https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

Atmospheric Chemistry and Physics Discussions

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
[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 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 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 eastern US, relative humidity alone cannot explain differences in ALW, suggesting emissions and *in situ* chemistry 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 causes cloud cover to change (Norris et al., 2016). Average cloud fraction values over the contiguous US (CONUS) are ~40% year-round with higher values in winter (44-54%) than summer (26-34%) (Ju and Roy, 2008; Kovalskyy and Roy, 2015). Clouds 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). Clouds are the primary drivers of vertical transport in the atmosphere, moving trace species from the boundary layer to the free troposphere (FT) (Ervens, 2015). The radiative impacts of aerosols in the FT are substantial, especially when located above clouds where they scatter and absorb both incoming solar radiation and diffuse back scatter from clouds (Seinfeld, 2008). Aerosol-cloud interactions are complex and a critical uncertainty in model projections (Fan et al., 2016).

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020


Atmospheric Chemistry and Physics Discussions

Atmospheric chemistry laboratory studies, ambient sampling, modelling, and analysis strategies are often designed in ways that minimize cloud and water influences. This leads to an implicit, yet persistent clear sky bias in the quantitative understanding of tropospheric composition. During atmospheric chemistry field campaigns, aircraft typically avoid clouds, and direct measurement of in-cloud particle chemical composition is rare (Wagner et al., 2015). There is increased error in remotely sensed aerosol optical thickness (AOT) retrieval techniques during cloudy times (Martin, 2008), and impacted retrievals are 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 (van Donkelaar et al., 2010; Guo et al., 2017; de Hoogh et al., 2016; Song et al., 2014; Tian and Chen, 2010) and cloud-free aircraft samples (Bray et al., 2017; McKeen et al., 2009). This biases model development and predictive skill toward cloud-free conditions, and hinders accurate prediction of trace species during cloudy time periods. Laboratory experiments to understand particulate matter formation are conducted under dry conditions (Lamkaddam et al., 2017; Ng et al., 2007) atypical of cloudy time periods. Should differences in aerosol physicochemical properties, including those that affect water uptake, 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.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020


Atmospheric Chemistry and Physics Discussions

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 mass concentrations and chemical speciation including aerosol liquid water (ALW) influence AOT (Christiansen et al., 2019; Malm et al., 1994; Nguyen et al., 2016; Pitchford et al., 2007), cloud microphysics, and mesoscale convective systems (Kawecki and Steiner, 2018), including storm morphology and precipitation patterns (Kawecki et al., 2016). Particle chemical composition modulates particle size via water uptake. Particle size is a determining factor in light scattering by particles, which is important for aerosol radiative calculations. An implication of this work is that if particle hygroscopicity changes from clear sky to cloudy time periods, when aerosol-cloud interactions are most important, a quantitative understanding remains unclear.

In this work, we test the hypothesis that there are quantitative differences in $PM_{2.5}$ chemical composition between cloudy and clear sky time periods in ways important for water uptake. 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, $PM_{2.5}$, and chemical speciation during cloudy and clear sky times using surface measurements from the IMPROVE network from 2010-2014 within the context of MODIS cloud flag values. 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).

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. Pairing of satellite and surface $PM_{2.5}$ mass measurements typically 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). For this reason, we use rural IMPROVE network sites that are located primarily in national parks, although improvements have been made for retrievals over bright surfaces (Hauser, 2005; Hsu et al., 2004, 2006, 2013; Zhang et al., 2016). We use 500 m resolution pixels that contain the IMPROVE sites. 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 it is a fundamental limit of the algorithm (Remer et al., 2013). IMPROVE monitors are frequently under a MODIS swath with valid retrievals even if the pixel containing the IMPROVE

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020


Atmospheric Chemistry and Physics Discussions

station is not successfully retrieved. As an alternative to the IMPROVE pixel, we employ a method for quality assurance, a 17x17 grid. This allows for any retrieval within a 50 km x 50 km area to represent the IMPROVE station. If all 17x17 pixels are not retrieved, then the state over the monitor is determined to be cloudy. The 17x17 grid approach is much more likely to attribute non-retrieved data to clouds (98.5%) than the containing pixel approach, which attributes 89.8% of non-retrieved data to clouds. 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. For example, 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 (K^+–Ca^{2+}–Mg^{2+}–NH_4^+–Na^+–SO_4^{2-}–NO_3^-–Cl^-–H_2O) 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 due to limited measurement availability. Dust and organic species are also not considered because water uptake properties are not well constrained (Jathar et al., 2016; Metzger et al., 2018), and there is large spatial heterogeneity in dust. Our approach to employing ISORROPIA introduces uncertainties (e.g., pH estimates would be unreliable (Guo et al., 2015)), but neglect of dust does not affect overall interpretation of ALW mass (Fig. S2), consistent with an earlier sensitivity using this technique that included organic species (Nguyen et al., 2015). The temperature and RH were extracted from the North American Regional Reanalysis (NARR) model (Kalnay et al., 1996) similar to Nguyen et al. 2016.

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 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

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020


Atmospheric Chemistry and Physics Discussions

largest in this region (Fig. S3), and it is in cloud often and consistently (cloud fraction 30-50% year-round) (Fig. S4). This makes statistical comparisons between Cloudy and Clear Sky times more robust than in the dry western US, where ALW concentrations and cloud fraction are low in most seasons. We group 24-hour average chemical composition and meteorology into Clear Sky and Cloudy bins and take monthly medians. We perform ALW estimations using the medians via three ISORROPIA calculation scenarios: 1) 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. S5). We use monthly medians 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 Mixed scenario in order to reproduce studies in which cloud free growth factors (Brock et al., 2016) are eventually applied in models that contain 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. Wet deposition is unconstrained in this analysis, but cloud droplets typically evaporate (Pruppacher and Klett, 2010).

Growth factors used in the Mid South region are estimated from a modified Kohler equation (Brock et al., 2016; Jefferson et al., 2017) (Eq. 1). 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) (Petters and Kreidenweis, 2007). Here, $gf(D)$ is the hygroscopic diameter growth.

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

Statistical significance for differences in measurement distributions of $PM_{2.5}$ 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 (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., 2018), the Studies of the Emissions and Atmospheric Composition, Clouds, and Climate Coupling by Regional Surveys (SEAC^{4}RS) (Toon et al., 2016), and the California Research at the Nexus of Air Quality and Climate Change (CalNex) (Ryerson et al., 2013) field 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).

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020


Atmospheric Chemistry and Physics Discussions

3 Results and Discussion

3.1 Hygroscopicity and Chemical Composition

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 differences that would arise from changes in meteorology alone (Fig. 1). These findings are consistent with an analysis in the desert southwest US that shows that chemical composition is an essential factor for improving cloud condensation nuclei predictions (Crosbie et al., 2015). 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). 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). When Clear Sky chemical composition is extrapolated 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"). Interestingly, monthly median Clear Sky and Cloudy scenario ALW concentrations do not differ significantly except during winter despite higher Cloudy RH (Fig. 2). This is consistent with chemical composition as a determining factor in ALW (Carlton and Turpin, 2013; Liao and Seinfeld, 2005), CCN (Crosbie et al., 2015), and extinction (Pitchford et al., 2007) on cloudy days because the pattern in ALW is opposite the pattern in RH.

Clear Sky/Cloudy patterns in SO_4^{2-} and NO_3^- mass concentrations, which affect particle hygroscopicity, vary regionally and seasonally. When aggregated over the eastern US, ALW estimates for the Mixed case are largest during summer and spring and can be explained by elevated Clear Sky SO_4^{2-} and NO_3^- concentrations and high Cloudy RH (Fig. 2). 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 S2). 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 has a determining effect on ALW mass concentrations (Nguyen et al., 2016), a critical element in the estimation of aerosol-cloud interactions and particle radiative impacts. 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.

Differences in daily mass concentrations of fine particle chemical constituents between 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

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020


Atmospheric Chemistry and Physics Discussions

region (Figs. 3-7, Tables S3-S7, Fig. S6). These patterns cannot be adequately described as a function of MODIS cloud fraction (Figs. S6-S7). If meteorological processes and physical transport are the only controlling factors, then patterns in mass concentrations among $PM_{2.5}$ and constituents should not vary. However, they do, suggesting differences in emissions and/or *in situ* chemical production of $PM_{2.5}$ during Cloudy and Clear Sky time periods. Where differences are significant for ALW, Cloudy ALW is higher than Clear Sky in all seasons, with few exceptions (Fig. 3, Table S3). Water uptake contributes to particle growth with a determining impact on particle size and radiative properties. $PM_{2.5}$ mass, greater during Clear Sky times in most regions and seasons, has nearly an opposite pattern to ALW spatial and seasonal trends (Fig. 4). The largest ALW differences are observed in the central and eastern US during winter. Wintertime Cloudy SO_4^{2-} mass concentrations are greater than Clear Sky (Fig. 5, Table S5), and the highest NO_3^- mass concentration differences are observed during Cloudy times in winter when temperatures are coldest (Fig. 6, Table S8). This promotes thermodynamic stability of nitrate in the condensed phase, increasing particle hygroscopicity and facilitating ALW.

Outside of winter, significant SO_4^{2-} mass concentrations are typically higher on Clear Sky days in the eastern US (Fig. 5, Table S5). 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 higher electricity demand (Farkas et al., 2016) associated with emissions that form sulfate.

TOC mass concentrations are nearly always higher during Clear Sky times than Cloudy (Fig. 7, Table S7) in all chemical climatology regions across the CONUS, with the largest differences during summer and fall. Precursor VOC emissions (e.g., biogenic) and subsequent derived PM that contributes to OC differ by season and region (Donahue et al., 2009; Gentner et al., 2017; Youn et al., 2013). Increased sunlight under clear sky conditions leads to higher biogenic VOC emissions (Sakulyanontvittaya et al., 2008) and enhanced photolysis rates that facilitate hydroxyl radical production important to secondary organic aerosol formation (Tang et al., 2003). Organic aerosol hygroscopicity and water uptake is highly uncertain (Christiansen et al., 2019; Nguyen et al., 2015), and yet has profound impacts on top-of-atmosphere radiative forcing calculations (Rastak et al., 2017). We note that TOC is also influenced by primary sources of OC including wildland fires in the west and prescribed burning in the east which are not influenced by cloud presence (Spracklen et al., 2007; Tian et al., 2009; Zeng et al., 2008).

3.2 $PM_{2.5}$ Mass Concentrations

Significant differences in $PM_{2.5}$ 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 (Fig. 4 and Table S4) and do not correlate with MODIS cloud fraction during any season in any region (Fig. S8). In all regions, Clear Sky $PM_{2.5}$ concentrations are generally higher than Cloudy. Satellite AOT products used to derive $PM_{2.5}$ may overestimate the atmospheric burden across the CONUS, particularly during summertime. Median All Sky $PM_{2.5}$ concentrations are also

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020


Atmospheric Chemistry and Physics Discussions

significantly different and typically lower than Clear Sky in multiple chemical climatology regions (Table S9). This suggests the clear sky bias in satellite data may impart a positive bias when assessing surface $PM_{2.5}$ trends in model applications for air quality, weather, and climate.

3.3 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, Fig. 8). RH in the region is high year-round during Cloudy and Clear Sky periods alike, with the median greater than 60%. Gas-phase water vapor mixing ratios are sufficiently high that water availability is 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. For example, 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). 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. This is consistent with independent humidified nephelometer measurements by Jefferson et al., who find that aerosol growth rates 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).

NO_3^- concentrations are generally lower than SO_4^{2-} in the Mid South, but NO_3^- is more hygroscopic and provides influence over ALW patterns. Sulfate is traditionally considered dominant in determining absolute ALW mass concentrations in this region, and sulfate mass fraction is highest in summer (Carlton and Turpin, 2013; Gasparini et al., 2006). Similar to other regions of the CONUS, SO_4^{2-} mass concentrations are greatest during summertime Clear Sky conditions due to transport (Parworth et al., 2015), increased rates of photochemistry (Stone et al., 2012), and increased electricity sector emissions during heat waves and stagnation events (Appel et al., 2011; Farkas et al., 2016), which generally occur on sunny days. Sulfate mass fraction is lowest in winter, when NO_3^- concentrations are high due to cooler temperatures and transport of precursor species from nearby agricultural and surrounding urban areas (Parworth et al., 2015). Year-round NO_3^- concentrations are higher during Cloudy conditions than Clear Sky, which are associated with lower temperatures. Under Cloudy conditions, the highest ALW concentrations and estimated growth factors occur during winter and spring, when NO_3^- mass fraction and RH are highest. In another continental location, the Po Valley in Italy, NO_3^- was found to control ALW concentrations with implications for secondary organic aerosol (Hodas et al., 2014). The Mid South is also a continental, agricultural area and aerosol growth may be subject to similar mechanisms.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020


Atmospheric Chemistry and Physics Discussions

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 formation processes are necessary to fully explain temporal and spatial patterns. Spatially and seasonally, $PM_{2.5}$ and particle speciation information that lends insight into water uptake, particle properties, and particle growth is incomplete when information is gathered only during Clear Sky times. The work presented here indicates aerosol growth due to water uptake is greatest during satellite periods identified as Cloudy in many regions, when satellites are unable to remotely sense 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 affects accurate representation of ALW on cloudy days and suggests that without *in situ* chemical information, aerosol-cloud interactions and subsequent estimates of radiative forcings in models (Lin et al., 2016; Vogelmann et al., 2012) will remain a large uncertainty.

Acknowledgements

This research was funded, in part, by NSF Grant AGS-1242155 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

Appel, K. W., Foley, K. M., Bash, J. O., Pinder, R. W., Dennis, R. L., Allen, D. J. and Pickering, K.: A multi-resolution assessment of the Community Multiscale Air Quality (CMAQ) model v4.7 wet deposition estimates for 2002–2006, Geoscientific Model Development, 4(2), 357–371, doi:10.5194/gmd-4-357-2011, 2011.

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.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 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 (NH3) predictions 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 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.

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.

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., 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, 2018.

Chow, J. C., Watson, J. G., Kuhns, H., Etyemezian, V., Lowenthal, D. H., Crow, D., Kohl, S. D., Engelbrecht, J. P. and Green, 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. 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.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

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: WSOC IN LA BASIN AND OUTFLOWS, Journal of Geophysical Research: Atmospheres, 116(D21), doi:10.1029/2011JD016674, 2011.

Ervens, B.: Modeling the Processing of Aerosol and Trace Gases in Clouds and Fogs, Chem. Rev., 115(10), 4157–4198, doi:10.1021/cr5005887, 2015.

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^+–$SO_4^{2\−}$–$NO_3^{\−}$–$Cl^{\−}$–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.

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., 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.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

Atmospheric Chemistry and Physics Discussions

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 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.

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), 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., Weinmayr, G., Brunekreef, B., Vienneau, D. and Hoek, G.: Development of West-European PM 2.5 and NO 2 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.

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: ENHANCED DEEP BLUE AEROSOL RETRIEVAL, Journal of Geophysical Research: Atmospheres, 118(16), 9296–9315, doi:10.1002/jgrd.50712, 2013.

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 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.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

Atmospheric Chemistry and Physics Discussions

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 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, 77(3), 437–471, doi:10.1175/1520-0477(1996)077<0437:TNYRP>2.0.CO;2, 1996.

Kawecki, S. and Steiner, A. L.: The Influence of Aerosol Hygroscopicity on Precipitation Intensity During a Mesoscale 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.

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 PM2.5 exposures for epidemiological studies using satellite aerosol optical depth measurements, Atmospheric Environment, 45(35), 6267–6275, 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 PM2.5 and aerosol optical depth in Delhi Metropolitan, Atmospheric Environment, 41(21), 4492–4503, doi:10.1016/j.atmosenv.2007.01.046, 2007.

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.

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.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

Lin, Y., Wang, Y., Pan, B., Hu, J., Liu, Y. and Zhang, R.: Distinct Impacts of Aerosols on an Evolving Continental Cloud 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 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.

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.

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 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.

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.

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., 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: ALW AND AOT, Geophysical Research Letters, 43(22), 11,903-11,912, doi:10.1002/2016GL070994, 2016.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020


Atmospheric Chemistry and Physics Discussions

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.

Parworth, C., Fast, J., Mei, F., Shippert, T., Sivaraman, C., Tilp, A., Watson, T. and Zhang, Q.: Long-term measurements of submicrometer aerosol chemistry at the Southern Great Plains (SGP) using an Aerosol Chemical Speciation Monitor (ACSM), Atmospheric Environment, 106, 43–55, doi:10.1016/j.atmosenv.2015.01.060, 2015.

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.

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.

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.

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., 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: CalNex 2010 FIELD PROJECT OVERVIEW, 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.: 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.

Seinfeld, J.: Black carbon and brown clouds: Atmospheric science, Nature Geoscience, 1(1), 15–16, doi:10.1038/ngeo.2007.62, 2008.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

505 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 PM2.5 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.

510 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: INTERANNUAL VARIABILITY OF OC AEROSOL, Geophys. Res. Lett., 34(16), doi:10.1029/2007GL030037, 2007.

515 Stone, D., Whalley, L. K. and Heard, D. E.: Tropospheric OH and HO2 radicals: field measurements and model comparisons, Chemical Society Reviews, 41(19), 6348, doi:10.1039/c2cs35140d, 2012.

Tai, A. P. K., Mickley, L. J. and Jacob, D. J.: Correlations between fine particulate matter (PM2.5) and meteorological variables in the United States: Implications for the sensitivity of PM2.5 to climate change, Atmospheric Environment, 44(32), 3976–3984, doi:10.1016/j.atmosenv.2010.06.060, 2010.

520 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 TRACE-P: 2. Three-dimensional study using a regional chemical transport model: 3-D PHOTOLYSIS AND PHOTOCHEMICAL STUDY, Journal of Geophysical Research: Atmospheres, 108(D21), doi:10.1029/2002JD003100, 2003.

525 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.

Tian, J. and Chen, D.: A semi-empirical model for predicting hourly ground-level fine particulate matter (PM2.5) concentration in southern Ontario from satellite remote sensing and ground-based meteorological measurements, Remote
530 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. and Pszenny, A.: Planning, implementation, and scientific goals of the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC ^{4} RS) field mission: Planning SEAC4RS, Journal of Geophysical
535 Research: Atmospheres, 121(9), 4967–5009, doi:10.1002/2015JD024297, 2016.

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.
540 H., Bucholtz, A., Collins, D. R., Diskin, G. S., Gerber, H., Lawson, R. P., Woods, R. K., Andrews, E., Yang, H.-J., Chiu, J. 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.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

Wagner, N. L., Brock, C. A., Angevine, W. M., Beyersdorf, A., Campuzano-Jost, P., Day, D., de Gouw, J. A., Diskin, G. S., Gordon, T. D., Graus, M. G., Holloway, J. S., Huey, G., Jimenez, J. L., Lack, D. A., Liao, J., Liu, X., Markovic, M. Z., Middlebrook, A. M., Mikoviny, T., Peischl, J., Perring, A. E., Richardson, M. S., Ryerson, T. B., Schwarz, J. P., Warneke, C., Welti, A., Wisthaler, A., Ziemba, L. D. and Murphy, D. M.: In situ vertical profiles of aerosol extinction, mass, and composition over the southeast United States during SENEX and SEAC⁴RS: observations of a modest aerosol enhancement aloft, Atmospheric Chemistry and Physics, 15(12), 7085–7102, doi:10.5194/acp-15-7085-2015, 2015.

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.

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: TOP-DOWN ESTIMATE OF DUST EMISSIONS, 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.

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: AQUEOUS SOA FORMATION IN 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 & Technology, 42(22), 8401–8406, doi:10.1021/es800363d, 2008.

Zhang, G., Rui, X. and Fan, Y.: Critical Review of Methods to Estimate PM2.5 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: ENHANCED VIIRS AOT RETRIEVAL ALGORITHM LAND, 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.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

Atmospheric Chemistry and Physics Discussions

585

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	1.33	1.50
Spr	1.46	1.79	0.37	0.50	2.48	4.02	0.62	0.76	1.25	1.41
Sum	1.91	1.69	0.20	0.19	2.92	3.57	0.59	0.72	1.21	1.39
Fall	1.05	1.17	0.18	0.33	1.56	2.74	0.57	0.73	1.18	1.37

590

595

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

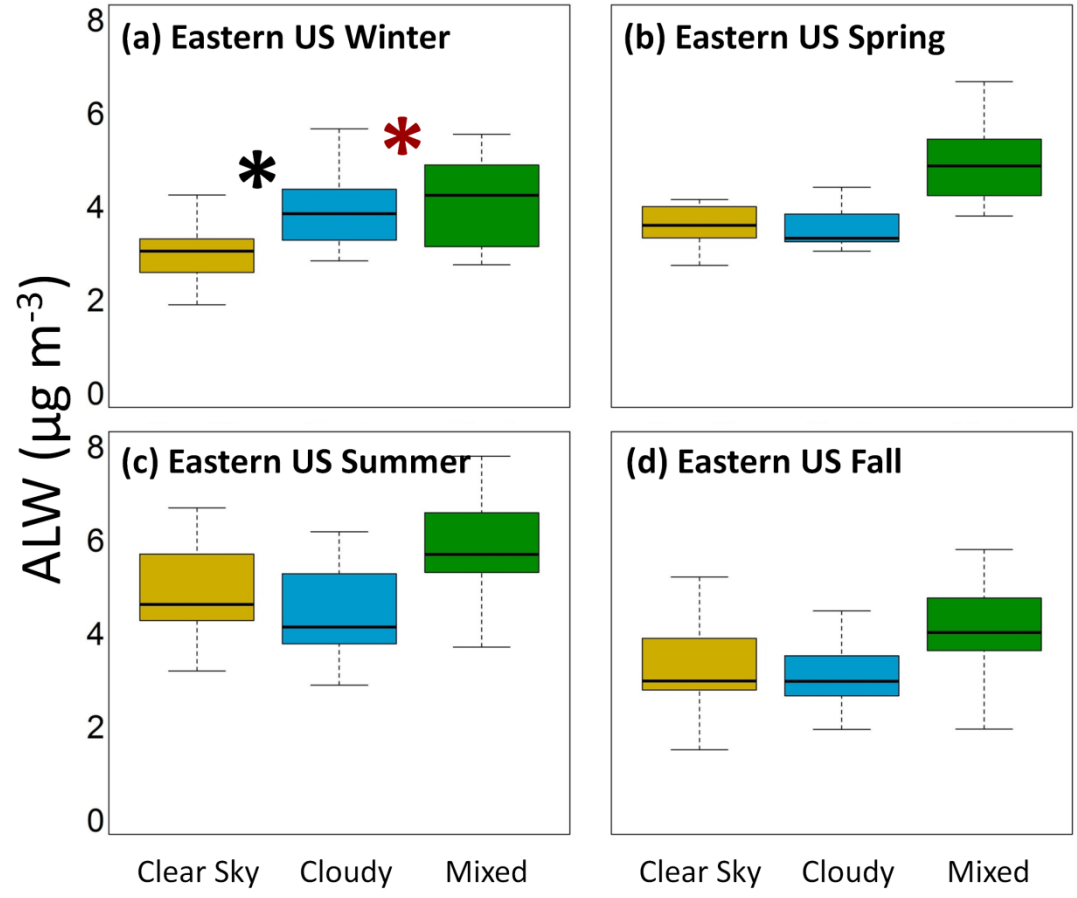


Figure 1: ALW mass concentrations are significantly different between Clear Sky and Cloudy time periods beyond what would arise from changes solely in meteorology (e.g., RH). Monthly median estimated ALW distributions at each IMPROVE monitor in the eastern US during Clear Sky times (yellow, Clear Sky scenario), Cloudy times (blue, Cloudy scenario), and Cloudy times employing Clear Sky particle chemical composition (green, Mixed scenario). The black asterisk in (a) indicates the only situation where Clear Sky and Cloudy scenarios differ significantly. The red asterisk in (a) indicates the only situation where the Cloudy and Mixed scenarios do not differ significantly. The midline in the box is the median, the box boundaries are the 25th and 75th percentiles, and the whiskers are the 10th and 90th percentiles. Potential outliers are not shown but are used in calculations.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

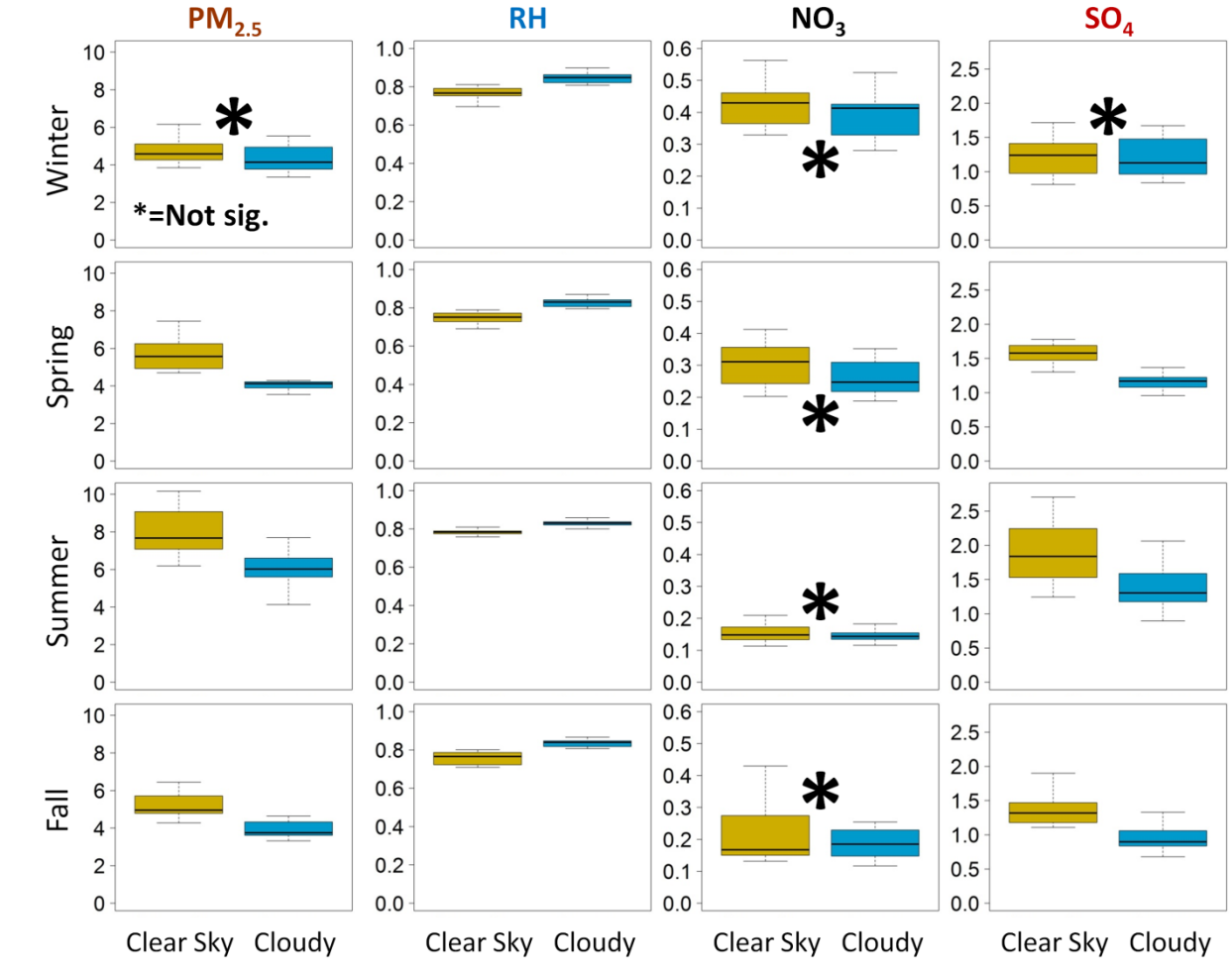
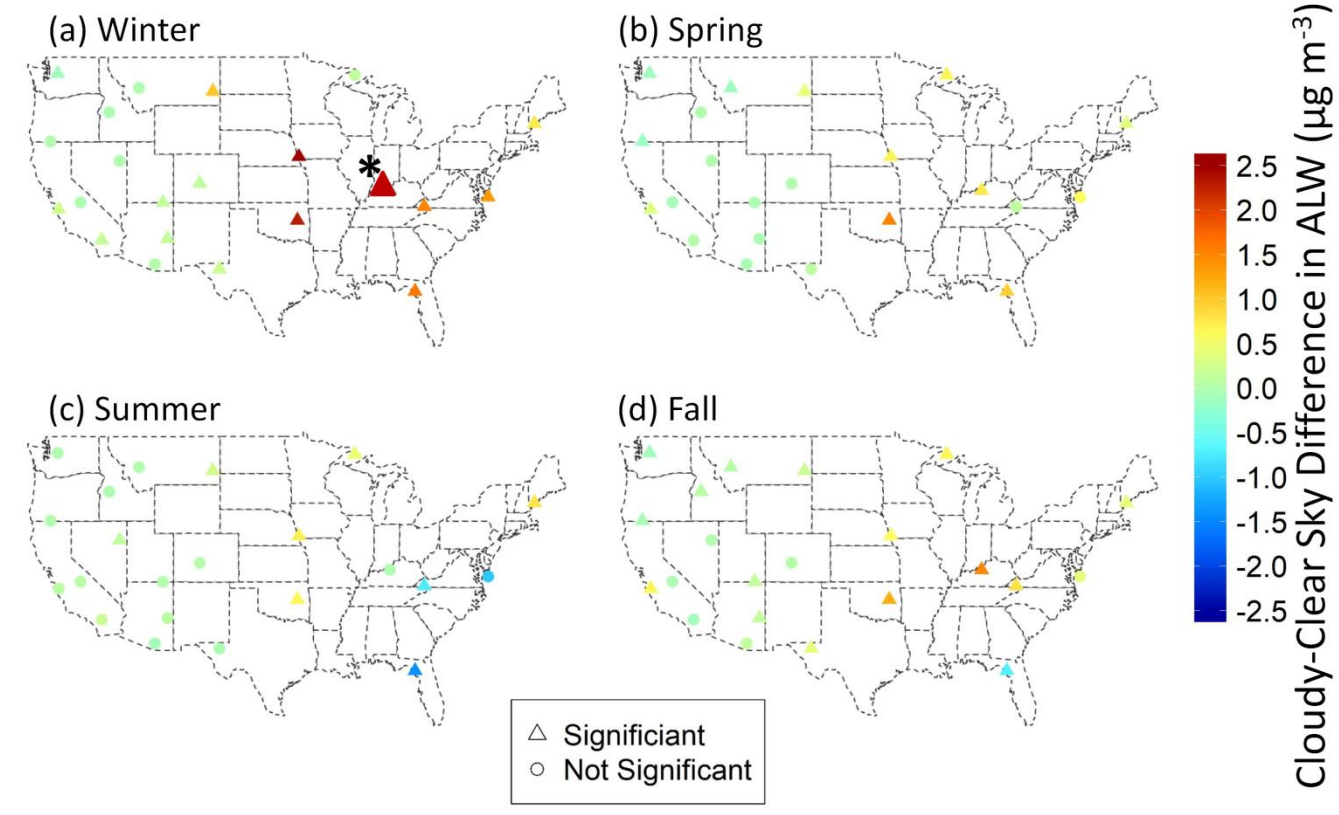


Figure 2: Box plots of $PM_{2.5}$, RH, NO_3^-, and SO_4^{2-} during clear sky times (yellow) and cloudy times (blue) across the eastern US. Note that potential outliers are not shown but are used in calculations. The width of the box plot is proportional to the number of observations. Asterisks denote Cloudy and Clear Sky differences that are *not* significant ($p<0.05$) by the Mann-Whitney U Test.

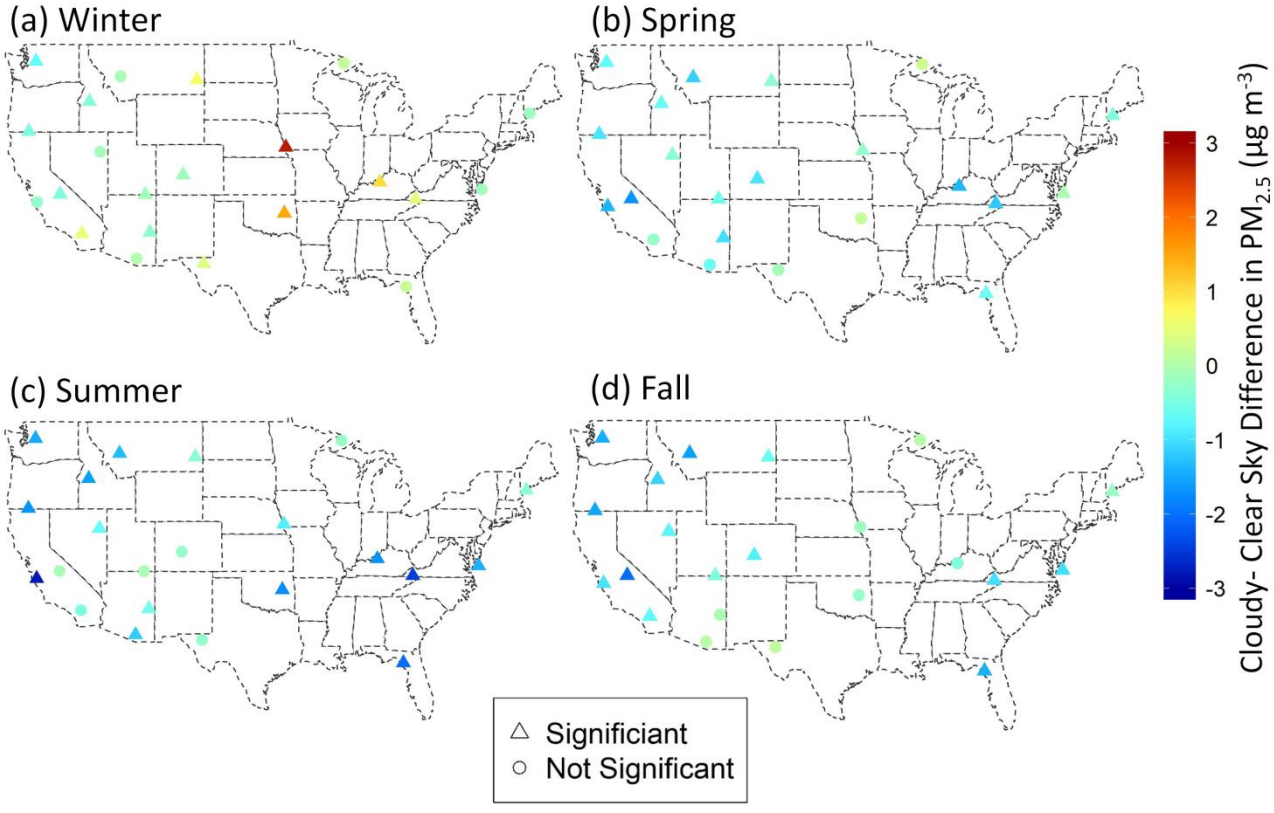
https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020



615 **Figure 3: 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 4.6 µg m^{-3} larger than Clear Sky).**

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

Atmospheric Chemistry and Physics Discussions

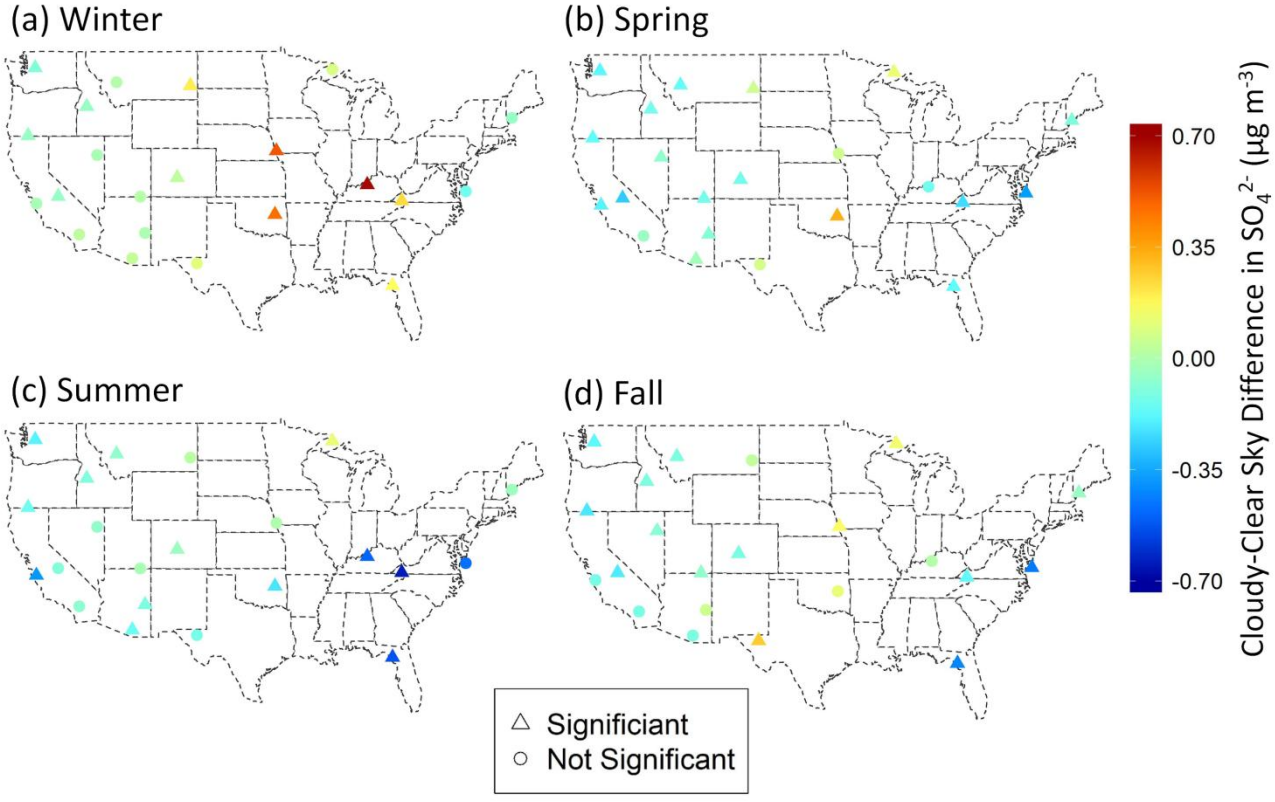


620

Figure 4: Maps of the difference in $PM_{2.5}$ 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.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

Atmospheric Chemistry and Physics Discussions



625

Figure 5: 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.

630

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

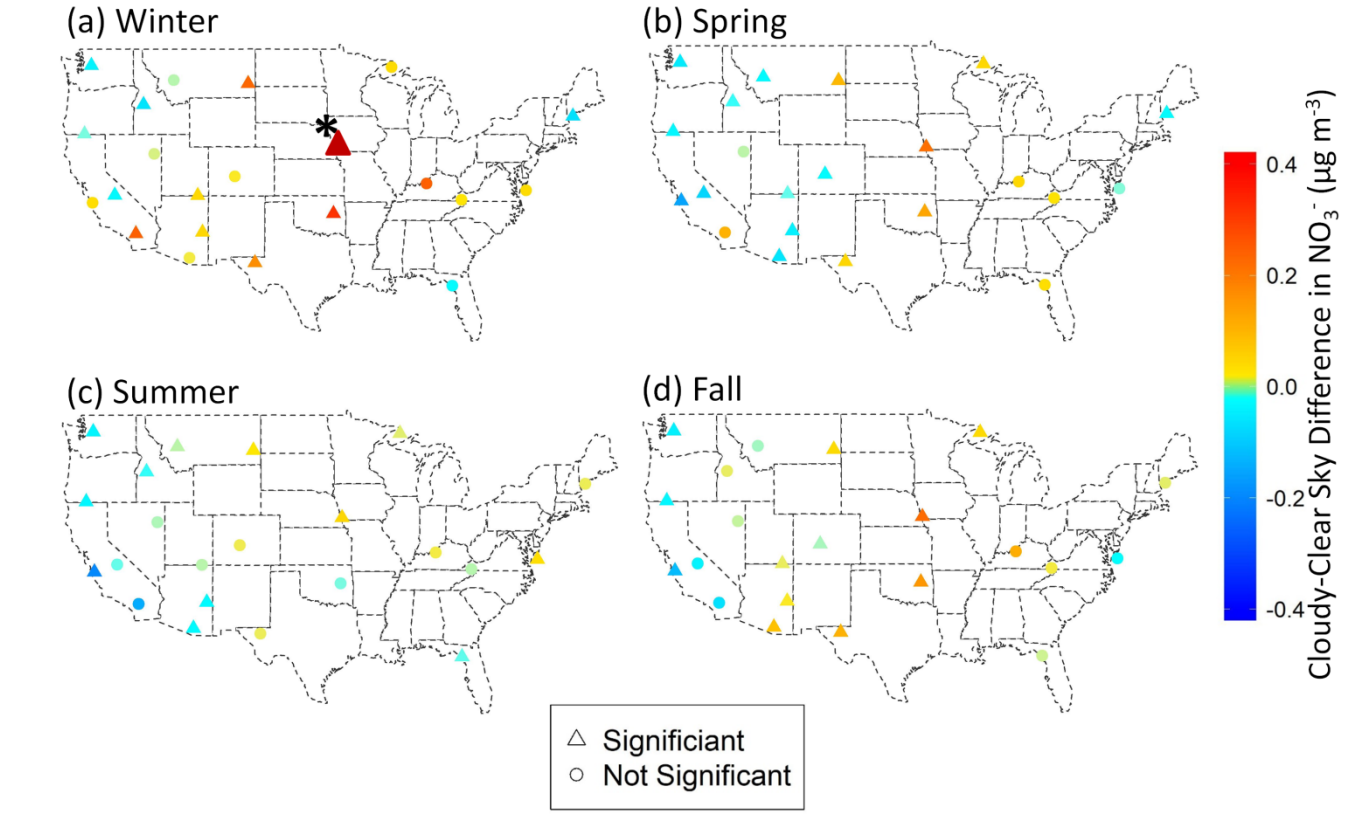
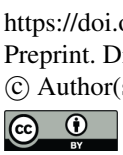


Figure 6: Maps of the difference in NO_3^- mass concentration medians (Cloudy-Clear Sky) for all regions from 2010-2014 for (a) winter, (b) spring, (c) summer, and (d) fall. The color of the point corresponds to the magnitude of the difference. Triangles indicate that median differences are significant by the Mann-Whitney U Test. Note that the difference in medians for daily NO_3^- 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).

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020



Atmospheric Chemistry and Physics Discussions

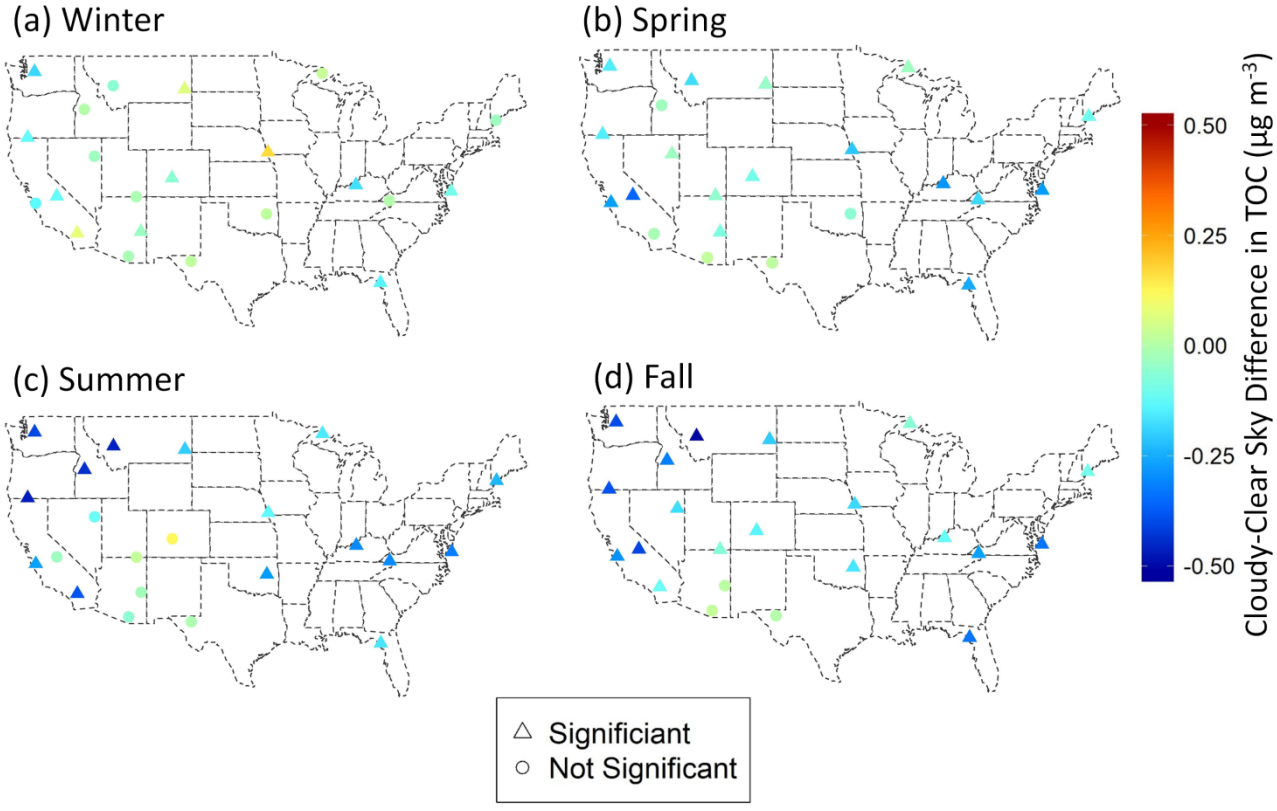


Figure 7: Maps of the difference in TOC mass concentration medians (Cloudy-Clear Sky) for all regions from 2010-2014 for (a) winter, (b) spring, (c) summer, and (d) fall. The color of the point corresponds to the magnitude of the difference. Triangles indicate that median differences are significant by the Mann-Whitney U Test.

https://doi.org/10.5194/acp-2020-184
Preprint. Discussion started: 23 March 2020

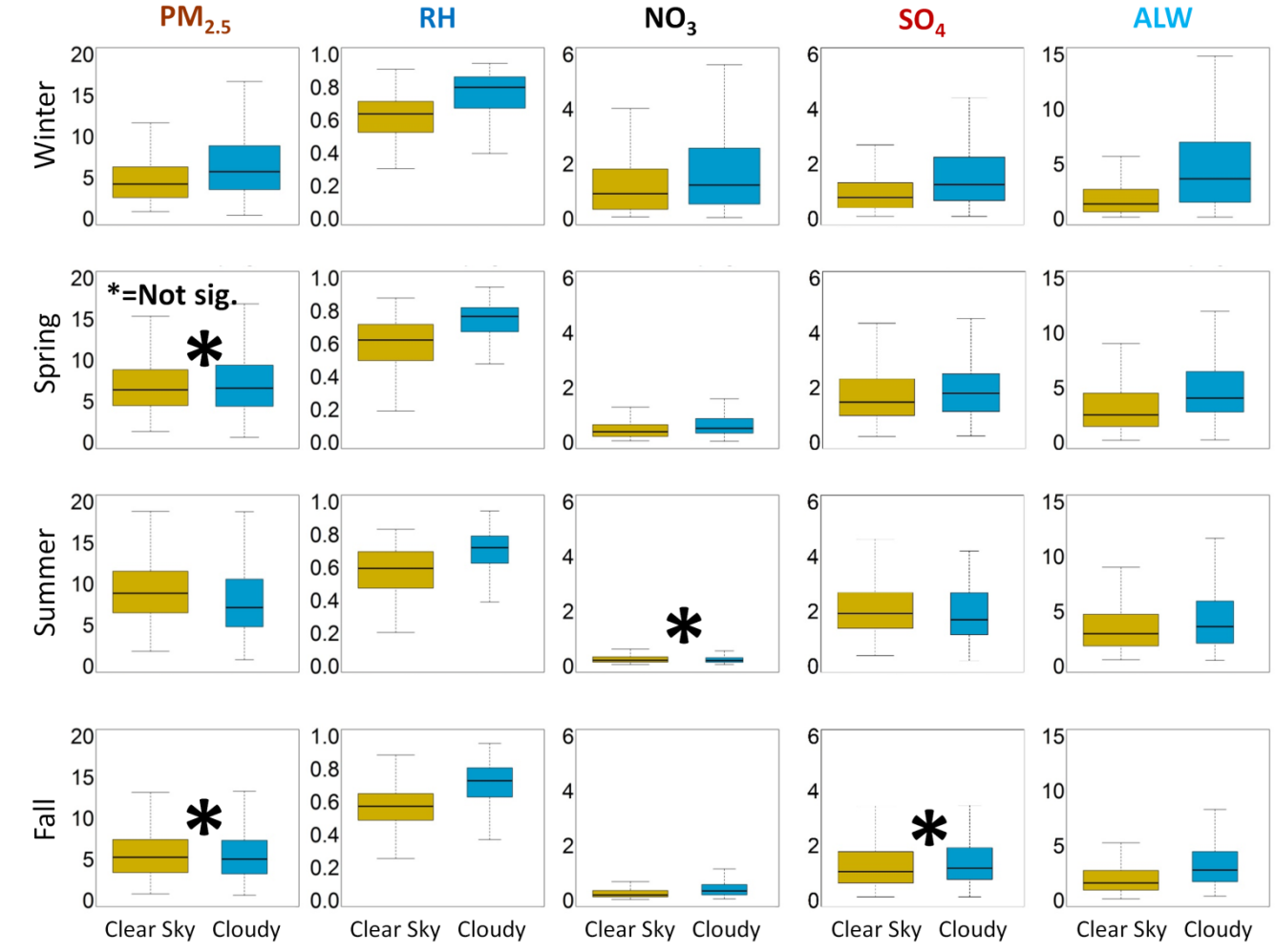


Figure 8: Box plots of cloudy and clear sky distributions of $PM_{2.5}$ and chemical constituent mass concentrations (μg m^{-3}) and RH in the Mid South for each season from 2010-2014. The width of the box plot is proportional to the number of observations. Note that potential outliers are not shown but are used in calculations. Asterisks denote Cloudy and Clear Sky differences that are *not* significant (p<0.05) by the Mann-Whitney U Test.