

Typically, techniques for measuring aerosol hygroscopic properties examine how particle growth responds to changes in RH relative to a dry reference state (e.g., ~5% RH) and do not explicitly measure water content of the unperturbed aerosol at ambient RH,³⁴ though ambient measurements have been taken (e.g., refs 9, 47, and 48). Field studies of aerosol hygroscopicity, from which ALW mass concentrations can be inferred, are conducted and provide valuable information. For example, the Southeastern Aerosol and Visibility Study (SEAVS) in the Great Smoky Mountains measured aerosol growth as a function of RH and found water uptake was greater than predicted because of inorganic species alone and the excess was positively associated with particle organic content.³⁴ Other studies suggest organic compounds present in ambient particulate matter can inhibit water uptake.^{49–51} However, studies in which estimates of ambient ALW mass concentration can be calculated are not routine and have primarily been short-term and regional in scope.^{9,34,48,52,53} Insufficient knowledge of ALW mass can lead to a misunderstanding regarding atmosphere–biosphere interactions and the fate and transport of trace species in the atmosphere and can hinder the development of effective control strategies for mitigating impacts of water-related particulate matter (PM) on air quality, climate, visibility, and human health and welfare.

Chemically characterized particle measurements with the AMS highlight the ubiquity and dominance of oxygenated organic species in aerosols in the anthropogenically influenced Northern Hemisphere midlatitudes⁵⁴ and in Southern Hemisphere locations.^{55–59} In this work, we estimate ALW mass concentrations from speciated AMS measurements at field campaign locations for which we can readily estimate campaign meteorological conditions to explore similar ubiquity and dominance. An explicit understanding and constraints in atmospheric models of ALW are essential. Uncertainties in the magnitude and direction of the direct and indirect effect of aerosols remain a predominant obstacle for reliable climate change prediction, especially when ALW, a controlling parameter for particle size, remains largely unmeasured in direct ways and model predictions remain poorly constrained. A global perspective on the presence of aerosol water represents a key knowledge gap.

MATERIALS AND METHODS

To explore global patterns in ALW for fine PM, we estimate mass concentrations at locations with consistent submicrometer aerosol composition measurements worldwide. We estimate and compare, in a relative sense, average ALW mass concentrations, fractions, and growth factors for 21 field campaigns with the thermodynamic model ISORROPIA version 2.1^{60,61} using AMS particle mass concentrations of inorganic species (NH_4^+ , SO_4^{2-} , and NO_3^-) from ref 54 and other data sets^{55–59} in the AMS Global Database,⁶² and RH and temperature data from the Climate Forecast System Reanalysis (CFSR) (Table S1).⁶³ ISORROPIA assumes thermodynamic equilibrium for a $\text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3^-$ metastable system and is valid within the errors associated with field measurements.^{64–66} The AMS campaigns take place primarily during the summer months, which are June, July, and/or August for Northern Hemisphere (NH) and December, January, and February for Southern Hemisphere (SH) locations. Winter campaigns and studies that span seasons are Pittsburgh (September; NH), Manaus (February and March; SH), Mexico City (April and May; NH), Edinburgh

(November; NH), Weybourne (April and May; NH), Duke Forest (September; NH), Hyytiälä (March and April; NH), Hohenpeissenberg (May; NH), Santiago (August through November; SH), and Welgegend (September 2010 through August 2011; SH). The AMS characterizes nonrefractory (excluding soot, dust, and sea salt) fine PM, with nearly 100% transmission efficiency for particles with aerodynamic diameters of 70–500 nm, and substantial transmission for particles from 30 to 70 and 500 nm to slightly above 1 μm .^{27,28} Hygroscopicity can change with particle size,^{9,67–69} and we note that limited size-resolved information introduces uncertainty into the absolute ALW mass estimates.

Meteorology data from CFSR version 1 (available 1979–2010) are used to obtain 1000 mb temperature and 2 m RH at $0.5^\circ \times 0.5^\circ$ spatial and 6 h temporal resolutions, averaged and paired in space and time for each of the respective AMS studies. As surface and 2 m temperature are unavailable in CFSR version 1, this may create an isobaric error in temperature that can reduce the estimated magnitude of ALW mass concentrations at mountainous sites such as Storm Peak and Jungfraujoch. The campaign at Welgegend (September 2010 to August 2011) spans the transition from CVSR version 1 to CFSR version 2, and RH for Welgegend was retrieved at 1000 mb. The difference in average RH between the two time periods is minimal (3%). Uncertainties in RH impact ALW estimates and growth factors exponentially, depending on the RH level (Figures S2 and S3). The meteorological data are averaged for the duration of the field campaign to match the speciated PM averages reported for the AMS data. ALW exhibits diurnal⁹ and seasonal²⁵ variations in which the particle water mass is largest during the daytime and the summer season. These variations depend on RH, temperature, and hygroscopicity changes and are not fully illuminated in this analysis. The resulting ALW thermodynamic estimates are limited to campaign-averaged values.

The effects of organic compounds on aerosol water are complex^{49–51,70,71} and depend on chemical composition.^{34,72–75} Though there is uncertainty, we apply κ -Kohler theory with the Zdanovskii–Stokes–Robinson (ZSR) mixing rule⁷⁶ to describe hygroscopic growth of aerosol mixtures that include organic compounds^{14,77,78} using eq 1.²⁵

$$V_{w,o} = V_o \kappa_{\text{org}} \frac{a_w}{1 - a_w} \quad (1)$$

where $V_{w,o}$ and V_o represent ALW and organic compound volumes, respectively (cubic micrometers per cubic centimeter), κ_{org} is the organic component hygroscopicity (dimensionless), and a_w is the water activity (dimensionless). V_o is calculated by dividing the organic matter mass measured during an AMS field campaign by an assumed organic density of 1.4 g/cm³.⁷⁹ Higher organic compound density values would decrease the amount of water, while lower values would result in an increase. We assume a_w is equivalent to RH for the sake of simplicity because of a lack of particle diameter data. A previous application of this approach to data from the SOAS campaign suggests this assumption may result in a 4–11% overestimate for hygroscopicity.⁹ We also calculate mass-based growth factors by dividing total aerosol mass concentrations (including water) by dry mass concentrations.

Estimates of ALW mass concentrations are influenced by uncertainties and limitations in the AMS measurements of aerosol size and chemical composition, meteorological parameters, and limited identification of organic compounds.

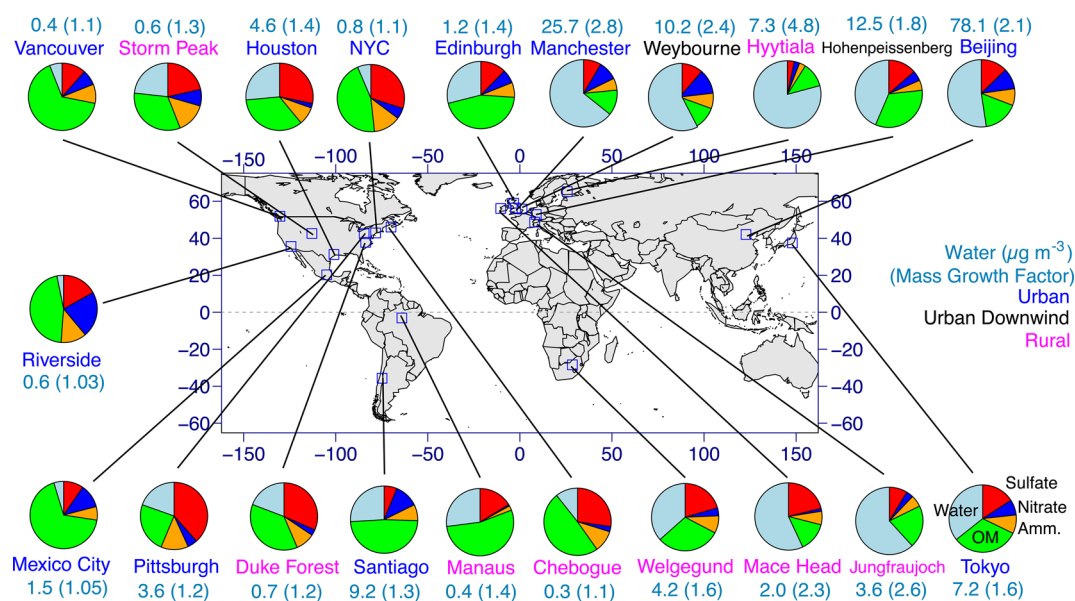


Figure 1. Aerosol species for urban (blue), urban downwind (black), and rural (pink) sites. Fractional species are sulfate (red), nitrate (dark blue), ammonium (orange), organic matter (green), and water (light blue). ALW mass concentrations are indicated in blue text, while mass-based growth factors are indicated in blue text in parentheses. ALW is estimated by ISORROPIA using inorganic compounds from AMS field studies and RH and temperature from CFSR. The campaign average ALW mass amounts are 12, 11, and 3 $\mu\text{g m}^{-3}$ for urban, urban downwind, and rural sites, respectively.

The simplifying assumptions in this work are likely lower-bound estimates of ALW mass that do not introduce a systematic bias to preclude assessment of ubiquity and relative abundance. Hygroscopicity of the particle organic fraction varies in the atmosphere. Typically, the organic fraction is hydrophobic near emission sources, such as urban centers, and becomes hygroscopic during transport due to oxidative processes.^{80,81} κ_{org} values are typically ~ 0.1 ,^{82–86} though κ_{org} has been found to vary from 0 to ~ 0.3 .^{80,87–90} In this work, we perform two κ_{org} sensitivity tests. In the first case, we apply a κ_{org} of 0 to all organic masses at all sites. In case two, we apply κ_{org} values of 0.08, 0.11, and 0.13 for urban, urban downwind, and rural sites, respectively, consistent with recent measurements^{47,52,80,82–86} and increasing hygroscopicity of the organic fraction during atmospheric processing. In addition, there are other species that impact particle hygroscopicity but are neglected in this application (e.g., chloride). Analysis of this ALW estimation approach to SOAS field data suggests an underestimation of the absolute water mass (largest underestimations from 7 to 9 a.m. local time) but with similar temporal profiles in measurements and predictions (Figure S1). Detailed chemical speciation of the organic fraction is necessary to refine this approach and is a critical next step.

RESULTS AND DISCUSSION

Globally, semiempirical observational estimates of ALW mass concentrations vary by amount and fractional contribution to total aerosol mass (Figure 1 and Table S1). As the AMS studies take place during different years and different seasons, it is important to note that the ALW estimates are snapshots in time meant to highlight the ubiquity and dominance of ALW rather than direct comparisons of representative concentrations among the different study locations. ISORROPIA estimates that ALW mass concentration is highest in humid urban areas with high concentrations of hygroscopic aerosol constituents such as sulfate. The Beijing study has the highest estimated

ALW concentrations ($78 \mu\text{g m}^{-3}$), while the Chebogogue study in rural Nova Scotia has the lowest estimated ALW concentrations ($0.35 \mu\text{g m}^{-3}$). The highest mass-based growth factor is estimated for the campaign in rural Hyytiälä at 4.8 (RH = 97%), while the lowest ratio is estimated for the Riverside, CA, study at 1.03 (RH = 17%). The general underprediction of ALW by our approach suggests that while there is uncertainty in the absolute value of the estimates, they are likely lower bounds. Because our approach predicts trends and patterns in ALW well (Figure S1), we have more confidence in the relative amounts and fractions for location categories than in the absolute predicted mass concentrations.

The campaign average ALW mass concentrations for all urban AMS field campaign locations exceed the estimate for Manaus, a site in the Brazilian rain forest, with the sole exception of Vancouver, BC. For example, the ALW masses estimated for the campaigns in Beijing, Manchester, and Houston are approximately 100, 60, and 11 times greater, respectively, than the value for Manaus. Even during dry campaigns in urban areas, such as Riverside, CA, where the average campaign RH was $<17\%$, the estimated ALW mass is still 50% higher than that in Manaus (average campaign RH of $>75\%$). There are interesting contrasts among the urban city campaigns. Even though Edinburgh experienced relatively high RH (78%) during the campaign, ALW mass is small ($1.2 \mu\text{g m}^{-3}$) compared to those of other urban campaigns. This is due to low mass concentrations of sulfate ($0.52 \mu\text{g m}^{-3}$), a highly hygroscopic aerosol constituent. ALW mass estimates for the sampling periods in New York City and Pittsburgh are also lower than for other urban locations, but for a different reason. Sulfate mass concentrations were substantial (3.9 and $7.0 \mu\text{g m}^{-3}$, respectively), but average campaign RH values were low (21 and 42%, respectively). The ALW fractional contribution to total particle mass and mass-based growth factors is largest in rural areas. Water is 79% of total aerosol mass during sampling in Hyytiälä, a rural area of Finland that experienced the highest

AMS campaign average RH of all the studies. The water mass fraction is lowest for Riverside, an urban area in California that experienced the lowest AMS campaign average RH, at 3.2% of total aerosol mass. The contrast in urban versus rural locations for ALW mass concentrations, fractional contributions, and growth factors demonstrates how complex interactions among meteorology, aerosol mass concentration, and chemical composition, in particular the presence of anthropogenic hygroscopic constituents, control aerosol water. Analysis of all variables is necessary to understand particle water and the subsequent impacts on particle chemistry and size.

Organic aerosol constituents vary in hygroscopicity and can add water to atmospheric aerosol or inhibit uptake depending on organic mass concentrations and the specific chemical identity of the organic compounds. When ALW estimates include water uptake employing the generalized κ values for urban, urban downwind, and rural categories for organic hygroscopicity, the estimated ALW mass concentration for Beijing is still the highest of all AMS sampled locations ($86 \mu\text{g m}^{-3}$), and the value from the Chebogue study remains the lowest ($0.42 \mu\text{g m}^{-3}$) (Figure 2 and Table S1). When the

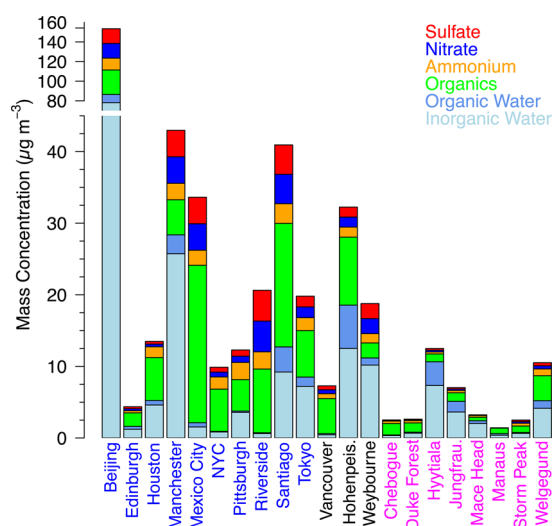


Figure 2. Aerosol species mass concentrations for urban (blue text locations), urban downwind (black text locations), and rural (pink text locations) sites. Fractional species are sulfate (red), nitrate (dark blue), ammonium (orange), organic matter (green), inorganic water (light blue), and organic water (darker light blue). Note that the names of sites Hohenpeissenberg and Jungfraujoch are shortened in the x -axis labels. Inorganic water refers to ALW estimated by ISORROPIA ($\kappa_{\text{org}} = 0$), while organic water refers to the ALW contribution by organics estimated in this study. The average ALW concentrations for urban, urban downwind, and rural areas are estimated to be 14, 15, and $3.2 \mu\text{g m}^{-3}$, respectively. The ALW:dry mass ratios are 0.53, 1.3, and 1.4, respectively. The ALW fraction is highest for the Hyytiälä study period, at 85% of total aerosol mass, and lowest for Riverside, at 3.7% of total aerosol mass, when the uptake of water by organic compounds is considered.

organic compound hygroscopicity ranges are considered, ALW mass concentrations increase by 21, 29, and 31% for urban, urban downwind, and rural areas, respectively, compared to the case in which $\kappa_{\text{org}} = 0$ for all organic masses in all locations, and general geographic trends in absolute ALW mass and fractional contribution are the same. This suggests that uptake of water by inorganic compounds dominates over contributions by organic compounds, and this is consistent with laboratory measure-

ments.⁷⁸ This work suggests there is more ALW in urban and urban downwind locations, and the water fraction is highest at rural campaign sites. General, global geospatial patterns in ALW are unlikely to change because of the addition of estimated water uptake by organic compounds; however, a more detailed analysis is needed, and this remains an open question.

Particle concentration and chemical speciation play critical roles that vary regionally and control ALW mass concentrations and its subsequent impacts on chemistry and transport. Consideration of local meteorology alone is insufficient to properly characterize ALW. Water vapor in the atmosphere is predicted to increase due to enhanced rates of evapotranspiration in a warmer world.^{87,88} Increasing global energy demand can impact atmospheric composition in ways that modulate ALW mass (e.g., sulfur emissions and subsequent sulfate formation). These factors may increase the amount of ALW and impact the fate and transport of trace species, in particular polar, water-soluble organic compounds, a major fraction of the atmospheric organic gas burden.⁹¹ Understanding the role of ALW in the atmosphere and accurately predicting how it varies in response to emissions from human activity are critical concerns for accurate predictions of future air quality in a changing world, and within the context of energy needs and choices. Future work requires a coordinated study among investigators and their varied data sets to conduct cross measurement comparisons with field data and modeling estimates. The findings suggest the need for more detailed studies of ALW with longer-term data sets to assess geographic representativeness and temporal trends because this work is limited to AMS studies and provides only snapshots in time.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.6b00167.

Table of locations and parameter values (Table S1), ISORROPIA uncertainty estimation (Figure S1), ALW versus RH (Figure S2), and growth factors versus RH (Figure S3) (PDF)

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Notes

The authors declare no competing financial interest.

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