Appendix 2.1. Monthly Varying Organic Carbon to Mass Ratio

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Converting organic carbon (OC) to particulate organic matter (POM) requires an assumption of an organic carbon to mass ratio (POM = (OM/OC) × OC) to account for unmeasured species such as hydrogen, oxygen, and other compounds associated with carbon. Previous work demonstrated that the OM/OC value of 1.8 used in earlier IMPROVE reconstructed mass and extinction algorithms may no longer be appropriate (Hand et al., 2019). The fine mass residual (equation 2.1.1), defined as the difference between $PM_{2.5}$ gravimetric mass (FM) and reconstructed fine mass (RCFM, equation 2.1.2), was found to vary seasonally and appeared to have increased since 2005.

$$\text{residual} = \text{FM} - \text{RCFM} \tag{2.1.1}$$

where

$$\text{RCFM} = \text{AS} + \text{AN} + \text{POM} + [\text{EC}] + [\text{FD}] + \text{SS} \tag{2.1.2}$$

Ammonium sulfate (AS) is calculated assuming sulfate is fully neutralized (AS = $1.375\times[SO_4^{2-}]$), nitrate is assumed to be ammonium nitrate (AN = $1.29 \times [NO_3^-]$), POM is calculated with an OM/OC ratio of 1.8 (POM = 1.8 × [OC]), fine dust (FD) is calculated assuming common oxides of crustal material (Malm et al., 1994), and sea salt (SS) is calculated using chloride ion data (SS = $1.8 \times [Cl^-]$). Chapter 2 includes more details regarding reconstructed fine mass algorithm assumptions. The daily network median residual has increased by 0.02 $\mu g\ m^{-3}\ yr^{-1}$ from 2005 through 2019, or by 0.29 $\mu g\ m^{-3}$ over 15 years (Hand et al., 2019). Measurement uncertainties in the residual are about 0.1 $\mu g\ m^{-3}$. A timeline of the daily network median residual is shown in Figure 2.1.1 in red. The residual is highly seasonal, with higher values during summer. The increase in the residual over time suggests either an increase in measurement biases associated with FM, a growing underestimation of RCFM, or both. Biases in FM were identified with particle bound water (PBW) associated with the gravimetric mass measurement after 2011 due to laboratory relative humidity (RH) issues (White, 2016; Hand et al., 2019). PBW was estimated by calculating aerosol water associated with AS, AN, and OC at laboratory RH. "Dry" FM (FM_{dry}) was estimated by subtracting PBW from measured FM (Hand et al., 2019). The results of the residual computed with FM_{dry} are also shown in Figure 2.1.1 (black). The magnitude of the "dry" residual decreased, as did the range in seasonality; however, some seasonality is still apparent.

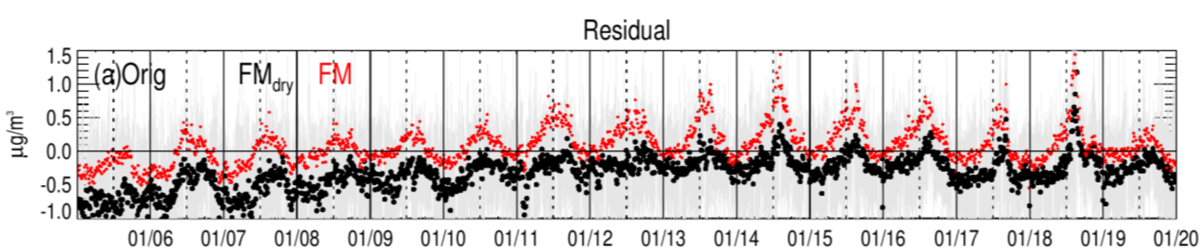

Figure 2.1.1. Daily network median residual (FM-RCFM) for dry $PM_{2.5}$ gravimetric fine mas (FM_{dry}, black) and original $PM_{2.5}$ gravimetric fine mass (FM, red) ($\mu g\ m^{-3}$).

A multiple linear regression (MLR) analysis indicated that the assumed OM/OC ratio also contributed to the residual (Hand et al., 2019). The MLR analysis included data from 2005 through 2019 for daily individual site data using equation (2.1.3):

$$FM\text{-}EC\text{-}SS = a_{AS}AS + a_{AN}AN + a_{OC}OC + a_{FD}FD \quad (2.1.3)$$

Elemental carbon (EC) was not included in the regression due to collinearities with OC, and SS was not included due to its high relative uncertainties. The derived coefficients (a_{AS}, a_{AN}, a_{OC}, for AS, AN, and OC, respectively) are interpreted as mass conversion factors that account for unmeasured compounds as well as effects of sampling or analytic biases. A coefficient of one for AS, AN, and FD suggests that the assumptions used in the reconstructed mass algorithm are appropriate. The OC coefficient is often interpreted as the OM/OC ratio. Regression coefficients for each species and site were considered statistically significant for $p \leq 0.05$ and were only included in seasonal (DFJ, MAM, JJA, SON) and spatial aggregations if they met this condition. The MLR analysis was performed with both FM and FM_{dry} to test the influence of PBW on the derived coefficients. MLR results using FM and aggregated over the entire network are shown in AS (Figure 2.1.2a), OC (Figure 2.1.2b), and FD (Figure 2.1.2c). Similar results are shown in Figure 2.1.3 for FM_{dry}. AN coefficients are not shown due to volatilization from the FM Teflon filter and will not be further considered.

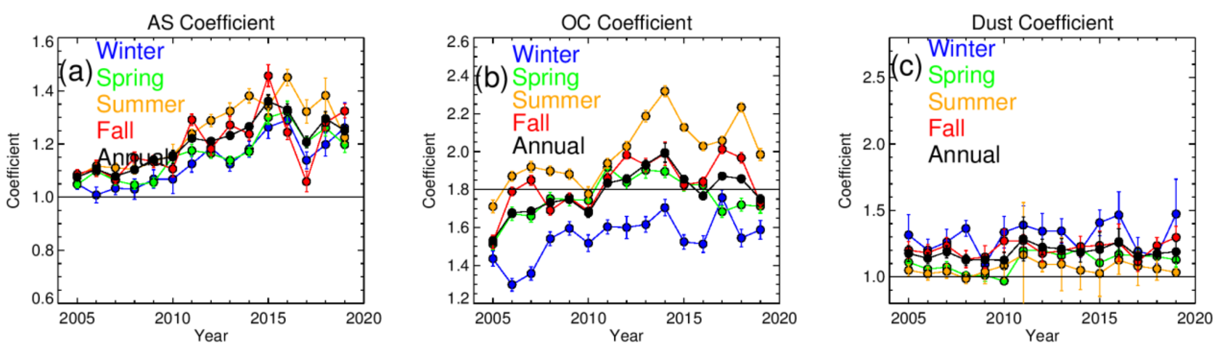

Figure 2.1.2. IMPROVE seasonal and annual network median multiple linear regression coefficients for 2005–2019 using original FM for (a) ammonium sulfate (AS), (b) organic carbon (OC), and (c) fine dust (FD). Error bars correspond to standard error.

AS coefficients were greater than one and increased over time for all seasons, especially after 2011. Values greater than one likely reflect the presence of PBW on the FM filter during weighing. Substituting FM_{dry} in equation (2.1.3) resulted in AS coefficients less than one (Figure 2.1.3a). Coefficients appeared to increase over time but were within 10–20% of one. AS coefficients below one may suggest that the assumption of fully neutralized sulfate was an overestimate of sulfate-related mass or could reflect an overestimate of PBW.

OC coefficients derived from the MLR analysis may include sampling or analytical biases. Seasonal and annual mean coefficients derived using FM are shown in Figure 2.1.2b, along with a constant value of 1.8 to reflect the value used in the reconstruction algorithm. From 2005 through 2010, OC coefficients were variable over time, increased from 2011 through 2014, and afterward decreased but remained variable through 2019. OC was considered weakly hygroscopic in the calculation of PBW, and regression results obtained with FM_{dry} (Figure 2.1.3b) suggested that PBW had little effect on the increase in the OC coefficient after 2011.

Interpreted as OM/OC ratios, the seasonal ranges in OC coefficients were consistent with other reported values, with higher summer values and lower values during winter (see Hand et al., 2019).

FD coefficients are shown in Figures 2.1.2c and 2.1.3c for FM and FM_{dry}, respectively. FD was considered nonhygroscopic; therefore, results in both analyses were similar. Coefficients were greater than one, suggesting that FD was underestimated in the reconstruction algorithm by 20–30%, consistent with previous work (Malm and Hand, 2007). The highest coefficients were associated with winter, which also corresponded to the lowest FD concentrations.

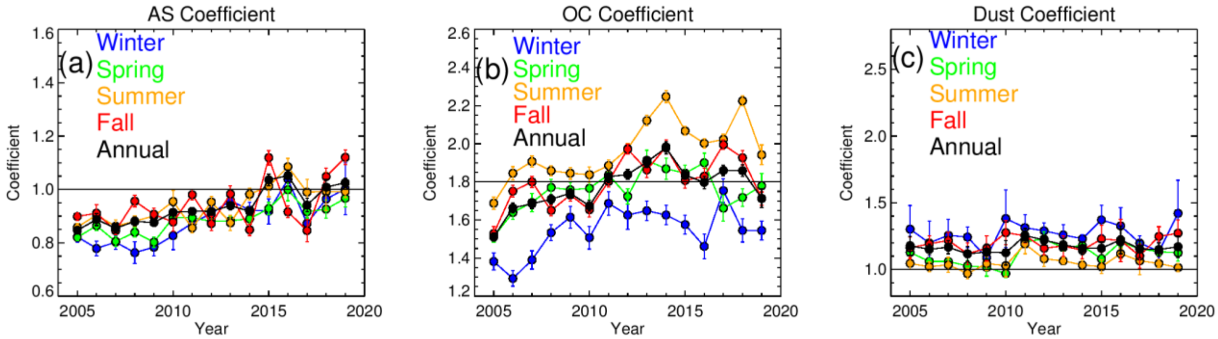

Figure 2.1.3. IMPROVE seasonal and annual network median multiple linear regression coefficients for 2005–2019 using FM_{dry} for (a) ammonium sulfate (AS), (b) organic carbon (OC), and (c) fine dust (FD). Error bars correspond to standard error.

The range in seasonal values of the OC coefficient suggests that some of the seasonality in the residual may be a result of using a constant OM/OC value of 1.8 in the reconstruction algorithm. POM is a major contributor to RCFM, and assumptions related to it have a significant influence on the residual. Hand et al. (2019) demonstrated that the positive summer residual was associated with the OM/OC ratio used in the reconstruction algorithm.

To further analyze the seasonality and regional variability in the OM/OC ratio, a MLR analysis was performed on monthly and regionally aggregated data from 2016 through 2019. This period coincided with new thermal optical analyzers that were upgraded in 2016 (see Chapter 1). Eight regions were defined based on similarities in aerosol composition and for summary purposes (Figure 2.1.4). The regions were larger groupings of the regions presented in Chapters 3 and 5. The regression was performed with the original FM using two methods: (1) the regression was performed on monthly, annually, and regionally aggregated data, and (2) the regression was performed on individual site data for a given month and year, and the median was calculated for all coefficients that met statistical significance criterion ($p \leq 0.05$) within a region. Both methods have advantages; the first method allows for more data in the regression, and the second allows for investigation of results from individual sites that do not meet the statistical significance requirements. Prior data filtering removed OC data greater than 10 µg m^{-3}.

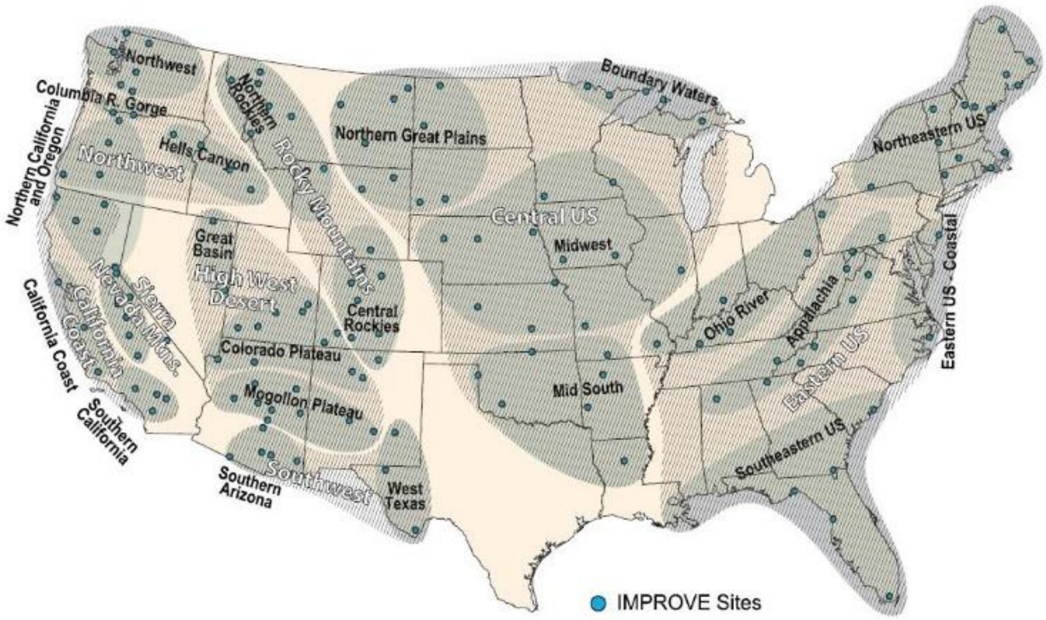

Figure 2.1.4. IMPROVE regions used to aggregate data for regional multiple linear regression analysis.

Regional monthly OC coefficients from the first method are shown in Figure 2.1.5. Some regional differences were observed, but all of the regions experienced lower coefficients during cold months and higher values during warm months. A network average over all the regions was calculated given the similarity in values.

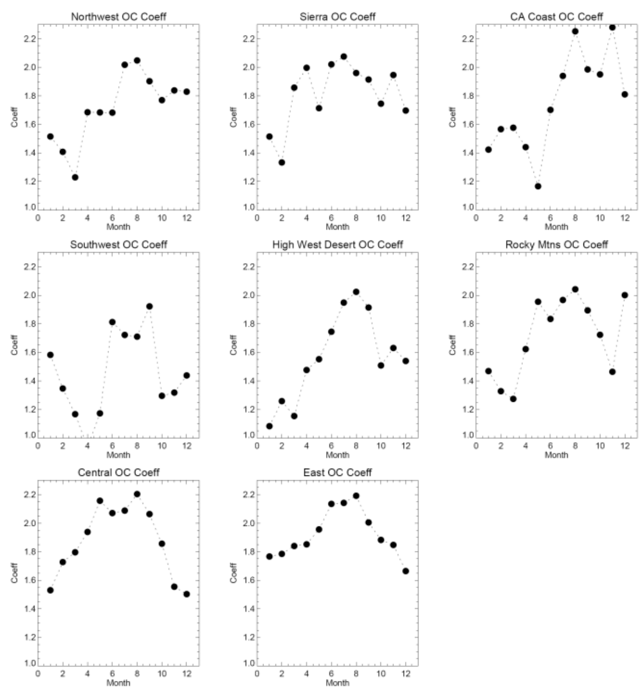

Figure 2.1.5. IMPROVE 2016–2019 regional monthly OC coefficients determined by aggregating data into regions (first method; see text).

Average OC coefficients, interpreted as OM/OC ratios, averaged for all regions and for both methods, are shown in Figure 2.1.6. The monthly differences in coefficients from the two methods were low. Method 1 (black) ranged from 1.5 in January to 2.1 in August, and the second method (orange) ranged from 1.4 in January to 2.1 in August. The annual means for both methods were 1.7, very close to the original OM/OC value of 1.8. The results from method 1 are used in this report and are listed in Table 2.1.1.

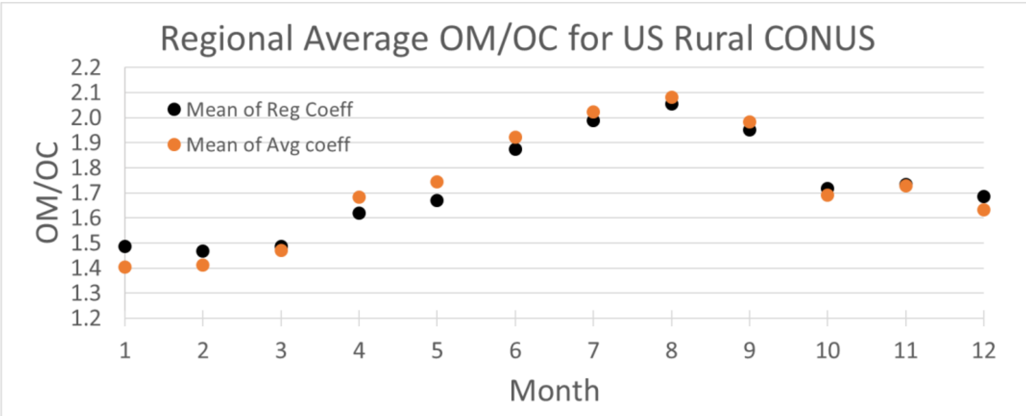

Figure 2.1.6. IMPROVE U.S. continental (CONUS) network averages of monthly regional OM/OC ratios for the regional multiple linear region method (black) and the regional average of site-specific multiple linear regression results (orange).

Table 2.1.1 IMPROVE network monthly OM/OC ratios applied in this report.

Month	OM/OC
Jan	1.5
Feb	1.5
Mar	1.5
Apr	1.6
May	1.7
Jun	1.9
Jul	2.0
Aug	2.1
Sept	2.0
Oct	1.7
Nov	1.7
Dec	1.7
Annual	1.7

The reconstructed mass algorithm in equation (2.1.2) was adjusted to apply monthly U.S. network average OM/OC values (Table 2.1.1) to all sites to calculate POM and to increase FD concentrations by 15%; all other components remained the same. Residuals were calculated using the original FM and the new algorithm from 2005 through 2019. Figure 2.1.7 shows the original daily network median residual (black) and the new adjusted residual (red). The assumptions in the adjusted algorithm resulted in lower seasonal variability in residuals, with lower but still positive residuals in summer. Beginning in 2019 gravimetric mass measurements were performed in an RH-controlled laboratory, which also contributed to a lower seasonal range in the residual due to a reduced PBW bias. Overall, the adjusted residual showed closer agreement between FM and RCFM, especially after 2017.

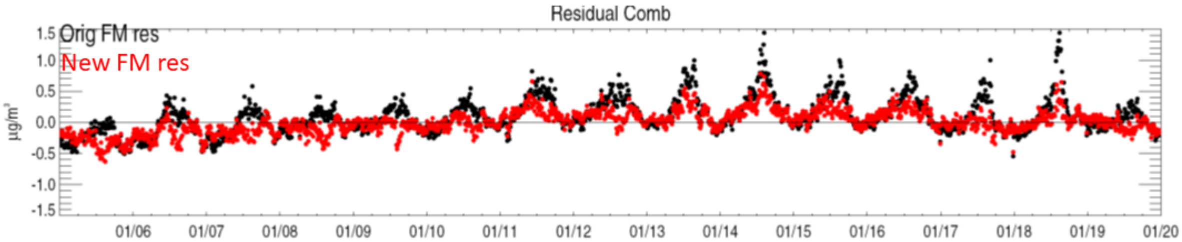

Figure 2.1.7. Daily network median residual for the original reconstruction algorithm (black) and adjusted algorithm (red) (µg m^{-3}).

An analysis of the biases and errors associated with three sets of residuals was performed for data from 2016 through 2019: (1) the original reconstruction algorithm, (2) seasonal OM/OC ratios (1.6, 1.8, 2.0, 1.8 for DJF, MAM, JJA, and SON, respectively) and a 15% increase in FD, and (3) monthly OM/OC ratios (Table 2.1.1) and a 15% increase in FD. The seasonal and monthly OM/OC ratios were applied to daily data, but results were evaluated over seasons for comparison purposes. The results for the entire U.S. network are reported in Table 2.1.2.

Table 2.1.2. Error metrics corresponding to the original reconstructed algorithm, seasonal OM/OC ratios and a 15% increase in FD, and monthly OM/OC ratios and a 15% increase in FD for winter (DJF), spring (MAM), summer (JJA), fall (JJA), and annual mean, for the entire U.S. CONUS network for 2016-2019.

Error Metric	Case	Winter	Spring	Summer	Fall	Annual
NRMSE[1]	**Original**	0.217	0.174	0.225	0.231	0.226
	Seasonal	0.207	0.167	0.172	0.226	0.196
	Monthly	0.209	0.174	0.169	0.220	0.194
MAB[2]	**Original**	0.052	-0.016	-0.103	-0.033	-0.042
	Seasonal	0.022	0.010	-0.028	-0.015	-0.009
	Monthly	0.016	-0.028	-0.021	-0.006	-0.013
MAE[3]	**Original**	0.349	0.352	0.683	0.415	0.452
(µg m^{-3})	**Seasonal**	0.325	0.341	0.490	0.403	0.392
	Monthly	0.327	0.351	0.472	0.381	0.384
MAD[4]	**Original**	0.217	0.223	0.335	0.248	1.031
(µg m^{-3})	**Seasonal**	0.199	0.216	0.295	0.242	0.766
	Monthly	0.200	0.214	0.284	0.227	0.696
Slope[5]	**Original**	0.967	1.033	1.119	1.071	1.087
	Seasonal	0.998	1.012	1.017	1.061	1.031
	Monthly	1.000	1.062	0.986	1.006	1.002
Average Residual[6]	**Original**	-0.140	0.054	0.587	0.127	0.166
(µg m^{-3})	**Seasonal**	-0.059	-0.034	0.158	0.058	0.034
	Monthly	-0.043	0.094	0.118	0.021	0.050

[1]Normalized Root Mean Square = $\frac{\sqrt{\frac{1}{N}\Sigma(RCFM_i - FM_i)^2}}{\overline{FM}}$; i = *individual sample*

[2]Mean Absolute Bias = $\frac{\frac{1}{N}\Sigma(RCFM_i - FM_i)}{\overline{FM}}$; i = *individual sample*

[3]Mean Absolute Error = $\frac{\sum|RCFM_i - FM_i|}{N}$; i = *individual sample*
[4]Mean Absolute Deviation = $MEDIAN(|Res_i - MEDIAN(Res_i)|)$, $Res_i = FM_i - RCFM_i$; i = *individual sample*
[5]Slope(x,y) = (RCFM,FM)
[6]Average Residual = $\overline{Res}$

For all of the error metrics listed in Table 2.1.2, both the seasonal and monthly OM/OC ratios resulted in lower errors and biases for the annual mean case and for most seasons when compared to the original algorithm (constant OM/OC ratio). For example, Figure 2.1.8a shows the original summer residual using a constant OM/OC ratio, compared to the adjusted case with monthly OM/OC ratios in Figure 2.1.8b. The residuals decreased at sites across the United States, but especially at sites in the eastern United States. For most cases, the monthly OM/OC case resulted in lower errors and biases than the seasonal OM/OC case. The residual calculated with monthly OM/OC ratios were less than the uncertainty of the residual.

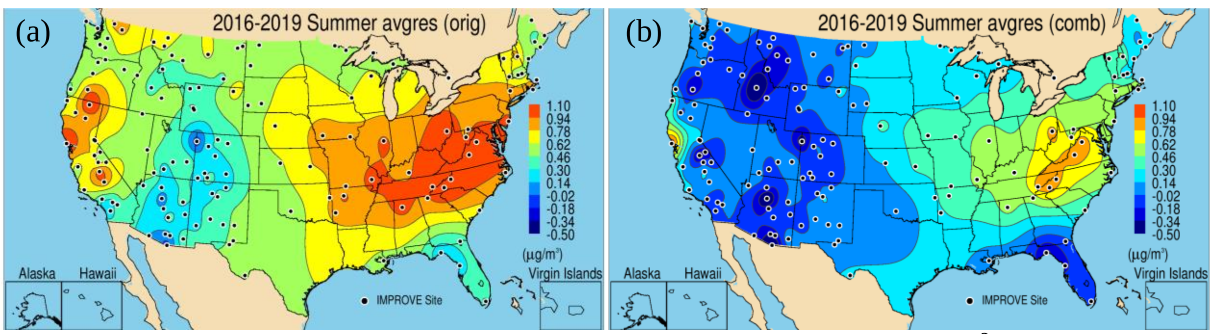

Figure 2.1.8 IMPROVE 2016-2019 summer (JJA) average residual (FM-RCFM, µg m^{-3}) using (a) original reconstruction algorithm with constant OM/OC ratio and (b) monthly OM/OC ratio and 15% increase in fine dust.

REFERENCES

Hand, J. L., Prenni, A. J., Schichtel, B. A., Malm, W. C., and Chow, J. C. (2019), Trends in remote PM2.5 residual mass across the United States: Implications for aerosol mass reconstruction in the IMPROVE network, *Atmospheric Environment*, *203*, 141-152, doi:10.1016/j.atmosenv.2019.01.049.

Malm, W. C., and Hand, J. L. (2007), An examination of the physical and optical properties of aerosols collected in the IMPROVE program, *Atmospheric Environment*, *41*(16), 3407-3427, doi:10.1016/j.atmosenv.2006.12.012.

Malm, W. C., Sisler, J. F., Huffman, D., Eldred, R. A., and Cahill, T. A. (1994), Spatial and seasonal trends in particle concentration and optical extinction in the United States, *Journal of Geophysical Research: Atmospheres*, *99*(D1), 1347-1370, https://doi.org/10.1029/93JD02916.

White, W. H. (2016), Increased variation of humidity in the weighing laboratory, *IMPROVE Data Advisory* (da0035), http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory/da0035/da0035_IncreasedRH.pdf.