Supporting Information for:

Chemically specific sampling bias: the ratio of $PM_{2.5}$ to surface AOD on average and peak days in the U.S.

Simon Rosanka, Madison M. Flesch, Yinting T. Chiu, and Annmarie G. Carlton*

University of California, Irvine Department of Chemistry, Irvine, CA

Corresponding author: Annmarie G. Carlton, agcarlto@uci.edu

Contents:

Introduction

This document includes information about the monitors used for the decadal and hourly analysis, methodology figures relating to aerosol liquid water, f(RH), and nitrate adjustment calculations, decadal planetary boundary layer height, sulfate, and f(RH) trends, comparison of reported and adjusted $PM_{2.5}$ mass concentrations, and differences in hourly model and observational median eta values.

Text S1

From Equation 1, we estimate f(RH) using mass concentrations of reported dry $PM_{2.5}$, $PM_{2.5}$ chemical constituents, estimates of ALW, and aerosol density:

$$f(RH) = \frac{\left(\frac{[ALW]}{\rho_w}\right)^{1/3} + \left(\frac{m_{d,dry}}{\rho_d}\right)^{1/3}}{\left(\frac{m_{d,spec}}{\rho_d}\right)^{1/3}}$$

Here, [ALW] is the mass concentration of ALW (μg m^{-3}), ρ_w is the density of water (1 g mL^{1}), $m_{d,dry}$ is the monitor-reported $PM_{2.5}$ mass (μg m^{-3}), $m_{d,spec}$ is the summed mass of the reported chemical constituents (sulfate, nitrate, OM, sodium, chloride, calcium, potassium, and magnesium; μg m^{-3}), and ρ_d is the density of dry aerosol as a mass-weighted average dependent on measured aerosol composition (g cm^{-3}). Note that f(RH) is typically measured at arbitrary "humid" and "dry" values, and in this work, we estimate particle diameters accounting for particle composition and ambient RH. Reported $PM_{2.5}$ mass concentrations average 5.3 μg m^{-3} greater than the speciated sum $PM_{2.5}$ totals. This is primarily due to missing chemical species measurements at some sites and limiting the calculation of the summed speciation mass to only the species used to determine dry aerosol density for consistency.

Movie S1. Movie of annual Pearson (ρ_P) correlations for regime-aggregated aerosol optical depth (AOD), $PM_{2.5}$, nitrate, and sulfate mass concentrations, and planetary boundary layer (PBL) height for the humid (left) and arid (right) regimes from 2006 to 2015. Red and positive numbers indicate strong correlation, blue and negative numbers a strong anticorrelation, and gray indicates little to no correlation between two variables.

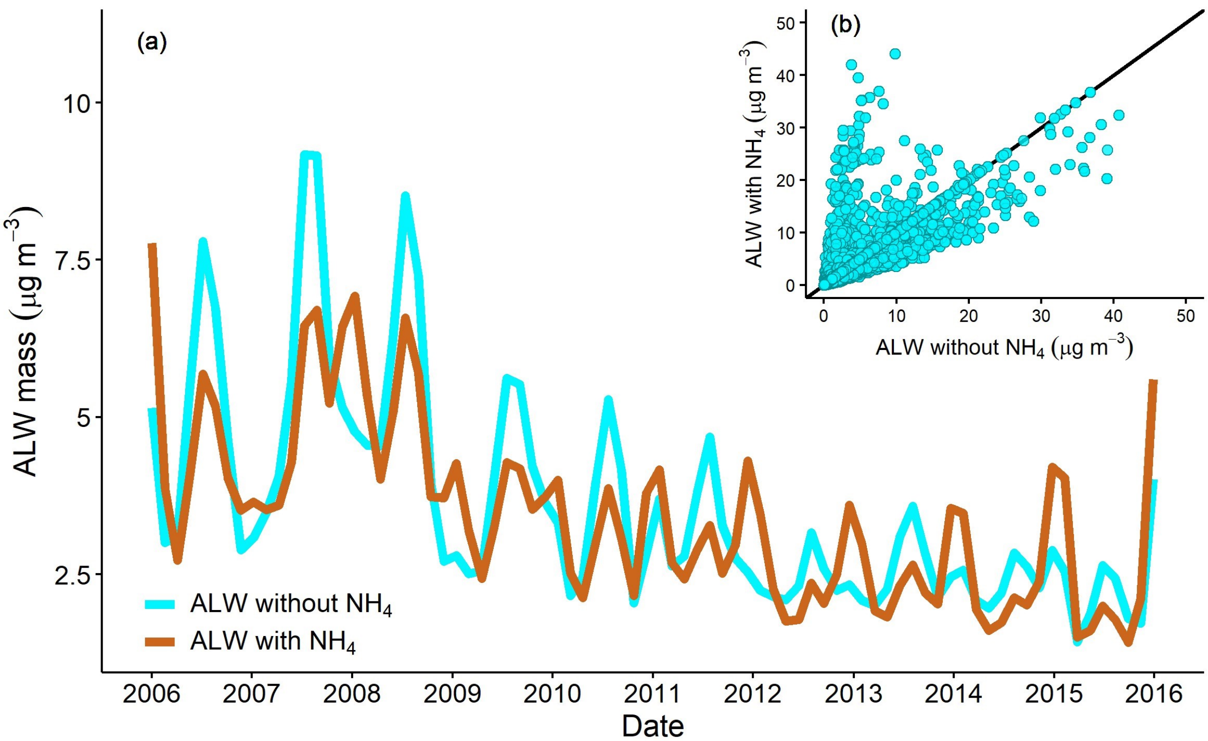

Figure S1. Sensitivity study of aerosol liquid water (ALW) with and without ammonium (NH_4) included in estimations via ISORROPIAv2.1 at 8 AERONET stations studied from 2006 to 2015 as a function of time (main figure) and against each other (inset). In the time series, the light blue fit excludes ammonium, and the brown fit includes ammonium. The black line in the inset represents the 1:1 line.

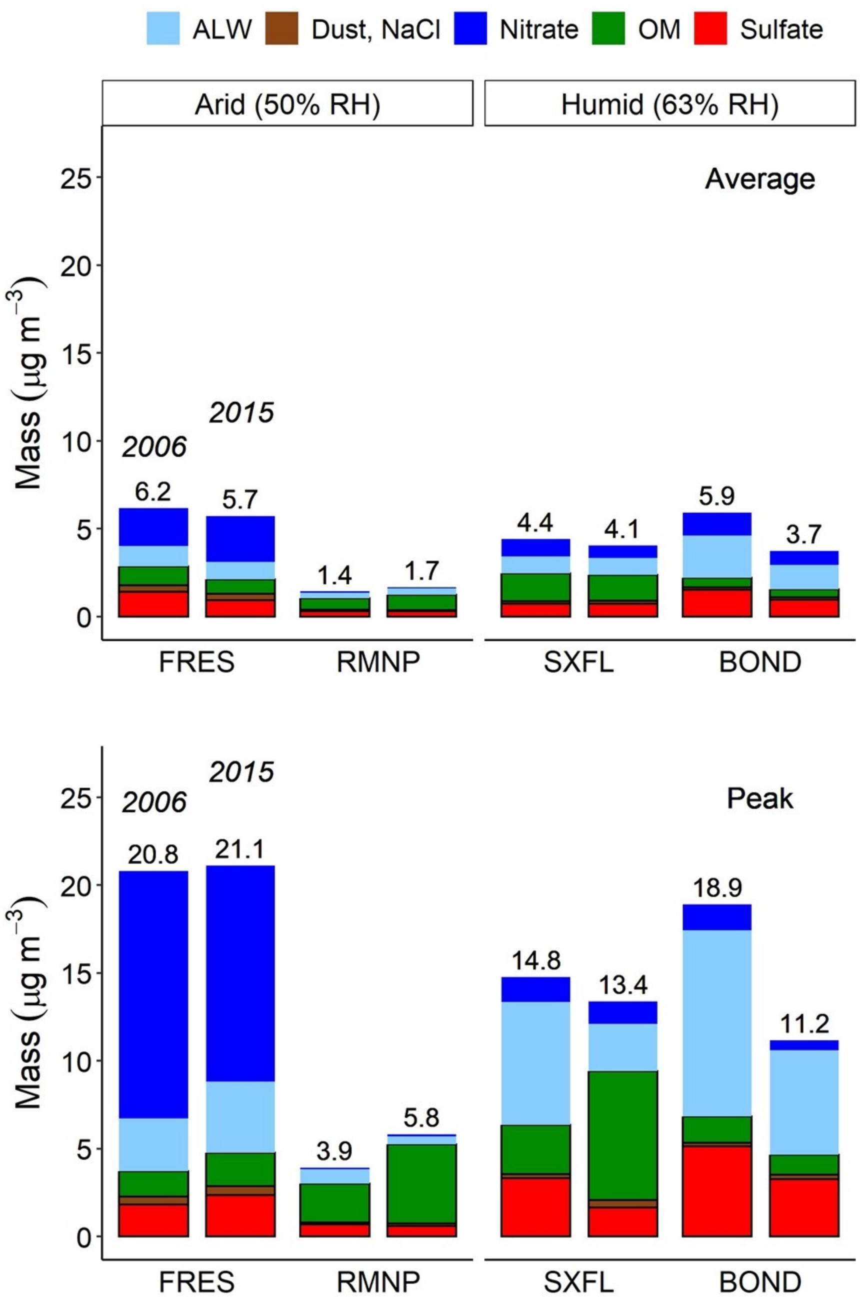

Figure S2. $PM_{2.5}$ chemical composition consisting of non-volatile species (sulfate, dust (calcium, magnesium, potassium), NaCl, and organic matter (OM)) and semi-volatile species (nitrate, aerosol liquid water (ALW)) on average (top) and peak (bottom, where AOD and $PM_{2.5}$ are both above their locally determined 75th percentile) days for the 4 stations with consistent organic species measurements in both 2006 (left bars) and 2015 (right bars).

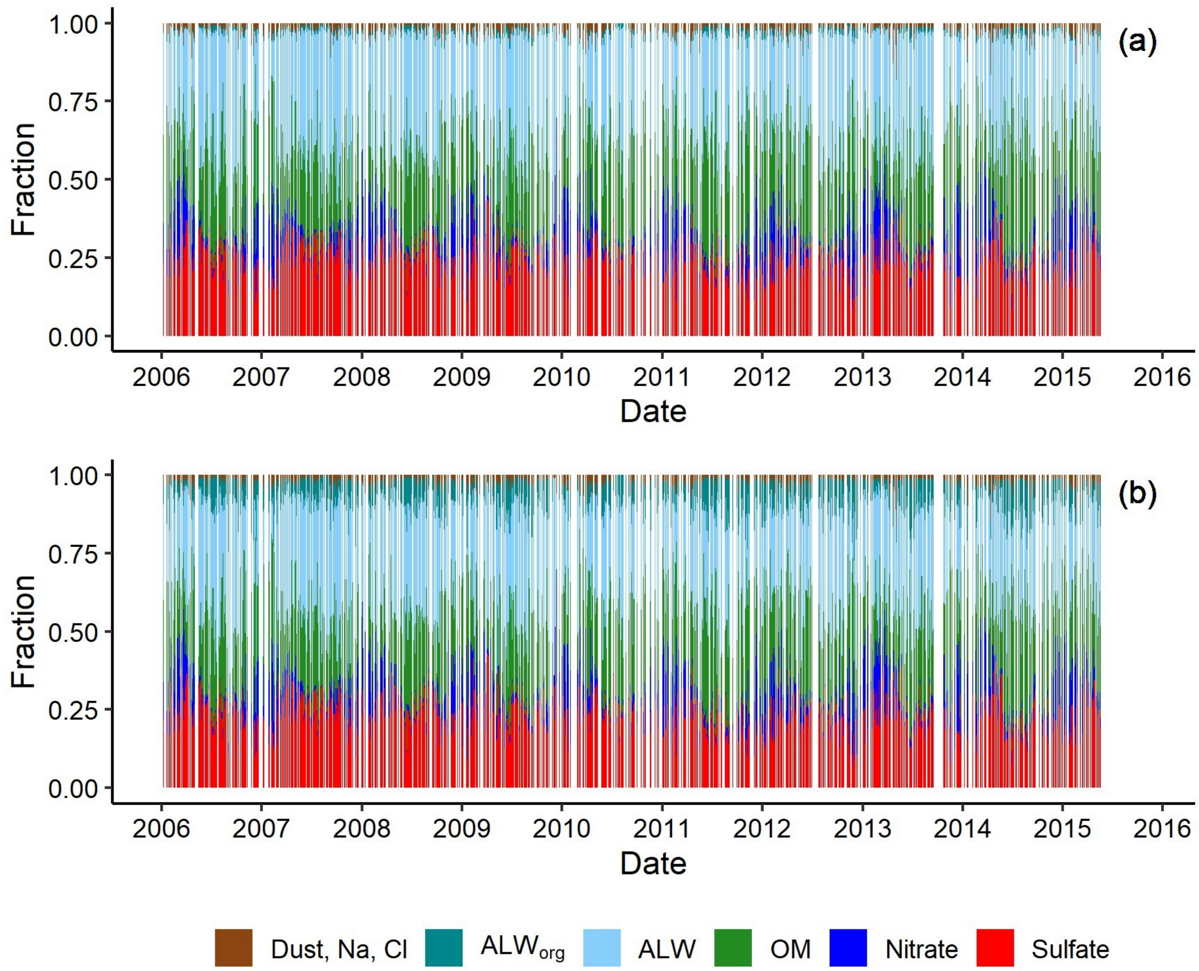

Figure S3. Sensitivity study of the fractional contribution of organic aerosol liquid water (ALW_{org}, teal) to $PM_{2.5}$ mass concentrations using hygroscopicity parameters of (a) $\kappa = 0.3$ and (b) $\kappa = 0.05$ at the GSFC monitoring location with IMPROVE $PM_{2.5}$ chemical composition from 2006 to 2015. Dust species include calcium, potassium, and magnesium.

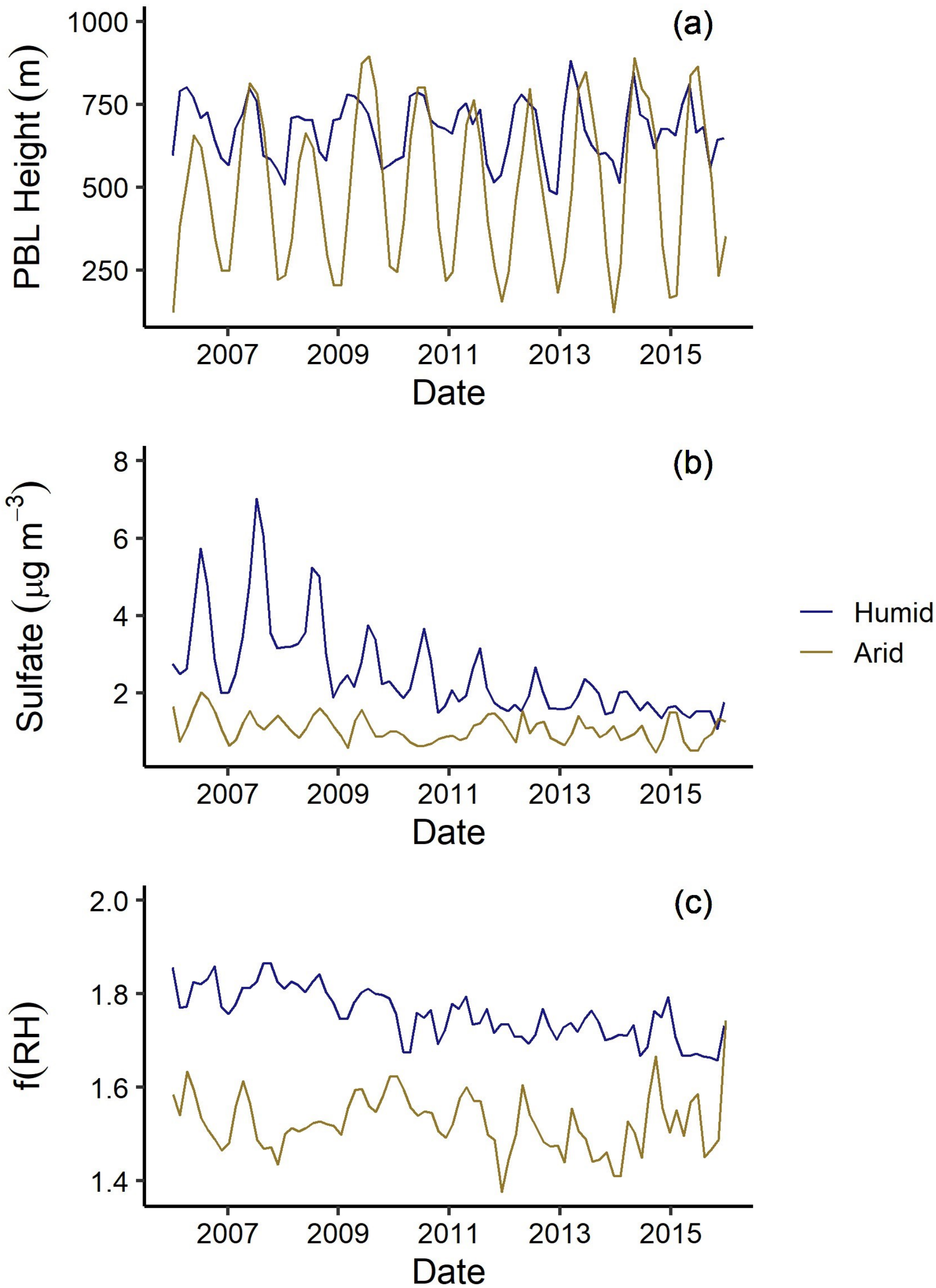

Figure S4. Time series of (a) planetary boundary layer (PBL) height, (b) sulfate mass concentrations, and (c) f(RH) for 8 AERONET locations in the humid (dark blue) and arid (dark gold) regions from 2006 to 2015.

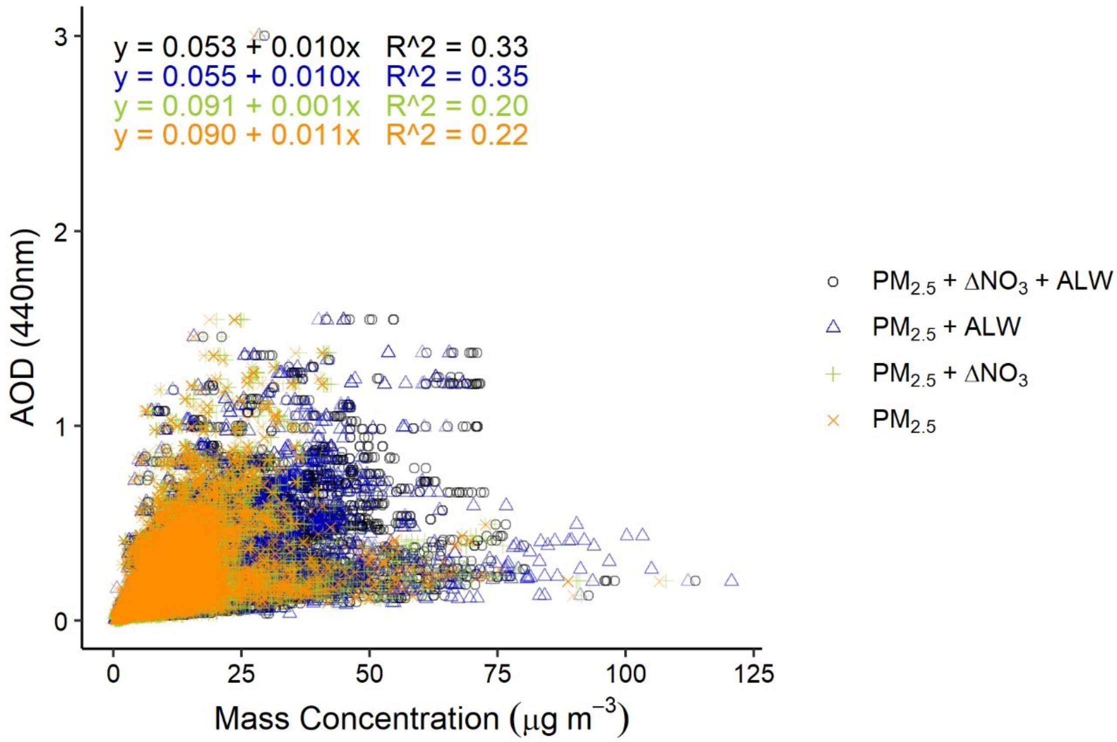

Figure S5. Comparison of various combinations of $PM_{2.5}$, aerosol liquid water (ALW), and nitrate (NO_3) correction mass concentrations against aerosol optical depth (AOD) at 440 nm with their respective equations of best fit and R^2 values.

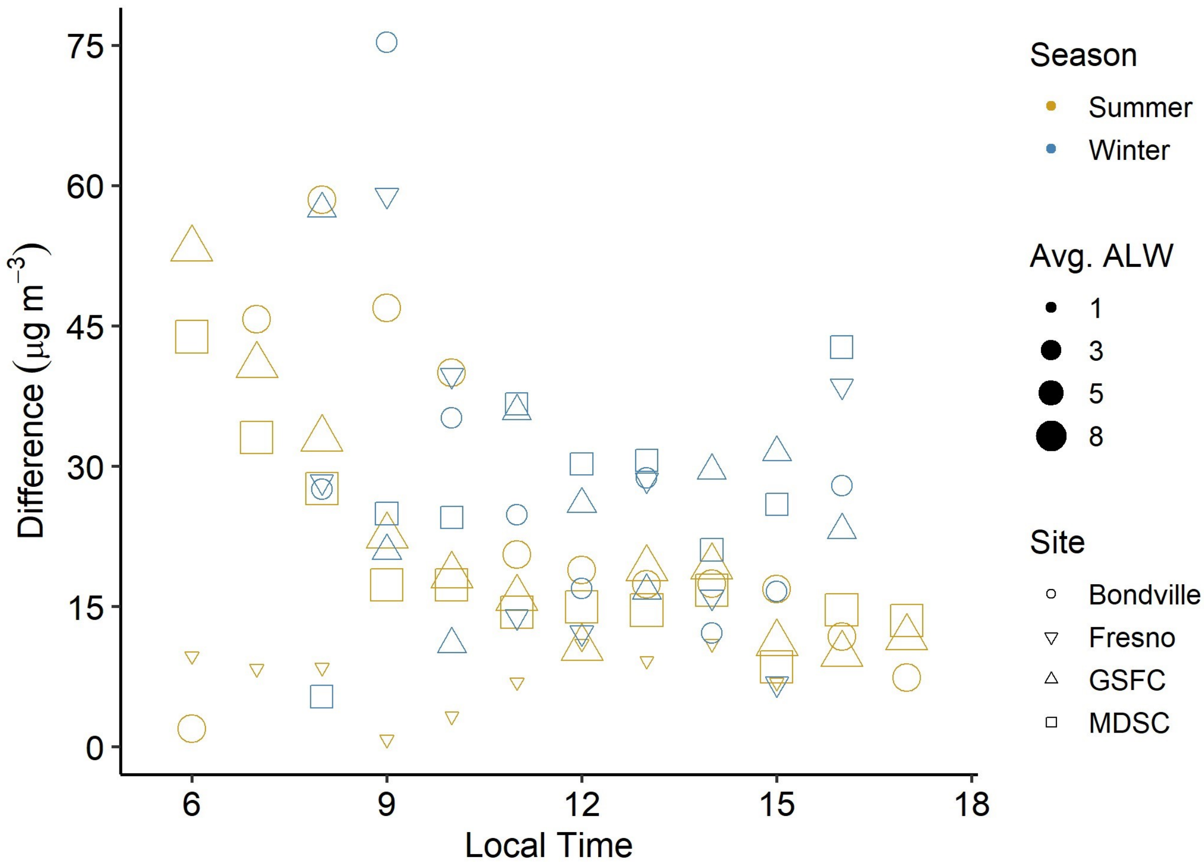

Figure S6. Differences in hourly CMAQ-simulated and surface observation median η values for the Bondville, Fresno, GSFC, and MDSC sites (point shape) in winter (blue) and summer (tan), grouped by each site's average winter and summer aerosol liquid water (ALW, μg m^{-3}; point size), respectively.

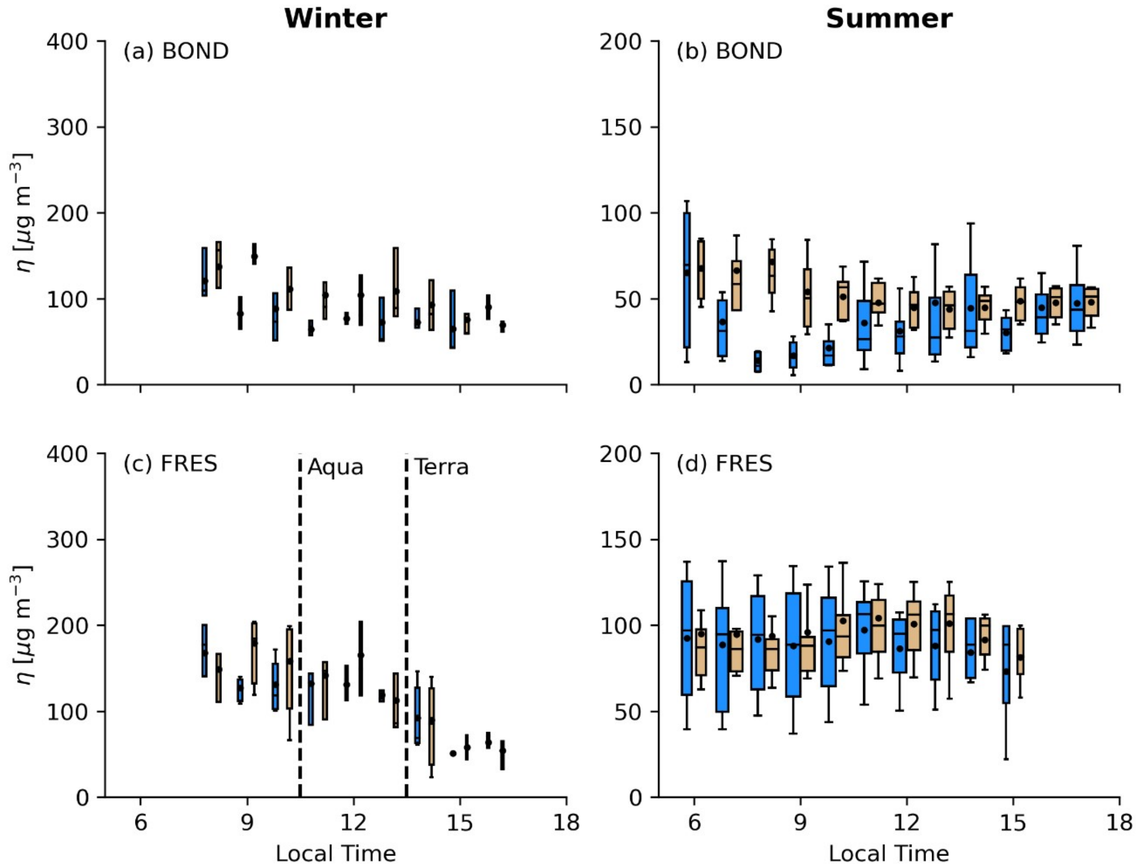

Figure S7. Diurnal distributions of eta (η) for January 2016 ("Winter" column) and August 2015 ("Summer" column) of surface-based hourly PM2.5 mass concentrations and AERONET AOD at 440 nm (blue boxes, points) and CMAQ model predictions using AOD at 550 nm (brown boxes, points) for BOND (a,b) and FRES (c,d). Points indicate the mean. Boxes represent the 25th to 75th percentile with the center horizontal line as the median and whiskers as the 10th and 90th percentile. The box width is proportional to the number of data pairs in each individual comparison set relative to the entire data set. Note the winter and summer y-axis scales differ. Vertical dashed lines in (c) indicate nominal overpass times for MODIS onboard the Aqua (10:30 a.m.) and Terra (1:30 p.m.) satellites.

Table S1. Site information for all AERONET, IMPROVE, EPA CSN, and ambient $PM_{2.5}$ mass concentration monitoring stations used in this study. $PM_{2.5}$ mass monitors include SLAMS (State or Local Air Monitoring Stations), SPM (Special Purpose Monitors), and Tribal monitors. Note that not all SLAMS or SPM stations may have associated site names.

Site Name/Code	Monitoring Network	Latitude	Longitude
Appalachian_State	AERONET	36.2146	-81.6938
Billerica	AERONET	42.52835	-71.2686
BONDVILLE	AERONET	40.05333	-88.3719
El_Segundo	AERONET	33.9125	-118.382
Fresno	AERONET	36.78173	-119.773
Fresno_2	AERONET	36.78537	-119.773
IMPROVE-MammothCave	AERONET	37.1318	-86.1479
NEON_CVALLA	AERONET	40.16063	-105.167
NEON_MOAB	AERONET	38.24833	-109.388
NEON_ORNL	AERONET	35.96413	-84.2826
NEON_RMNP	AERONET	40.2759	-105.546
NEON_SCBI	AERONET	38.89292	-78.1395
Pagosa_Springs	AERONET	37.27028	-107.05
Red_Mountain_Pass	AERONET	37.90745	-107.711
Santa_Monica_Colg	AERONET	34.01685	-118.471
Sevilleta	AERONET	34.35472	-106.885
Sioux_Falls	AERONET	43.73648	-96.626
Table_Mountain	AERONET	40.125	-105.237
Tallahassee	AERONET	30.44583	-84.2994
Thompson_Farm	AERONET	43.10877	-70.9483
Tucson	AERONET	32.233	-110.953
UCSB	AERONET	34.41543	-119.845
USGS_Flagstaff_ROLO	AERONET	35.21484	-111.634
CCNY	AERONET	42.52835	-71.2686
Georgia_Tech	AERONET	33.7802	-84.3995
GSFC	AERONET	38.9925	-76.8398
MD_Science_Center	AERONET	39.28123	-76.6121
LIGO1	IMPROVE	35.9723	-81.9331
LOND1	IMPROVE	42.8624	-71.3801
BOND1	IMPROVE	40.052	-88.3733
SAGA1	IMPROVE	34.2969	-118.028
FRES1	IMPROVE	36.7818	-119.773
MACA1	IMPROVE	37.1318	-86.1479
ROMO1	IMPROVE	40.2783	-105.546
CANY1	IMPROVE	38.4587	-109.821
GRSM1	IMPROVE	35.6334	-83.9416
SHEN1	IMPROVE	38.5229	-78.4348
SHMI1	IMPROVE	37.3038	-107.484

WEMI1	IMPROVE	37.6594	-107.800
BOAP1	IMPROVE	33.8695	-106.852
BLMO1	IMPROVE	43.7158	-96.1913
SAMA1	IMPROVE	30.0926	-84.1614
SAGU1	IMPROVE	32.1746	-110.737
SAWE1	IMPROVE	32.2486	-111.218
RAFA1	IMPROVE	34.7339	-120.007
SYCA1	IMPROVE	35.1406	-111.969
ATLA1	IMPROVE	33.6878	-84.2905
WASH1	IMPROVE	39.31083	-76.4744
Clovis-Villa	SLAMS	36.81945	-119.71643
HU-Beltsville	SLAMS	39.05528	-76.87833
Rockville	SLAMS	39.11431	-77.10688
Oldtown	SLAMS	39.29773	-76.60460
Madera-City	SLAMS	36.95326	-120.03420
3425 N FIRST ST, FRESNO	SLAMS	36.78133	-119.77319
Picayune Rancheria	TRIBAL	37.21360	-119.69907
MCMILLAN NCore-PAMS	SLAMS	38.92185	-77.01318
Edgewood	SLAMS	39.41019	-76.29695
Hanford-Irwin	SLAMS	36.31567	-119.64345
Fresno – Garland	SLAMS	36.78538	-119.77321
ISWS CLIMATE STATION	SLAMS	40.05278	-88.37251
Padonia	SLAMS	39.46048	-76.63354
Visalia-Church	SLAMS	36.33218	-119.29123
Lee District Park	SLAMS	38.77335	-77.10468
HAINS POINT PM-2.5 AND IMPROVE SITE ON ROOF OF PARK POLICE BLDG.	SLAMS	38.87626	-77.03406
Essex	SLAMS	39.31083	-76.47444
DUDLEY SQUARE ROXBURY	SLAMS	42.32950	-71.08260
PEARL ST MUNICIPAL PARKING LOT	SLAMS	42.99578	-71.46253
MOOSEHILL SCHOOL	SLAMS	42.86253	-71.38014
	SPM	40.81722	-74.04376
	SLAMS	40.81681	-74.04367
	SLAMS	40.83311	-74.04346
Newark Firehouse	SLAMS	40.72099	-74.19289
New Brunswick	SLAMS	40.47283	-74.42240
Rutgers University	SLAMS	40.46218	-74.42944
Elizabeth Lab	SLAMS	40.64144	-74.20837
MORRISANIA	SLAMS	40.83606	-73.92009
BOTANICAL GARDEN	SLAMS	40.86585	-73.88083
IS 52	SLAMS	40.81600	-73.90200
DIVISION STREET	SLAMS	40.71436	-73.99518
QUEENS COLLEGE 2	SLAMS	40.73614	-73.82153
SD School for the Deaf	SLAMS	43.54792	-96.70077
Fresno – Garland	EPA CSN	36.78538	-119.77321
DUDLEY SQUARE ROXBURY	EPA CSN	42.32950	-71.08260

IS 52	EPA CSN	4081600	-73.90200
DIVISION STREET	EPA CSN	40.71436	-73.9518
QUEENS COLLEGE 2	EPA CSN	40.73614	-73.82153

Table S2. Annual changes in aerosol optical depth (AOD) and surface mass concentrations of PM2.5 and several chemical constituents at sites in the eastern and western U.S. from 2006 to 2015. Statistically significant linear regression coefficients ($p < 0.05$) are denoted with asterisks.

Region	Parameter	Rate of Change
East	AOD	$-6.70 \times 10^{-3}\,(yr^{-1})^{*}$
	$PM_{2.5}$	$-0.38\,(\mu g\, m^{-3}\, yr^{-1})^{*}$
	Nitrate	$-0.06\,(\mu g\, m^{-3}\, yr^{-1})^{*}$
	Sulfate	$-0.23\,(\mu g\, m^{-3}\, yr^{-1})^{*}$
	ALW	$-0.40\,(\mu g\, m^{-3}\, yr^{-1})^{*}$
East	AOD	$-3.50 \times 10^{-3}\,(yr^{-1})$
	$PM_{2.5}$	$-0.13\,(\mu g\, m^{-3}\, yr^{-1})$
	Nitrate	$-0.06\,(\mu g\, m^{-3}\, yr^{-1})^{*}$
	Sulfate	$-0.01\,(\mu g\, m^{-3}\, yr^{-1})$
	ALW	$-0.03\,(\mu g\, m^{-3}\, yr^{-1})$

Table S3. Standard CMAQ performance metrics for all observation stations. The abbreviations used in this table are as follows: STDEV – standard deviation, NMB –

normalizes mean bias, MB – mean bias, and RMSE – root mean square error. The MB, NMB, and RMSE are calculated based on Equation 2, 3, and 4 in Appel et al. 2021*, respectively. Statistically insignificant linear regression coefficients ($p > 0.05$) are colored in red.

Year	Month	#Stations	Obs mean	Model mean	STDEV obs	STDEV model	NMB	MB	RMSE	r
2005	August	12	38.68	64.78	11.06	19.03	26.10	67.47	32.60	0.16
2006	January	12	129.51	123.25	57.60	55.72	-6.36	-4.83	44.71	0.67
2015	August	25	62.45	52.28	19.99	13.00	-10.17	-16.29	20.61	0.45
2016	January	20	132.03	92.92	67.18	41.55	-39.11	-29.62	68.07	0.53

*Appel, K. W., Bash, J. O., Fahey, K. M., Foley, K. M., Gilliam, R. C., Hogrefe, C., Hutzell, W. T., Kang, D., Mathur, R., Murphy, B. N., Napelenok, S. L., Nolte, C. G., Pleim, J. E., Pouliot, G. A., Pye, H. O. T., Ran, L., Roselle, S. J., Sarwar, G., Schwede, D. B., Sidi, F. I., Spero, T. L., and Wong, D. C.: The Community Multiscale Air Quality (CMAQ) model versions 5.3 and 5.3.1: system updates and evaluation, Geosci. Model Dev., 14, 2867–2897, https://doi.org/10.5194/gmd-14-2867-2021, 2021.