks et al., 2002; Choi and Chan, 2002; Cruz and Pandis, 2000; Hansson et al., 1998). The impact of this behavior is likely widespread as highly soluble, low-DRH WSOC was ubiquitous during these studies. In all SPL WSM samples, hysteresis was limited, despite the general expectation that ~~SNA~~ sulfate-nitrate aerosols have~~s~~ 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., 2009). T~~; t~~he 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~~ inorganic compounds can be expected to contribute more to aerosol water in the presence of ~~highly soluble~~ low-DRH WSOC. The atmospheric impact of this behavior could be significant in dry climates where crystalline aerosol would otherwise form.

3.54 ~~Enhanced WSOC water uptake at low RH in mixtures with highly soluble, acidic sulfate~~GRSM Summer: Mixtures dominated by acidic sulfate

~~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.~~

~~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.~~

~~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.~~ Only two other WSM samples, corresponding to GRSM Summer Samples 4 and 6, were produced and analyzed as part of these studies. Unlike the SPL study, composition had to be inferred from simultaneous daily filter measurements. The GRSM Summer aerosol was also quite distinct from that at SPL. It was dominated by sulfate (9.0 μg/m^3), had limited ammonium (1.9 μg/m^3), and while organic mass was relatively abundant (5.2 μg/m^3) only 24% was soluble.

The differences between predicted and measured WSM hygroscopicity for these samples, shown in Fig. 6, may stem from uncertainties in inferred composition. WSM hygroscopicity is much lower than predicted. For both samples, closure is possible by assuming the relative concentration of WSOC is 550% higher. Closure cannot be achieved by assuming realistic changes in the WSOC or inorganic hygroscopicity (i.e., WSOC hygroscopicity is unlikely to be negative). And only a small percentage of WSOC hygroscopicity can be attributed to the lower sulfate cleaning efficiency for GRSM Summer samples (~5%). Because composition is inferred, it is difficult to speculate whether this error implies a higher than reported ambient WSOC concentration or simply a difference between the samples and daily filter measurements.

As with the SPL samples there is an ion imbalance. The molar ratio of ammonium to sulfate inferred for Samples 4 and 6 are 1.04 and 0.86, respectively. But there is less justification for assuming that ammonium is under-reported. Though sulfate levels have since dropped, GRSM has long been characterized by acidic sulfate aerosol in summer (Lowenthal et al., 2015). Nor was significant nitrate detected, which would have implied neutralized sulfate. The measured Sample 6 WSM hygroscopicity does show behavior consistent with the presence of letovicite, $(NH_4)_3H(SO_4)_2$, which would imply an ammonium to sulfate ratio greater than 1.

Though these results are uncertain, there are several features worth noting, including a potential depression of the deliquescence point of letovicite. Because the dominant fraction of both samples is acidic sulfate, the aerosols are expected to be fully aqueous at all measurement RH. Ammonium bisulfate does exhibit deliquescence (39% DRH) and a crystalline form, but its efflorescence point (17% ERH) is below the range of the H-TDMA used in this analysis. Reflecting this, the formation of crystalline ammonium bisulfate is suppressed in the E-AIM estimates shown in Fig. 6. Despite this expectation, Sample 6 exhibits a distinct deliquescence transition near 50% RH. As noted above, this behavior appears to be most consistent with a fraction of crystalline letovicite. Figure 6 illustrates the impact of assuming different ammonium to sulfate ratios (i.e., assuming ammonium was under-reported to differing degrees). Depressed κ(RH) at low RH is due to the formation of crystalline letovicite. As is shown, the expected DRH differs from the measured DRH. E-AIM predicts some depression of DRH of letovicite, as some will dissolve into the surrounding aqueous solution. This is illustrated by the lower DRH of letovicite at lower ammonium-to-sulfate ratios in Fig. 6. There is more aqueous volume in proportion to letovicite and it is entirely consumed at lower RH. Here, the predicted depression was less than measured, suggesting that the presence of aqueous WSOC contributes to the effect.

3.6 Irregular particle morphology rationalization for anomalous growth factor at low RH~~Variability in generated aerosol shape~~

This section addresses a measurement artifact that has been observed in other similar studies (Boreddy and Kawamura, 2016; Mikhailov et al., 2009; Mikhailov et al., 2004; Gysel et al., 2004). 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, t~~The measured GF from these projects was also consistently below unity at low RH (as illustrated in Fig. ~~6~~7, showing the results from GRSM winter)~~. Similar behavior was observed in the measurements of WSOC conducted by Gysel et al. (2004).~~ These results indicate a reduction in particle size as the aerosol is processed between the two DMAs in the TDMA. Though there are several plausible explanations for this behavior, including evaporation of volatile aerosol phase components, the parallels in Gysel et al. (2004) and Mikhailov et al. (2009) support the hypothesis that the size loss is due to the collapse of irregularly shaped particles. Regardless of the cause, in all measurements the pre-desiccated and pre-hydrated profiles eventually overlap and the smallest detected pre-hydrated size is assumed to be the most accurate assessment of dry volume for κ(RH) calculations and inferring bulk WSOC hygroscopic properties.

~~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 an enhanced shape factor.~~

~~This hypothesis explains the lower-than-unity growth factor as the result of the irregularly shaped aerosol collapsing.~~

The separation between the pre-desiccated and pre-hydrated measurements appears to relate to the aerosol being rehydrated. The aerosol entering the first DMA has been dried to low RH (<20%). The pre-hydrated aerosol is in the collapsed form even during measurements at very low RH because its conditioning begins with rehydration in the humidifying Nafion tube bundle (Fig. 1), while the pre-desiccated particles only collapse when the controlled RH is sufficient for them to substantially dissolve. This link with dissolution is supported by the observance of this behavior only during the GRSM Winter, MORA and SPL projects: As shown in Fig. 3, the WSOC samples from these projects are the only samples that exhibit DRH greater than 30% RH, while the GRSM summer and ACAD WSOC samples appear fully dissolved at the lowest RH measured. The link to dissolution is consistent with both the collapse of an irregularly shaped aerosol and kinetically limited evaporation. Nor are these rationalizations exclusive as evaporation can produce void fractions within a gel-like aerosol (Mikhailov et al. 2004).

Gysel et al. (2004), Mikhailov et al. (2009), and Boreddy and Kawamura (2016) each report on similar behavior for various WSOC. The report of Gysel et al. is most analogous and attributes this behavior to restructuring. Along with filter extracts of WSOC, they reproduced the phenomenon using Nordic reference humic and fulvic acids and Aldrich humic salts—i.e., substances unlikely to volatilize (Baltensperger et al., 2005). SEM micrographs in Gysel et al. (2004) depict approximately spherical particles; each of the three reports cited above suggest fissures and void fractions account for the apparent reduction in particle density of spray-dried aerosol. Mikhailov et al. (2009) detected similar behavior by oxalic acid aerosol. Though some dicarboxylic acids have been shown to exhibit evaporative losses in TDMAs, Mikhailov et al. (2009) demonstrated the stability of oxalic acid by varying its residence time within the system. Notably, Mikhailov et al. (2009) reported that rapidly drying atomized organic matter in its native, highly charged state could produce high void fraction (40-50%) aerogel-like aerosol. Here, as in Mikhailov et al. (2009), the initial drying of the highly-charged atomizer spray is rapid and distinct from the drying of singly-charged particles within the TDMA system. The initial drying in this study was not as drastic (~25% vs. ~5% RH) but the similarities in process and result are convincing. These findings parallel other work linking drying rate (Wang et al., 2010) and particle charge (Berkland et al., 2004) to particle morphology. Alternatively, for succinic acid, the solvent used in the spray suspension has been found to dramatically affect morphology and void fraction (Carver and Snyder, 2012).

In sum, this behavior appears to be a measurement artifact. There is little direct evidence from this study to determine whether it is caused by irregularly shaped particles or evaporative losses, but similar findings by others support the former. For the purposes of this study, the cause is irrelevant and the minimum size reached by the pre-hydrated scan is assumed to most accurately reflect the amount of aerosol material involved in hygroscopic growth. ~~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 (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 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 κ(RH) curves from SPL, above, indicate that the pre-hydrated 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 was ubiquitous in PM2.5 ~~gathered~~collected during five month-long studies at various sites and was ~~were~~ characterized by hygroscopic growth parameters (κ) ranging from 0.05 to 0.15. WSOC samples from GRSM Winter, MORA, and SPL deliquesced near 30% RH, while WSOC samples from GRSM Summer and ACAD did not display deliquescence, but were aqueous at all measured RH. ~~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 WSOC samples~~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, low-DRH 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 increases~~d~~ 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%
Sulfate~~SO_4~~ 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·C/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

Table 2: Concentration (ng/m^3) of Inorganic Ions, Organic Carbon, and Organic Mass in WSM Extracts

Storm Peak Lab WSM Samples*

Sample Number	1	2	3	4	6
Na^+	6.5	2	11	8.9	6.4
$SO4_4^{2-}$	544	330 (449)	452	77 (488)	242
NH_4^+	85	58 (80)	41	66 (112)	33
NO_3^-	83	83 (105)	137	126 (124)	50
Cl^-	4.4	4.3	2.6	5.6	0.4
Ca^{2+}	28	27	27	33	33
K^+	42	46	54	44	29
Mg^{2+}	5	4.6	6	7	2.2
Total Inorganic Ions	797	555 (718)	730	368 (810)	396
WSOC (ng·C/m^3)	525	1,932	601	596	490
WSOC Recovery (%)	55	87	81	92	52
WSOM (x2.1)	1,070	3,942 (1,387)	1,226	1,215	999

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GRSM Summer WSM Samples**

Sample Number	4	6
$SO4_4^{2-}$	13,172	12,043
NH_4^+	2,580	1,949
NO_3^- [†]	---	---
Total Inorganic Ions	15,752	13,992
WSOC (ng·C/m^3)	1,637	533
WSOC Recovery (%)[††]	---	---
WSOM (x1.8)	2,946	960

*Direct analysis of SPL samples was performed and reported by Samburova et al. (2013). Values in parenthesis were inferred from concurrent daily PM2.5 filter analysis reported by Hallar et al. (2013).

**WSM composition was not reported for GRSM Summer. The given values are inferred from concurrent dailyPM2.5filter analysis performed and reported by Lowenthal et al. (2009).

[†] Daily nitrate was not reported; Lowenthal et al. indicated that 50 ng/m^3 was typical during this study.

[††] Daily WSOC Recovery was not reported for these samples; Lowenthal et al. indicated an average WSOC Recovery of 46% for GRSM Summer.

Figures

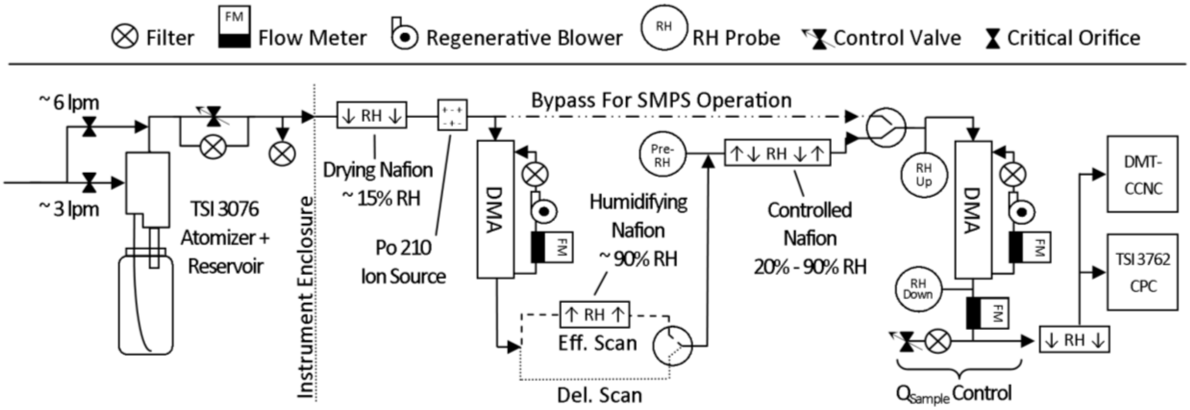

Figure 1: TDMA and SMPS-CCNc configuration.

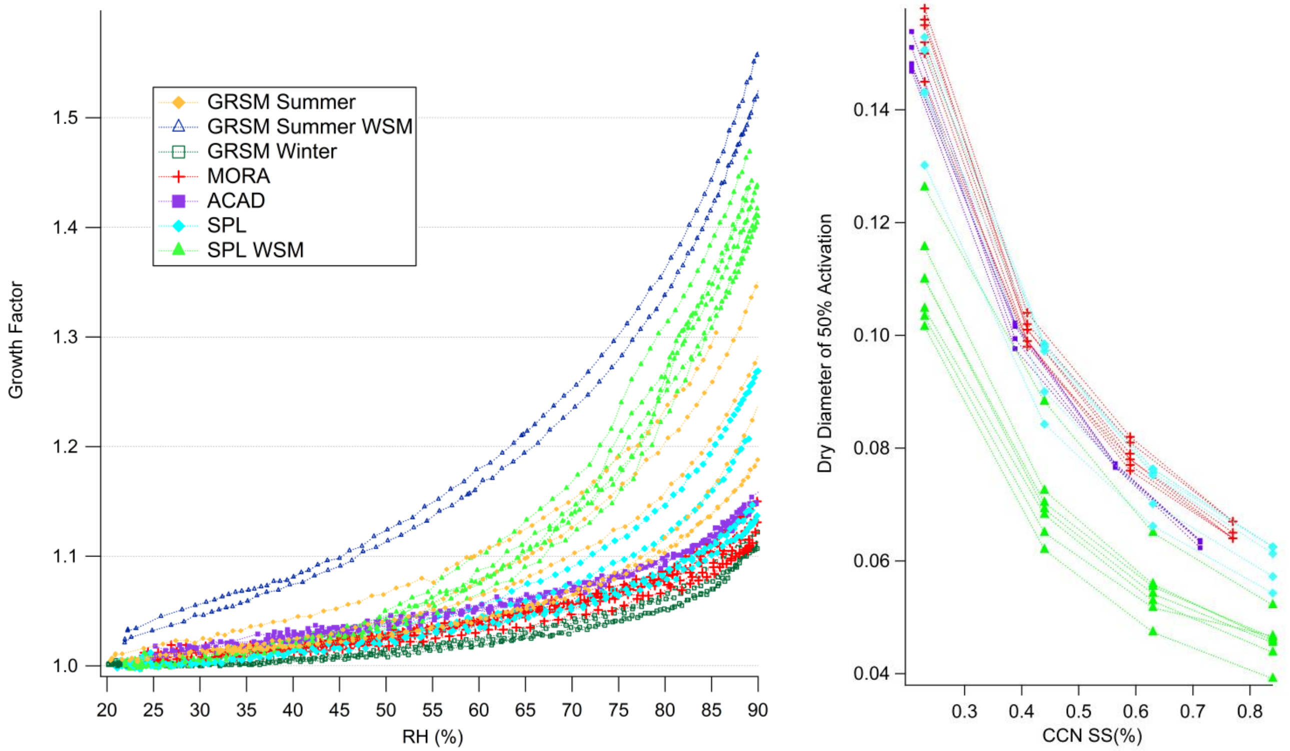

Figure 2: Hygroscopic growth curves for initially hydrated aerosol samples (designed to detect efflorescence) and CCN activity results. Hygroscopic growth was measured for all samples~~: From Great Smoky Mountains Summer (GRSM I), both total Water Soluble aerosol Material (WSM) and isolated WSOC; from 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 samples (both WSM and WSOC).

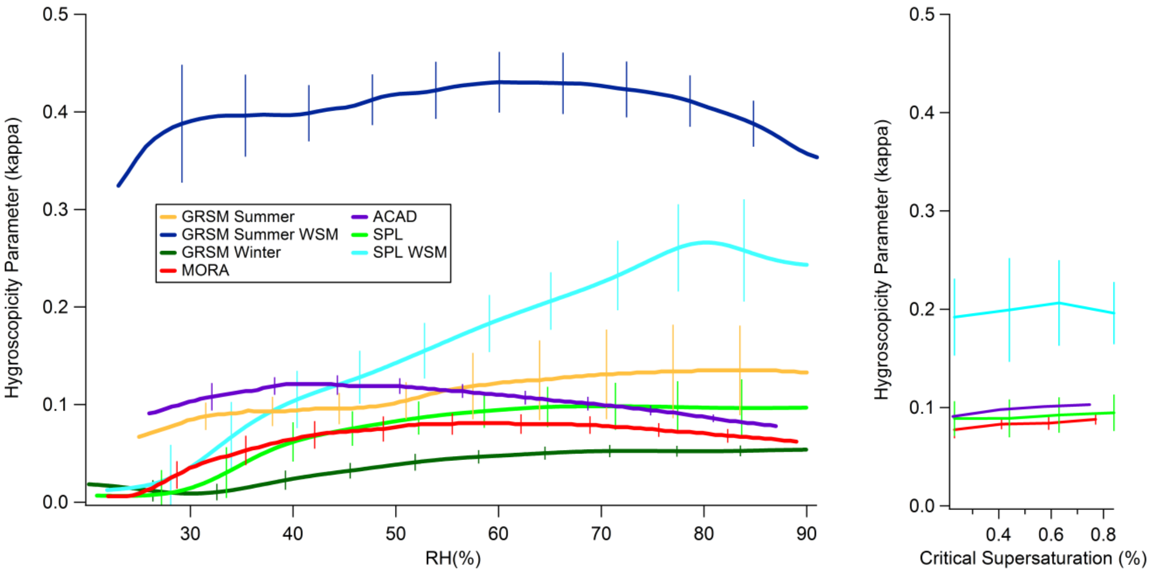

Figure 3: Average κ(RH) and κ(SS$_c$) from all initially hydrated hygroscopicity measurements for all WSOC and ~~total Water Soluble aerosol Material (WSM) samples from Great Smoky Mountains Summer and Winter (GRSM I and II), Mount Rainier (MORA), Acadia (ACAD), and Storm Peak Lab (SPL)~~WSM samples.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

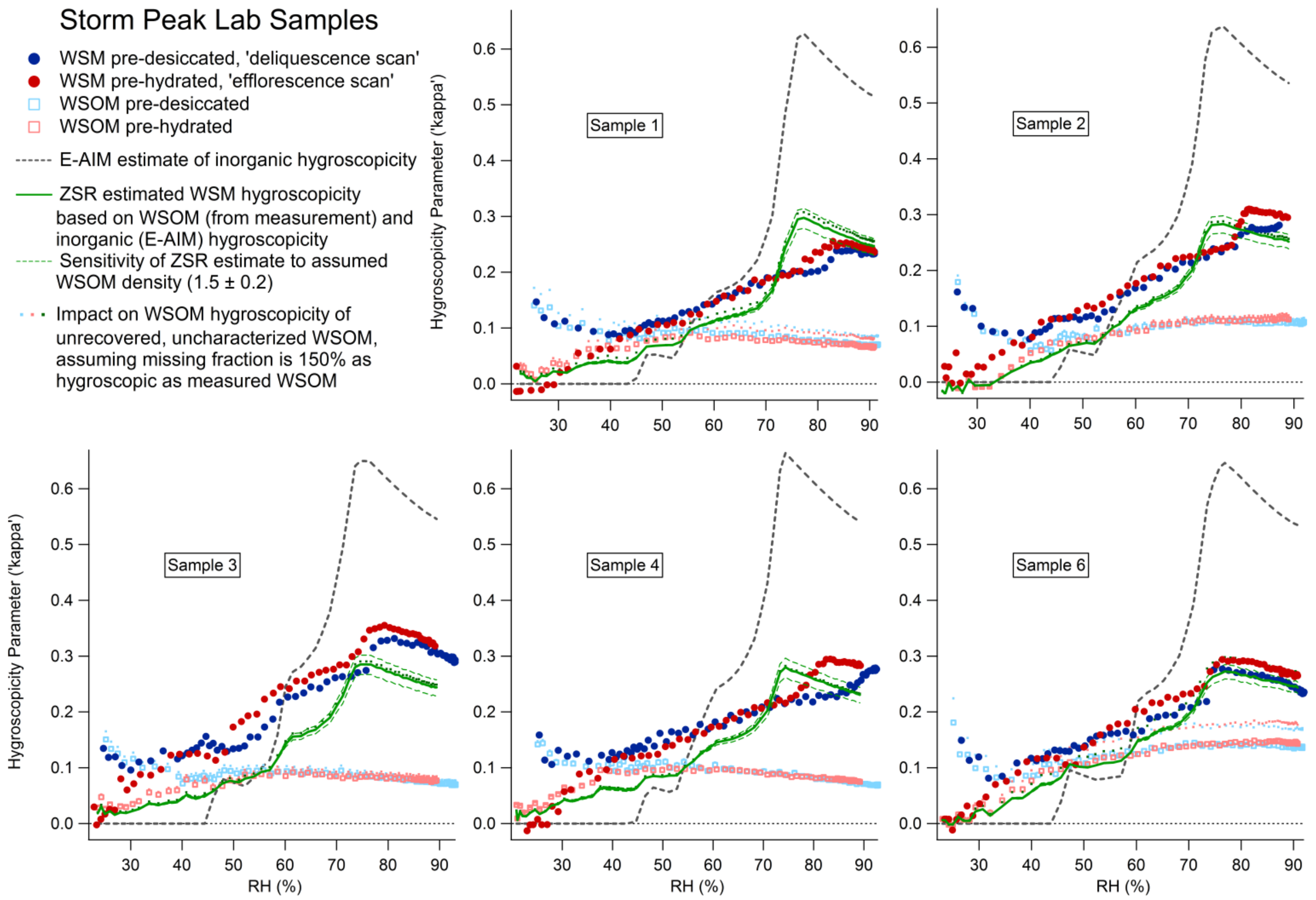

Figure 4: ~~Contrasting hygroscopic growth of WSOC and total Water Soluble aerosol Material (WSM) of samples from Great Smoky Mountains National Park in summer. For Sample 6, WSOC appears to dissolve at lower RH when associated with the WSM mixture.~~Comparison of the measured hygroscopicity of SPL WSM samples to expected WSM hygroscopicity assuming no interaction between the organic and inorganic components. WSM hygroscopicity (in green) was estimated from independent assessments of the hygroscopicity of the organic fraction (from WSOC measurements) and of the inorganic fraction (predicted from composition using the E-AIM model). For each sample, WSM hygroscopicity is underestimated below 70% RH, driven by the expectation of the model that the majority of the inorganic fraction will not dissolve until RH reaches ~65%. This suggests that WSOC can significantly depress inorganic DRH, enhancing water uptake below 70% RH.

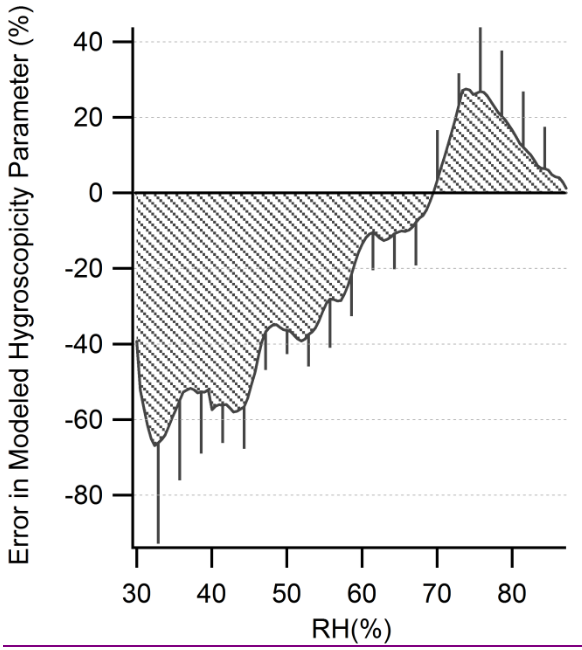

Figure 5: Average error in predicted WSM κ(RH). Error is defined as (κ(RH)$_{measured}$- κ(RH)$_{predicted}$)/ κ(RH)$_{measured}$. Whiskers depict the standard deviation (of error) between the five samples.

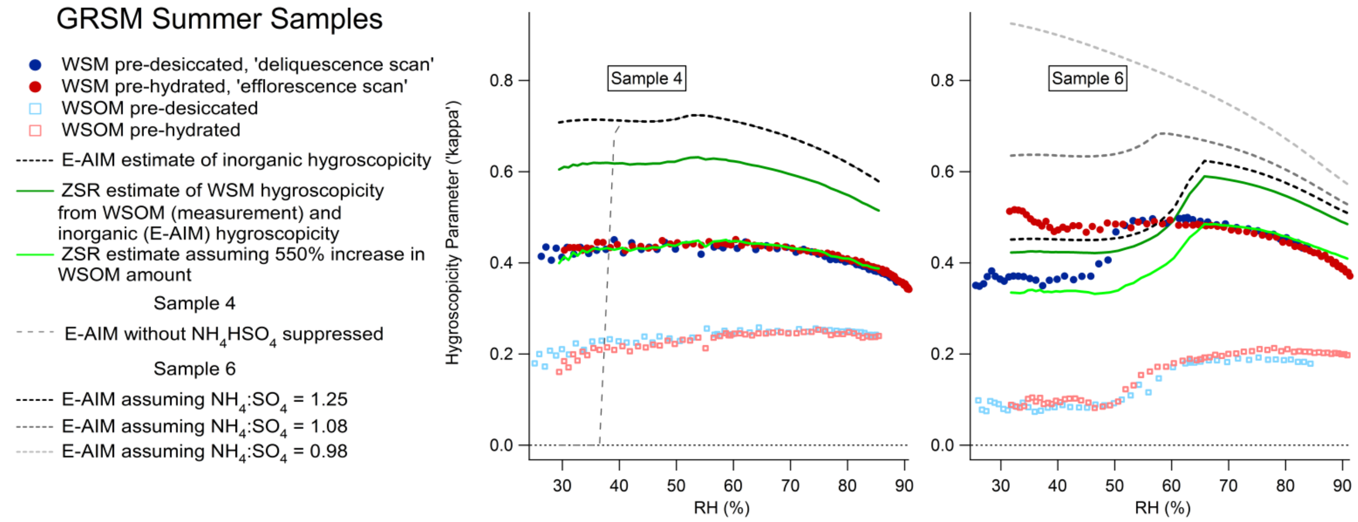

Figure ~~5~~6: ~~Contrasting hygroscopic growth of WSOC and total Water Soluble aerosol Material (WSM) samples from Storm Peak Lab. All WSM samples exhibit continuous, increasing dissolution with increasing RH.~~ Contrasting expected and measured WSM hygroscopicity for samples taken during GRSM Summer.

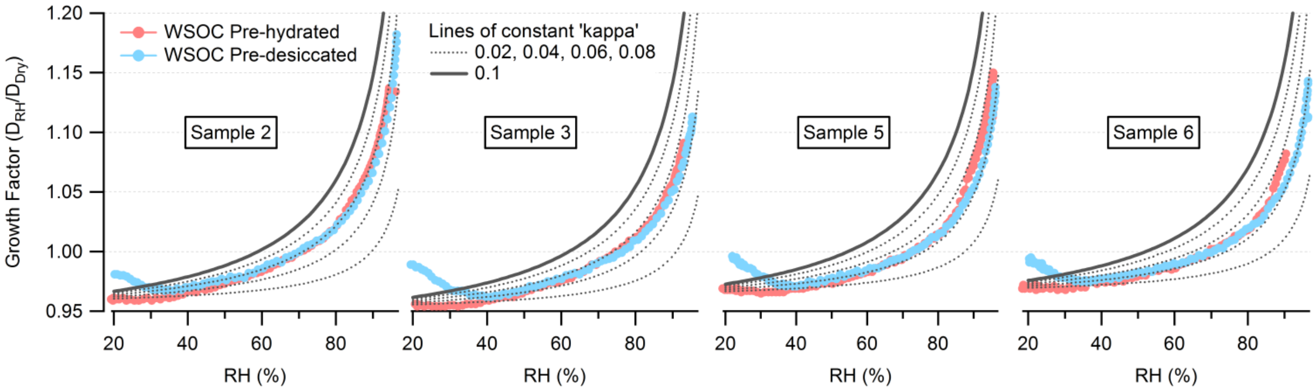

Figure <u>7</u>~~6~~: Hygroscopic growth measurements of WSOC samples ~~from Great Smoky Mountains National Park in winter~~<u>from GRSM Winter illustrating below unity growth factor and gradual collapse of pre-desiccated scans at low RH</u>.