Differences in Fine Particle Chemical Composition on Clear and Cloudy Days

Amy E. Christiansen[1], Annmarie G. Carlton[1], Barron H. Henderson[2]

[1]Department of Chemistry, University of California, Irvine, CA 92697, USA

5   [2]Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27709, USA

Correspondence to: Annmarie G. Carlton (agcarlto@uci.edu)

Abstract. Clouds are prevalent and alter fine particulate matter ($PM_{2.5}$) mass and chemical composition. Cloud-affected satellite retrievals are subject to higher uncertainty and are often removed from data products, hindering quantitative estimates

10   of tropospheric chemical composition during cloudy times. We examine surface $PM_{2.5}$ chemical constituent concentrations in the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network in the United States during Cloudy and Clear Sky times defined using Moderate Resolution Imaging Spectroradiometer (MODIS) cloud flags from 2010-2014 with a focus on differences in particle species that affect hygroscopicity and aerosol liquid water (ALW). Cloudy and Clear Sky periods exhibit significant differences in $PM_{2.5}$ mass and chemical composition that vary regionally and seasonally. In the

15   eastern US, relative humidity alone cannot explain differences in ALW, suggesting emissions and *in situ* chemistry related to anthropogenic sources exert determining impacts. An implicit clear sky bias may hinder efforts to quantitatively understand and improve representation of aerosol-cloud interactions, which remain dominant uncertainties in models.

1 Introduction

At any given time, visible clouds cover over 60% of the Earth's surface (King et al., 2013), and a warming climate changes

20   cloud patterns (Norris et al., 2016). Average cloud fraction over the contiguous US (CONUS) is ~40% year-round and higher in winter (44-54%) than summer (26-34%) (Ju and Roy, 2008; Kovalskyy and Roy, 2015). Convective cloud droplets act as atmospheric aqueous phase reactors, and their condensed phase oxidative chemistry generates particle mass aloft, such as sulfate (Zhou et al., 2019), water-soluble organic carbon (Carlton et al., 2008; Duong et al., 2011), and organo-sulfur compounds (Pratt et al., 2013). Cloud processing alters physical and chemical parameters of boundary layer aerosol that served

25   as cloud condensation nuclei (CCN). Aqueous chemistry changes aerosol size distribution (Meng and Seinfeld, 1994), hygroscopicity and oxygen to carbon (O:C) ratio (Ervens et al., 2018). Aerosol-cloud interactions and impacts are complex and a critical uncertainty in model projections (Fan et al., 2016).

Atmospheric chemistry strategies are often designed in ways that minimize cloud and water influences. Laboratory

30   experiments to understand organic particulate matter formation are historically conducted under dry conditions (Ng et al.,

2007) and aircraft typically avoid clouds during atmospheric chemistry field campaigns. Recent laboratory experiments include RH influence (e.g., Hinks et al., 2018; Lamkaddam et al., 2017), and understanding the impact on the amount of aerosol liquid water is critical (Kamens et al., 2011). With respect to satellites, there is increased error in remotely sensed aerosol optical thickness (AOT) retrieval techniques during cloudy times (Martin, 2008). AOT quantification above cloud is improving but impacted retrievals are often screened from final data products to avoid measurement artifacts. Most validation of satellite-derived AOT through comparison to surface measurements, such as those from sun photometers used to retrieve AOT from the ground up, is conducted for cloud-free periods (Liu et al., 2018). Air quality models are often evaluated with cloud-free satellite retrievals and aircraft samples (van Donkelaar et al., 2010; Guo et al., 2017; de Hoogh et al., 2016; Song et al., 2014; Tian and Chen, 2010; Bray et al., 2017; McKeen et al., 2009). This biases model development and predictive skill toward cloud-free conditions. Should differences in aerosol physicochemical properties exist between cloudy and clear sky time periods, current approaches are limited in their ability to quantitatively assess those differences. This is a key knowledge gap.

Characterization of fine particulate matter (PM$_{2.5}$) mass and chemical composition in the US primarily relies on surface measurements from relatively sparsely spaced monitors. At various locations across the CONUS, the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network samples every 3 days, and the Chemical Speciation Network (CSN) samples every 3 or 6 days (US Environmental Protection Agency, 2008). To improve upon surface network spatial and temporal limitations, data can be interpolated to describe particle mass (Li et al., 2014; Zhang et al., 2018) and chemical composition over larger areas (Liu et al., 2009; Tai et al., 2010). Satellite information can also be used (van Donkelaar et al., 2015b), such as the Moderate Resolution Imaging Spectroradiometer (MODIS) instruments aboard the Aqua and Terra satellite platforms. These view the entire Earth surface every 1 to 2 days and are used to impart information for use in air quality applications (van Donkelaar et al., 2015b; Gupta et al., 2006; Kloog et al., 2011; Sorek-Hamer et al., 2016). Many advanced satellite AOT models translate space-based radiation measurements to surface PM$_{2.5}$ (van Donkelaar et al., 2010, 2015b, 2015a; Gupta et al., 2006; Kessner et al., 2013; Kloog et al., 2011; Kumar et al., 2007; Liu et al., 2011; Schaap et al., 2009; Wang et al., 2012; Wang and Christopher, 2003) and employ sophisticated techniques which account for aerosol size and type, vertical extinction, mass, and relative humidity (RH) (van Donkelaar et al., 2010). Evaluation of AOT-to-PM$_{2.5}$ techniques finds that monthly aggregated AOT can robustly estimate relationships spanning five years of daily mean values over North America (R>0.77) (van Donkelaar et al., 2010). While temporal and geospatial satellite AOT is useful for understanding trends in PM$_{2.5}$ concentrations (van Donkelaar et al., 2015b; Sorek-Hamer et al., 2016; Wang and Christopher, 2003), an implicit constraint for this and other similar findings is that such agreement is for clear sky conditions.

Surface networks record PM$_{2.5}$ mass and chemical composition during clear sky and cloudy time periods alike. The difference between spatially and temporally aggregated PM$_{2.5}$ mass concentrations in the CONUS for cloudy and all sky (cloudy + clear sky) conditions is estimated to be ±2.5 µg m$_{-3}$ (Christopher and Gupta, 2010). Less attention has been given to clear sky and cloudy differences in PM$_{2.5}$ chemical composition, especially with regards to particle hygroscopicity and water uptake. Aerosol

65   mass concentrations and chemical speciation including aerosol liquid water (ALW) influence AOT (Christiansen et al., 2019; Malm et al., 1994; Nguyen et al., 2016a; Pitchford et al., 2007), cloud microphysics, and mesoscale convective systems (Kawecki and Steiner, 2018), including storm morphology and precipitation patterns (Kawecki et al., 2016). ALW provides a plausible contribution to reconcile surface $PM_{2.5}$ and remotely sensed AOT (Babila et al., 2020; Nguyen et al., 2016a). An implication of this work is that if particle hygroscopicity changes from clear sky to cloudy time periods, when aerosol-cloud

70   interactions are most important, a quantitative understanding suitable for atmospheric models remains unclear.

In this work, we test the hypothesis that there are quantitative differences in surface $PM_{2.5}$ chemical composition between cloudy and clear sky time periods in ways important for water uptake. We employ MODIS because it is frequently utilized in air quality estimates of surface $PM_{2.5}$ concentrations at global and regional scales (van Donkelaar et al., 2015b; Gupta et al.,

75   2006; Kloog et al., 2011; Sorek-Hamer et al., 2016). Our goal is to assess differences in $PM_{2.5}$ chemical composition between Cloudy and Clear Sky times under all cloud scenarios, as high and low clouds both interfere with successful satellite retrievals. We employ a combination of satellite products, surface measurements, and thermodynamic modeling to analyze annual and seasonal trends in chemical climatology regions across the CONUS. We assess and quantify seasonal statistical significance (Kahn, 2005) for differences in distributions of RH, surface $PM_{2.5}$, and chemical speciation during cloudy and clear sky times

80   using surface measurements from the IMPROVE network from 2010-2014 within the context of MODIS cloud flags. Further, we examine one chemical climatology region in detail, the Mid South, as a case study. This region encompasses the location of the Atmospheric Radiation Measurement Southern Great Plains (SGP) site in an area of the CONUS that experiences varied weather patterns, a broad range of cloud conditions, and distinct seasonal variations in temperature and humidity (Sisterson et al., 2016).

85   **2 Data and Methods**

Cloudy and clear sky classifications are determined using publicly available data (National Aeronautics and Space Administration, 2018) from MODIS on the Aqua and Terra satellites. We classify the scene based on the MODIS AOD 3 km product retrieval flags (Remer et al., 2013). We do not differentiate between high and low clouds, and acknowledge that boundary layer aerosol interacts only with low-level clouds. Pairing of satellite and surface $PM_{2.5}$ mass measurements typically

90   works best in rural and vegetated locations, where the spectral properties of the background tend to be dark and vary little over the space of a satellite grid cell (Hauser, 2005; Jones and Christopher, 2010), although improvements have been made for retrievals over bright surfaces (Hauser, 2005; Hsu et al., 2004, 2006, 2013; Zhang et al., 2016). In this work, we use rural IMPROVE network sites located primarily in national parks and focus on the eastern half of the CONUS. MODIS overpasses occur once per day for each satellite platform, at 10:30 (Terra) and 13:30 (Aqua) local time. IMPROVE measurements are 24-

95   hour samples. Further, we analyse surface measurements only and do not address aloft extinction, which can be substantial at IMPROVE sites (Christiansen et al., 2019). The mismatch in timing and poorly captured vertical and diurnal variations in both

clouds and particle composition adds uncertainty to this analysis and represent a limitation. We employ MODIS 3 km resolution pixels that contain each IMPROVE site. Retrievals are flagged as cloudy if QA flags specifically identified clouds as preventing retrieval, or if 2.1-micrometer reflectance was too high ($r > 0.35$) and the fraction of 500 m sub pixels that were cloudy was greater than 44.4%. We choose 44.4% because more cloudy subpixels could prevent acquisition of a sufficient number of subpixels for the 3 km pixel solution (Remer et al., 2013). IMPROVE monitors are frequently under a MODIS swath with valid retrievals even if the pixel containing the IMPROVE station is not successfully retrieved. Note that the effects of clouds on AOT extend at least 20 km farther than the cloud itself (Twohy et al., 2009), and our wide area helps to properly encompass "Cloudy" conditions. Misidentifying non-retrievals as cloudy is unlikely to substantially affect interpretation, as the sample size is large ($N > 70,000$ total observations, and $N > 1500$ for an individual region).

IMPROVE network data were downloaded on 13 July 2015 and 26 May 2016 from public archives (http://vista.cira.colostate.edu/Improve/) (IMPROVE Network, 2019) for 132 unique sites across the CONUS with complete data records for the years 2010-2014 (Fig. S1a). IMPROVE data is collected every 3 days. We investigate 24-hour average PM$_{2.5}$ mass, ALW, RH, sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), and total organic carbon (TOC) mass concentrations. Other species affect particle hygroscopic properties but are not widely measured in routine networks. We investigate TOC as a whole even though primary and secondary species affect water uptake differently. There is no direct measurement of either in routine monitoring network operations, although fractionation can sometimes be used to infer information about sources and formation processes (Aswini et al., 2019; Cao et al., 2005; Chow et al., 2004). We group IMPROVE sites across the CONUS into 22 chemical climatology regions defined by the IMPROVE network (Fig. S1b) (Hand et al., 2011; Malm et al., 2017). PM$_{2.5}$ mass and composition is provided directly from the IMPROVE database, while ALW is estimated.

ALW is a function of RH, particle concentration, and chemical composition. We estimate ALW using a metastable assumption in the inorganic aerosol thermodynamic equilibrium model ISORROPIAv2.1 (Fountoukis and Nenes, 2007). We use the reverse, open-system problem because only aerosol measurements are available. Particle mass concentration inputs of SO$_4^{2-}$ and NO$_3^-$ are taken from IMPROVE measurements. Ammonium ion is not considered and this impacts absolute values, but not overall temporal trends (Figure S2). Dust is not considered because water uptake properties are not well constrained (Metzger et al., 2018), and there is large spatial heterogeneity in dust concentrations over the area of satellite grid cell. Our approach to employing ISORROPIA introduces uncertainties (e.g., pH estimates would be unreliable (Guo et al., 2015)), and we are more confident in overall trends than absolute values of ALW mass (Fig. S3). Organic hygroscopicity values are uncertain (Metzger et al., 2018; Nguyen et al., 2015) and the magnitude of water uptake varies by location (Jathar et al., 2016), but is typically less than the contribution from inorganic constituents at IMPROVE sites (Christiansen et al., 2019) and surface locations globally (Nguyen et al., 2016b). We provide an estimate of organic ALW using a relevant hygroscopicity value for rural aerosol of 0.3 (Chang et al., 2010; Nguyen et al., 2014). Organic speciation at IMPROVE locations changes in time and space (Christiansen et al., 2020) and the suitability of applying a constant value for organic hygroscopicity is difficult to

quantitatively assess. Organic ALW is estimated as in Christiansen et al. (2019) and Nguyen et al. (2015). Briefly, we use κ-Kohler theory and the Zdanovskii-Stokes-Robinson (ZSR) mixing rule (Eq. 1).

$$V_{w,o} = V_o \kappa_{org} \frac{a_w}{1-a_w} \tag{1}$$

135

Here, the water activity (a_w) is assumed to be equivalent to RH, V_o and $V_{w,o}$ are the volumes of organic matter and water from organic species, respectively, and κ_{org} is the organic hygroscopicity parameter. V_o is determined by dividing organic mass (OM) by 1.4 g cm-3 (Christiansen et al., 2019). OM is calculated from IMPROVE-measured OC with site- and time-specific OM:OC ratios, which are estimated via a mass balance method, as described in Malm et al. (2020) and Christiansen et al.

140   (2020). Temperature and RH values were extracted from the North American Regional Reanalysis (NARR) model (Kalnay et al., 1996) similar to Nguyen et al. (2016a).

Cloudy and Clear Sky differences in ALW are investigated in two ways. First, we compare ALW estimated using 24-hour average chemical composition and meteorology and group results into Clear Sky and Cloudy bins using the MODIS cloud

145   flag. We use these daily values when comparing ALW within chemical climatology regions. Second, we investigate trends across the eastern US to isolate the effect of chemical composition. We select the eastern US since ALW concentrations are largest in this region (Fig. S4) and it is in cloud often and consistently (cloud fraction 30-50% year-round) (Fig. S5). This makes statistical comparisons between Cloudy and Clear Sky times more robust than in the western US, where Cloudy counts are low in most seasons. We perform ALW estimations using the medians via three ISORROPIA calculation scenarios: 1)

150   Clear Sky chemical composition and Clear Sky meteorology ("Clear Sky" scenario), 2) Cloudy chemical composition and Cloudy meteorology ("Cloudy"), and 3) Clear Sky chemical composition and Cloudy meteorology ("Mixed") (Table S1, Fig. S6). We group 24-hour average chemical composition and meteorology into Clear Sky and Cloudy bins and take monthly medians to mitigate the impact of outliers and to avoid complications that arise from differing numbers of Cloudy and Clear Sky days in the Mixed scenario. To investigate meteorology and chemical composition impacts separately, we perform the

155   Mixed scenario in order to reproduce studies in which cloud free growth factors (Brock et al., 2016) are eventually applied to models and used to simulate cloudy meteorological conditions (Bar-Or et al., 2012). When the Mixed scenario is significantly different than Cloudy, we can reject the hypothesis that RH and temperature alone explain the difference. The impacts of wet deposition due to precipitation and dry deposition (i.e., particles are physically larger and more likely to deposit when water uptake is higher (Carlton et al., 2020)) are unconstrained in this analysis.

160

Growth factors used in the Mid South region are estimated from a modified Kohler equation (Brock et al., 2016; Jefferson et al., 2017) (Eq. 2). We use RH from the NARR and estimate κ_d, the particle hygroscopicity, from IMPROVE-measured

chemical composition mass concentrations and individual species κ values (κ_{SO4}=0.5, κ_{NO3}=0.7, $\kappa_{org} = 0.3$) (Chang et al., 2010; Nguyen et al., 2014; Petters and Kreidenweis, 2007). Here, $gf(D)$ is the hygroscopic diameter growth.

165

$$gf(D) = (1 + \kappa_d \frac{RH}{100-RH})^{1/3} \qquad\qquad (2)$$

Statistical significance for differences in measurement distributions of PM2.5 chemical composition and properties between Cloudy and Clear Sky time periods from 2010-2014 is determined using the Mann-Whitney U Test in R statistical software

170 (R Core Team, 2013). The Mann-Whitney U Test is a non-parametric test that compares two samples to assess whether population distributions differ (McKnight and Najab, 2010). 2010-2014 encompasses typical conditions and coincides with several intensive observation periods including the Southeast Atmosphere Studies (SAS) (Carlton et al., 2018b), the Studies of the Emissions and Atmospheric Composition, Clouds, and Climate Coupling by Regional Surveys (SEAC4RS) (Toon et al., 2016), and the California Research at the Nexus of Air Quality and Climate Change (CalNex) (Ryerson et al., 2013) field

175 campaigns. We define cloud fraction for each region as the number of MODIS-flagged cloudy IMPROVE sampling days over the total number of IMPROVE sampling days. Further, we define winter as December, January, and February (DJF), spring as March, April, and May (MAM), summer as June, July, and August (JJA), and fall as September, October, and November (SON).

3 Results and Discussion

180 **3.1 PM2.5 Mass Concentrations**

There is evidence that successful retrieval frequency contributes to a clear sky bias in satellite AOT products when compared to surface PM2.5 measurements at IMPROVE monitoring locations in the Eastern U.S. Across the CONUS, significant differences in PM2.5 mass concentrations measured at IMPROVE monitoring locations are observed between Cloudy and Clear Sky conditions in the majority (>60%) of regions in any given season during 2010-2014 (Figures 1, A1; Table S2), especially

185 during summer. Median All Sky PM2.5 concentrations are also significantly different and typically lower than Clear Sky in multiple chemical climatology regions (Table S3). Similarly, Christopher and Gupta (2010) found Cloudy and All Sky PM2.5 surface mass concentrations differed by 2.5 µg m-3 for the CONUS in 2006, but differences in that work were not statistically significant as they are here. This may be due to differing regional and temporal aggregation, the considered timeframes, and Clear Sky definitions. In that work, a day was defined as Clear Sky if one pixel in the 5x5 grid had a successful AOT retrieval,

190 whereas we take the 44.4% approach described above. In all regions, Clear Sky PM2.5 concentrations are generally higher than Cloudy with some exceptions during winter. There is an increased likelihood of aerosol removal due to scavenging by precipitation during Cloudy times, and this may contribute to differences in mass concentrations. However, the cloud definition employed here uses the entire column (i.e., non-precipitating cirrus and stratus clouds are included), and the majority of cloud

droplets evaporate (Pruppacher and Klett, 2010). Further, differences in PM$_{2.5}$ mass concentrations are not a quantitative function of MODIS cloud fraction values during any season in any region (Fig. S7), yet this work suggests further study with a more sophisticated analysis of cloud properties is warranted.

3.2 PM$_{2.5}$ Chemical Composition

Differences in daily mass concentrations during Cloudy and Clear Sky periods across the CONUS are spatially and temporally different among PM$_{2.5}$ mass and its chemical constituents except in the Northwest region (Figures 2, A2-A5; Tables S2, S4-S12). Overall patterns for individual chemical constituents cannot be quantitatively described as a function of MODIS cloud fraction (Figs. S7, S9). If physical meteorology was the only controlling factor differentiating aerosol concentrations between Clear Sky and Cloudy times, then patterns among PM$_{2.5}$ and constituents should be similar. However, they vary (Figure 2). This suggests changing emissions and/or *in situ* chemistry contribute to distinct patterns among PM$_{2.5}$ chemical constituents.

Clear Sky/Cloudy patterns in SO$_4^{2-}$ and NO$_3^-$ mass concentrations, which affect particle hygroscopicity, vary regionally and seasonally. Outside of winter, sulfate mass concentrations are significantly higher on Clear Sky days in the eastern US (Fig. 2, Table S4), while nitrate concentrations are consistently highest under Cloudy conditions. Higher Clear Sky SO$_4^{2-}$ concentrations during summertime are associated with heat waves and stagnation events, which are characterized by a lack of ventilation in high pressure systems (Jacob and Winner, 2009; Wang and Angell, 1999) and increased electricity demand (Farkas et al., 2016) associated with emissions that form sulfate. The sharpest Clear Sky vs. Cloudy differences in sulfate mass occur in the East Coast, Appalachia, Southeast, and Ohio River Valley. The highest nitrate concentrations occur during Cloudy days in winter (Figure 2, Table S5), which are cooler (Table S8) and promote the thermodynamic stability of nitrate in the condensed phase. The sharpest differences in nitrate occur in the Central Great Plains.

Mass concentrations of TOC are nearly always higher during Clear Sky times than Cloudy (Figure 3, Table S6) in all chemical climatology regions across the CONUS, with the largest differences during summer and fall. The patterns are unique among the PM$_{2.5}$ chemical constituents and consistent with SOA. Summertime wildland fires in the west and prescribed burning during spring and fall in the east may obscure interpretation due to large episodic primary OC emissions (Spracklen et al., 2007; Tian et al., 2009; Zeng et al., 2008). However, at IMPROVE monitoring locations, secondary organic aerosol (SOA) contribution to TOC dominates over primary sources (Carlton et al., 2018a). The most pronounced differences in Clear Sky and Cloudy TOC occur in summer in regions where precursor biogenic VOC emissions that form SOA are substantial (Donahue et al., 2009; Gentner et al., 2017; Youn et al., 2013). Further, increased sunlight and higher temperatures under Clear Sky conditions (Table S8) lead to higher biogenic VOC emissions that form SOA (Laothawornkitkul et al., 2009; Sakulyanontvittaya et al., 2008) and enhanced photolysis rates that facilitate hydroxyl radical production important to SOA

formation (Tang et al., 2003). These findings indicate that TOC mass concentrations are different on Clear Sky and Cloudy days and suggest organic composition changes as well.

Cloudy period ALW mass concentrations are higher than Clear Sky in all seasons from both inorganic and organic
230 contributions, with few exceptions (Figure 4, Table S7). The largest Cloudy and Clear Sky ALW differences are observed in the central and eastern US during winter. The pattern of higher ALW during Cloudy periods is opposite the pattern of dry $PM_{2.5}$ mass and arises from a combination of higher RH and changing aerosol composition that affects hygroscopicity. Nitrate is the most hygroscopic species considered in this analysis and high Cloudy NO_3^- mass concentrations increase particle hygroscopicity to facilitate ALW during these times, despite lower overall dry $PM_{2.5}$ mass. Clear Sky and Cloudy changes in
235 the precise chemical composition of organic compounds and their impacts on ALW remain critical open questions.

3.3 ALW and Growth Factor Scenarios in the Eastern US

Distributions in monthly particle chemical composition across the eastern US in 2010-2014 are sufficiently changed between MODIS-defined Cloudy and Clear Sky times to affect hygroscopicity and alter predicted ALW mass concentrations beyond
240 differences that would arise from changes in meteorology alone (Figure 5). The only difference between the Mixed and Cloudy ALW calculations is that the Mixed scenario employs Clear Sky chemical composition (rather than Cloudy chemical composition) extrapolated to Cloudy meteorology. This type of scenario can occur in model development or satellite validation applications when $PM_{2.5}$-AOD relationships or growth factors remain unmeasured for Cloudy periods (Brock et al., 2016; van Donkelaar et al., 2010; de Hoogh et al., 2016; Tian and Chen, 2010). When Clear Sky chemical composition is extrapolated
245 to Cloudy period meteorology ("Mixed"), monthly median ALW concentrations in the eastern US, in all seasons except winter, are significantly different from our best estimate, which employs the actual chemical composition during cloudy periods ("Cloudy"). These findings are consistent with analyses that show chemical composition is an essential factor for improving cloud condensation nuclei predictions (Crosbie et al., 2015), determining ALW (Carlton and Turpin, 2013; Liao and Seinfeld, 2005), and calculating extinction (Pitchford et al., 2007).
250

Generally, Mixed ALW concentrations in the eastern US are higher than for the Cloudy scenario because Clear Sky chemical composition facilitates greater hygroscopicity and Cloudy RH is elevated (Table S7). A notable exception is the Ohio River Valley during winter, where Cloudy SO_4^{2-}, NO_3^-, and RH are higher than Clear Sky. In this case, Cloudy period ALW concentrations are higher than for the Mixed scenario. These findings highlight that a changing $PM_{2.5}$ chemical composition
255 has a determining effect on ALW mass concentrations (Nguyen et al., 2016b), a critical element in the estimation of aerosol-cloud interactions and particle radiative impacts. Previous work using climate models shows that application of ALW uptake that is influenced by incorrect chemical composition significantly affects top of atmosphere radiative forcing estimates and attribution of anthropogenic climate impacts (Rastak et al., 2017). During cloudy periods, when the accurate prediction of ALW and aerosol-cloud interactions is most critical, *in situ* knowledge of $PM_{2.5}$ chemical composition is required.

3.4 Case Study: The Mid South

ALW concentrations are significantly higher during Cloudy times than Clear Sky in the Mid South during all seasons (Table 1, Figure 5). RH in the region is high year-round during Cloudy and Clear Sky periods alike, with the median greater than 60%. This suggests that gas-phase water vapor mixing ratios are not limiting for ALW in the region for any season. Aerosol mass concentrations and chemical composition vary, however, and the effects on particle hygroscopicity can be seen in contrasting Cloudy and Clear Sky ALW concentrations among the seasons. During Clear Sky conditions, the highest ALW mass concentrations occur during summer and spring, which correspond to the highest SO_4^{2-} concentrations in the Mid South, and not when Clear Sky RH is highest (i.e., during winter). Year-round NO_3^- concentrations are higher during Cloudy conditions than Clear Sky. The largest absolute ALW concentrations and estimated growth factors occur during Cloudy times in the winter and spring, when NO_3^- mass fraction and RH are highest. Nitrate concentrations are generally lower than SO_4^{2-}, and while sulfate is thought to determine ALW mass concentrations in the region (Carlton and Turpin, 2013; Gasparini et al., 2006), NO_3^- is more hygroscopic. The Mid South is a continental, agricultural area and in a separate but similar location, the Po Valley in Italy, NO_3^- was found to control ALW concentrations (Hodas et al., 2014). Independent humidified nephelometer measurements demonstrate that aerosol growth factors are highest in the winter and spring at the SGP site within the Mid South chemical climatology region, and identify nitrate and RH as determining factors (Jefferson et al., 2017). Observed growth factors by Jefferson et al. (2017) are higher than those estimated here, and we suspect this arises due to the presence of hygroscopic species such as ammonium, which is common to agricultural regions and not included in our ALW estimates.

Patterns in estimated growth factors suggest that the chemistry of water uptake by aerosol is different during Cloudy and Clear Sky periods and is related to changes in particle hygroscopicity driven by sulfate and nitrate pollution. Contributions from SOA, enhanced by anthropogenic emissions (Carlton et al., 2018a) also plays a role, though it is difficult to accurately quantify. These patterns in changing aerosol hygroscopicity are consistent with findings for the central U.S. that demonstrate cloud microphysics, mesoscale convective systems, and precipitation are impacted by anthropogenically influenced aerosol (Kawecki et al., 2016; Kawecki and Steiner, 2018).

4 Conclusions

Across the CONUS, statistically discernible differences among PM$_{2.5}$ and chemical constituent concentrations under Cloudy and Clear Sky conditions cannot be explained solely by physical mechanisms. The chemical properties of aerosol are important to explain differences in water uptake and particle composition under different meteorological conditions. While meteorological phenomena such as pressure systems, winds, and air mixing affect PM$_{2.5}$ and chemical component concentrations, they are insufficient to explain chemical constituent differences between Cloudy and Clear Sky times. *In situ* chemical information is necessary to fully explain temporal and spatial patterns. Spatially and seasonally, PM$_{2.5}$ and particle speciation information that lend insight into water uptake, particle properties, and particle growth is incomplete when information is gathered only during Clear Sky times. Differences in PM$_{2.5}$ concentrations under different cloud conditions suggest a potential bias in the understanding of PM$_{2.5}$ and AOT when using information only from Clear Sky times. The work presented here indicates aerosol growth due to water uptake is greatest during MODIS-defined periods identified as Cloudy in many regions, when satellites are unable to remotely sense surface particle properties and impacts. This limits understanding of atmospheric particle burden and its climate-relevant physicochemical properties, which have implications for the prediction of weather (Kawecki and Steiner, 2018), air quality, and climate. This indicates that the clear sky bias can affect accurate representation of ALW on cloudy days and suggests that without *in situ* chemical information, aerosol-cloud interactions, subsequent estimates of radiative forcings in models (Lin et al., 2016; Vogelmann et al., 2012), and feedbacks will remain a large uncertainty. This work suggests further study employing new satellite algorithms and geostationary analysis is warranted.

Acknowledgements

This research was funded, in part, by NSF Grant AGS-1242155, DOE Grant DE-SC0018349, and NASA Grant #80NSSC19K0987. The views expressed in this manuscript are those of the authors and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency. The IMPROVE database can be found at http://vista.cira.colostate.edu/Improve/. NCEP Reanalysis data are available from the NOAA/OAR/ESRL PSD in Boulder, Colorado, United States, at http://www.esrl.noaa.gov/psd/. MODIS data were acquired from the NASA Global Change Master Directory (GCMD) at https://gcmd.nasa.gov/. The authors thank Virendra Ghate for support in retrieving NCEP Reanalysis data, and Divya Srivistava and Julia Daniels for technical support. The authors also thank Athanasios Nenes for the development and public availability of ISORROPIA.

References

Aswini, A. R., Hegde, P., Nair, P. R. and Aryasree, S.: Seasonal changes in carbonaceous aerosols over a tropical coastal location in response to meteorological processes, Science of The Total Environment, 656, 1261–1279, doi:10.1016/j.scitotenv.2018.11.366, 2019.

320   Babila, J. E., Carlton, A. G., Hennigan, C. J. and Ghate, V. P.: On Aerosol Liquid Water and Sulfate Associations: The Potential for Fine Particulate Matter Biases, Atmosphere, 11(2), 194, doi:10.3390/atmos11020194, 2020.

Bar-Or, R. Z., Koren, I., Altaratz, O. and Fredj, E.: Radiative properties of humidified aerosols in cloudy environment, Atmospheric Research, 118, 280–294, doi:10.1016/j.atmosres.2012.07.014, 2012.

Bray, C. D., Battye, W., Aneja, V. P., Tong, D., Lee, P., Tang, Y. and Nowak, J. B.: Evaluating ammonia (NH_3) predictions
325   in the NOAA National Air Quality Forecast Capability (NAQFC) using in-situ aircraft and satellite measurements from the CalNex2010 campaign, Atmospheric Environment, 163, 65–76, doi:10.1016/j.atmosenv.2017.05.032, 2017.

Brock, C. A., Wagner, N. L., Anderson, B. E., Attwood, A. R., Beyersdorf, A., Campuzano-Jost, P., Carlton, A. G., Day, D. A., Diskin, G. S., Gordon, T. D., Jimenez, J. L., Lack, D. A., Liao, J., Markovic, M. Z., Middlebrook, A. M., Ng, N. L., Perring, A. E., Richardson, M. S., Schwarz, J. P., Washenfelder, R. A., Welti, A., Xu, L., Ziemba, L. D. and Murphy, D. M.: Aerosol
330   optical properties in the southeastern United States in summer – Part 1: Hygroscopic growth, Atmospheric Chemistry and Physics, 16(8), 4987–5007, doi:10.5194/acp-16-4987-2016, 2016.

Cao, J. J., Wu, F., Chow, J. C., Lee, S. C., Li, Y., Chen, S. W., An, Z. S., Fung, K. K., Watson, J. G., Zhu, C. S. and Liu, S. X.: Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China, Atmospheric Chemistry and Physics, 5(11), 3127–3137, doi:10.5194/acp-5-3127-2005, 2005.

335   Carlton, A. G. and Turpin, B. J.: Particle partitioning potential of organic compounds is highest in the Eastern US and driven by anthropogenic water, Atmospheric Chemistry and Physics, 13(20), 10203–10214, doi:10.5194/acp-13-10203-2013, 2013.

Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S. P., Mathur, R., Roselle, S. J. and Weber, R. J.: CMAQ Model Performance Enhanced When In-Cloud Secondary Organic Aerosol is Included: Comparisons of Organic Carbon Predictions with Measurements, Environmental Science & Technology, 42(23), 8798–8802, doi:10.1021/es801192n, 2008.

340   Carlton, A. G., Pye, H. O. T., Baker, K. R. and Hennigan, C. J.: Additional Benefits of Federal Air-Quality Rules: Model Estimates of Controllable Biogenic Secondary Organic Aerosol, Environmental Science & Technology, 52(16), 9254–9265, doi:10.1021/acs.est.8b01869, 2018a.

Carlton, A. G., de Gouw, J., Jimenez, J. L., Ambrose, J. L., Attwood, A. R., Brown, S., Baker, K. R., Brock, C., Cohen, R. C., Edgerton, S., Farkas, C. M., Farmer, D., Goldstein, A. H., Gratz, L., Guenther, A., Hunt, S., Jaeglé, L., Jaffe, D. A., Mak, J.,
345   McClure, C., Nenes, A., Nguyen, T. K., Pierce, J. R., de Sa, S., Selin, N. E., Shah, V., Shaw, S., Shepson, P. B., Song, S., Stutz, J., Surratt, J. D., Turpin, B. J., Warneke, C., Washenfelder, R. A., Wennberg, P. O. and Zhou, X.: Synthesis of the Southeast Atmosphere Studies: Investigating Fundamental Atmospheric Chemistry Questions, Bulletin of the American Meteorological Society, 99(3), 547–567, doi:10.1175/BAMS-D-16-0048.1, 2018b.

Carlton, A. G., Christiansen, A. E., Flesch, M. M., Hennigan, C. J. and Sareen, N.: Multiphase atmospheric chemistry in liquid
350   water: impacts and controllability of organic aerosol, Accounts of Chemical Research, 2020. *In press.*

Chang, R. Y.-W., Slowik, J. G., Shantz, N. C., Vlasenko, A., Liggio, J., Sjostedt, S. J., Leaitch, W. R. and Abbatt, J. P. D.: The hygroscopicity parameter (κ) of ambient organic aerosol at a field site subject to biogenic and anthropogenic influences: relationship to degree of aerosol oxidation, Atmos. Chem. Phys., 10(11), 5047–5064, doi:10.5194/acp-10-5047-2010, 2010.

Chow, J. C., Watson, J. G., Kuhns, H., Etyemezian, V., Lowenthal, D. H., Crow, D., Kohl, S. D., Engelbrecht, J. P. and Green,
355   M. C.: Source profiles for industrial, mobile, and area sources in the Big Bend Regional Aerosol Visibility and Observational study, Chemosphere, 54(2), 185–208, doi:10.1016/j.chemosphere.2003.07.004, 2004.

Christiansen, A., Carlton, A. M. G. and Porter, W. C.: The changing nature of organic carbon over the United States, Environ. Sci. Technol., acs.est.0c02225, doi:10.1021/acs.est.0c02225, 2020.

Christiansen, A. E., Ghate, V. P. and Carlton, A. G.: Aerosol Optical Thickness: Organic Composition, Associated Particle Water, and Aloft Extinction, ACS Earth and Space Chemistry, 3(3), 403–412, doi:10.1021/acsearthspacechem.8b00163, 2019.

Christopher, S. A. and Gupta, P.: Satellite Remote Sensing of Particulate Matter Air Quality: The Cloud-Cover Problem, Journal of the Air & Waste Management Association, 60(5), 596–602, doi:10.3155/1047-3289.60.5.596, 2010.

Crosbie, E., Youn, J.-S., Balch, B., Wonaschütz, A., Shingler, T., Wang, Z., Conant, W. C., Betterton, E. A. and Sorooshian, A.: On the competition among aerosol number, size and composition in predicting CCN variability: a multi-annual field study in an urbanized desert, Atmos. Chem. Phys., 15(12), 6943–6958, doi:10.5194/acp-15-6943-2015, 2015.

Donahue, N. M., Robinson, A. L. and Pandis, S. N.: Atmospheric organic particulate matter: From smoke to secondary organic aerosol, Atmospheric Environment, 43(1), 94–106, doi:10.1016/j.atmosenv.2008.09.055, 2009.

van Donkelaar, A., Martin, R. V., Brauer, M., Kahn, R., Levy, R., Verduzco, C. and Villeneuve, P. J.: Global Estimates of Ambient Fine Particulate Matter Concentrations from Satellite-Based Aerosol Optical Depth: Development and Application, Environmental Health Perspectives, 118(6), 847–855, doi:10.1289/ehp.0901623, 2010.

van Donkelaar, A., Martin, R. V., Spurr, R. J. D. and Burnett, R. T.: High-Resolution Satellite-Derived $PM_{2.5}$ from Optimal Estimation and Geographically Weighted Regression over North America, Environmental Science & Technology, 49(17), 10482–10491, doi:10.1021/acs.est.5b02076, 2015a.

van Donkelaar, A., Martin, R. V., Brauer, M. and Boys, B. L.: Use of Satellite Observations for Long-Term Exposure Assessment of Global Concentrations of Fine Particulate Matter, Environmental Health Perspectives, 123(2), 135–143, doi:10.1289/ehp.1408646, 2015b.

Duong, H. T., Sorooshian, A., Craven, J. S., Hersey, S. P., Metcalf, A. R., Zhang, X., Weber, R. J., Jonsson, H., Flagan, R. C. and Seinfeld, J. H.: Water-soluble organic aerosol in the Los Angeles Basin and outflow regions: Airborne and ground measurements during the 2010 CalNex field campaign, Journal of Geophysical Research: Atmospheres, 116(D21), doi:10.1029/2011JD016674, 2011.

Ervens, B., Sorooshian, A., Aldhaif, A. M., Shingler, T., Crosbie, E., Ziemba, L., Campuzano-Jost, P., Jimenez, J. L. and Wisthaler, A.: Is there an aerosol signature of chemical cloud processing?, Atmos. Chem. Phys., 18(21), 16099–16119, doi:10.5194/acp-18-16099-2018, 2018.

Fan, J., Wang, Y., Rosenfeld, D. and Liu, X.: Review of Aerosol–Cloud Interactions: Mechanisms, Significance, and Challenges, Journal of the Atmospheric Sciences, 73(11), 4221–4252, doi:10.1175/JAS-D-16-0037.1, 2016.

Farkas, C. M., Moeller, M. D., Felder, F. A., Henderson, B. H. and Carlton, A. G.: High Electricity Demand in the Northeast U.S.: PJM Reliability Network and Peaking Unit Impacts on Air Quality, Environmental Science & Technology, 50(15), 8375–8384, doi:10.1021/acs.est.6b01697, 2016.

Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K_+-Ca_{2+}-Mg_{2+}-NH_{4+}-Na_+-SO_{42-}-NO_3-Cl_--H_2O aerosols, Atmospheric Chemistry and Physics, 7(17), 4639–4659, doi:10.5194/acp-7-4639-2007, 2007.

Gasparini, R., Li, R., Collins, D. R., Ferrare, R. A. and Brackett, V. G.: Application of aerosol hygroscopicity measured at the Atmospheric Radiation Measurement Program's Southern Great Plains site to examine composition and evolution, J. Geophys. Res., 111(D5), D05S12, doi:10.1029/2004JD005448, 2006.

395 Gentner, D. R., Jathar, S. H., Gordon, T. D., Bahreini, R., Day, D. A., El Haddad, I., Hayes, P. L., Pieber, S. M., Platt, S. M., de Gouw, J., Goldstein, A. H., Harley, R. A., Jimenez, J. L., Prévôt, A. S. H. and Robinson, A. L.: Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions, Environmental Science & Technology, 51(3), 1074–1093, doi:10.1021/acs.est.6b04509, 2017.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite, J. R., Carlton, A. G., Lee, S.-H., Bergin, M. H., Ng, N. L.,
400 Nenes, A. and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmospheric Chemistry and Physics, 15(9), 5211–5228, doi:10.5194/acp-15-5211-2015, 2015.

Guo, Y., Tang, Q., Gong, D.-Y. and Zhang, Z.: Estimating ground-level PM2.5 concentrations in Beijing using a satellite-based geographically and temporally weighted regression model, Remote Sensing of Environment, 198, 140–149, doi:10.1016/j.rse.2017.06.001, 2017.

405 Gupta, P., Christopher, S. A., Wang, J., Gehrig, R., Lee, Y. and Kumar, N.: Satellite remote sensing of particulate matter and air quality assessment over global cities, Atmospheric Environment, 40(30), 5880–5892, doi:10.1016/j.atmosenv.2006.03.016, 2006.

Hand, J. L., Copeland, S. A., Day, D. E., Dillner, A. M., Indresand, H., Malm, W. C., McDad, C. E., Moore, Jr., C. T., Pitchford, M. L., Schichtel, B. A. and Watson, J. G.: Spatial and Seasonal Patterns and Temporal Variability of Haze and its Constituents
410 in the United States: Report V, [online] Available from: http://vista.cira.colostate.edu/improve/wp-content/uploads/2016/08/IMPROVE_V_FullReport.pdf (Accessed 18 March 2018), 2011.

Hauser, A.: NOAA AVHRR derived aerosol optical depth over land, Journal of Geophysical Research, 110(D8), doi:10.1029/2004JD005439, 2005.

Hinks, M. L., Montoya-Aguilera, J., Ellison, L., Lin, P., Laskin, A., Laskin, J., Shiraiwa, M., Dabdub, D. and Nizkorodov, S.
415 A.: Effect of relative humidity on the composition of secondary organic aerosol from the oxidation of toluene, Atmos. Chem. Phys., 18(3), 1643–1652, doi:10.5194/acp-18-1643-2018, 2018.

Hodas, N., Sullivan, A. P., Skog, K., Keutsch, F. N., Collett, J. L., Decesari, S., Facchini, M. C., Carlton, A. G., Laaksonen, A. and Turpin, B. J.: Aerosol Liquid Water Driven by Anthropogenic Nitrate: Implications for Lifetimes of Water-Soluble Organic Gases and Potential for Secondary Organic Aerosol Formation, Environmental Science & Technology, 48(19),
420 11127–11136, doi:10.1021/es5025096, 2014.

de Hoogh, K., Gulliver, J., Donkelaar, A. van, Martin, R. V., Marshall, J. D., Bechle, M. J., Cesaroni, G., Pradas, M. C., Dedele, A., Eeftens, M., Forsberg, B., Galassi, C., Heinrich, J., Hoffmann, B., Jacquemin, B., Katsouyanni, K., Korek, M., Künzli, N., Lindley, S. J., Lepeule, J., Meleux, F., de Nazelle, A., Nieuwenhuijsen, M., Nystad, W., Raaschou-Nielsen, O., Peters, A., Peuch, V.-H., Rouil, L., Udvardy, O., Slama, R., Stempfelet, M., Stephanou, E. G., Tsai, M. Y., Yli-Tuomi, T.,
425 Weinmayr, G., Brunekreef, B., Vienneau, D. and Hoek, G.: Development of West-European PM2.5 and NO2 land use regression models incorporating satellite-derived and chemical transport modelling data, Environmental Research, 151, 1–10, doi:10.1016/j.envres.2016.07.005, 2016.

Hsu, N. C., Tsay, S.-C., King, M. D. and Herman, J. R.: Aerosol Properties Over Bright-Reflecting Source Regions, IEEE Transactions on Geoscience and Remote Sensing, 42(3), 557–569, doi:10.1109/TGRS.2004.824067, 2004.

430   Hsu, N. C., Tsay, S.-C., King, M. D. and Herman, J. R.: Deep Blue Retrievals of Asian Aerosol Properties During ACE-Asia, IEEE Transactions on Geoscience and Remote Sensing, 44(11), 3180–3195, doi:10.1109/TGRS.2006.879540, 2006.

Hsu, N. C., Jeong, M.-J., Bettenhausen, C., Sayer, A. M., Hansell, R., Seftor, C. S., Huang, J. and Tsay, S.-C.: Enhanced Deep Blue aerosol retrieval algorithm: The second generation, Journal of Geophysical Research: Atmospheres, 118(16), 9296–9315, doi:10.1002/jgrd.50712, 2013.

435   IMPROVE Network: Federal Land Manager Environmental Database, [online] Available from: http://views.cira.colostate.edu/fed/DataWizard/Default.aspx (Accessed 26 May 2016), 2019.

Jacob, D. J. and Winner, D. A.: Effect of climate change on air quality, Atmospheric Environment, 43(1), 51–63, doi:10.1016/j.atmosenv.2008.09.051, 2009.

Jathar, S. H., Mahmud, A., Barsanti, K. C., Asher, W. E., Pankow, J. F. and Kleeman, M. J.: Water uptake by organic aerosol
440   and its influence on gas/particle partitioning of secondary organic aerosol in the United States, Atmospheric Environment, 129, 142–154, doi:10.1016/j.atmosenv.2016.01.001, 2016.

Jefferson, A., Hageman, D., Morrow, H., Mei, F. and Watson, T.: Seven years of aerosol scattering hygroscopic growth measurements from SGP: Factors influencing water uptake: Aerosol Scattering Hygroscopic Growth, Journal of Geophysical Research: Atmospheres, 122(17), 9451–9466, doi:10.1002/2017JD026804, 2017.

445   Jones, T. A. and Christopher, S. A.: Satellite and Radar Remote Sensing of Southern Plains Grass Fires: A Case Study, Journal of Applied Meteorology and Climatology, 49(10), 2133–2146, doi:10.1175/2010JAMC2472.1, 2010.

Ju, J. and Roy, D. P.: The availability of cloud-free Landsat ETM+ data over the conterminous United States and globally, Remote Sensing of Environment, 112(3), 1196–1211, doi:10.1016/j.rse.2007.08.011, 2008.

Kahn, R. A.: Multiangle Imaging Spectroradiometer (MISR) global aerosol optical depth validation based on 2 years of
450   coincident Aerosol Robotic Network (AERONET) observations, Journal of Geophysical Research, 110(D10), doi:10.1029/2004JD004706, 2005.

Kalnay, E., Kanamitsu, M., Kistler, R., Collins, W., Deaven, D., Gandin, L., Iredell, M., Saha, S., White, G., Woollen, J., Zhu, Y., Leetmaa, A., Reynolds, R., Chelliah, M., Ebisuzaki, W., Higgins, W., Janowiak, J., Mo, K. C., Ropelewski, C., Wang, J., Jenne, R. and Joseph, D.: The NCEP/NCAR 40-Year Reanalysis Project, Bulletin of the American Meteorological Society,
455   77(3), 437–471, doi:10.1175/1520-0477(1996)077<0437:TNYRP>2.0.CO;2, 1996.

Kamens, R. M., Zhang, H., Chen, E. H., Zhou, Y., Parikh, H. M., Wilson, R. L., Galloway, K. E. and Rosen, E. P.: Secondary organic aerosol formation from toluene in an atmospheric hydrocarbon mixture: Water and particle seed effects, Atmospheric Environment, 45(13), 2324–2334, doi:10.1016/j.atmosenv.2010.11.007, 2011.

Kawecki, S. and Steiner, A. L.: The Influence of Aerosol Hygroscopicity on Precipitation Intensity During a Mesoscale
460   Convective Event, Journal of Geophysical Research: Atmospheres, 123(1), 424–442, doi:10.1002/2017JD026535, 2018.

Kawecki, S., Henebry, G. M. and Steiner, A. L.: Effects of Urban Plume Aerosols on a Mesoscale Convective System, Journal of the Atmospheric Sciences, 73(12), 4641–4660, doi:10.1175/JAS-D-16-0084.1, 2016.

Kessner, A. L., Wang, J., Levy, R. C. and Colarco, P. R.: Remote sensing of surface visibility from space: A look at the United States East Coast, Atmospheric Environment, 81, 136–147, doi:10.1016/j.atmosenv.2013.08.050, 2013.

465   King, M. D., Platnick, S., Menzel, W. P., Ackerman, S. A. and Hubanks, P. A.: Spatial and Temporal Distribution of Clouds Observed by MODIS Onboard the Terra and Aqua Satellites, IEEE Transactions on Geoscience and Remote Sensing, 51(7), 3826–3852, doi:10.1109/TGRS.2012.2227333, 2013.

Kloog, I., Koutrakis, P., Coull, B. A., Lee, H. J. and Schwartz, J.: Assessing temporally and spatially resolved PM$_{2.5}$ exposures for epidemiological studies using satellite aerosol optical depth measurements, Atmospheric Environment, 45(35), 6267–6275,
470   doi:10.1016/j.atmosenv.2011.08.066, 2011.

Kovalskyy, V. and Roy, D.: A One Year Landsat 8 Conterminous United States Study of Cirrus and Non-Cirrus Clouds, Remote Sensing, 7(1), 564–578, doi:10.3390/rs70100564, 2015.

Kumar, N., Chu, A. and Foster, A.: An empirical relationship between PM$_{2.5}$ and aerosol optical depth in Delhi Metropolitan, Atmospheric Environment, 41(21), 4492–4503, doi:10.1016/j.atmosenv.2007.01.046, 2007.

475   Lamkaddam, H., Gratien, A., Pangui, E., Cazaunau, M., Picquet-Varrault, B. and Doussin, J.-F.: High-NO$_x$ Photooxidation of *n* -Dodecane: Temperature Dependence of SOA Formation, Environmental Science & Technology, 51(1), 192–201, doi:10.1021/acs.est.6b03821, 2017.

Laothawornkitkul, J., Taylor, J. E., Paul, N. D. and Hewitt, C. N.: Biogenic volatile organic compounds in the Earth system, New Phytologist, 183(1), 27–51, doi:10.1111/j.1469-8137.2009.02859.x, 2009.

480   Li, L., Gong, J. and Zhou, J.: Spatial Interpolation of Fine Particulate Matter Concentrations Using the Shortest Wind-Field Path Distance, edited by Q. Sun, PLoS ONE, 9(5), e96111, doi:10.1371/journal.pone.0096111, 2014.

Liao, H. and Seinfeld, J. H.: Global impacts of gas-phase chemistry-aerosol interactions on direct radiative forcing by anthropogenic aerosols and ozone, J. Geophys. Res., 110(D18), D18208, doi:10.1029/2005JD005907, 2005.

Lin, Y., Wang, Y., Pan, B., Hu, J., Liu, Y. and Zhang, R.: Distinct Impacts of Aerosols on an Evolving Continental Cloud
485   Complex during the RACORO Field Campaign, Journal of the Atmospheric Sciences, 73(9), 3681–3700, doi:10.1175/JAS-D-15-0361.1, 2016.

Liu, B., Ma, Y., Gong, W., Zhang, M., Wang, W. and Shi, Y.: Comparison of AOD from CALIPSO, MODIS, and Sun Photometer under Different Conditions over Central China, Scientific Reports, 8(1), doi:10.1038/s41598-018-28417-7, 2018.

Liu, Y., Schichtel, B. A. and Koutrakis, P.: Estimating Particle Sulfate Concentrations Using MISR Retrieved Aerosol
490   Properties, IEEE Journal of Selected Topics in Applied Earth Observations and Remote Sensing, 2(3), 176–184, doi:10.1109/JSTARS.2009.2030153, 2009.

Liu, Y., Wang, Z., Wang, J., Ferrare, R. A., Newsom, R. K. and Welton, E. J.: The effect of aerosol vertical profiles on satellite-estimated surface particle sulfate concentrations, Remote Sensing of Environment, 115(2), 508–513, doi:10.1016/j.rse.2010.09.019, 2011.

495   Malm, W. C., Sisler, J. F., Huffman, D., Eldred, R. A. and Cahill, T. A.: Spatial and seasonal trends in particle concentration and optical extinction in the United States, Journal of Geophysical Research, 99(D1), 1347, doi:10.1029/93JD02916, 1994.

Malm, W. C., Schichtel, B. A., Hand, J. L. and Collett, J. L.: Concurrent Temporal and Spatial Trends in Sulfate and Organic Mass Concentrations Measured in the IMPROVE Monitoring Program: Trends in Sulfate and Organic Mass, Journal of Geophysical Research: Atmospheres, 122(19), 10,462-10,476, doi:10.1002/2017JD026865, 2017.

500   Martin, R. V.: Satellite remote sensing of surface air quality, Atmospheric Environment, 42(34), 7823–7843, doi:10.1016/j.atmosenv.2008.07.018, 2008.

McKeen, S., Grell, G., Peckham, S., Wilczak, J., Djalalova, I., Hsie, E.-Y., Frost, G., Peischl, J., Schwarz, J., Spackman, R., Holloway, J., de Gouw, J., Warneke, C., Gong, W., Bouchet, V., Gaudreault, S., Racine, J., McHenry, J., McQueen, J., Lee, P., Tang, Y., Carmichael, G. R. and Mathur, R.: An evaluation of real-time air quality forecasts and their urban emissions over
505   eastern Texas during the summer of 2006 Second Texas Air Quality Study field study, Journal of Geophysical Research, 114, doi:10.1029/2008JD011697, 2009.

McKnight, P. E. and Najab, J.: Mann-Whitney U Test, in The Corsini Encyclopedia of Psychology, edited by I. B. Weiner and W. E. Craighead, John Wiley & Sons, Inc., Hoboken, NJ, USA., 2010.

Meng, Z. and Seinfeld, J. H.: On the Source of the Submicrometer Droplet Mode of Urban and Regional Aerosols, Aerosol
510   Science and Technology, 20(3), 253–265, doi:10.1080/02786829408959681, 1994.

Metzger, S., Abdelkader, M., Steil, B. and Klingmüller, K.: Aerosol water parameterization: long-term evaluation and importance, Atmospheric Chemistry and Physics Discussions, 1–41, doi:10.5194/acp-2018-450, 2018.

National Aeronautics and Space Administration: Global Change Master Directory, [online] Available from: https://gcmd.nasa.gov/, 2018.

515   Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C. and Seinfeld, J. H.: Secondary organic aerosol formation from *m*-xylene, toluene, and benzene, Atmospheric Chemistry and Physics, 7(14), 3909–3922, doi:10.5194/acp-7-3909-2007, 2007.

Nguyen, T. K. V., Petters, M. D., Suda, S. R., Guo, H., Weber, R. J. and Carlton, A. G.: Trends in particle-phase liquid water during the Southern Oxidant and Aerosol Study, Atmospheric Chemistry and Physics, 14(20), 10911–10930, doi:10.5194/acp-
520   14-10911-2014, 2014.

Nguyen, T. K. V., Capps, S. L. and Carlton, A. G.: Decreasing Aerosol Water Is Consistent with OC Trends in the Southeast U.S., Environmental Science & Technology, 49(13), 7843–7850, doi:10.1021/acs.est.5b00828, 2015.

Nguyen, T. K. V., Ghate, V. P. and Carlton, A. G.: Reconciling satellite aerosol optical thickness and surface fine particle mass through aerosol liquid water, Geophysical Research Letters, 43(22), 11,903-11,912, doi:10.1002/2016GL070994, 2016a.

525   Nguyen, T. K. V., Zhang, Q., Jimenez, J. L., Pike, M., Carlton, A. G.: Liquid Water: Ubiquitous Contributor to Aerosol Mass, Environmental Science & Technology, 3(7), 257-263, 2016b.

Norris, J. R., Allen, R. J., Evan, A. T., Zelinka, M. D., O'Dell, C. W. and Klein, S. A.: Evidence for climate change in the satellite cloud record, Nature, 536(7614), 72–75, doi:10.1038/nature18273, 2016.

530   Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmospheric Chemistry and Physics, 7(8), 1961–1971, doi:10.5194/acp-7-1961-2007, 2007.

Pitchford, M., Malm, W., Schichtel, B., Kumar, N., Lowenthal, D. and Hand, J.: Revised Algorithm for Estimating Light Extinction from IMPROVE Particle Speciation Data, Journal of the Air & Waste Management Association, 57(11), 1326–1336, doi:10.3155/1047-3289.57.11.1326, 2007.

535   Pratt, K. A., Fiddler, M. N., Shepson, P. B., Carlton, A. G. and Surratt, J. D.: Organosulfates in cloud water above the Ozarks' isoprene source region, Atmospheric Environment, 77, 231–238, doi:10.1016/j.atmosenv.2013.05.011, 2013.

Pruppacher, H. R. and Klett, J. D.: Microphysics of clouds and precipitation, Springer, Dordrecht ; New York., 2010.

R Core Team: R: A language and environment for statistical computing., R Foundation for Statistical Computing, Vienna, Austria. [online] Available from: http://www.R-project.org/, 2013.

540   Rastak, N., Pajunoja, A., Acosta Navarro, J. C., Ma, J., Song, M., Partridge, D. G., Kirkevåg, A., Leong, Y., Hu, W. W., Taylor, N. F., Lambe, A., Cerully, K., Bougiatioti, A., Liu, P., Krejci, R., Petäjä, T., Percival, C., Davidovits, P., Worsnop, D. R., Ekman, A. M. L., Nenes, A., Martin, S., Jimenez, J. L., Collins, D. R., Topping, D. O., Bertram, A. K., Zuend, A., Virtanen, A. and Riipinen, I.: Microphysical explanation of the RH-dependent water affinity of biogenic organic aerosol and its importance for climate, Geophys. Res. Lett., 44(10), 5167–5177, doi:10.1002/2017GL073056, 2017.

545   Remer, L. A., Mattoo, S., Levy, R. C. and Munchak, L. A.: MODIS 3 km aerosol product: algorithm and global perspective, Atmos. Meas. Tech., 6(7), 1829–1844, doi:10.5194/amt-6-1829-2013, 2013.

Ryerson, T. B., Andrews, A. E., Angevine, W. M., Bates, T. S., Brock, C. A., Cairns, B., Cohen, R. C., Cooper, O. R., de Gouw, J. A., Fehsenfeld, F. C., Ferrare, R. A., Fischer, M. L., Flagan, R. C., Goldstein, A. H., Hair, J. W., Hardesty, R. M., Hostetler, C. A., Jimenez, J. L., Langford, A. O., McCauley, E., McKeen, S. A., Molina, L. T., Nenes, A., Oltmans, S. J.,
550   Parrish, D. D., Pederson, J. R., Pierce, R. B., Prather, K., Quinn, P. K., Seinfeld, J. H., Senff, C. J., Sorooshian, A., Stutz, J., Surratt, J. D., Trainer, M., Volkamer, R., Williams, E. J. and Wofsy, S. C.: The 2010 California Research at the Nexus of Air Quality and Climate Change (CalNex) field study, Journal of Geophysical Research: Atmospheres, 118(11), 5830–5866, doi:10.1002/jgrd.50331, 2013.

Sakulyanontvittaya, T., Duhl, T., Wiedinmyer, C., Helmig, D., Matsunaga, S., Potosnak, M., Milford, J. and Guenther, A.:
555   Monoterpene and Sesquiterpene Emission Estimates for the United States, Environmental Science & Technology, 42(5), 1623–1629, doi:10.1021/es702274e, 2008.

Schaap, M., Apituley, A., Timmermans, R. M. A., Koelemeijer, R. B. A. and de Leeuw, G.: Exploring the relation between aerosol optical depth and PM$_{2.5}$ at Cabauw, the Netherlands, Atmospheric Chemistry and Physics, 9(3), 909–925, doi:10.5194/acp-9-909-2009, 2009.

560   Sisterson, D. L., Peppler, R. A., Cress, T. S., Lamb, P. J. and Turner, D. D.: The ARM Southern Great Plains (SGP) Site, Meteorological Monographs, 57, 6.1-6.14, doi:10.1175/AMSMONOGRAPHS-D-16-0004.1, 2016.

Song, W., Jia, H., Huang, J. and Zhang, Y.: A satellite-based geographically weighted regression model for regional PM$_{2.5}$ estimation over the Pearl River Delta region in China, Remote Sensing of Environment, 154, 1–7, doi:10.1016/j.rse.2014.08.008, 2014.

565   Sorek-Hamer, M., Just, A. C. and Kloog, I.: Satellite remote sensing in epidemiological studies, Current Opinion in Pediatrics, 28(2), 228–234, doi:10.1097/MOP.0000000000000326, 2016.

Spracklen, D. V., Logan, J. A., Mickley, L. J., Park, R. J., Yevich, R., Westerling, A. L. and Jaffe, D. A.: Wildfires drive interannual variability of organic carbon aerosol in the western U.S. in summer, Geophys. Res. Lett., 34(16), doi:10.1029/2007GL030037, 2007.

570   Tai, A. P. K., Mickley, L. J. and Jacob, D. J.: Correlations between fine particulate matter (PM$_{2.5}$) and meteorological variables in the United States: Implications for the sensitivity of PM$_{2.5}$ to climate change, Atmospheric Environment, 44(32), 3976–3984, doi:10.1016/j.atmosenv.2010.06.060, 2010.

Tang, Y., Carmichael, G. R., Uno, I., Woo, J.-H., Kurata, G., Lefer, B., Shetter, R. E., Huang, H., Anderson, B. E., Avery, M. A., Clarke, A. D. and Blake, D. R.: Impacts of aerosols and clouds on photolysis frequencies and photochemistry during

575 TRACE-P: 2. Three-dimensional study using a regional chemical transport model, Journal of Geophysical Research: Atmospheres, 108(D21), doi:10.1029/2002JD003100, 2003.

Tian, D., Hu, Y., Wang, Y., Boylan, J. W., Zheng, M. and Russell, A. G.: Assessment of Biomass Burning Emissions and Their Impacts on Urban and Regional $PM_{2.5}$: A Georgia Case Study, Environmental Science & Technology, 43(2), 299–305, doi:10.1021/es801827s, 2009.

580 Tian, J. and Chen, D.: A semi-empirical model for predicting hourly ground-level fine particulate matter ($PM_{2.5}$) concentration in southern Ontario from satellite remote sensing and ground-based meteorological measurements, Remote Sensing of Environment, 114(2), 221–229, doi:10.1016/j.rse.2009.09.011, 2010.

Toon, O. B., Maring, H., Dibb, J., Ferrare, R., Jacob, D. J., Jensen, E. J., Luo, Z. J., Mace, G. G., Pan, L. L., Pfister, L., Rosenlof, K. H., Redemann, J., Reid, J. S., Singh, H. B., Thompson, A. M., Yokelson, R., Minnis, P., Chen, G., Jucks, K. W.
585 and Pszenny, A.: Planning, implementation, and scientific goals of the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys ($SEAC_4RS$) field mission: Planning SEAC4RS, Journal of Geophysical Research: Atmospheres, 121(9), 4967–5009, doi:10.1002/2015JD024297, 2016.

Twohy, C. H., Coakley, J. A. and Tahnk, W. R.: Effect of changes in relative humidity on aerosol scattering near clouds, J. Geophys. Res., 114(D5), D05205, doi:10.1029/2008JD010991, 2009.

590 US Environmental Protection Agency: Ambient Air Monitoring Strategy for State, Local, and Tribal Air Agencies, [online] Available from: https://www3.epa.gov/ttnamti1/files/ambient/monitorstrat/AAMS%20for%20SLTs%20%20-%20FINAL%20Dec%202008.pdf, 2008.

Vogelmann, A. M., McFarquhar, G. M., Ogren, J. A., Turner, D. D., Comstock, J. M., Feingold, G., Long, C. N., Jonsson, H. H., Bucholtz, A., Collins, D. R., Diskin, G. S., Gerber, H., Lawson, R. P., Woods, R. K., Andrews, E., Yang, H.-J., Chiu, J.
595 C., Hartsock, D., Hubbe, J. M., Lo, C., Marshak, A., Monroe, J. W., McFarlane, S. A., Schmid, B., Tomlinson, J. M. and Toto, T.: Racoro Extended-Term Aircraft Observations of Boundary Layer Clouds, Bulletin of the American Meteorological Society, 93(6), 861–878, doi:10.1175/BAMS-D-11-00189.1, 2012.

Wang, J. and Christopher, S. A.: Intercomparison between satellite-derived aerosol optical thickness and $PM_{2.5}$ mass: Implications for air quality studies, Geophysical Research Letters, 30(21), 2095, doi:10.1029/2003GL018174, 2003.

600 Wang, J., Xu, X., Henze, D. K., Zeng, J., Ji, Q., Tsay, S.-C. and Huang, J.: Top-down estimate of dust emissions through integration of MODIS and MISR aerosol retrievals with the GEOS-Chem adjoint model, Geophysical Research Letters, 39(8), n/a-n/a, doi:10.1029/2012GL051136, 2012.

Wang, J. X. and Angell, J. K.: Air stagnation climatology for the United States, [online] Available from: https://www.arl.noaa.gov/documents/reports/atlas.pdf, 1999.

605 Youn, J.-S., Wang, Z., Wonaschütz, A., Arellano, A., Betterton, E. A. and Sorooshian, A.: Evidence of aqueous secondary organic aerosol formation from biogenic emissions in the North American Sonoran Desert, Geophys. Res. Lett., 40(13), 3468–3472, doi:10.1002/grl.50644, 2013.

Zeng, T., Wang, Y., Yoshida, Y., Tian, D., Russell, A. G. and Barnard, W. R.: Impacts of Prescribed Fires on Air Quality over the Southeastern United States in Spring Based on Modeling and Ground/Satellite Measurements, Environmental Science &
610 Technology, 42(22), 8401–8406, doi:10.1021/es800363d, 2008.

Zhang, G., Rui, X. and Fan, Y.: Critical Review of Methods to Estimate $PM_{2.5}$ Concentrations within Specified Research Region, ISPRS International Journal of Geo-Information, 7(9), 368, doi:10.3390/ijgi7090368, 2018.

Zhang, H., Kondragunta, S., Laszlo, I., Liu, H., Remer, L. A., Huang, J., Superczynski, S. and Ciren, P.: An enhanced VIIRS aerosol optical thickness (AOT) retrieval algorithm over land using a global surface reflectance ratio database, Journal of Geophysical Research: Atmospheres, 121(18), 10,717-10,738, doi:10.1002/2016JD024859, 2016.

Zhou, S., Collier, S., Jaffe, D. A. and Zhang, Q.: Free tropospheric aerosols at the Mt. Bachelor Observatory: more oxidized and higher sulfate content compared to boundary layer aerosols, Atmospheric Chemistry and Physics, 19(3), 1571–1585, doi:10.5194/acp-19-1571-2019, 2019.

615

620

625

630

Table 1: Particle chemical constituent concentrations, meteorology, and growth factors during Cloudy (Cl) and Clear Sky (CS) times in the Mid South.

	SO$_4^{2-}$		NO$_3^-$		ALW		RH		Growth Factors	
	CS	Cl	CS	Cl	CS	Cl	CS	Cl	CS	Cl
Win	0.77	1.24	0.90	1.22	1.32	3.61	0.64	0.80	1.24	1.45
Spr	1.46	1.79	0.37	0.50	2.48	4.02	0.62	0.76	1.20	1.37
Sum	1.91	1.69	0.20	0.19	2.92	3.57	0.59	0.72	1.17	1.28
Fall	1.05	1.17	0.18	0.33	1.56	2.74	0.57	0.73	1.16	1.31

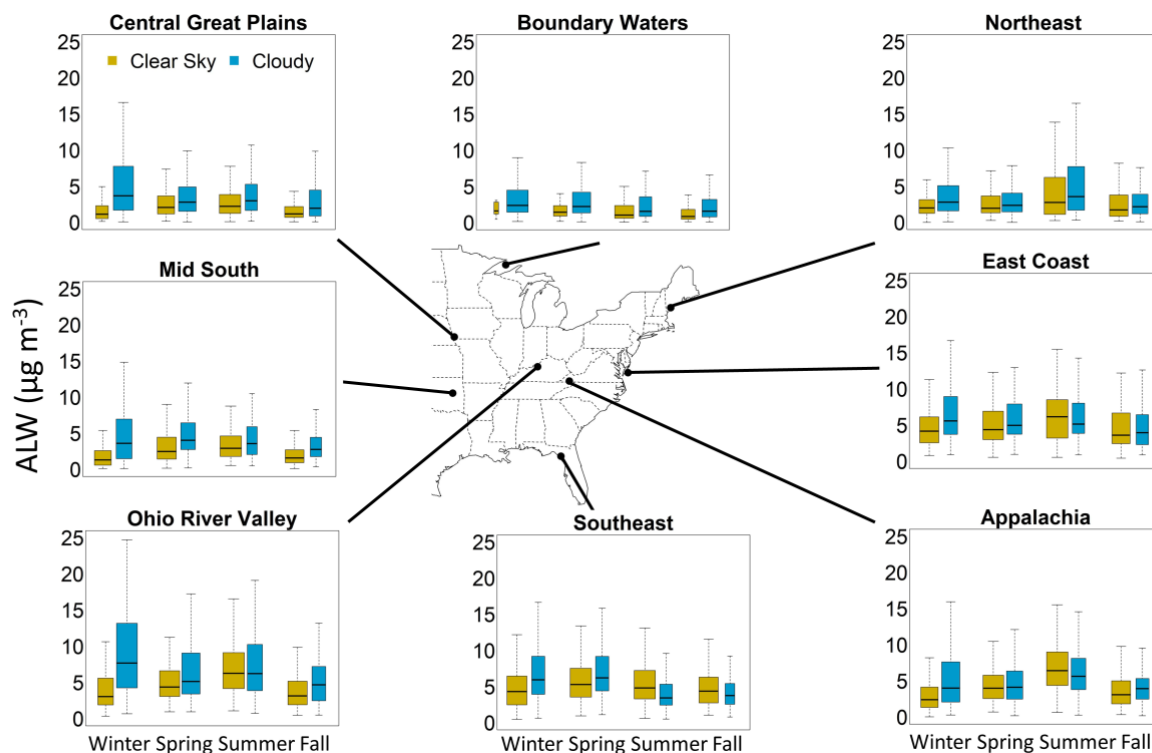
635

640

Figure 1. Differences in PM$_{2.5}$ mass concentrations in the Eastern U.S. Clear sky values are yellow and

Cloudy are blue. Median values are shown as midline with box boundaries as the 75th and 25th percentiles. Whiskers are 90th and 10th percentiles. Outliers are not shown but are included in calculations. PM2.5 mass is typically highest during Clear Sky conditions with the exception of winter.

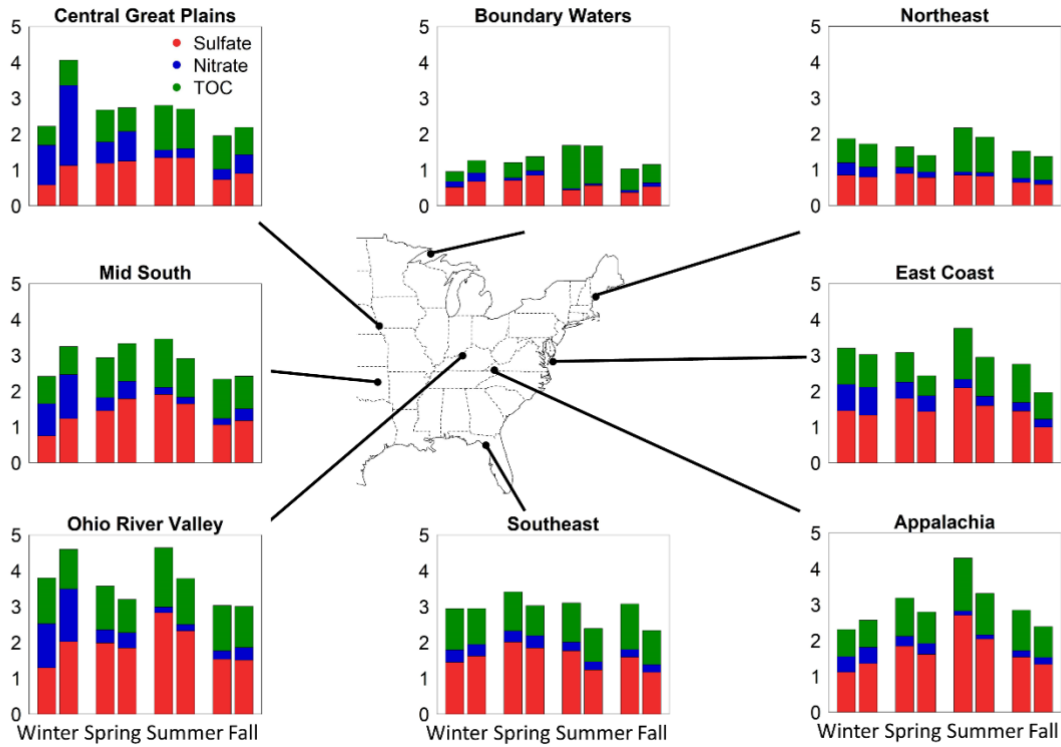



Figure 2. Seasonal median values of PM2.5 chemical constituent in the Eastern U.S. during MODIS-defined Clear sky (left stacked bar in each pair) and Cloudy (right stacked bar in each pair) conditions. Total organic carbon mass concentration are nearly universally higher during Clear Sky conditions in all regions and this pattern is unique among PM2.5 chemical constituents.

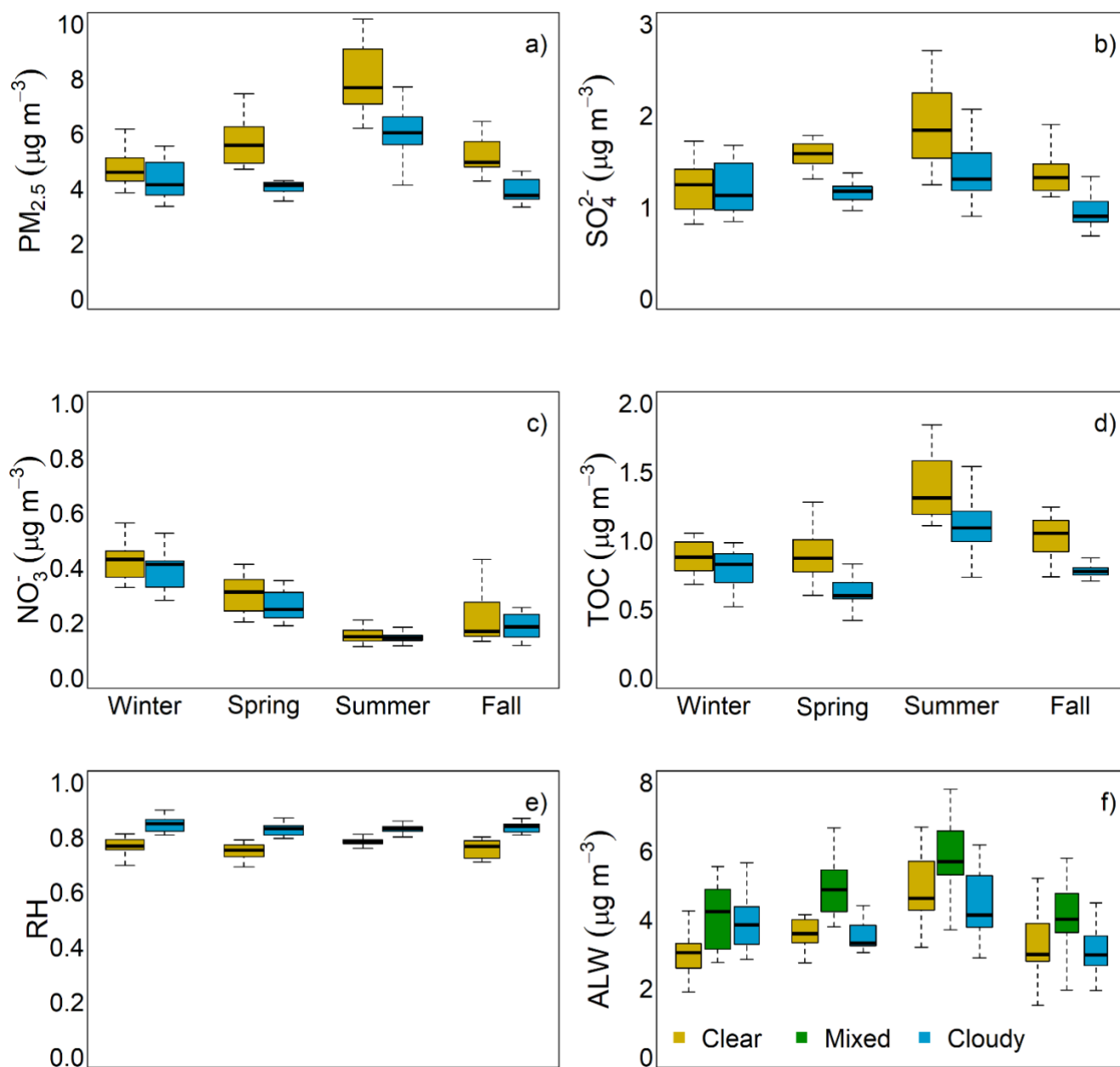



Figure 3. Distributions of a) PM2.5, b) SO4, c) NO3, d) TOC, e) RH, and f) ALW mass concentrations during all seasons in the eastern US. Yellow boxplots indicate Clear Sky times, and blue boxplots indicate Cloudy times. In b), the green boxplots represent the Mixed ALW scenario.

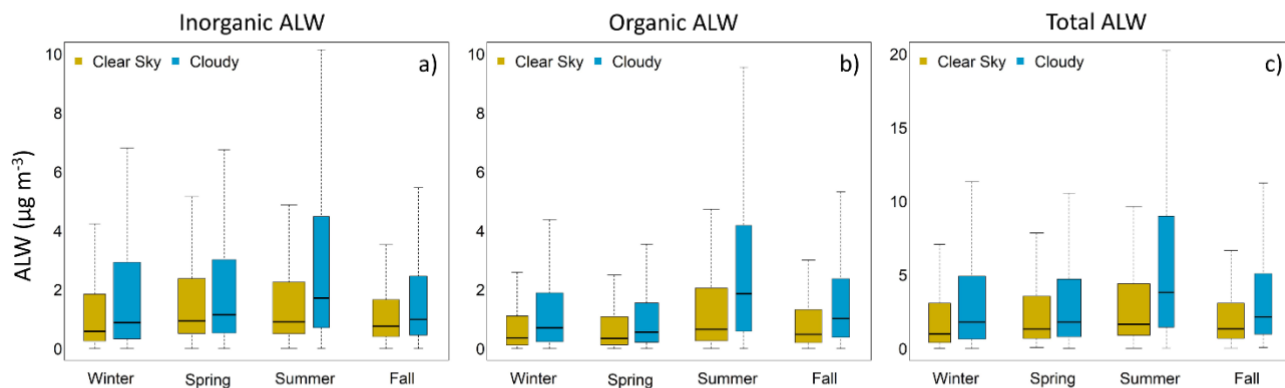



Figure 4. Distributions of a) inorganic ALW, b) organic ALW, and c) total (inorganic + organic) ALW during Clear Sky (yellow) and Cloudy (blue) times in all seasons across the CONUS. The width of the boxplot is proportional to the amount of observations that make up each distribution. Note that potential outliers are not shown, but are used in calculations.

665

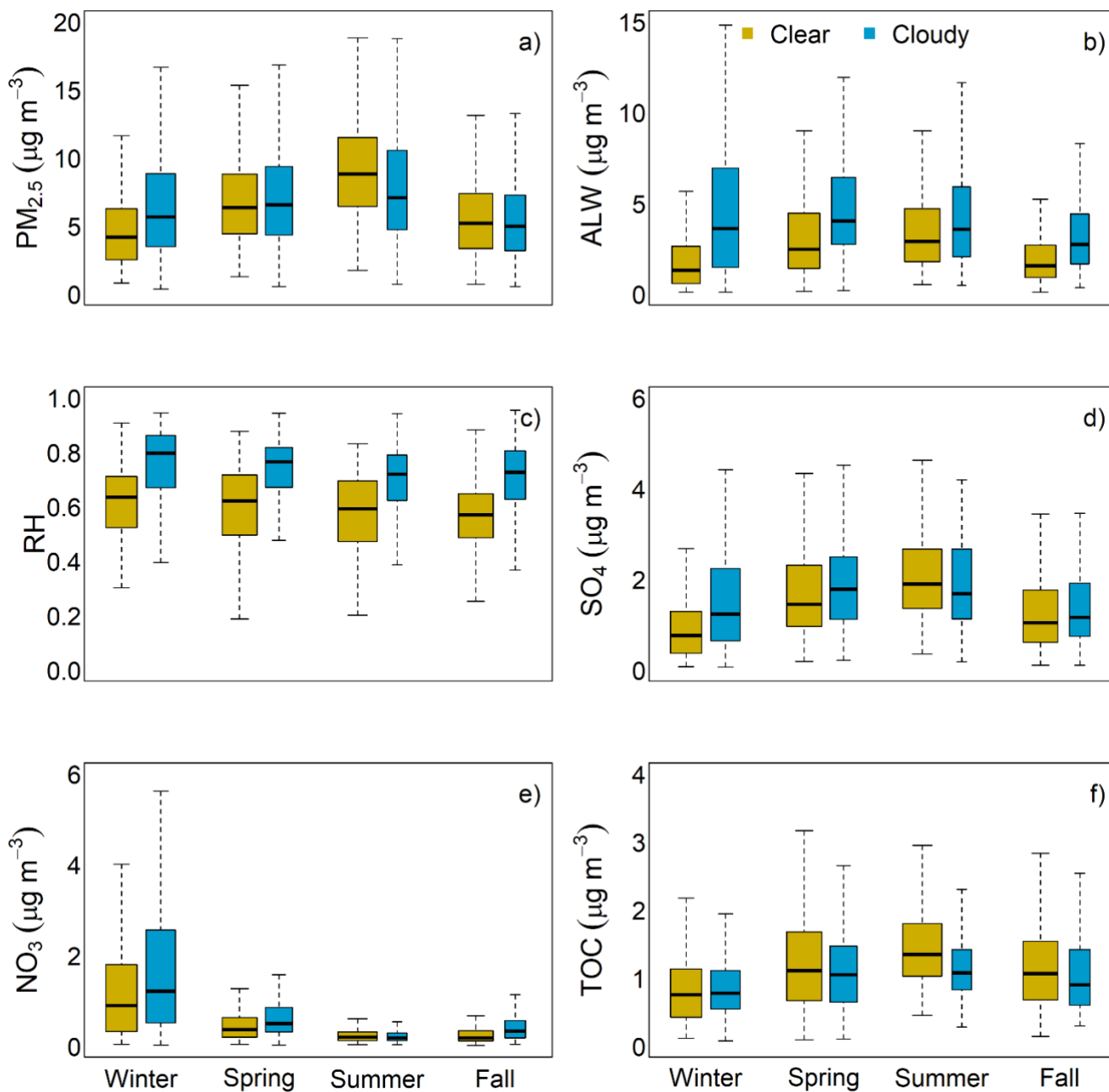



Figure 5. Distributions of a) PM2.5, b) ALW, c) RH, d) SO4, e) NO3, and f) TOC mass concentrations in all seasons in the Mid South. Yellow boxplots indicated Clear Sky times, and blue boxplots indicate Cloudy times. The width of the boxplots is proportional to the number of observations in each. Note that potential outliers are not shown, but are used in calculations.

670

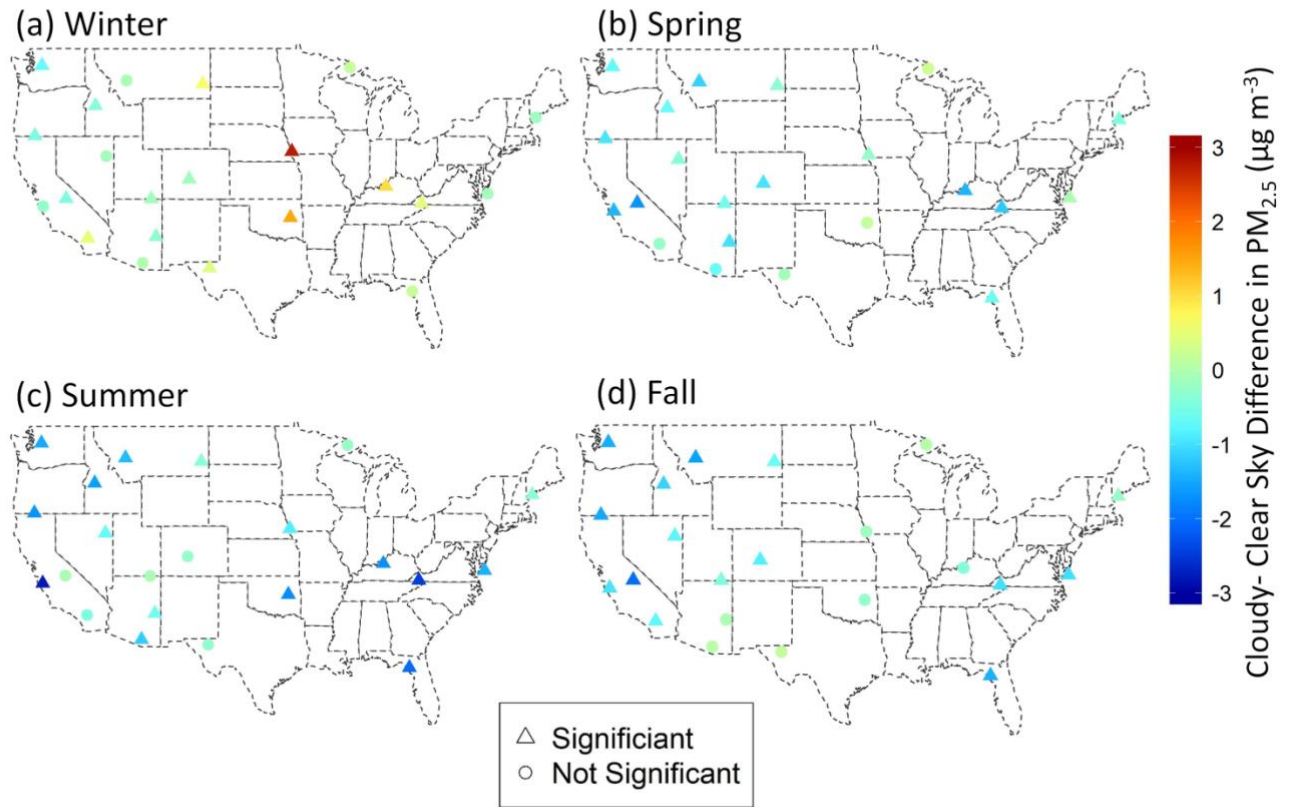



Figure A1: Maps of the difference in PM2.5 mass concentration medians (Cloudy-Clear Sky) for all regions from 2010-2014 for (a) winter, (b) spring, (c) summer, and (d) fall. The color of the point corresponds to the magnitude of the difference. Triangles indicate that median differences are significant by the Mann-Whitney U Test.

675

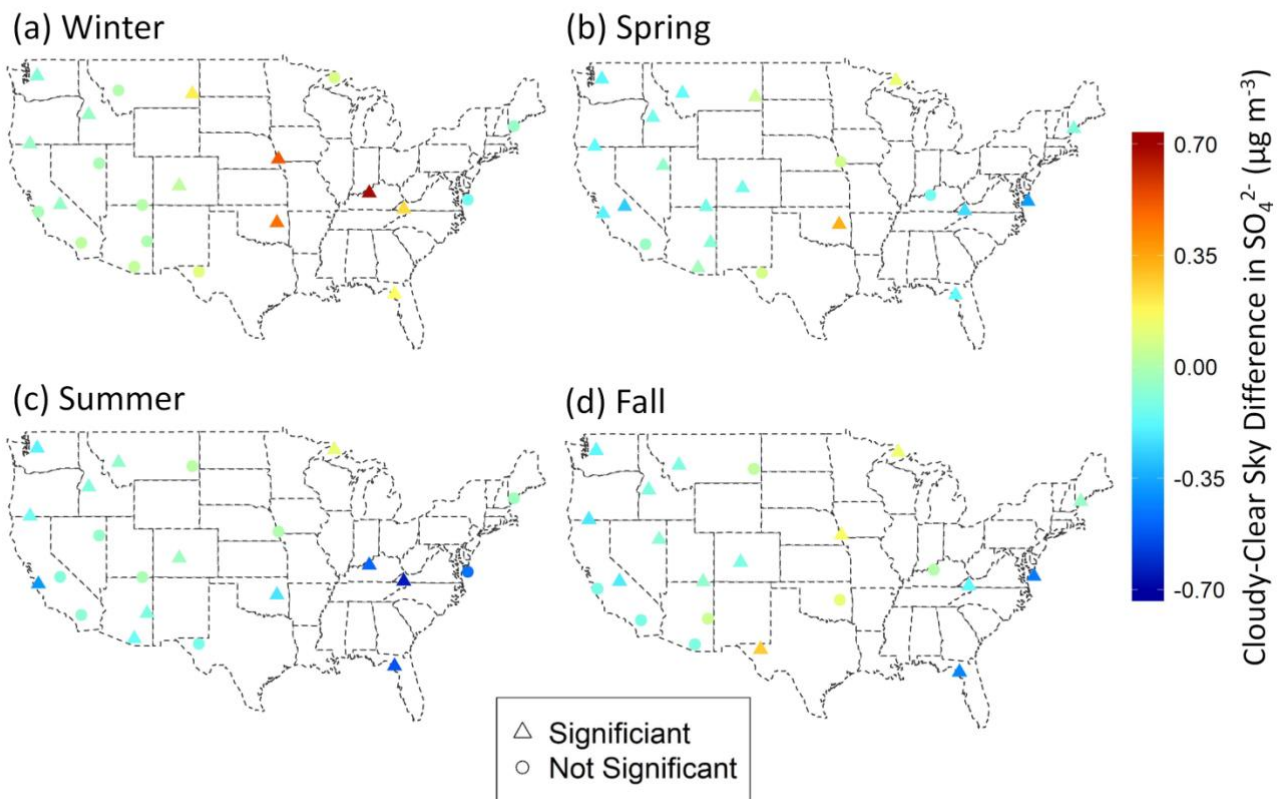



Figure A2: Maps of the difference in SO$_4^{2-}$ mass concentration medians (Cloudy-Clear Sky) for all regions from 2010-2014 for (a)
winter, (b) spring, (c) summer, and (d) fall. The color of the point corresponds to the magnitude of the difference. Triangles indicate
that median differences are significant by the Mann-Whitney U Test.

680

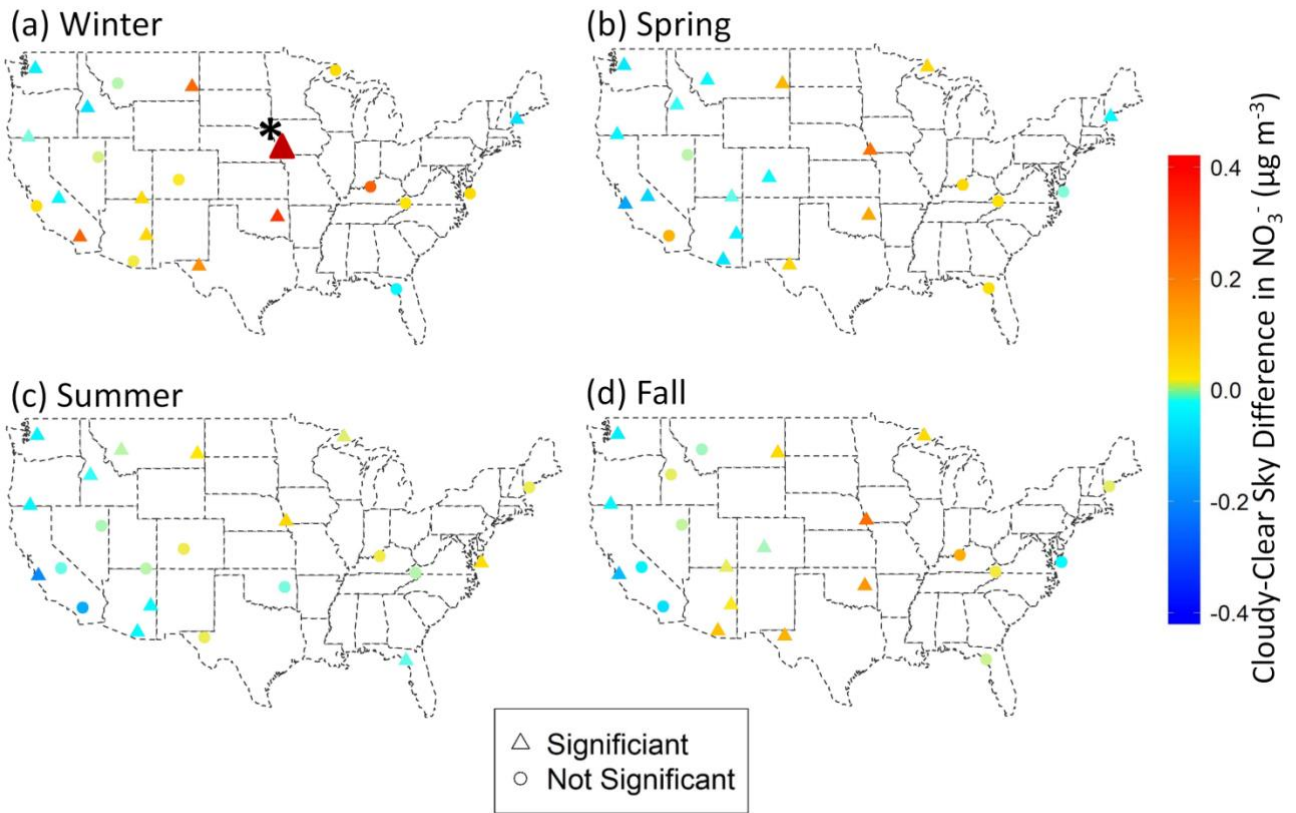



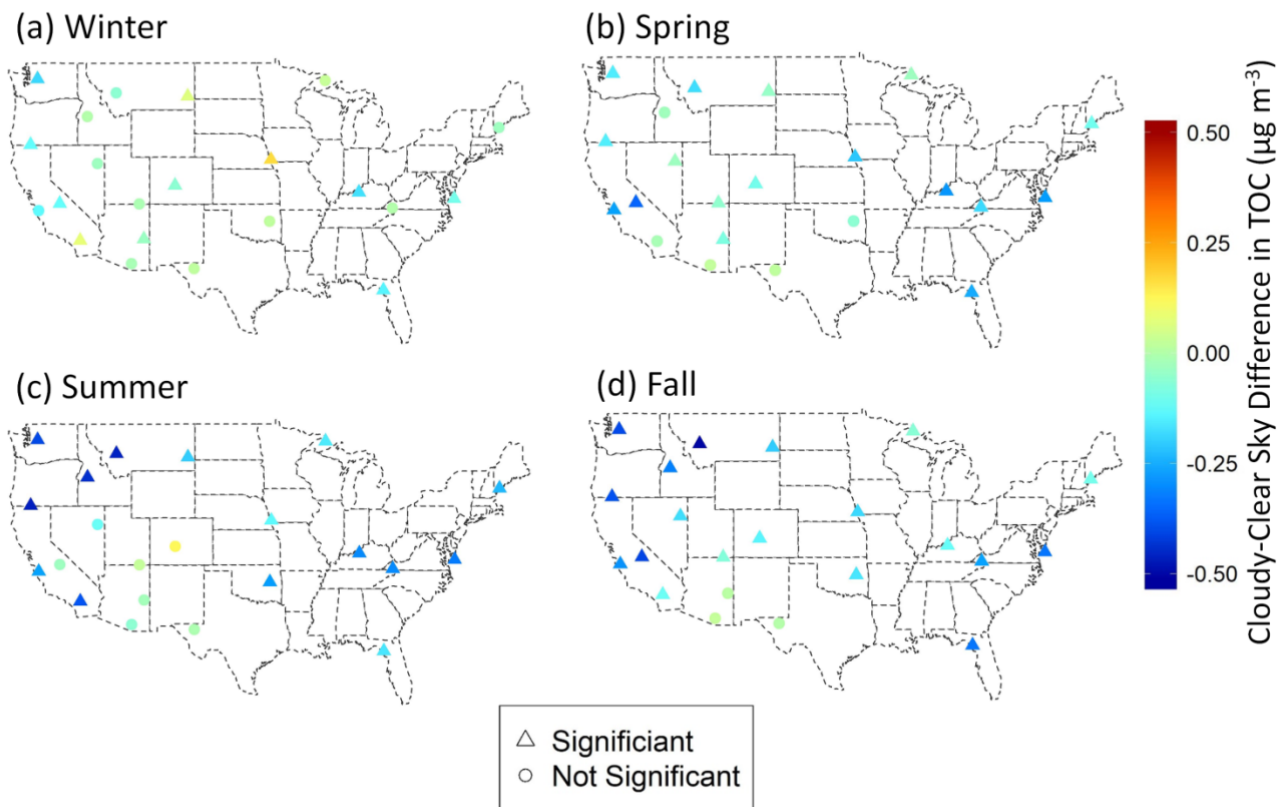
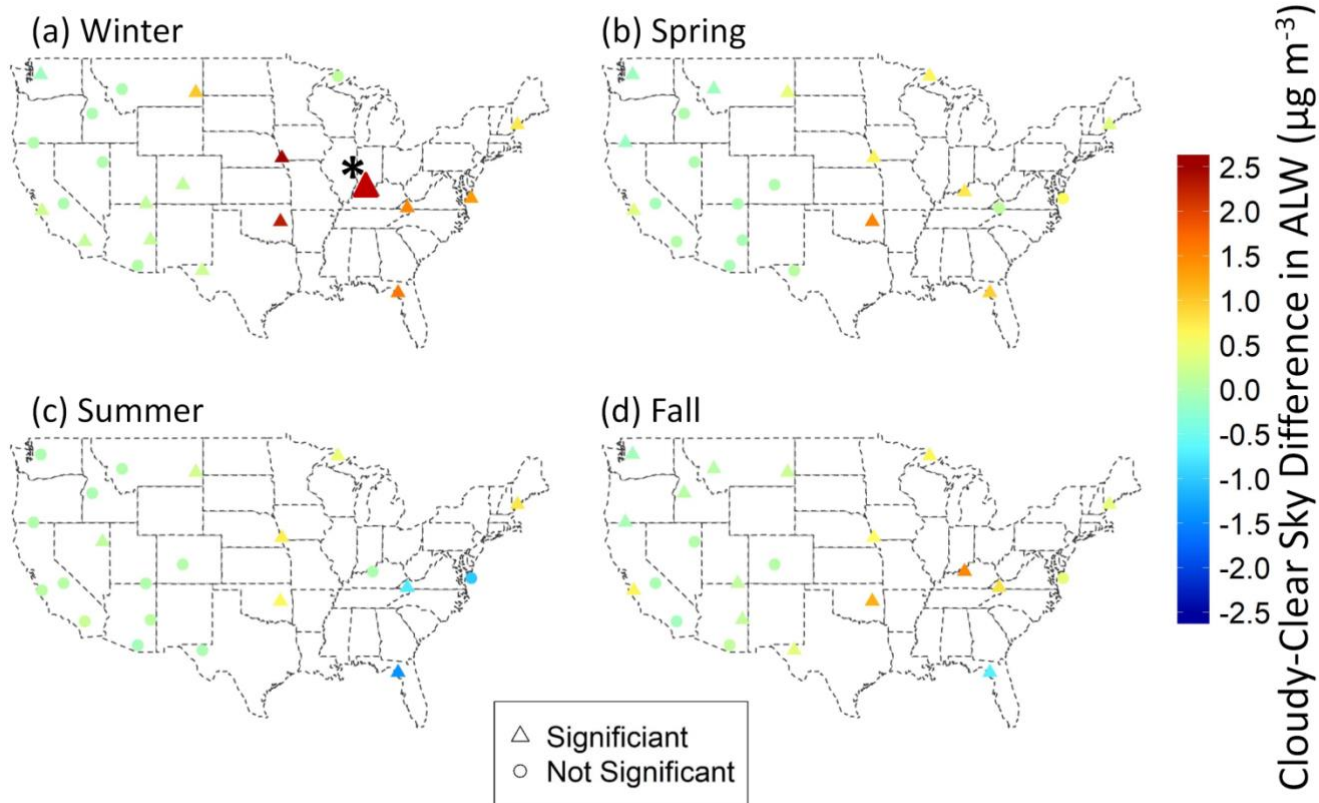
Figure A3: Maps of the difference in NO₃⁻ mass concentration medians (Cloudy-Clear Sky) for all regions from 2010-2014 for (a) winter, (b) spring, (c) summer, and (d) fall. The color of the point corresponds to the magnitude of the difference. Triangles indicate that median differences are significant by the Mann-Whitney U Test. Note that the difference in medians for daily NO₃⁻ concentrations in winter for the Central Great Plains (denoted with asterisk) is substantially larger than other regions (Cloudy median value is 1.07 μg m⁻³ larger than Clear Sky).

690 Figure A4: Maps of the difference in TOC mass concentration medians (Cloudy-Clear Sky) for all regions from 2010-2014 for (a) winter, (b) spring, (c) summer, and (d) fall. The color of the point corresponds to the magnitude of the difference. Triangles indicate that median differences are significant by the Mann-Whitney U Test.

695

Figure A5: Maps of the difference in ALW mass concentration medians (Cloudy-Clear Sky) for all regions from 2010-2014 for (a) winter, (b) spring, (c) summer, and (d) fall. The color of the point corresponds to the magnitude of the difference. Triangles indicate that median differences are significant by the Mann-Whitney U Test. Note that the difference in wintertime medians for daily ALW concentrations in the Ohio River Valley (denoted with asterisk) is substantially larger than other regions (Cloudy median value is

700 **4.6 μg m-3 larger than Clear Sky).**