Appendix 1.1. A New Cost-Effective Analytical Method for IMPROVE: Nondestructive Infrared Analysis of PTFE Filters to Measure Organic, Elemental, and Total Carbon, Inorganic Ions, Soil Elements, Organic Matter (OM), and Organic Functional Groups

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For the last decade, the use of Fourier transform – infrared (FT-IR) spectroscopy has been explored to cost-effectively reproduce existing IMPROVE speciation data and to measure additional speciation data in the form of organic functional groups (Figure 1.1.1). For this new effort, FT-IR spectra are collected from IMPROVE PTFE (Teflon) filters without damaging the sample so there is no disruption to routine IMPROVE operations. FT-IR spectra for a few sites were measured in 2011 and for a few more sites in 2013. Since 2015, all $PM_{2.5}$ PTFE samples in the IMPROVE network are analyzed by FT-IR. Analysis time is 5 minutes and undergraduate students at UC Davis analyze the filters under the guidance of a laboratory supervisor at the Air Quality Research Center, UC Davis.

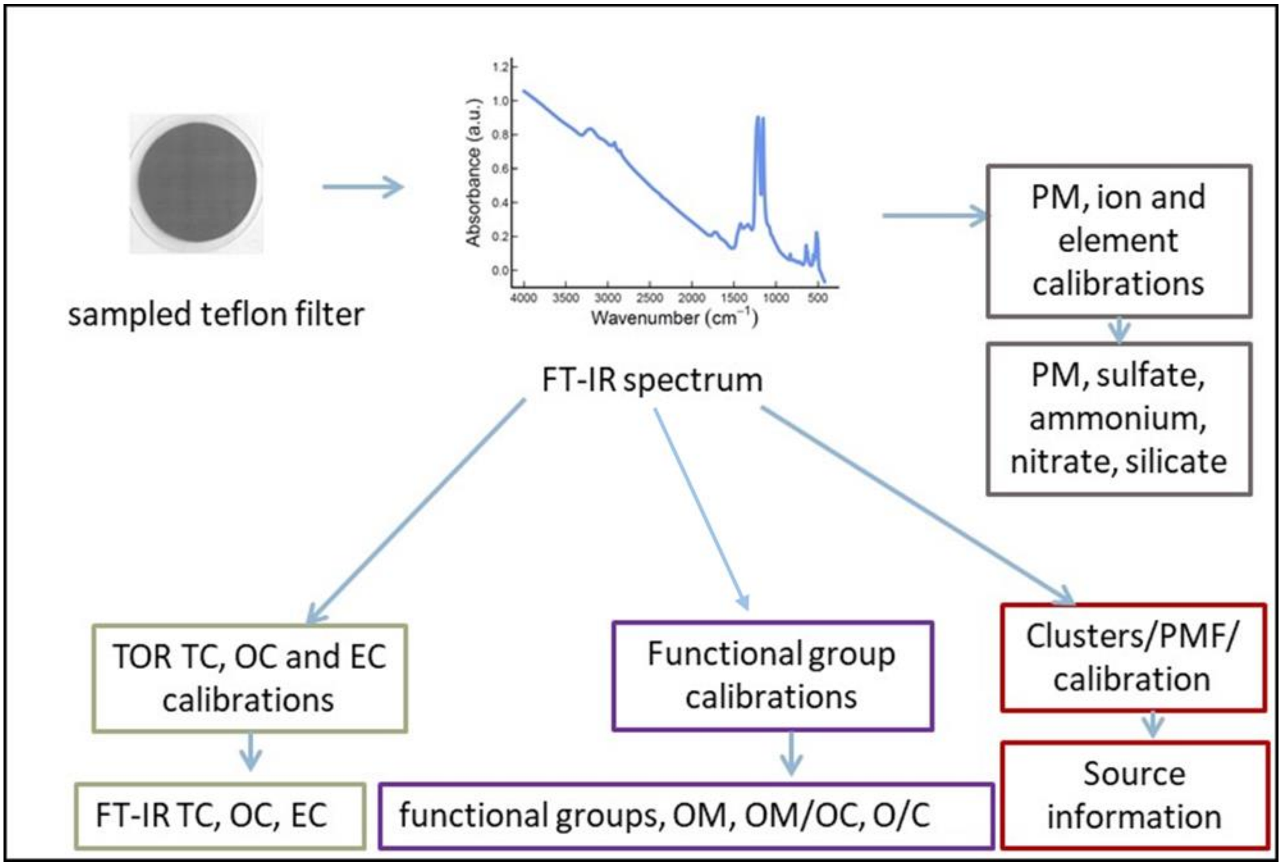

Figure 1.1.1. An FT-IR spectrum of a Teflon (PTFE) filter can be used to reproduce existing data (green and black boxes), measure additional compositional data (purple boxes) and identify sources and atmospheric transformations (red boxes). An FT-IR spectrum is acquired in five minutes without modifying the sample.

This multitude of compositional data is able to be obtained from FT-IR analysis because all of these constituents have bonds that absorb infrared light. Figure 1.1.2 shows three spectra from the Fresno, California IMPROVE site in the winter of 2013. The figure is annotated with the organic functional groups including from left to right, alcohol OH, carboxylic acid OH, aliphatic CH, and carbonyl and inorganic ions including ammonium and nitrate. A large double peak associated the PTFE filter is also visible. The organic functional groups enable the measurement of organic carbon and assist with measuring elemental carbon. Elemental carbon is also able to be measured due to peaks at 1600 cm^{-1} and 868 cm^{-1} (not visible but still useful in the calibration methods) and broad absorption between 1500 cm^{-1} and 4000 cm^{-1}. Figure 1.1.3 shows spectra from Birmingham Alabama which highlight inorganic sulfate and ammonium as well as carbonyl and suggest the location of organosulfate peaks.

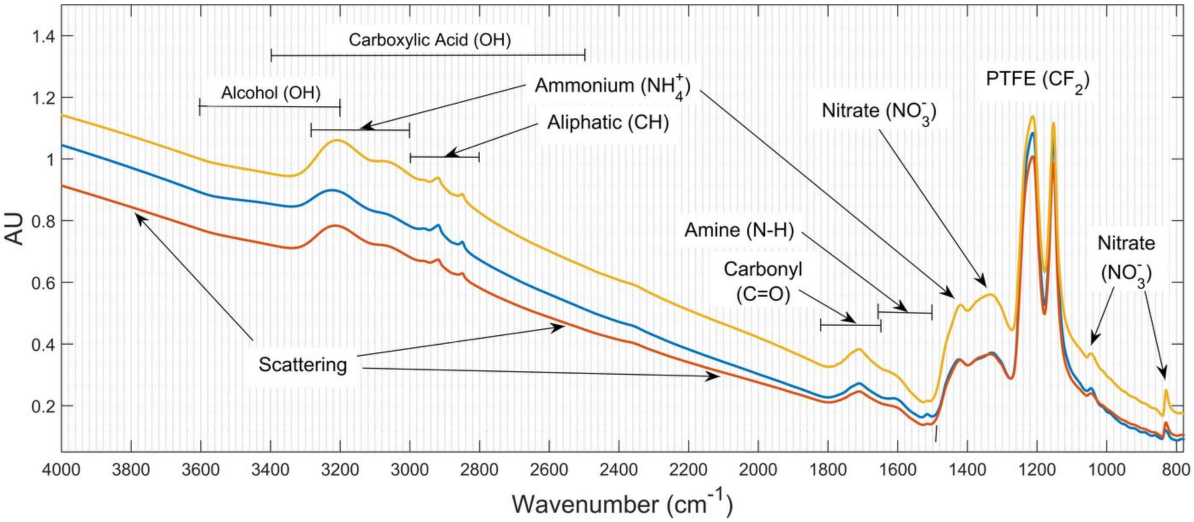

Figure 1.1.2. Spectra from the Fresno, CA IMPROVE site collected in January of 2013. Each colored line is the spectrum from a single PTFE filter.

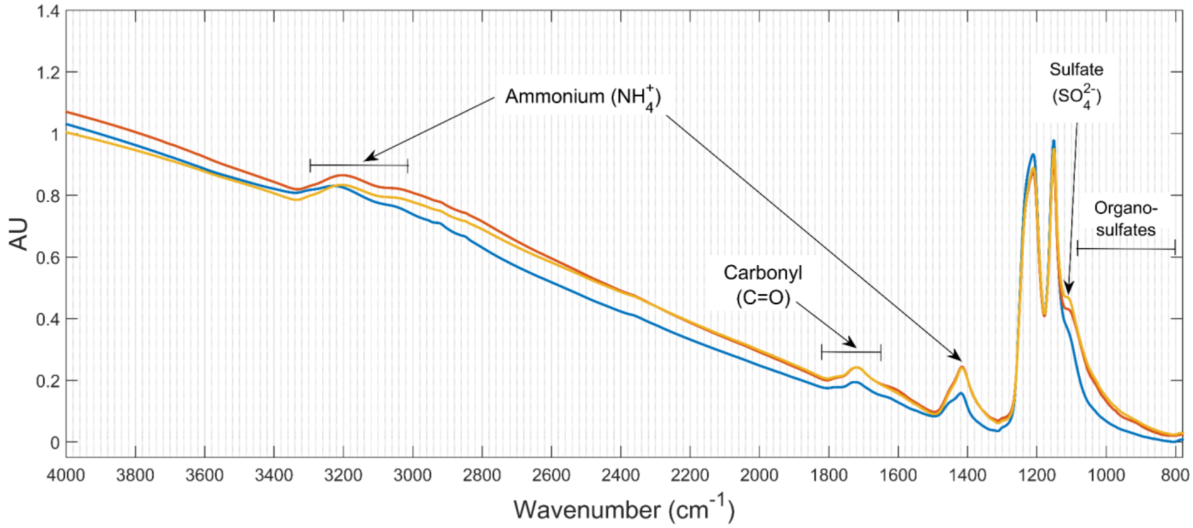

Figure 1.1.3. Spectra from the Birmingham Alabama IMPROVE site collected in August and September of 2013. The sulfate peak is located to the right of the large PTFE peaks.

Reproducing existing data using only one filter type and one analytical technique (FT-IR) could be used to (1) expand the IMPROVE network without incurring the full cost of a new site, (2) enhance quality control and data validation on existing IMPROVE data (3) replace missing data and (4) for some species could be used to replace most of the existing analytical measurements (particularly for OC, EC and TC). The functional group composition of organic matter (OM) is also measured from FT-IR spectra and can provide additional information about the sources and atmospheric processes of carbonaceous particulate matter. Currently, organic matter (OM) is estimated for all samples by multiplying organic carbon by an estimated OM/OC value of 1.8 (Pitchford et al., 2007). Using FT-IR spectra, OM is measured by summing the measured organic functional groups for that sample providing a sample-specific concentration of OM.

Strengths of the method include not changing or destroying the sample during analyses, no gas phase adsorption onto the Teflon (sampling artifact), providing a new data stream of functional groups and most of the current suite of composition data and lower cost. Limitations of FT-IR include the use of the PTFE filters which can no longer be obtained with consistent Teflon material, the scattering and absorption by PTFE which causes sloping baseline in the spectra and obscures peaks useful for measuring carbonaceous components, the lack of strong and unique absorptions related to EC, and the complexity of the spectra requiring advanced mathematical tools.

1.1.1. REPRODUCING EXISTING IMPROVE SPECIATION DATA

Proof of concept work began with efforts to reproduce thermal optical reflectance (TOR) organic carbon (OC) and elemental carbon (EC) data at the seven collocated PTFE filter sites in IMPROVE in 2011 (Dillner and Takahama, 2015a; Dillner and Takahama, 2015b) and extended to 11 additional sites in 2013 (Reggente et al., 2016). In this work, we learned that a select group of spectra can be calibrated to TOR OC and EC to accurately predict FT-IR OC and EC in all other samples as long as the mass range and chemical composition of samples in the calibration set was similar to the samples to be measured. It also showed that samples from one year could be used to predict samples in another year. The next step was to analyze all samples in the IMPROVE network and all of the Chemical Speciation Network samples for further evaluation. This requires three FT-IR instruments that are operated by students during regular work hours. Our analysis (Debus et al., 2019) shows that these instruments can be used interchangeably as long as environmental conditions for the filters and the instruments were maintained over time. This enables us to make one calibration for all three instruments rather than the more conventional method of calibrating each instrument separately. Considerations for calibrations to be used for measuring FT-IR OC and EC network wide include the likely need for more than one calibration for each constituent to be measured (OC, EC, TC) due to the large variability in samples across the network, particularly the difference between heavily loaded samples collected during forest fires or prescribed burns and more typical rural samples at IMPROVE sites (Takahama et al., 2019).

This calibration method is conceptually different than other analyses in IMPROVE which are calibrated to laboratory standards. However, the complexities of the carbonaceous fraction is not rivaled by other constituents (ions and elements) and calibration to ambient standards analyzed continuously provides a robust means of spanning the mass loadings, composition and interferents as well as predicting operationally defined constituents for which there are no agreed upon standards.

Using network wide data from 2015 through 2017, calibration methods and measurements of FT-IR OC, EC and TC, as well as inorganic ions sulfate and nitrate and soil elements, (Si, Al, Ca, Ti, Fe), light absorption, and PM$_{2.5}$ mass were made for all sites (except the South Korean site) (Debus et al., 2022). Speciation data from TOR as well as ion chromatography, x-ray fluorescence, gravimetry and HIPs are used for calibration. To make this procedure operationally practical, select IMPROVE sites are used for calibration and the remainder of the sites are predicted using FT-IR spectra. The calibration sites are selected to represent the diversity of PM concentration and composition across the IMPROVE network. The sites are selected by creating clusters (groups) from all of the FTIR spectra from one year. We chose 21 clusters and then selected the site that had the most samples within that cluster to be representative. The selected sites and their annual average concentrations are shown in Figure 1.1.4. This list of sites is not unique such that if one site closes down, another site from that cluster can be used to replace it.

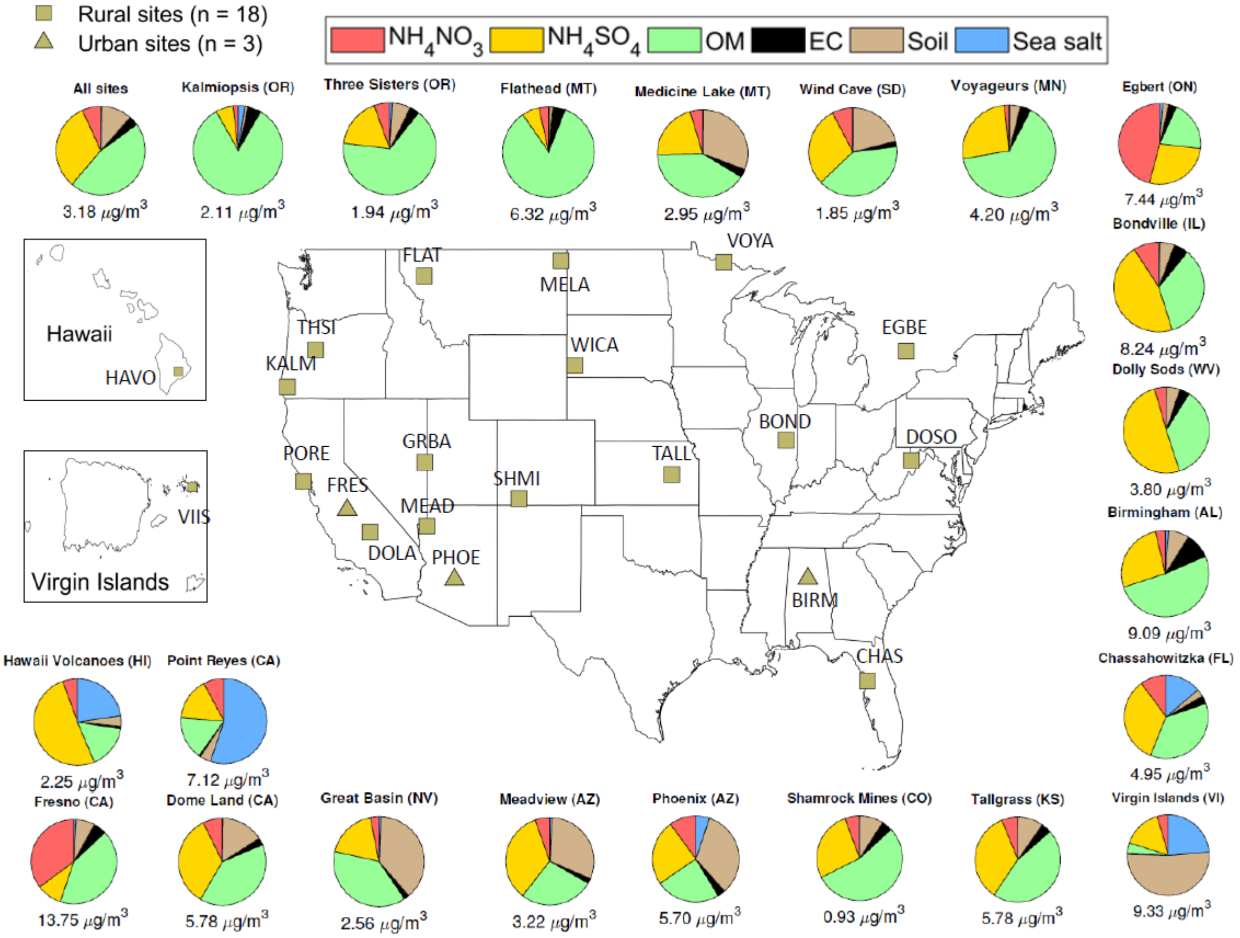

Figure 1.1.4. Annual median PM$_{2.5}$ concentration and composition for the 21 representative sites selected as calibration samples. The first pie chart representing the median PM$_{2.5}$ composition and mass concentration across all sites and samples over a one year period is given for comparison. (Debus et al., 2022).

FT-IR measured concentrations are compared to routine IMPROVE data for all constituents. Reliable predicted concentrations are obtained for a broad range of atmospheric constituents with detectable infrared signatures such as OC, EC, TC, sulfate, soil elements (Si, Al, Ca, Ti, Fe), light absorption, and $PM_{2.5}$ mass. Due to volatilization off the PTFE filter, nitrate measurements were found to be unsatisfactory. Initial results were obtained for 2015. Using the same calibration sites, similar quality data was obtained for 2016 and 2017.

The method has been partially implemented into the UCDavis IMPROVE database including storage of all spectra, metadata, and QC analyses and prediction of TC, OC, EC along with soil elements and ions, using calibrations developed as part of the research effort. QC analysis is currently done outside of the database as is calibration development. These two pieces can be added to the IMPROVE database for complete implementation.

1.1.2. MEASURING ORGANIC FUNCTIONAL GROUP

A compelling use of FT-IR spectra is to measure organic matter and its constituents, organic functional groups (Coury and Dillner, 2009; Boris et al., 2019; Boris et al., 2021; Bürki et al., 2020; George et al., 2015; Kamruzzaman et al., 2018; Landis et al., 2018; Reggente et al., 2019; Ruthenburg et al., 2014; Allen et al., 2015). Organic functional groups are not currently available in IMPROVE and provide a better representation of OM than OC multiplied by a fixed OM/OC factor. In addition functional groups are the building blocks of OM composition which can be used to elucidate atmospheric processes and identify sources (Russell et al., 2011; Russell et al., 2009; Takahama et al., 2013; Boris et al., 2021). Functional groups provide additional specificity for the carbonaceous PM composition but are not as specific as individual compounds measured by more time and cost intensive techniques. They are more specific than the mass fragments obtained in online aerosol measurements such as the Aerodyne Aerosol Mass Spectrometer (AMS).

Functional group measurements use the traditional approach of using laboratory standards for calibration. Because there are thousands of organic compounds in particles and only a fraction (less than half) of those are known, only a small representative group of standards can be made in the laboratory for the purposes of calibration.

In the IMPROVE network, functional groups have been measured for seven sites in 2011 (Ruthenburg et al., 2014) and 16 sites in 2013 (Kamruzzaman et al., 2018). Figure 1.1.5 shows the annual mean composition of the OM/OC by functional group for IMPROVE sites in 2013. This figure illustrates the variability of OM/OC (it is not 1.8 for all sites and samples) by site with additional variability occurring among individual samples (not shown). In addition, the composition of OM/OC varies by sites indicating differences in sources and atmospheric processes.

More recently, measurements of functional groups at four Southeastern Aerosol Research and Characterization (SEARCH) network sites were made from 2009 to 2016 (Boris et al., 2019; Boris et al., 2021). During this time period, mass of OM decreases while the relative contribution of OM (measured from functional groups) to particulate mass increased (not shown) due to a decrease in sulfate. Figure 1.1.6 shows that this increase in fractional PM was dominated by aliphatic CH, carboxylic acids and alcohol OH moieties. The composition of OM also changes during this time period. Highly oxygenated functional groups (carboxylic acids and carboxylates) decreased which is attributed to anthropogenic SO_2 and/or volatile organic compound (VOC) emissions reductions. Less oxygenated functional groups (non-acid carbonyls and alcohol OH) increased slightly with plausible influences from decreasing NO_x and/or increasing O_3 concentrations. Aliphatic CH remained relatively constant.

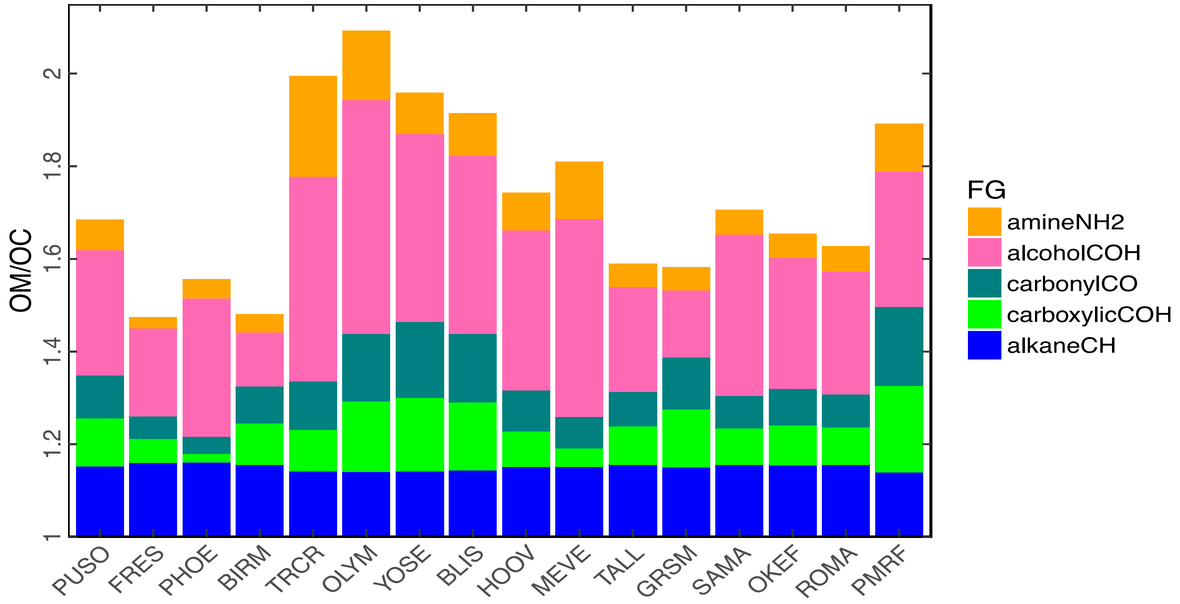

Figure 1.1.5. Functional group composition of OM/OC at 16 sites in IMPROVE in 2013. (Kamruzzaman et al., 2018)

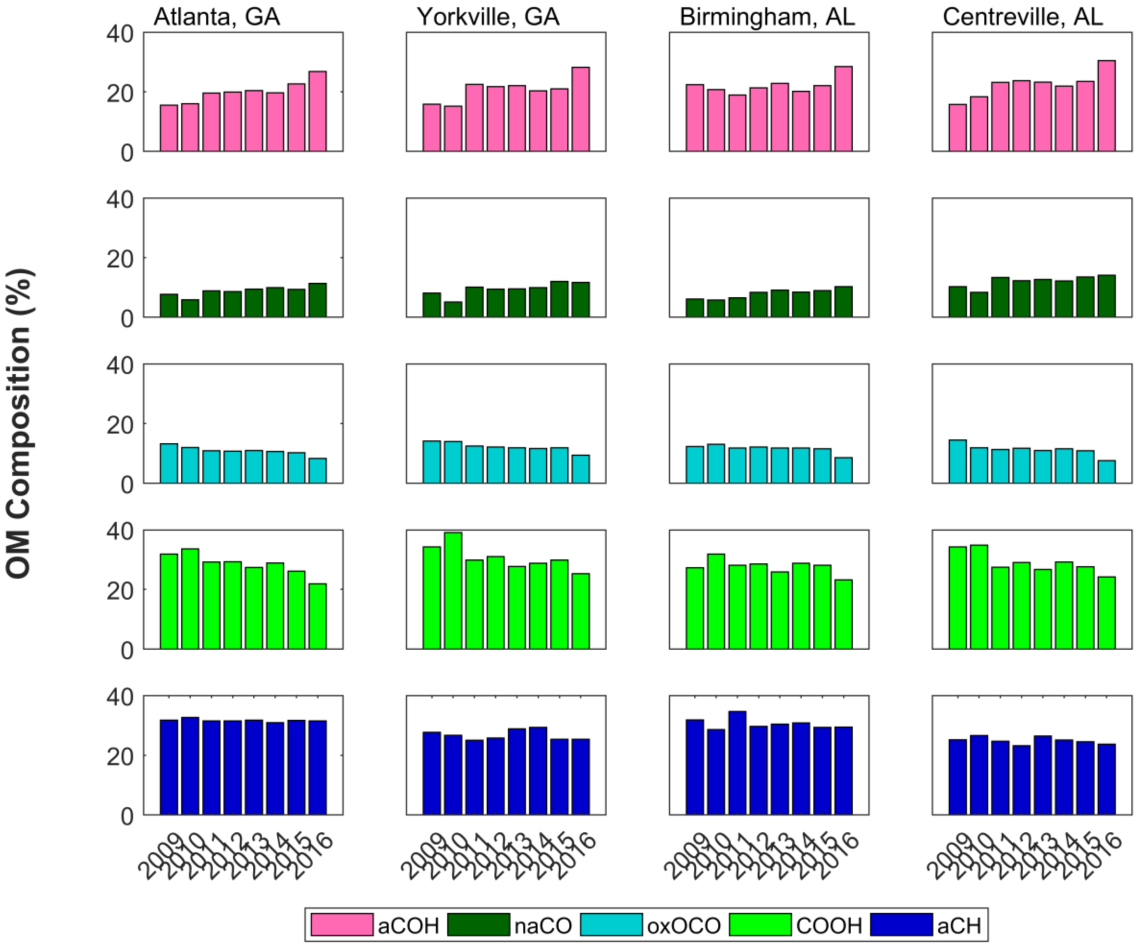

Figure 1.1.6. Annual average functional composition at four sites in the SEARCH network from 2009 to 2016. Note that the more highly oxidized functional groups carbonylic acids (COOH) and oxalate (oxOCO) are decreasing while the moderately oxidized functional groups, non-acid carbonyl (naCO) and alcohol OH (aCOH) are increasing (Boris et al., 2021).

In summary, FT-IR methods are a fast, cost-effective method that can be added to the IMPROVE network without disrupting routine analyses. A new data stream of functional groups, OM and OM/OC on a per filter basis can be added to existing sites. Replicating existing data, OC, EC, TC, sulfate, and soil elements could be useful for adding new site cost effectively, QCing data, replacing missing data or mostly eliminating TOR analysis from the network.

REFERENCES

Allen, H. M., Draper, D. C., Ayres, B. R., Ault, A., Bondy, A., Takahama, S., Modini, R. L., Baumann, K., Edgerton, E., Knote, C., Laskin, A., Wang, B., and Fry, J. L. (2015), Influence of crustal dust and sea spray supermicron particle concentrations and acidity on inorganic NO3-aerosol during the 2013 Southern Oxidant and Aerosol Study, *Atmospheric Chemistry and Physics*, *15*(18), 10669-10685, doi:10.5194/acp-15-10669-2015.

Boris, A. J., Takahama, S., Weakley, A. T., Debus, B. M., Fredrickson, C. D., Esparza-Sanchez, M., Burki, C., Reggente, M., Shaw, S. L., Edgerton, E. S., and Dillner, A. M. (2019), Quantifying organic matter and functional groups in particulate matter filter samples from the southeastern United States – Part 1: Methods, *Atmos. Meas. Tech.*, *12*(10), 5391-5415, doi:10.5194/amt-12-5391-2019.

Boris, A. J., Takahama, S., Weakley, A. T., Debus, B. M., Shaw, S. L., Edgerton, E. S., Joo, T., Ng, N. L., and Dillner, A. M. (2021), Quantifying organic matter and functional groups in particulate matter filter samples from the southeastern United States – Part 2: Spatiotemporal trends, *Atmos. Meas. Tech.*, *14*(6), 4355-4374, doi:10.5194/amt-14-4355-2021.

Bürki, C., Reggente, M., Dillner, A. M., Hand, J. L., Shaw, S. L., and Takahama, S. (2020), Analysis of functional groups in atmospheric aerosols by infrared spectroscopy: Method development for probabilistic modeling of organic carbon and organic matter concentrations, *Atmos. Meas. Tech.*, *13*(3), 1517-1538, doi:10.5194/amt-13-1517-2020.

Coury, C., and Dillner, A. M. (2009), ATR-FTIR characterization of organic functional groups and inorganic ions in ambient aerosols at a rural site, *Atmospheric Environment*, *43*(4), 940-948, https://doi.org/10.1016/j.atmosenv.2008.10.056.

Debus, B., Takahama, S., Weakley, A. T., Seibert, K., and Dillner, A. M. (2019), Long-term strategy for assessing carbonaceous particulate matter concentrations from multiple Fourier transform infrared (FT-IR) instruments: Influence of spectral dissimilarities on multivariate calibration performance, *Applied Spectroscopy*, *73*(3), 271-283, https://opg.optica.org/as/abstract.cfm?URI=as-73-3-271.

Debus, B., Weakley, A. T., Takahama, S., George, K. M., Amiri-Farahani, A., Schichtel, B., Copeland, S., Wexler, A. S., and Dillner, A. M. (2022), Quantification of major particulate matter species from a single filter type using infrared spectroscopy – Application to a large-scale monitoring network, *Atmos. Meas. Tech.*, *15*(9), 2685-2702, doi:10.5194/amt-15-2685-2022.

Dillner, A. M., and Takahama, S. (2015a), Predicting ambient aerosol thermal-optical reflectance (TOR) measurements from infrared spectra: organic carbon, *Atmos. Meas. Tech.*, *8*(3), 1097-1109, doi:10.5194/amt-8-1097-2015.

Dillner, A. M., and Takahama, S. (2015b), Predicting ambient aerosol thermal–optical reflectance measurements from infrared spectra: elemental carbon, *Atmos. Meas. Tech.*, *8*(10), 4013-4023, doi:10.5194/amt-8-4013-2015.

George, K. M., Ruthenburg, T. C., Smith, J., Yu, L., Zhang, Q., Anastasio, C., and Dillner, A. M. (2015), FT-IR quantification of the carbonyl functional group in aqueous-phase secondary organic aerosol from phenols, *Atmospheric Environment*, *100*, 230-237, https://doi.org/10.1016/j.atmosenv.2014.11.011.

Kamruzzaman, M., Takahama, S., and Dillner, A. M. (2018), Quantification of amine functional groups and their influence on OM/OC in the IMPROVE network, *Atmospheric Environment*, *172*, 124-132, https://doi.org/10.1016/j.atmosenv.2017.10.053.

Landis, M. S., Edgerton, E. S., White, E. M., Wentworth, G. R., Sullivan, A. P., and Dillner, A. M. (2018), The impact of the 2016 Fort McMurray Horse River wildfire on ambient air pollution levels in the Athabasca Oil Sands Region, Alberta, Canada, *Science of The Total Environment*, *618*, 1665-1676, https://doi.org/10.1016/j.scitotenv.2017.10.008.

Pitchford, M., Malm, W. C., Schichtel, B. A., Kumar, N., Lowenthal, D., and Hand, J. L. (2007), 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.

Reggente, M., Dillner, A. M., and Takahama, S. (2016), Predicting ambient aerosol thermal–optical reflectance (TOR) measurements from infrared spectra: extending the predictions to different years and different sites, *Atmos. Meas. Tech.*, *9*(2), 441-454, doi:10.5194/amt-9-441-2016.

Reggente, M., Dillner, A. M., and Takahama, S. (2019), Analysis of functional groups in atmospheric aerosols by infrared spectroscopy: systematic intercomparison of calibration methods for US measurement network samples, *Atmos. Meas. Tech.*, *12*(4), 2287-2312, doi:10.5194/amt-12-2287-2019.

Russell, L. M., Takahama, S., Liu, S., Hawkins, L. N., Covert, D. S., Quinn, P. K., and Bates, T. S. (2009), Oxygenated fraction and mass of organic aerosol from direct emission and atmospheric processing measured on the R/V Ronald Brown during TEXAQS/GoMACCS 2006, *Journal of Geophysical Research: Atmospheres*, *114*(D7), https://doi.org/10.1029/2008JD011275.

Russell, L. M., Bahadur, R., and Ziemann, P. J. (2011), Identifying organic aerosol sources by comparing functional group composition in chamber and atmospheric particles, *Proceedings of the National Academy of Sciences*, *108*(9), 3516-3521, doi:10.1073/pnas.1006461108.

Ruthenburg, T. C., Perlin, P. C., Liu, V., McDade, C. E., and Dillner, A. M. (2014), Determination of organic matter and organic matter to organic carbon ratios by infrared spectroscopy with application to selected sites in the IMPROVE network, *Atmospheric Environment*, *86*, 47-57, http://dx.doi.org/10.1016/j.atmosenv.2013.12.034.

Takahama, S., Dillner, A. M., Weakley, A. T., Reggente, M., Bürki, C., Lbadaoui-Darvas, M., Debus, B., Kuzmiakova, A., and Wexler, A. S. (2019), Atmospheric particulate matter characterization by Fourier transform infrared spectroscopy: a review of statistical calibration strategies for carbonaceous aerosol quantification in US measurement networks, *Atmospheric Measurement Techniques*, *12*(1), 525-567, https://doi.org/10.5194/amt-12-525-2019.

Takahama, S., Johnson, A., and Russell, L. M. (2013), Quantification of carboxylic and carbonyl functional groups in organic aerosol infrared absorbance spectra, *Aerosol Science and Technology*, *47*(3), 310-325, doi:10.1080/02786826.2012.752065.