1 **Quantification of major particulate matter species from a single filter type using**

2 **infrared spectroscopy – Application to a large-scale monitoring network**

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16 **Abstract**

17 To enable chemical speciation, monitoring networks collect particulate matter (PM) on different

18 filter media, each subjected to one or more analytical techniques to quantify PM composition

19 present in the atmosphere. In this work, we propose an alternate approach that uses one filter

20 type (teflon or polytetrafluoroethylene, PTFE, commonly used for aerosol sampling) and one

21 analytical method, Fourier Transform Infrared (FT-IR) spectroscopy to measure almost all of the

22 major constituents in the aerosol. In the proposed method, measurements using the typical

23 multi-filter, multi-analytical techniques are retained at a limited number of sites and used as

24 calibration standards. At all remaining sites, only sampling on PTFE and analysis by FT-IR is

25 performed. This method takes advantage of the sensitivity of the mid-IR domain to various

26 organic and inorganic functional groups and offers a fast and inexpensive way of exploring sample

27 composition. As a proof of concept, multiple years of samples collected within the Interagency

28 Monitoring of PROtected Visual Environment network (IMPROVE) are explored with the aim of

29 retaining high quality predictions for a broad range of atmospheric compounds including mass,

30 organic (OC), elemental (EC) and total (TC) carbon, sulfate, nitrate and crustal elements. Findings

31   suggest that models based on only 21 sites, covering spatial and seasonal trends in atmospheric
32   composition, are stable over a three year period within the IMPROVE network with acceptable
33   prediction accuracy (R^2 > 0.9, median bias less than 3%) for most constituents. The major
34   limitation is measuring nitrate as it is known to volatilize off of PTFE filters. Incorporating
35   additional sites at low cost, partially replacing existing, more time and cost intensive techniques
36   or using the FT-IR data for quality control or substitute for missing data, are among the potential
37   benefits of the one-filter, one-method approach.

1 Introduction

In the United States, filter-based chemical speciation of ambient aerosols has been in operation for decades to quantify trends, assess transport and atmospheric transformation, identify sources of air pollution, evaluate impacts of pollution regulations, assess impacts on visibility, radiative forcing, human and ecosystem health and evaluate atmospheric and climatological models. The two federally funded speciation networks, the Interagency Monitoring of PROtected Visual Environments (IMPROVE) and the Chemical Speciation Network (CSN) collect 24-hour filter samples using three filter media: polytetrafluoroethylene (PTFE) for analysis by gravimetry, x-ray fluorescence (XRF) and hybrid integrating plate and sphere (HIPS), quartz for thermal optical reflectance (TOR) and nylon for ion chromatography. Over the decades of operation, the analytical methods have evolved with efforts to maintain consistency in trends while also adopting improved methodology and retiring obsolete equipment. Impacts of many of these changes have been addressed in the literature (Hyslop et al., 2015, 2012; White et al., 2016; Zhang et al., 2021; Chow et al., 2007a, 2015) and in data advisories posted on the IMPROVE website (http://vista.cira.colostate.edu/Improve/data-advisories/).

In this paper, we explore the use of Fourier transform-infrared spectroscopy (FT-IR) to reproduce most of the existing speciation data based on the optical activity of the components in the mid-IR. The number and bands of organic compounds are numerous, but generally group frequencies can be found above 1500 cm^{-1} and compound-specific spectral patterns ("fingerprint region") below this frequency; down to approximately 700 cm^{-1} (for example, Weakley et al., 2016; Mayo et al., 2004). Graphitic carbon displays peaks near 1600 cm^{-1} due to lattice defects (Tuinstra and Koenig, 1970; Friedel and Carlson, 1971), displacement vibrations near 868 cm^{-1} (Nemanich et al., 1977), and a broad, sloping absorbance between 4000 and 1500 cm^{-1} due to the tail of the electronic transition more strongly observed in the UV (Parks et al., 2021). Inorganic substances containing polyatomic ions such as sulfate, nitrate, and ammonium have strong vibrational modes above 600 cm^{-1} (Mayo, 2004). Crystalline and amorphous geological minerals in the form of oxides (which include hydroxides and oxyhydroxides) have distinct internal vibrational modes influenced by the electronegativity of the metal to which the oxygen is bonded (Busca and Resini, 2006; Chukanov and Chervonnyi, 2016; Margenot et al., 2017).

FT-IR spectra with partial least squares (PLS) calibrations have been shown to reproduce OC and EC concentrations using organic and graphitic carbon absorption bands, respectively, at a limited number of sites in the IMPROVE network (Dillner and Takahama, 2015a, b; Reggente et al., 2016), CSN (Weakley et al., 2016, 2018a) and FRM network (Weakley et al., 2018b). Takahama et al. (2019) reviewed these findings and the overall framework to be used for the two phases of such statistical calibrations: model building (sample selection, spectral preparation, model generation, model selection, model evaluation, and model understanding) and operation (error anticipation and model updating).   Inorganic ions and geological mineral absorption bands have been used

75 for chemical speciation of these substances using FT-IR in prior studies (e.g., Cunningham et al.,
76 1974; McClenny et al., 1985; Pollard et al., 1990; Bogard et al., 1982; Foster and Walker, 1984).

77 Organic absorption bands are useful for measuring OC but also provide spectral information
78 needed to add detailed knowledge of composition not currently measured in air quality
79 monitoring networks – such as organic matter (OM) and organic functional group composition –
80 which is the subject of other work (Reggente et al., 2019; Boris et al., 2019, 2021; Burki et al.,
81 2020). Such calibrations, also combined with factor analytic approaches, can provide source
82 characterization on par with more costly mass spectrometric techniques (Boris et al., 2021;
83 Yazdani et al., 2021a; Hawkins et al., 2010; Takahama et al., 2011; Liu et al., 2012; Corrigan et al.,
84 2013).

85 Although FT-IR shows promise for measuring many constituents in aerosol, it is not without its
86 challenges. One limitation is that not all PM constituents can be measured, or measured with
87 high sensitivity, from the FT-IR spectrum. For instance, NaCl and $MgCl_2$ do not have IR-active
88 substituents. While a multitude of spectral signatures associated with mineral dust arise from
89 their constituent bonds – e.g., the metal-oxygen bonds in oxides (the oxide form is explicitly
90 assumed in estimating dust mass concentrations from elemental composition for the IMPROVE
91 network), some must be predicted from correlation with other constituents (e.g., some forms of
92 iron) if IR-activity is lacking. Other substances are IR-active but have weak responses, such as
93 graphitic carbon (Niyogi et al., 2006; Parks et al., 2021).   The absorption and scattering by the
94 PTFE filter also pose challenges for quantitative analysis. The PTFE-based material changes over
95 time due to change in manufacturer or manufacturing process, and is difficult to fully characterize
96 a priori or treat with simple blank subtraction techniques. PTFE absorption limits full access to
97 the range of spectroscopic information in the mid-IR, for instance in the region of carbon-oxygen
98 bonds that can lead to less than full recovery of OM mass. Additionally, scattering leads to
99 broadly-varying slope in the group frequency region. This scattering artifact is minimized by
100 baselining (Kuzmiakova et al., 2016) and using many standards that have a range of scattering
101 and absorption observed in the network (Debus et al., 2019), yet these techniques can still lead
102 to errors in quantification. Weakley et al., (2018b) demonstrated that calibrations built using one
103 brand of filter can be accurately extended to another brand of PTFE filter with numerically
104 marginal but statistically significant increase in method error (e.g., +2% error for $\alpha=0.05$).
105 However, these studies are insufficient to generalize findings to all types of sampling filters.

106 The goal of this work is to assess the capability of using FT-IR to measure the aerosol chemical
107 composition at all IMPROVE sites. FT-IR quickly and non-destructively collects information-rich
108 spectra from routinely collected PTFE filter samples. Ambient samples from strategically-
109 selected IMPROVE sites are used for calibration and reasonably mimic the composition, matrix
110 effects and substrates of the unknowns, all of which theoretically lead to accurate estimations of
111 concentrations. Using all samples from selected sites reduces maintenance, shipping, processing

112 and coordinating required to maintain intermittent quartz and nylon filter sampling at every site.
113 Sites are selected using data from 2015 and are used for calibrating samples from 2015-2017.
114 Samples from all other (non-calibration) IMPROVE sites are predicted and compared to routine
115 IMPROVE data to assess the quality of prediction. Aerosol components to be measured include
116 TC, OC, EC, inorganic ions, soil elements, particulate mass, and light absorption.

2   Methods

2.1   Network data

119 IMPROVE samples collected every third day at all North American sites (Section S1) from January
120 2015 through December 2017 are included in this study. Fine particulate matter (aerodynamic
121 diameter less than 2.5 micrometers) is deposited on 25 mm diameter filters
122 polytetrafluoroethylene (PTFE, Teflo, Pall Gelman) and quartz filters by sampling air at a nominal
123 flowrate of 22.8 liters per minute from midnight to midnight local time. Parallel 37 mm nylon
124 filters are collected at the same flow flowrate. PTFE filters are analyzed by multiple instruments
125 and archived for future analysis. Nylon filters and a portion of each quartz filter undergoes
126 destructive analysis and the remaining part of the quartz filters are retained for archive.

127 Over the period covered in this study, two different TOR instruments were employed to measure
128 OC, EC and TC. Quartz filters sampled prior to 2016 where analyzed on a DRI Model 2001 thermal
129 optical carbon analyzers (Chow et al., 1993) while filters collected beginning in January of 2016
130 were analyzed on a DRI Model 2015 multi-wavelength thermal optical carbon instrument (Magee
131 Scientific – Berkley, USA)(Chow et al., 2015). Both instruments use the IMPROVE_A protocol
132 (Chow et al., 2007b), which outlines the temperature step, gaseous environment in the
133 instrument and that reflectance is used to define the split point between OC and EC. To correct
134 for gas phase adsorption onto the quartz filter, the monthly median field blank OC concentration
135 is subtracted from each OC measurement during that sample month. Carbon concentrations are
136 reported in $\mu g/m^3$.

137 An in-house Hybrid Integrating Plate and Sphere (HIPS) system evaluates light absorption from
138 the PTFE filters in the IMPROVE network (White et al., 2016). In this work, the measured
139 absorption coefficient (*Fabs*) is converted into a TOR EC equivalent concentration assuming a
140 Fabs / EC ratio of 10 m^2g^{-1} (Malm et al., 1994). The resulting value, referred to as HIPS Black
141 Carbon (HIPS BC), is used as part of a quality control procedure to evaluate potential outliers in
142 TOR EC measurements.

143 Data from gravimetry and X-ray fluorescence (XRF) analysis obtained from PTFE filters and ion
144 chromatography from the nylon filters are also used in this study. Additional information on
145 routine IMPROVE methods can be found on the IMPROVE website
146 (http://vista.cira.colostate.edu/Improve/). IMPROVE data are available online at
147 (http://views.cira.colostate.edu/fed).

2.2 Outlier removal

Data were screened for outliers to eliminate their influence on the results. Out of the ~61,500 total number of samples in the three-year period, fewer than 800 were excluded from the analysis due sampling issues or missing TOR, XRF or IC data. In addition, 65 samples collected at the Wheeler Peak Wilderness (New Mexico) site between November 2015 and April 2016 were excluded due to an EC contamination caused by a diesel-powered ski lift.

Potential outliers in TOR measurements were investigated by regressing TOR EC against HIPS BC concentrations. Samples with differences exceeding a predefined threshold value (0.68 µg/m^3) were flagged as potential outliers (section S2). The status of these samples was confirmed by building separate TOR EC and HIPS BC calibrations. The poor agreement between TOR EC and FT-IR EC concentrations contrasts with the nearly 1:1 relationship HIPS BC and FT-IR BC predicted values indicating that TOR EC concentrations were likely compromised (Section S2). For the period considered in this study, 112 samples with faulty TOR EC values were identified and excluded from further analysis. The number of valid sample spectra retained in this study is 61,462.

2.3 Fourier-transform infrared (FT-IR) analyses

Since 2015, all PTFE in the IMPROVE network have been analyzed by infrared spectroscopy for research and evaluation purposes. FT-IR measurement occurs after gravimetric analysis and prior to XRF and HIPS to prevent possible loss of volatile species under the mild vacuum in XRF. Three FT-IR spectrometers including one Tensor 27 and two Tensor 2 instruments (Bruker Optics, Billerica, MA) equipped with a pre-aligned mid-IR source and a liquid nitrogen-cooled wide-band mercury cadmium telluride (MCT) detector were used for spectra acquisition in the range 4000 - 420 cm^{-1} by averaging 512 scans at a nominal resolution of 4 cm^{-1}. The single beam signal associated with each PTFE filter was converted to an absorbance spectrum using the most recent zero reference signal, updated hourly.

Previously, it was determined that calibration transfer between multiple FT-IR instruments is not required as long as their spectral response is carefully matched by controlling a set of key environmental and instrumental parameters (Debus et al., 2019). Briefly, each mercury cadmium telluride (MCT) detector is connected to an automatic liquid nitrogen micro dosing system (NORHOF, Ede, Netherlands) designed to improve signal stability and maintain a high signal to noise ratio. The repeatability and reproducibility of the filter position relative to the IR beam is controlled via a house-built sample chamber (4.0 × 5.1 × 4.5 cm) mounted inside the instrument sample compartment. Details regarding the chamber design have been published elsewhere (Debus et al., 2019). Finally, the contribution of water vapor and carbon dioxide to the signal was minimized by continuously purging both the sample chamber and the optical bench with a VCD Series CO_2 adsorber / dryer system (PureGas LLC, Broomfield, CO). For each sample, the acquisition procedure involves a 4 minute purge followed by pectrum collection lasting about 1

185 minute. An in-house macro interfaced to the OPUS software (Bruker Optics, Billerica, MA)
186 controls each step. PTFE filters were measured in transmission mode without sample
187 preparation. No interpolated data (from zero-filling) are included in the final raw spectra.
188 Collected spectra are subjected to weekly quality control procedures detailed in (Debus et al.,
189 2019). Duplicate and replicate measurements were also performed to evaluate instrument
190 stability and found to be within +/- 10%.

191 ## 2.4   Multivariate Calibration Model - Partial Least Squares (PLS) Regression
192 While the presence of certain category of atmospheric compounds can be identified qualitatively
193 from an FT-IR spectrum, an accurate quantification of their concentration requires calibration.
194 PLS is a commonly used algorithm to relate a multi-wavenumber measurement to any particular
195 sample properties such as concentration (Wold et al., 2001). In brief, PLS maximizes the co-
196 variance between a set of response variables (species measurements) and a reference
197 measurement (FT-IR spectra) from which equivalent predicted values are desired. In so doing,
198 the optimal combination of response variables best describing the reference measurement is
199 identified and the selected features are used to build a multivariate calibration. With all least-
200 squares calibration methodologies, concentration-dependent biases in residuals that are
201 determined by the quality of fit (R^2) and dynamic range of the data are expected due to the nature
202 of least-squares estimation (Besalú et al., 2006; Draper and Smith, 1998, pp. 63-64,173,638). For
203 further discussion of these biases, see Section S1.

204 The applicability of PLS to quantify carbonaceous aerosol species (Reggente et al., 2016; Weakley
205 et al., 2016, 2018a) or functional groups (Boris et al., 2019; Ruthenburg et al., 2014) collected on
206 PTFE filters in various monitoring networks and field campaigns has been successfully
207 demonstrated. A complete review of the implementation of PLSR calibration in the framework
208 of atmospheric particulate matter characterization has been recently published (Takahama et al.,
209 2019).

210 To evaluate model performance, FT-IR predicted concentrations were regressed against their
211 reference measurement to quantify residuals and a series of metrics. Reported figures of merit
212 include the coefficient of determination (R^2), bias, error and the method detection limit (MDL).
213 Residuals are defined as the difference between predicted and reference concentrations, bias
214 corresponds to the median residual while error is the median absolute residual. To facilitate
215 inter-model comparison, relative performance metrics were calculated by normalizing the
216 values by their reference value. FT-IR PLSR calibration MDL was estimated from field blank
217 predicted concentrations as the 95th percentile minus the median residuals, as is done for other
218 species in the IMPROVE network http://vista.cira.colostate.edu/improve/wp-
219 content/uploads/2021/07/IMPROVE-SOP-351_Data-Processing-and-Validation_2021_final.pdf.
220 Performance is reported for all samples together regardless if the samples were included in the
221 calibration. This enables comparison between models with different samples used for

222 calibration. Maps of annual median values of the reference method concentration and
223 performance metric are generated for each aerosol component. Isopleths on the maps are
224 calculated using an ordinary Kriging algorithm and are intended to guide the eye to capture the
225 regional nature of the concentrations and performance quality. For the MDL map, the
226 difference between the percent of samples below MDL for the reference method is subtracted
227 from the percent below MDL for FT-IR to indicate if the reference method or FT-IR have more
228 samples below MDL.

229 For further insight into model prediction accuracy, the distribution in FT-IR residuals is
230 qualitatively compared with residuals from collocated measurements. Collocated quartz filters
231 are collected at the Everglades (FL), Hercules-Glades (MO), Medicine Lake (MT) and Phoenix (AZ)
232 sites. Similarly, collocated Teflon filters are sampled at Mesa Verde (CO), Proctor Maple Research
233 Facility (VT), Saint Marks National Wildlife Refuge (FL), Yosemite (CA) and Phoenix (AZ) sites while
234 collocated nylon filters are featured at the Phoenix (AZ), Frostburg Reservoir (MD), Mammoth
235 Cave (KY) and San Gabriel (CA) sites.

236 Data handling and analysis was performed in Matlab R2018a (The MatWorks, Inc, Natick, MA,
237 United States) using the statistics and signal processing toolboxes. PLS was computed via the
238 libPLS Matlab package (v1.9) (Li et al., 2018).

2.5   FT-IR Calibrations for Predicting PM Composition

240 This section presents the design of calibrations for quantifying the concentration of major
241 atmospheric species by taking advantage of the composition-based information embedded
242 within an FT-IR spectrum. In practice, spectra are calibrated against reference measurements
243 from TOR, XRF, IC, HIPS and gravimetric analysis with the aim of predicting concentrations of
244 atmospheric constituents using only spectra of PTFE filters as input.

245 A multilevel model (Snijders and Bosker, 2011; Takahama et al., 2019) is proposed in which
246 dedicated calibration models for subgroups of samples are constructed, and applied according
247 to a predetermined selection criterion for each sample. This model considers two subgroups: i)
248 samples determined to be dominated by biomass burning, which are calibrated with similar
249 samples, and ii) the remaining samples, which are calibrated with samples from a limited number
250 of sites.

251 To establish baseline performance metrics for comparison, a "Global model" in which a single
252 calibration (for each species) is constructed from all samples considered together is described in
253 Section S1 (Supplement).

254 The first step in the development of the Multilevel model consists of screening for biomass
255 burning samples. These samples are removed from consideration during the site selection
256 process. A simple detection method combining estimates of key functional group spectral peak

257 areas and spectral dissimilarity metrics were used to segregate biomass burning samples from all
258 other samples. Next, a Gaussian Mixture Model (GMM) was applied to the spectra of all non-
259 biomass burning samples. The GMM exploits the specificity of the infrared signal for organic and
260 inorganic species. The GMM was implemented with the aim of clustering the non-biomass
261 burning FT-IR spectra into groups sharing similar spectral features (Section 2.5.2). Those groups
262 were later used as part of the methodology for selecting sites with representative atmospheric
263 composition. Spectra from the year 2015 were used as a benchmark to validate the biomass
264 burning detection strategy, build the GMM and establish the list of representative sites where
265 multi-filter collection/multi-analyses should be retained (section 2.5.2). The identified biomass
266 burning samples are used to build a calibration for biomass burning samples (Section 2.5.1).

267 ## 2.5.1 Biomass burning model
268 FT-IR spectra were used to estimate functional group areas and calculate spectral dissimilarities
269 metrics to segregate biomass burning samples from all other samples. Although this paper
270 focuses on using FT-IR to measure the major aerosol components in routine speciated aerosol
271 monitoring networks, FT-IR is more frequently used to measure organic functional groups (e.g.
272 (Russell et al., 2011; Ruthenburg et al., 2014; Boris et al., 2019). Specific regions in the IR spectra
273 correspond to specific functional groups. Peak areas, calculated from baseline corrected spectra
274 (see Section S3 for baseline procedure), for carbonyl, OH and CH were used rather than functional
275 group calibrations for simplicity. Because the relative functional group peak area tends to
276 increase significantly as the cumulative peak area decreases, especially for low mass deposition
277 samples, an estimate of spectral dissimilarities, the squared Mahalanobis distance (D_i^2), for each
278 site is also considered to minimize false detection. The Mahalanobis distance (Mahalanobis,
279 1936; Cios et al., 1998) is a measure of the spectral dissimilarity between a given spectrum at a
280 site and the mean spectrum at the site. Taking advantage of D_i^2 and relative functional group
281 areas, a set of criteria were established from observations at known wildfire sites during wildfire
282 season (O'Dell et al., 2019). First, samples collected under heavy smoke conditions whose spectra
283 fulfill C–H ≥ 2 %, C=O ≥ 15 % and $D_i^2 \geq 3\ \overline{D^2}$ were detected (Section S3). This group of spectra
284 tend to have large D_i^2 values and, consequently, the $3\ \overline{D^2}$ threshold often excludes samples with
285 low to moderate biomass burning contributions. For a more inclusive detection, spectra from the
286 first group were removed from consideration, the D_i^2 values are updated for each sample and
287 the plots were regenerated. The cut-off value for the relative carbonyl functional group area was
288 lowered to 8 % while other parameters were not changed. Spectra identified by the first and
289 second rounds are considered biomass burning samples. This procedure is performed for each
290 site and for each year of sample collection (Section S.3)

291 Recent work has shown that smoke samples may be identified using techniques such as cluster
292 analysis (Burki et al., 2020) similar to the GMM used here and through detection of molecular
293 markers – levoglucosan and lignin – or peak profiles in FT-IR spectra (Yazdani et al., 2021a, b).

294   For the large data set in this work (~20,000 samples in 2015), cluster analysis resulted in
295   multiple clusters that could be associated with smoke-impacted samples likely due to the
296   variations in fuel, oxidation conditions, and contributions from other sources. Therefore, for
297   this work we selected a single group of smoke-impacted samples based on specific organic
298   features known to be present in FT-IR spectra. While the criteria for selecting smoke-impacted
299   samples can be defined differently according to each intended purpose, the method presented
300   here is demonstrated to sufficiently partition the samples for building accurate submodels to
301   predict concentrations of PM constituents.

302   While ions and crustal species are not necessary correlated with wildfire emissions, the Biomass
303   Burning sub-model accounts for interferences that are used to maintain high prediction accuracy
304   for samples collected on smoky days.

305   2.5.2 Limited Sites Model

306   To assess major $PM_{2.5}$ composition regimes in the network and to identify representative sites to
307   use as calibration standards in the Limited Sites model, screening of all FT-IR spectra (except
308   samples identified as biomass burning samples) across all locations and seasons was performed
309   by building a Gaussian Mixture Model (GMM) (Bilmes, J. A., 1998; Hastie, T et al., 2009). The basic
310   idea behind GMM is to group FT-IR spectra into clusters of similar spectral shape using a
311   probabilistic approach describing the likelihood that any given spectrum belongs to a particular
312   class. To minimize the concentration dependence and emphasize composition, raw spectra were
313   transformed to second derivative spectra using a 2nd order, 21 point, Savitzky-Golay filter
314   (Savitzky and Golay, 1964), differenced with filter blank spectra and divided by their respective
315   Euclidean norm (Bro and Smilde, 2003). Additional details about the GMM pre-processing and
316   implementation as well as cluster interpretation are provided in Section S4.

317   After classification, a single site per cluster was selected to represent the atmospheric
318   composition captured in that cluster. For any given cluster, the retained location was defined as
319   the site with the largest number of classified spectra with the highest probabilities of belonging
320   to that cluster. To prevent misleading site selection and enhance spatial coverage, the following
321   set of decision rules were used: *i)* if the same site is representative of two clusters, it is ascribed
322   to the cluster with the largest number of classified spectra from that site, *ii)* if none of the
323   retained sites accounts for a given spatial region or known source type in the network, an
324   additional site with the highest number of classified spectra is selected from a nearby cluster,
325   and *iii)* only sites under continuous operation between 2015 and 2017 are eligible for selection.
326   Criteria *ii)* was invoked once to add a site in the Midwest to improve spatial coverage in that
327   region and to capture prescribed fire emissions in Kansas. All non-biomass burning samples from
328   selected sites were used as FT-IR calibration standards for all species and all non-biomass burning
329   samples are predicted with these models. Once established, the selected sites are not re-
330   evaluated but instead are used in all subsequent years as would occur in practice.

331   2.5.3 Application of Multilevel Model
332   The Multilevel model is the combination of the FT-IR predicted concentrations from the Limited
333   sites and Biomass burning models. Multilevel modeling will be discussed in the context of
334   carbonaceous aerosols before extending the modeling to other atmospheric constituents with
335   detectable infrared signatures. In addition to OC and EC, species evaluated for FT-IR prediction
336   include $PM_{2.5}$ mass, soil elements (silicon, aluminum, calcium, titanium, iron), anions (sulfate,
337   nitrate) and HIPS BC. As mentioned previously, NaCl is not IR active and so there is no direct
338   measure of seasalt from FT-IR. Next, the years 2016 and 2017 will be examined to assess the
339   long-term stability of the proposed Multilevel strategy by screening for smoke samples and re-
340   calibrating each year using the sites selected using 2015 data.

3   Results and discussion

342   In the following sections, the quality of FT-IR based calibrations for quantifying aerosol
343   composition across continental US and their long-term applicability to large speciation
344   monitoring networks will be assessed. Section 3.1 describes the selected calibration samples for
345   the Biomass Burning and Limited Sites models. In Section 3.2, Biomass Burning and Limited
346   model performance will be briefly reviewed before exploring the Multilevel FT-IR predictions for
347   all samples. Initially focused on carbonaceous species on PTFE samples collected in 2015, FT-IR
348   predictions will be extended to other atmospheric constituents and years.

3.1   Multilevel modeling – Calibration sample selection

350   Biomass burning sample selection
351   Using the methods described above, 492 samples impacted by biomass burning emissions were
352   identified in 2015 (2.5 % of the network), 288 samples in 2016 (1.5 %), and 817 samples in 2017
353   (3.7 %). The mean OC concentration of the biomass burning samples range was 5.6 – 8.3 μg/m^3
354   with maximum concentrations extending from 44 to 97 μg/m^3 over the three year period.
355   Similarly, per year, the mean EC concentration varies between 0.6 – 0.9 μg/m^3 with maximums
356   up to 2.9 – 3.9 μg/m^3. Mean OC/EC ratios are larger than 7, in agreement with past literature
357   (Schichtel et al., 2008; Sorooshian et al., 2011). Analysis of the detected samples shows reliable
358   spatial and seasonal distributions, consistent with biomass burning emissions predominantly in
359   summer and fall across the Pacific North West and Northwestern US (Section S3). Two-thirds of
360   the identified samples were selected (Section S5) as calibration standards for the calibration and
361   resulting model was applied to the remaining third of the smoke impacted samples.

362   Limited Sites model – clusters and retained sites
363   Figure 1 shows the spatial distribution and annual average composition (from routine IMPROVE
364   data) of the 21 sites selected for the Limited sites model calibration. From a spatial standpoint,
365   retained sites appear reasonably scattered across the network including Hawaii and the Virgin
366   Islands. Clusters are represented by a distribution of urban and rural sites. One urban cluster is

represented by Fresno and contains mostly urban samples from Fresno and Phoenix. All other clusters contain mostly rural and pristine sites. However, two other urban sites were retained, Phoenix and Birmingham. The Phoenix cluster contains samples from the southwest in the spring. The Birmingham site along with the Tallgrass site represent a non-western cluster in the spring and summer.

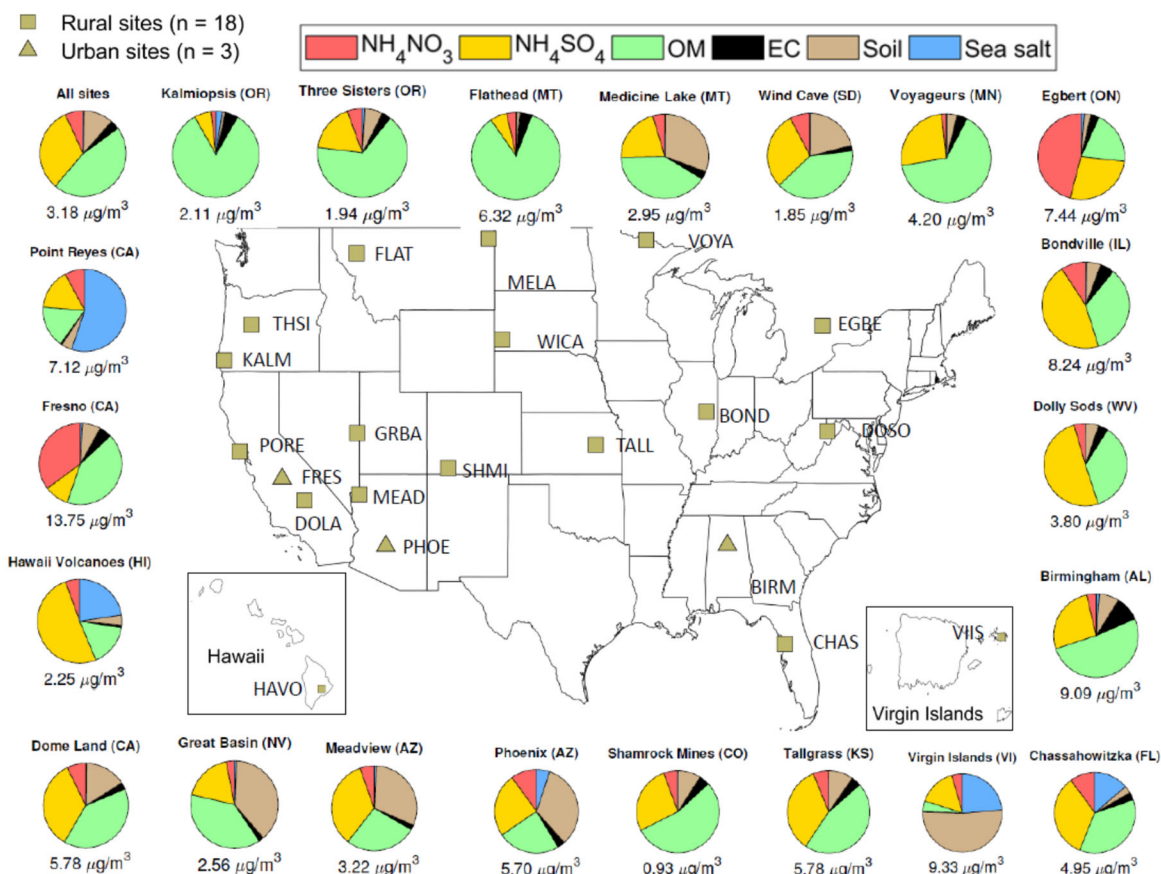
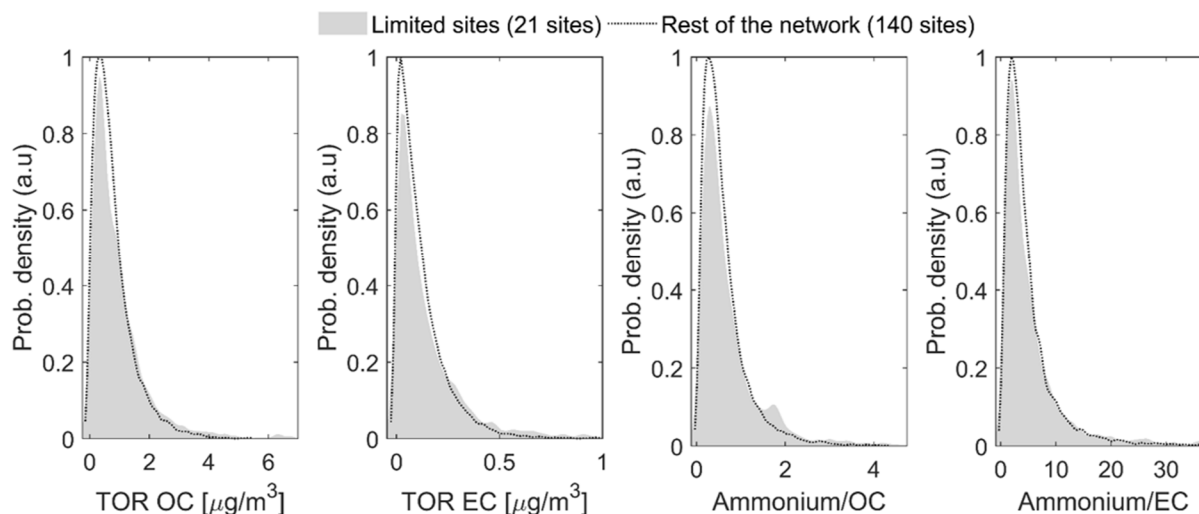



Figure 1: Spatial distribution, median PM$_{2.5}$ concentration and composition of the 21 representative sites. The composition is obtained from routine IMPROVE (non-FT-IR) measurements and the IMPROVE reconstructed fine mass equation (http://vista.cira.colostate.edu/Improve/reconstructed-fine-mass/) to calculate soil and seasalt. Sites are identified by the four letter site code which is the first four letters of a single word site name (Fresno = FRES) or the first two letters of the first and second word for two word site names (Dome Land = DOLA). The top left pie chart shows the median PM$_{2.5}$ composition across all sites and samples for comparison.

382   The clusters are also seasonally distributed (Section S6): five clusters are dominated by fall -
383   winter samples, ten clusters containing summer samples (along with varying number of spring
384   and fall samples), two clusters are predominately spring and one is spring - fall. Three clusters
385   have little seasonality.

386   Because FT-IR spectra are clustered based on composition, the first step in assessing the
387   representativeness of the 21 sites is to compare the concentration ranges. For this purpose,
388   distributions in TOR OC and EC concentrations excluding biomass burning samples are compared
389   for the 21 sites used for calibration and the 140 remaining sites. In Fig. 2, the two probability
390   density functions are very similar for both OC and EC despite large differences in sample
391   populations (2572 and 16,543, respectively). In addition to matching the range of carbonaceous
392   concentrations observed in the rest of the network, the presence of species interfering with
393   organic functional groups should also be accounted for by the calibration. Because ammonium
394   absorptions overlap with carbonaceous absorptions, situations where ammonium to OC and
395   ammonium to EC ratios are different between calibration samples and samples to be predicted
396   were associated with additional sources of bias and error (Dillner and Takahama, 2015a, b).
397   Although not measured in IMPROVE, ammonium concentration is approximated from nitrate and
398   sulfate assuming both species are fully neutralized. The corresponding probability distribution in
399   Fig. 2 confirms the equivalence between the ranges of ammonium/OC and ammonium/EC
400   concentrations spanned by the Limited sites samples and the overall network. In section S6, Fig.
401   S6-3 shows reasonable agreement between the selected sites and the rest of the network for
402   PM2.5 mass, ions, elements and HIPS BC. Together, these results suggest the list of 21 sites is a
403   suitable representation of network variations in OC and EC and their relative proportion to
404   ammonium, and for all other predicted constituents.

405

The spatial and seasonal as well as the urban and rural diversity supports the compositional diversity of the selected sites as shown in Fig. 1. The three urban sites have distinct characteristics. At the Fresno, CA site, the composition is dominated by nitrate (35 %) and organic matter (42 %). A large number of autumn – winter samples were included in the cluster which is consistent with agriculture and residential wood burning activities (Ngo et al., 2010) as well as with the formation of secondary aerosols during stagnation events and a low inversion layer (Watson and Chow, 2002). Phoenix, AZ site features a strong soil component (33%) associated with spring dust storms and windblown dust and equal proportions of ammonium sulfate (25 %) and OM (24 %) occurring mostly in spring and summer. The ammonium sulfate and organic matter has been attributed to regional power production and traffic (Brown et al. 2007). In contrast, Birmingham samples show little seasonal trend with elevated OM (52 %) and EC (10 %) fractions originating from various combustion processes including vehicle exhaust, biomass burning and biogenic secondary organic aerosols (Blanchard et al. 2016). The other dominant species at this site is ammonium sulfate (26 %), characteristic of coal burning and industrial activities in the Eastern US (Watson et al. 2015).

Among rural sites, four noticeable patterns in $PM_{2.5}$ composition are distinguishable. The first corresponds to OM fractions accounting for more than two-thirds of the filter mass. High OM samples are encountered at four locations in Northwestern US, namely the Kalmiopsis (OR), Three Sisters (OR), Flathead (MT) and Voyageurs (MT) sites. Samples from Voyageurs (MN) and Flathead (MT) sites are from Summer-Fall and present elevated median $PM_{2.5}$ concentrations (4.20 $\mu g/m^3$ and 6.32 $\mu g/m^3$, respectively) and very large percentage of OM consistent with biomass burning emissions. Kalmiopsis (OR) and Three Sisters (OR) samples have a lower and nearly identical median $PM_{2.5}$ concentration ($\approx$ 2 $\mu g/m^3$) but differ in their monthly distribution with the former displaying more winter samples than any other season whereas the later shows little seasonality.

The second type of sites have high OM and sulfate concentrations. Both Shamrock Mines (CO) and Tallgrass Prairie (KS) sites have larger OM than sulfate content. However, the Colorado site has more autumn – winter samples, represents samples in the Rockies and Alaska and an overall small median $PM_{2.5}$ concentration (< 1 $\mu g/m^3$). The Kansas site has a majority of spring samples, representing non-western samples and has a significantly larger $PM_{2.5}$ concentration ($\approx$ 6 $\mu g/m^3$) that is attributed to prescribed burning near the Tallgrass site (Whitehill et al. 2019). Other sites have higher median sulfate concentrations (~50%) than OM concentrations (~40%) such as Dolly Sods (WV) and Bondville (IL). The monthly sample distribution indicates seasonal influences: Bondville (IL) samples are mostly from the summer and the concentrations are relatively high

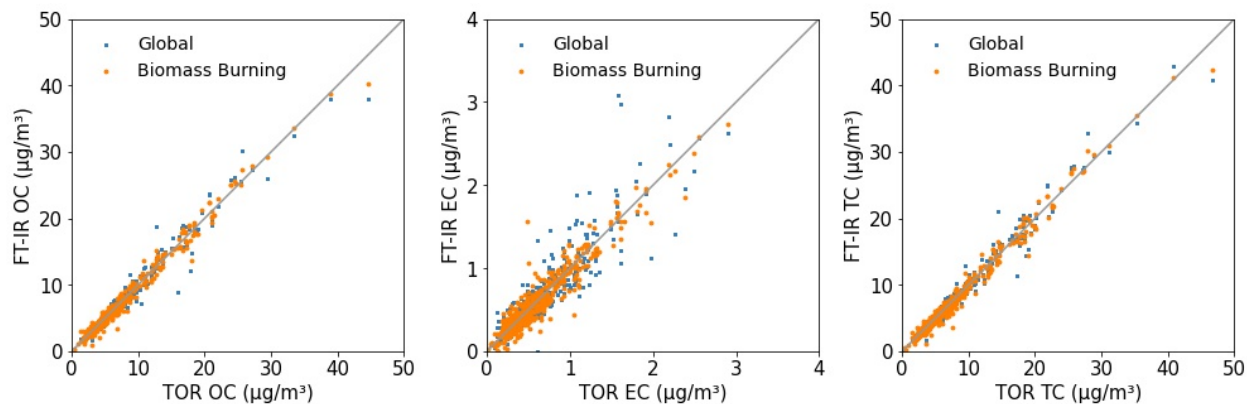
443   while the Dolly Sods (WV) site samples are mostly not in the summer with lower concentrations.
444   Because the spectra were normalized to minimize influence of concentration, these two clusters
445   likely have different organic composition even though the relative amount of OM is the same.
446   Finally, sites where sulfate and OM are present in equal proportions (≈ 36 %) are reported at the
447   Dome Land (CA) and Chassahowitzka (FL) pristine sites mainly featuring spring – summer and
448   winter samples, respectively.

449   A third group of rural sites contains a large fraction of soil (> 20 % of the total mass). The Virgin
450   Islands (VI) site presents the highest soil fraction across the network with 52 % of the total $PM_{2.5}$
451   mass from soil, mostly originating from long-range Sahara soil dust transport (Holmes and Miller
452   2004). In addition to sulfate and OM, elevated soil contributions are observed for the Wind Cave
453   (SD), Meadview (AZ), Medicine Lake (MT), and Great Basin (NV) sites with soil content between
454   20 and 40%. Although the seasonality is somewhat different between these sites, they all have
455   many samples from the spring suggesting the dust is due at least in part to spring dust storms
456   and may also contain resuspended road dust and more localized dust sources.

457   A fourth and final distinct category of $PM_{2.5}$ composition includes a collection of sites with unique
458   local atmospheric pollution sources, specific to those locations. The Hawaii Volcanoes (HI) site
459   where sulfur is emitted as part of the volcanic activity, contains 51% sulfate along with sea salt
460   (23 %). Another location with unique composition is the Point Reyes (CA) site where the sea salt
461   contribution reaches 55% of the median filter mass for the clustered samples, larger than any
462   other marine site in the network. Finally, the Egbert (ON) Canadian site, representing the upper
463   Midwest in winter is dominated by nitrate (46 %), sulfate (27 %) and OM (20 %).

464   As described above, the 21 sites retained for the Limited sites sub-calibration present seasonal,
465   regional and compositional features consistent with known or expected trends in $PM_{2.5}$ across
466   the network. The median $PM_{2.5}$ mass at those locations covers a broad range of concentrations
467   ranging from 0.93 μg/m^3 to 13.75 μg/m^3 and includes both urban and rural sites. Capturing the
468   large variability in $PM_{2.5}$ composition and concentration is essential to ensure the proposed site
469   list is a representative subset of the parent network. However, it should be mentioned that the
470   proposed site list is not unique but is one of the many feasible solutions since sites whose samples
471   clustered together in the GMM are likely interchangeable.

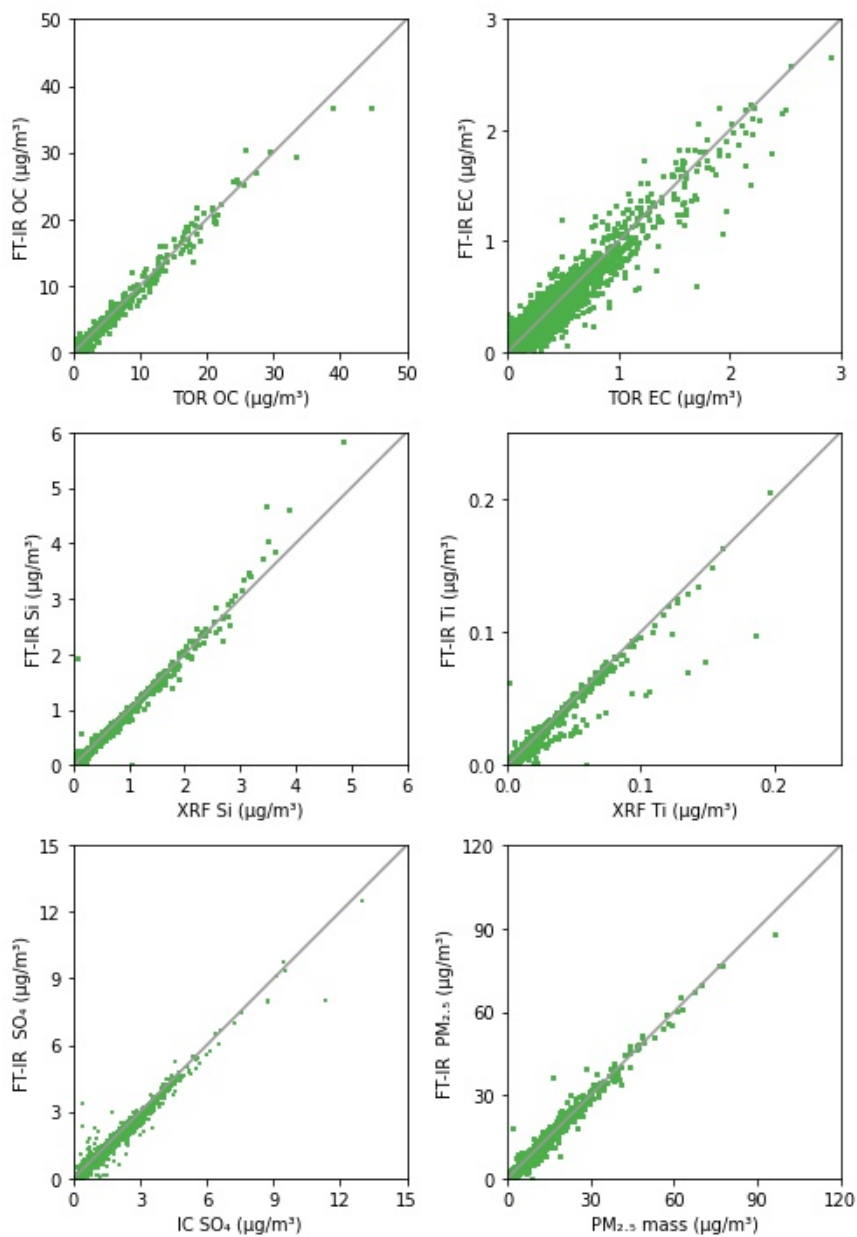
472   ## 3.2   Evaluation of Biomass Burning Model
473   Prior to describing the overall results from the Multilevel model, the Biomass Burning model is
474   evaluated to determine if the biomass burning model improves predictions for those samples.
475   To evaluate the quality of the biomass burning model, the predictions are compared to a global
476   model (section S1) which contains a few samples from all 160 sites. Due to the selection
477   method of calibration standards for the global modal, most of the samples are non-smoke
478   samples but a few smoke samples are included. Visual inspection of Fig. 3 suggests the

479 equivalence of the biomass burning models to the global model at the lower end of the
480 concentration range. However, improvement in prediction accuracy can be claimed at high
481 concentrations for the Biomass Burning model. The gain in model performance is subtle for OC
482 and TC; however, for EC, predictions benefit from having a dedicated calibration for samples
483 impacted by wildfire emissions, with an increase in R^2 from 0.747 to 0.902 (Section S7).

484

485 **Figure 3:** Inter-model OC (left), EC (middle), TC (right) comparison between global (section S1)
486 and Biomass Burning predicted concentrations for the 492 samples classified as biomass burning
487 in 2015. EC prediction, in particular, benefit from having a dedicated Biomass Burning calibration
488 model.

489 Therefore, we retain the biomass burning model as part of the multilevel model and present
490 the results for the Multilevel model below.

491 3.3   Multilevel modeling – Performance evaluation
492 3.3.1   Carbonaceous aerosol predictions
493 Figure 4 shows the correspondence between FT-IR Multilevel concentrations for OC and EC and
494 TOR OC and EC measurements for 2015 (plot for TC can be found in Section S9) and Table 1 lists
495 the prediction metrics for all 3 carbonaceous components. The visual agreement between FT-
496 IR and the reference measurements of TOR OC and EC is high but EC shows higher scatter than
497 the other measurements. Table 1 indicates that FT-IR OC and TC has higher prediction quality
498 than EC but both perform satisfactorily. FT-IR OC and TC error is on par with TOR precisions
499 (Table 1) indicating that on average FT-IR does not add significant additional error to the
500 measurement. FT-IR EC predictions, however, have higher error than TOR precision. With
501 respect to reference (TOR) measurements, concentration-dependent biases in residuals that
502 are determined by the quality of fit (R^2) and dynamic range of the data are expected due to the
503 nature of least-squares estimation (Besalú et al., 2006; Draper and Smith, 1998). For bias
504 defined as FT-IR predictions minus the reference (TOR) measurement, least-squares estimator
505 causes an apparent linear bias which is positive at the low end of the concentration range and

506   negative at the high end of the concentration range (see Section S8 for further discussion). The
507   satisfactory agreement between FT-IR and TOR concentrations as well as the equivalence
508   agreements using the global model (Section S1) support the validity of the proposed Multilevel
509   modeling in the context of carbonaceous aerosols prediction from PTFE filters in large
510   speciation networks.

511

512 **Figure 4**: Comparison of predicted FT-IR OC, EC, Si, Ti, SO_4 and mass concentrations using the
513 Multilevel model against their reference measurements. Each subplot contains all 19,608
514 samples collected in the year 2015.

515

516 **Table 1**: Summary of Multilevel model performance for IR-active atmospheric constituents for
517 19,608 spectra analyzed by FT-IR in the year 2015.

Species	R^2	Bias [μg/m³]	Bias (%)	Error [μg/m³]	Error (%)	Reference Data Error[1] (%)	MDL [μg/m³]	< MDL (%)
OC	0.983	0.01	1.6	0.08	12	10	0.06	0.9
EC	0.912	0	1.7	0.02	30	15	0.04	20.7
TC	0.984	0.01	1.2	0.08	12	11	0.07	1.3
BC	0.92	0	-0.3	0.03	23	---	0.04	19.3
Si	0.983	0	2.2	0.01	11	13	0.01	9.7
Al	0.985	0	2.2	0	12	10	0	4.7
Ca	0.979	0	1.1	0	13	9	0	6.9
Ti	0.941	0	2.7	0	21	16	0	14.9
Fe	0.95	0	1.1	0	25	8	0.01	19
SO_4	0.983	0	0.1	0.03	6	2	0.03	0.9
NO_3	0.927	0.02	15.3	0.07	54	8	0.07	21.8
$PM_{2.5}$ Mass	0.985	0.03	1	0.18	6	6	0.25	1.1

518 [1]Median relative error for TOR, XRF, IC and gravimetric analysis. OC, EC and TC median relative error estimated
519 from collocated sampling as measurement error/uncertainty is not reported by IMPROVE for this components.
520 For all other components, the normalized error was calculated as the uncertainty divided by the concentration
521 prior to selecting the median. BC is not reported by IMPROVE so measurement error is not estimated.

522 In addition to OC, EC and TC, light absorption which is predominantly due to black carbon, is also
523 a measure of one fraction of the carbonaceous aerosol. FT-IR calibrations are found to be
524 adequate for replicating HIPS BC measurements (Section S9). As expected, the corresponding
525 model is similar in performance to EC with R^2 and relative error of 0.920 and 23.3 %, respectively
526 (Table 1). FT-IR BC residuals have a broader interquartile range than in the HIPS BC collocated
527 data (Section S9). We attribute this effect to a difference in signal to noise ratio and sensitivity to
528 chemical interferents between the two analytical techniques. While HIPS exploits the strong
529 absorption properties of refractory carbon in the visible domain, the weak absorptivity of EC in
530 the mid-infrared domain (Niyogi et al., 2006) and the presence of overlapping species makes the
531 quantification less accurate.

532 Further exploration of the regional and site by site quality of data is made via contiguous United
533 States (CONUS) maps of annual median reference method concentrations (left), difference in %
534 below MDL between FTIR and reference method (middle) and relative error (right) are shown in
535 Figure 5 for OC and EC. TC is very similar to OC and BC is very similar to EC.

536 Maps for all constituents with annual median FTIR and reference method concentrations, as well
537 as annual median prediction metrics are shown in Section S10.

538

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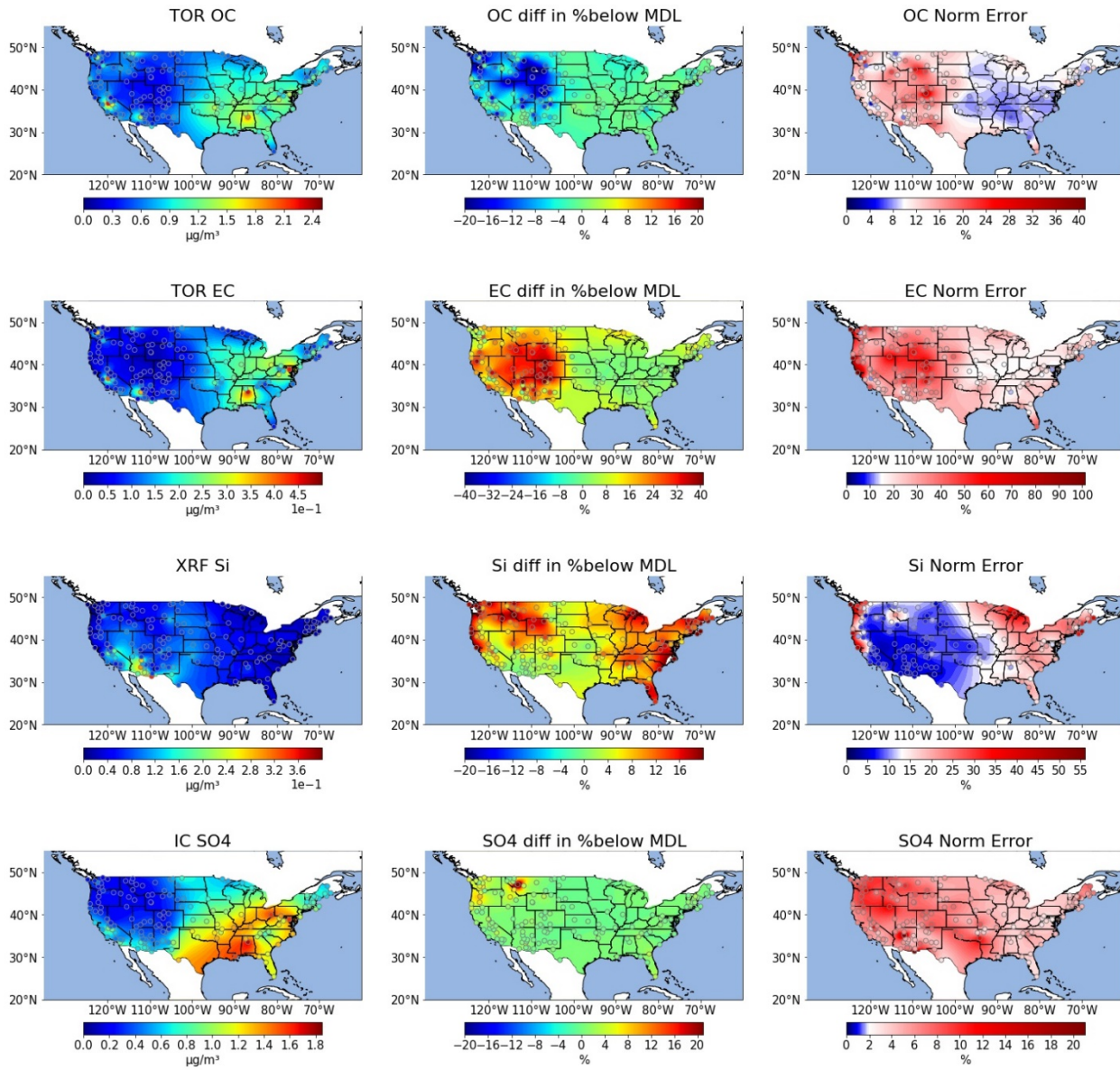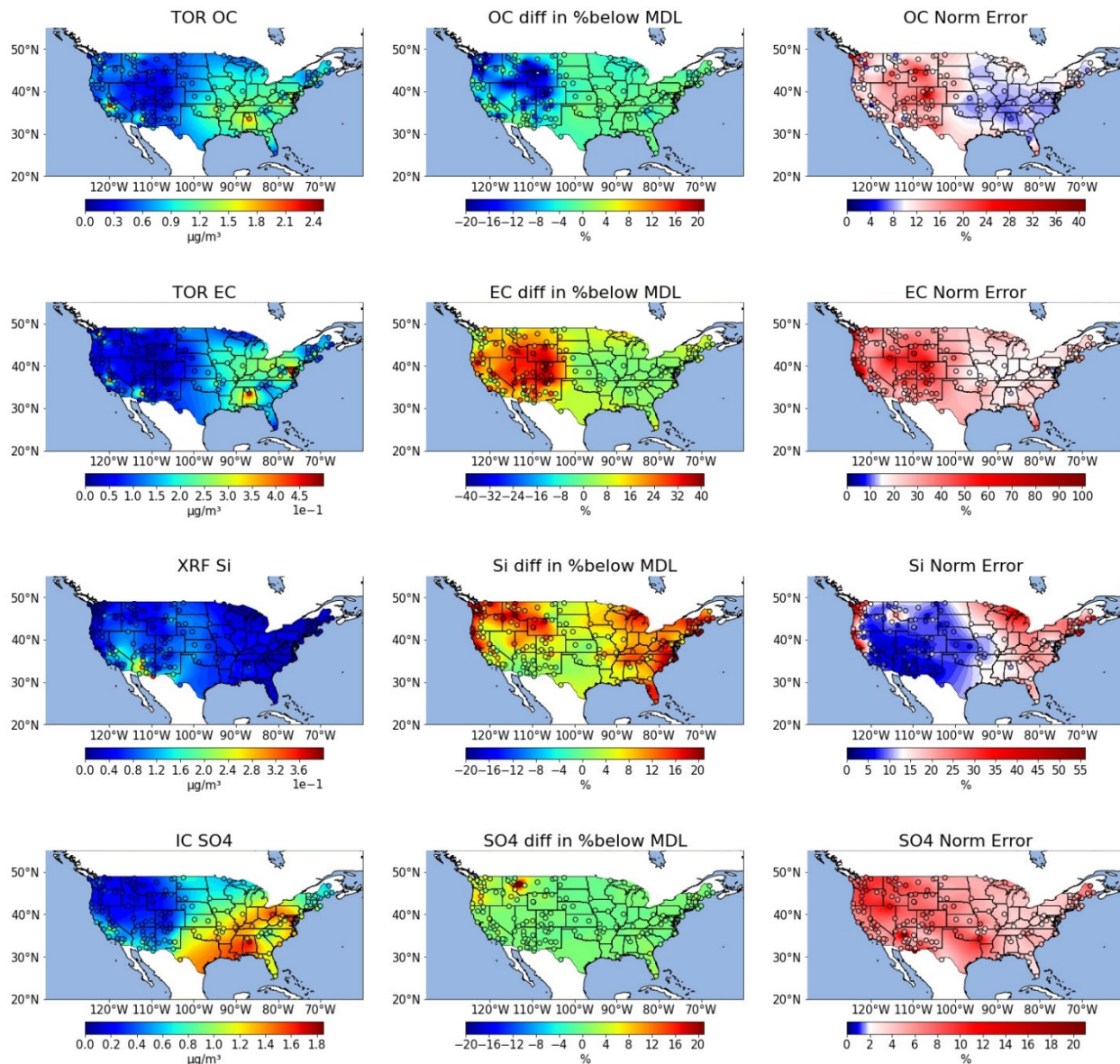
Figure 5. Annual median reference method concentrations (left), difference in % below MDL (middle) and normalized relative error (right) per site for OC, EC, silicon, and sulfate for CONUS for 2015. For the MDL plot, sites in green and blue indicate that the FTIR has the same or fewer samples below MDL than the reference method. Sites in yellow and red have more samples below MDL for FTIR than for the reference method. For the relative error maps, the median relative error of the reference method estimated using methods described in Table 1 is white. For sites in blue, FTIR has lower relative error than the reference method and sites in red are higher.

549   Annual median maps of FT-IR OC and TOR OC as well as maps of FT-IR EC and TOR EC

550   (Supplemental material S10) are nearly identical. As shown in Figure 5, annual median OC and

551   EC concentrations are highest at the four urban IMPROVE sites of Seattle, WA, Fresno, CA,

552   Phoenix, AZ and Birmingham, AL than the rural sites and are higher in the east than in the west.

553   For OC, the relative error is lower than the TOR relative error in the east (where concentrations

554   are higher) and higher than TOR relative error in the west. FT-IR OC has an equal or lower

555   number of samples below MDL than TOR at all sites. For EC, FTIR relative error is higher than

556   TOR relative error at almost all sites. The percentage of samples of EC that are below MDL for

557   FTIR is similar to or are slightly higher than TOR in the eastern US where EC concentrations are

558   higher and are significantly higher than TOR in the western US where concentrations are lower.

559   These patterns indicate that FTIR does not add error to OC measurements when concentrations

560   are above ~0.75 μg/m^3 but does add some error at lower OC concentrations and for EC

561   measurements.

562   ### 3.3.2   Elemental oxide predictions

563   Taking advantage of known mineral absorbance bands in the mid-infrared range (Hahn et al.,

564   2018; Madejová and Komadel, 2001; Senthil Kumar and Rajkumar, 2013) (Section S9), Multilevel

565   calibrations for soil elements were evaluated for the five crustal elements commonly used to

566   estimate soil: silicon, aluminum, calcium, titanium, and iron (Table 1 and Fig. 4 for Si and Ti). All

567   models present a satisfactory agreement between XRF and FT-IR predicted concentrations (R^2 >

568   0.94).   The quality of prediction of the elemental oxides falls into two groups. The first group

569   includes silicon, aluminum and calcium and is characterized by moderate relative errors (11 – 13

570   %), similar in magnitude to the FT-IR OC model (12 %) and have similar errors to XRF

571   measurements. This indicates that like OC and TC, on-average FT-IR does not add additional

572   uncertainty. The second group includes titanium and iron which have larger relative errors (20.9

573   – 24.8 %), analogous to HIPS BC and EC models (23.3 – 30 %). Comparing residuals to collocated

574   XRF measurements (Section S9) shows that the FT-IR based models have a larger interquartile

575   range. For Fe, XRF uncertainty is quite low and FT-IR adds additional uncertainty to the

576   measurement. XRF Ti measurements have higher error than the other elements but there is an

577   incremental increase in error due to FT-IR. In addition, cross plots of titanium concentrations

578   show a bifurcation (Fig. 4). While most samples fall near their expected titanium concentration,

579   samples collected at the Sycamore Canyon (AZ) site present a systematic negative bias, consistent

580   across years, tentatively attributed to a site-specific soil composition not accounted for by the

581   Limited calibration. Takahama et al. (2019) demonstrated several methods to identify the

582   possible occurrence of anomalous predictions in OC and EC based on comparison of new sample

583   spectra to calibration spectra based on projected PLS scores and regression residual vectors.

584   These samples with systematic negative bias in titanium predictions can presumably be identified

585 using such an approach, provided that compositional differences are detected in the IR spectrum.
586 Although distinct IR fingerprints exist, FT-IR calibrations for quantifying mineral contents should
587 be interpreted with care as specific elements may be indirectly quantified through their
588 correlation with another element even in the absence of clear IR signature (Hahn et al., 2018).
589 For instance, the variable importance in projection (VIP) scores for the Si, Al, and Ti calibrations
590 suggests use of similar spectral variables, with small differences, for prediction of these species
591 (Section S9). However, the 21 GMM sites coverage still meet the necessary requirements for
592 providing a reliable insight into soil composition in the IMPROVE network.

593 Figure 5 shows the distribution of concentrations of XRF Si across CONUS. The highest
594 annual median concentrations are in the southwest. Similar patterns are found for Al, Ca,
595 Ti and Fe except that high Fe concentrations are also observed at the urban sites,
596 particularly Fresno, CA and Birmingham, AL (Figures S10-6 through S10-9). For Si, FTIR
597 normalized error is lower than XRF in the west where concentrations are higher. For Ca, Ti
598 and Al, FT-IR normalized error is lower only in the southwest. For Fe, FT-IR is above XRF
599 normalized error. The percentage of samples below MDL are similar to XRF (0-10%
600 different) in the southwest and central US and modestly higher (15-20%) in the northwest
601 and eastern US for Si. For Fe, the spatial pattern is similar but the FTIR % below MDL is up
602 to 50 % higher than XRF. However, for Al, Ca, and Ti, FTIR percent below MDL is
603 approximately the same or lower than XRF at all sites.
604

605 3.3.3   Inorganic ions

606 The two most abundant inorganic anions quantified in the network, nitrate and sulfate, can also
607 be measured by FT-IR (absorption bands used for prediction are discussed in Section S9). FT-IR
608 sulfate concentrations display a satisfactory agreement with the reference IR measurements
609 (Fig. 4). Model performance metrics include R^2 above 0.98 and relative error of 6 %. The relative
610 error is the same as for FT-IR PM$_{2.5}$ and lower than OC, TC, and Si (Table 1). However, IC
611 measurements have even lower error than FT-IR sulfate. Compared to sulfate, FT-IR nitrate
612 concentrations (Section S9) are characterized by a moderate drop in the overall model
613 performance (R^2 = 0.927) while relative bias and error exceed 15 % and 50 %, respectively and
614 the error far exceeds reference IC nitrate measurement error. A direct comparison against
615 differential nitrate concentrations at collocated sites highlights the broad uncertainty in
616 determining nitrate content from PTFE filters (Section S9, Figure S9-3). Unlike nylon filters for
617 which nitrate is trapped on the surface, nitrate is known to evaporate from PTFE filters and the
618 extent of volatilization is dependent on temperature and relative humidity during and after
619 sampling. This causes a discrepancy between the mass of nitrate deposited onto the nylon filter
620 and the mass of nitrate on the PTFE filter (Eldred and Ashbaugh, 2004), therefore FT-IR

621   calibrations with the nitrate measurements by IC from nylon filters as the reference should be
622   used with caution. Although there are physical limitations to measuring ambient nitrate on
623   PTFE filters, a measure of nitrate on PTFE filters which corresponds to its contribution to the
624   gravimetric mass is useful for mass closure and data validation. FT-IR has been shown to be
625   useful for measuring and evaluating nitrate under controlled laboratory conditions (ex. Wu et
626   al., 2007). For network samples, nitrate could be measured using laboratory calibration
627   standards and this effort will be addressed in future work.

628   The annual median sulfate concentrations by IC are shown in Figure 5. Annual median
629   concentrations are highest in the southeast and eastern US with a gradient in concentrations
630   observed across the midwest. The median relative error for sulfate by IC is only 2% and all FTIR
631   sulfate has higher relative error. There are however, spatial differences. In the eastern US
632   sulfate relative error is less than 15% but in the west, it is considerably higher, peaking in
633   Wyoming where concentrations are very low.   The % below MDL is very similar for FTIR and IC
634   across the continent. Due to volatility of nitrate, the nitrate metrics for FTIR are poor compared
635   to sulfate (Figure S10-11).

636   3.3.4   PM$_{2.5}$ mass predictions
637   Since the major aerosol species are shown to be reasonably well measured by FT-IR, it was
638   anticipated that PM$_{2.5}$ mass calibration would perform well. The PM$_{2.5}$ model presents reliable
639   filter mass predictions (R^2 = 0.985) characterized by relative bias and error that are 1/3 to 1/2 of
640   those for OC and on par with gravimetric error (Table 1). The cross plot of gravimetric mass and
641   FT-IR predictions (Fig. 4) and maps of predictions metrics (Figure S10-12) show that PM$_{2.5}$ mass
642   can be accurately predicted across a broad concentration range indicating that FT-IR spectra of
643   PTFE filters do not contain interferents or other limitations that make PM mass predictions error
644   prone.

645   3.4   Long term stability
646   Finally, Multilevel calibrations are extended to 2016 and 2017 to evaluate the inter-year
647   consistency and determine if the assumptions behind Limited Sites and Biomass Burning models
648   remain valid over time. For each sampling year, new calibrations were developed following the
649   framework established for 2015. Models were recalibrated with data from the 21 sites and
650   biomass burning samples were detected by the functional group screening procedure. Fig. 6
651   shows the median relative bias (top) and error (bottom) for the three years of data (cross plots
652   and prediction metrics shown for all predicted species for 2016 and 2017 in Section S11). These
653   results indicate that the modeling methodology provided reasonably consistent results across all
654   three years.

655   Normalized bias for most species is below 3% and normalized error is consistent for all species
656   across all three years. The relative bias for EC and BC are similar to other species in 2015 and

657 2017 but in 2016 they are larger in magnitude than the other two years and different in sign.
658 2016 is the first year of TOR data from the multiwavelength TOR instruments (Chow et al., 2015)
659 so higher bias could be potentially be related to the new instruments. However, the HIPS
660 instrument was overhauled beginning in 2017 which provides no explanation for high bias in 2016
661 (http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory/da0041/da0041_HIPSmodificat
662 ions.pdf).   Further, the EC and BC calibrations are independent of each other except for using
663 the same filters for calibrations (as all species do) so the fact that the median bias is roughly equal
664 but opposite in sign is not due to codependence of the models.

665 In future work, calibrations models will be updated more frequently than annually with the most
666 recent year of ambient samples which may smooth biases and errors due to changes to
667 atmospheric condition and instrument drift.

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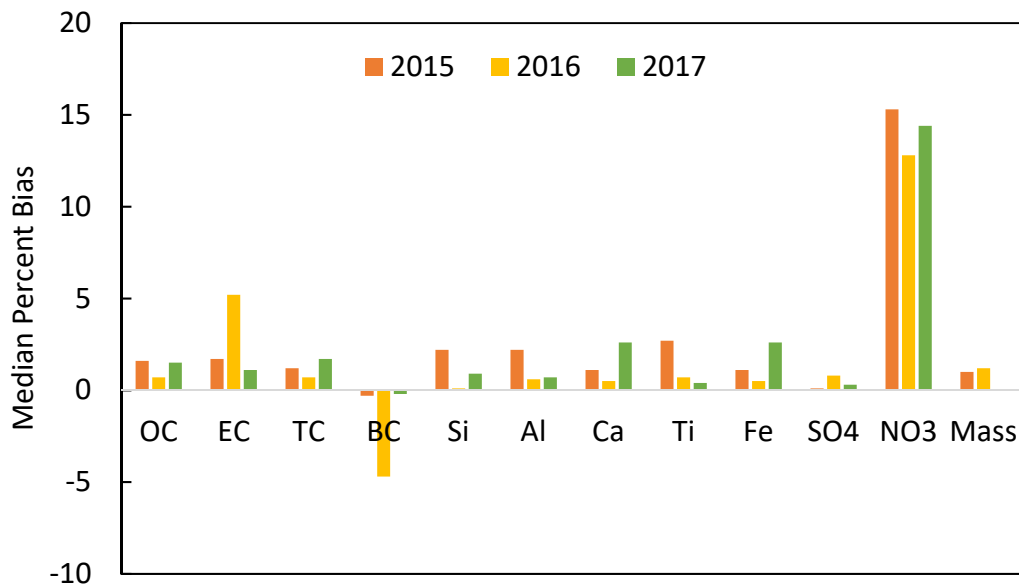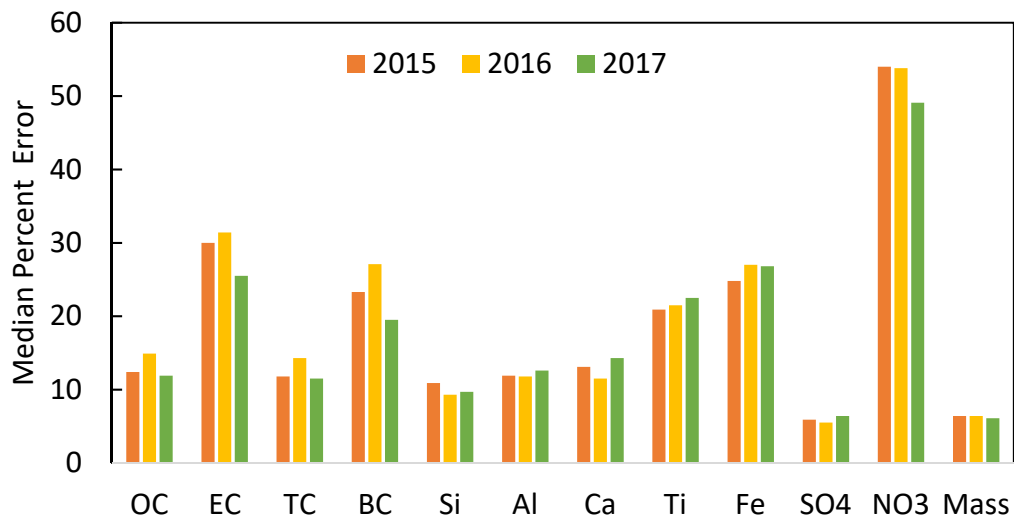
Figure 6. (top) Median Percent Bias and (bottom) Median Percent Error for each constituent measured for each year.

672

4 Conclusion

In this paper, we investigate the feasibility of using FT-IR to measure speciated PM2.5 concentrations in a large monitoring network. In this method, all sites in the network collect PTFE

676 filters for FT-IR analysis. A few select sites, used for calibration, retain all sampling and analyses
677 of current IMPROVE sites to enable re-calibration of the FTIR method on a routine basis. Re-
678 calibration is especially important as atmospheric changes occur and as conditions in the network
679 evolve over time, for example new reference instruments, new or significantly modified FT-IR
680 instruments, changes to sampling protocol or changes in filter material. The validity of such a
681 design was evaluated with all PTFE filters collecting $PM_{2.5}$ aerosols at 161 IMPROVE sites in 2015
682 and then tested for all filters in 2016 and 2017.

683 A multi-level modeling algorithm was used whereby smoke impacted samples are identified and
684 predicted by one model and the rest of the samples are predicted by another model developed
685 from 21 selected IMPROVE sites. The data from the two models are combined to evaluate
686 performance of the FT-IR method. The selection of sites was performed such that if one of the
687 21 sites ceases to operate, another site, selected from the same compositional cluster can be
688 used for calibration.

689 The cross-plots and prediction metrics indicate that the Multilevel model is equivalent to
690 conventional calibrations built from samples from every available site. Reliable performance in
691 predicted concentrations were reported for a broad range of atmospheric constituents with
692 detectable infrared signatures such as OC, EC, TC, sulfate, soil elements (Si, Al, Ca, Ti, Fe), light
693 absorption, and $PM_{2.5}$ mass. Due to volatilization off the PTFE filter, nitrate measurements were
694 found to be unsatisfactory. NaCl is not active in the infrared and cannot be measured. The
695 calibration method was developed using data from 2015, and the same methodology was applied
696 to 2016 and 2017. The model performance metrics in all three years were similar. Results across
697 ~61,500 FT-IR spectra highlight the suitability of the Multilevel calibration design to quantify
698 multiple atmospheric $PM_{2.5}$ species in large monitoring networks.

699 This work presents an alternative, lower cost, filter analysis method to measure speciated aerosol
700 in a routine monitoring network. This could be a valuable addition to routine speciated aerosol
701 monitoring networks, such as IMPROVE, by incorporating monitoring sites that collect samples
702 on only a PTFE filter for subsequent analysis. This would provide the opportunity to have a subset
703 of less expensive monitoring site, which could be used for scoping studies to understand the
704 aerosol composition in unmonitored locations. It could also serve as a network cost savings
705 method by having a subset of network sites collect aerosol samples on Teflon filters only.
706 However, the inability to measure particulate nitrate is a significant deficiency for using this
707 method to replace existing monitoring sites. The FTIR derived aerosol concentrations are also a
708 semi-independent measurement from the routine speciated aerosol measurements. Therefore,
709 routine FTIR measurements would provide valuable QA/QC information for any speciated
710 monitoring network. In addition, FTIR derived concentrations could be used to substitute for
711 missing concentrations in the case where the Teflon sample is valid, but filter samples or analyses
712 on the nylon or quartz fiber filters are not.

713   For IMPROVE's urban counterpart, the CSN network, after evaluation of the quality of

714   predictions in CSN, this framework could be used to accomplish goals similar to those of

715   IMPROVE. Additionally, this method could be used to predict samples collected in the Federal

716   Reference Method (FRM) network which is a PM mass only network. In addition, this method,

717   with appropriate ambient standards, could be applied at other regional or international

718   monitoring networks or sites to provide low-cost comprehensive composition data. As shown

719   in our previous work, additional data, including an estimate of organic matter and it's functional

720   group composition, can also be obtained from FT-IR spectra of PTFE filters, further increasing

721   the utility of infrared spectroscopy of aerosol samples.

5   Data availability

Data is available at https://doi.org/10.25338/B8TP8V.

6   Author contribution

BD developed the software, performed the formal analysis and visualization for much of the manuscript and wrote the original draft of the manuscript, ATW developed software, performed formal analysis and visualization of the GMM work, ST participated in conceptualization, methodology software, visualization and reviewing and editing the manuscript. KMG developed parts of the biomass burning identification methodology. AAF performed the final visualizations for parts of the paper and was responsible for additional visualizations made to the paper based on reviewer comments. BS, SC and ASW, provided input throughout the project and reviewed and edited the manuscript, AMD conceptualized of and acquired funding for this project, developed methodology, performed project administration and supervision and reviewed, edited and finalized the manuscript.

7   Competing interests

The authors declare that they have no conflict of interest.

8   Acknowledgments

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9   References

Allen, D. T., Palen, E. J., Haimov, M. I., Hering, S. V., and Young, J. R.: Fourier Transform Infrared Spectroscopy of Aerosol Collected in a Low Pressure Impactor (LPI/FTIR): Method Development and Field Calibration, Aerosol Science and Technology, 21, 325–342, https://doi.org/10.1080/02786829408959719, 1994.

Besalú, E., Julián-Ortiz, J. V. de., Iglesias, M., and Pogliani, L.: An overlooked property of plot methods, Journal of Mathematical Chemistry, 39, 475–484, https://doi.org/10.1007/s10910-005-9035-z, 2006.

Bilmes, J. A.: A gentle tutorial of the EM algorithm and its application to parameter estimation for Gaussian mixture and hidden Markov models, 4:126, 1998.

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.: Quantifying organic matter and functional groups in particulate matter filter samples from the southeastern United States – Part 1: Methods, Atmos. Meas. Tech., 12, 5391–5415, https://doi.org/10.5194/amt-12-5391-2019, 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.: Quantifying organic matter and functional groups in particulate matter filter samples from the southeastern United States - Part 2: Spatiotemporal trends, 14, 4355–4374, https://doi.org/10.5194/amt-14-4355-2021, 2021.

Bro, R. and Smilde, A. K.: Centering and scaling in component analysis, Journal of Chemometrics, 17, 16–33, https://doi.org/10.1002/cem.773, 2003.

Burki, C., Reggente, M., Dillner, A. M., Hand, J. L., Shaw, S. L., and Takahama, S.: Analysis of functional groups in atmospheric aerosols by infrared spectroscopy: method development for probabilistic modeling of organic carbon and organic matter concentrations, 13, 1517–1538, https://doi.org/10.5194/amt-13-1517-2020, 2020.

Busca, G. and Resini, C.: Vibrational Spectroscopy for the Analysis of Geological and Inorganic Materials, in: Encyclopedia of Analytical Chemistry, John Wiley & Sons, Ltd, 2006.

Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G.: The dri thermal/optical reflectance carbon analysis system: description, evaluation and applications in U.S. Air quality studies, 27, 1185–1201, https://doi.org/10.1016/0960-1686(93)90245-T, 1993.

Chow, J. C., Watson, J. G., Chen, L. W. A., Chang, M. C. O., Robinson, N. F., Trimble, D., and Kohl, S.: The IMPROVE_A Temperature Protocol for Thermal/Optical Carbon Analysis: Maintaining Consistency with a Long-Term Database, 57, 1014–1023, https://doi.org/10.3155/1047-3289.57.9.1014, 2007a.

Chow, J. C., Watson, J. G., Chen, L. W. A., Chang, M. C. O., Robinson, N. F., Trimble, D., and Kohl, S.: The IMPROVE_A Temperature Protocol for Thermal/Optical Carbon Analysis: Maintaining Consistency with a Long-Term Database, 57, 1014–1023, https://doi.org/10.3155/1047-3289.57.9.1014, 2007b.

Chow, J. C., Wang, X., Sumlin, B. J., Gronstal, S. B., Chen, L.-W. A., Trimble, D. L., Watson, J. G., Kohl, S. D., Mayorga, S. R., Riggio, G., Hurbain, P. R., Johnson, M., and Zimmermann, R.: Optical Calibration and Equivalence of a Multiwavelength Thermal/Optical Carbon Analyzer, 15, 1145–1159, https://doi.org/10.4209/aaqr.2015.02.0106, 2015.

Chukanov, N. V. and Chervonnyi, A. D.: Infrared Spectroscopy of Minerals and Related Compounds, Springer International Publishing, 2016.

Cios, K., Pedrycz, W., and Swiniarski, R. W.: Data Mining Methods for Knowledge Discovery, Kluwer Academic Publishers, Norwell, MA, USA, 495 pp., 1998.

786 Corrigan, A. L., Russell, L. M., Takahama, S., Äijälä, M., Ehn, M., Junninen, H., Rinne, J., Petäjä, T.,
787 Kulmala, M., Vogel, A. L., Hoffmann, T., Ebben, C. J., Geiger, F. M., Chhabra, P., Seinfeld, J. H., Worsnop,
788 D. R., Song, W., Auld, J., and Williams, J.: Biogenic and biomass burning organic aerosol in a boreal forest
789 at Hyytiälä, Finland, during HUMPPA-COPEC 2010, 13, 12233–12256, https://doi.org/10.5194/acp-13-
790 12233-2013, 2013.

791 Debus, B., Takahama, S., Weakley, A. T., Seibert, K., and Dillner, A. M.: Long-Term Strategy for Assessing
792 Carbonaceous Particulate Matter Concentrations from Multiple Fourier Transform Infrared (FT-IR)
793 Instruments: Influence of Spectral Dissimilarities on Multivariate Calibration Performance, 73, 271–283,
794 https://doi.org/10.1177/0003702818804574, 2019.

795 Dillner, A. M. and Takahama, S.: Predicting ambient aerosol thermal-optical reflectance measurements
796 from infrared spectra: Elemental carbon, 8, 4013–4023, https://doi.org/10.5194/amt-8-4013-2015,
797 2015a.

798 Dillner, A. M. and Takahama, S.: Predicting ambient aerosol thermal-optical reflectance (TOR)
799 measurements from infrared spectra: Organic carbon, 8, 1097–1109, https://doi.org/10.5194/amt-8-
800 1097-2015, 2015b.

801 Draper, N. R. and Smith, H.: Applied Regression Analysis, 1998.

802 Eldred, Robert. and Ashbaugh, L. L.: Loss of particle nitrate from Teflon sampling filters: Effects on
803 measured gravimetric mass in California and in the IMPROVE network, 54, 93–104,
804 https://doi.org/10.1080/10473289.2004.10470878, 2004.

805 Friedel, R. A. and Carlson, G. L.: Infrared spectra of ground graphite, 75, 1149–1151,
806 https://doi.org/10.1021/j100678a021, 1971.

807 Hahn, A., Vogel, H., Andó, S., Garzanti, E., Kuhn, G., Lantzsch, H., Schüürman, J., Vogt, C., and Zabel, M.:
808 Using Fourier transform infrared spectroscopy to determine mineral phases in sediments, Sedimentary
809 Geology, 375, 27–35, https://doi.org/10.1016/j.sedgeo.2018.03.010, 2018.

810 Hastie, T, Tibshirani, R, and Friedman, J: The Elements of Statistical Learning: Data Mining, Inference,
811 and Prediction, Second Edition, Springer New York, New York, NY, 2009.

812 Hawkins, L. N., Russell, L. M., Covert, D. S., Quinn, P. K., and Bates, T. S.: Carboxylic acids, sulfates, and
813 organosulfates in processed continental organic aerosol over the southeast Pacific Ocean during
814 VOCALS-REx 2008, 115, https://doi.org/10.1029/2009jd013276, 2010.

815 Hyslop, N. P., Trzepla, K., and White, W. H.: Reanalysis of Archived IMPROVE PM2.5 Samples Previously
816 Analyzed over a 15-Year Period, Environ. Sci. Technol., 46, 10106, 2012.

817   Hyslop, N. P., Trzepla, K., and White, W. H.: Assessing the Suitability of Historical PM2.5 Element
818   Measurements for Trend Analysis, Environ. Sci. Technol., 49, 9247–9255,
819   https://doi.org/10.1021/acs.est.5b01572, 2015.

820   Kuzmiakova, A., Dillner, A. M., and Takahama, S.: An automated baseline correction protocol for infrared
821   spectra of atmospheric aerosols collected on polytetrafluoroethylene (Teflon) filters, 9, 2615–2631,
822   https://doi.org/10.5194/amt-9-2615-2016, 2016.

823   Li, H.-D., Xu, Q.-S., and Liang, Y.-Z.: libPLS: An integrated library for partial least squares regression and
824   linear discriminant analysis, 176, 34–43, https://doi.org/10.1016/j.chemolab.2018.03.003, 2018.

825   Liu, S., Ahlm, L., Day, D. A., Russell, L. M., Zhao, Y., Gentner, D. R., Weber, R. J., Goldstein, A. H., Jaoui,
826   M., Offenberg, J. H., Kleindienst, T. E., Rubitschun, C., Surratt, J. D., Sheesley, R. J., and Scheller, S.:
827   Secondary organic aerosol formation from fossil fuel sources contribute majority of summertime organic
828   mass at Bakersfield, 117, https://doi.org/10.1029/2012JD018170, 2012.

829   Madejová, J. and Komadel, P.: Baseline studies of the clay minerals society source clays: Infrared
830   methods, Clays and Clay Minerals, 49, 410–432, https://doi.org/10.1346/CCMN.2001.0490508, 2001.

831   Mahalanobis, P., C,: On the generalized distance in statistics, 2, 49–55, 1936.

832   Malm, W. C., Sisler, J. F., Huffman, D., Eldred, R. A., and Cahill, T. A.: Spatial and seasonal trends in
833   particle concentration and optical extinction in the United States, 99, 1347–1370,
834   https://doi.org/10.1029/93jd02916, 1994.

835   Margenot, A. J., Calderón, F. J., Goyne, K. W., Mukome, F. N. D., and Parikh, S. J.: IR Spectroscopy, Soil
836   Analysis Applications, in: Encyclopedia of Spectroscopy and Spectrometry (Third Edition), edited by:
837   Lindon, J. C., Tranter, G. E., and Koppenaal, D. W., Academic Press, Oxford, 448–454,
838   https://doi.org/10.1016/B978-0-12-409547-2.12170-5, 2017.

839   Mayo, D. W., Miller, F. A., and Hannah, R. W.: Course Notes on the Interpretation of Infrared and Raman
840   Spectra, John Wiley & Sons, Hoboken, NJ, 2004.

841   Nemanich, R. J., Lucovsky, G., and Solin, S. A.: Infrared active optical vibrations of graphite, Solid State
842   Communications, 23, 117–120, https://doi.org/10.1016/0038-1098(77)90663-9, 1977.

843   Ngo, M. A., Pinkerton, K. E., Freeland, S., Geller, M., Ham, W., Cliff, S., Hopkins, L. E., Kleeman, M. J.,
844   Kodavanti, U. P., Meharg, E., Plummer, L., Recendez, J. J., Schenker, M. B., Sioutas, C., Smiley-Jewell, S.,
845   Haas, C., Gutstein, J., and Wexler, A. S.: Airborne particles in the San Joaquin Valley may affect human
846   health, 64, 12–16, https://doi.org/10.3733/ca.v064n01p12, 2010.

847   Niyogi, S., Bekyarova, E., Itkis, M. E., McWilliams, J. L., Hamon, M. A., and Haddon, R. C.: Solution
848   Properties of Graphite and Graphene, 128, 7720–7721, https://doi.org/10.1021/ja060680r, 2006.

849 O'Dell, K., Ford, B., Fischer, E. V., and Pierce, J. R.: Contribution of wildland-fire smoke to US PM2.5 and
850 its influence on recent trends, 53, 1797–1804, https://doi.org/10.1021/acs.est.8b05430, 2019.

851 Parks, D. A., Griffiths, P. R., Weakley, A. T., and Miller, A. L.: Quantifying elemental and organic carbon in
852 diesel particulate matter by mid-infrared spectrometry, null, 55, 1014–1027,
853 https://doi.org/10.1080/02786826.2021.1917764, 2021.

854 Reggente, M., Dillner, A. M., and Takahama, S.: Predicting ambient aerosol thermal-optical reflectance
855 (TOR) measurements from infrared spectra: Extending the predictions to different years and different
856 sites, 9, 441–454, https://doi.org/10.5194/amt-9-441-2016, 2016.

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

860 Russell, L. M., Bahadur, R., and Ziemann, P. J.: Identifying organic aerosol sources by comparing
861 functional group composition in chamber and atmospheric particles, 108, 3516–3521,
862 https://doi.org/10.1073/pnas.1006461108, 2011.

863 Ruthenburg, T. C., Perlin, P. C., Liu, V., McDade, C. E., and Dillner, A. M.: Determination of organic matter
864 and organic matter to organic carbon ratios by infrared spectroscopy with application to selected sites in
865 the IMPROVE network, 86, 47–57, https://doi.org/10.1016/j.atmosenv.2013.12.034, 2014.

866 Savitzky, A. and Golay, M. J. E.: Smoothing and differentiation of data by simplified least squares
867 procedures, 36, 1627–1639, https://doi.org/10.1021/ac60214a047, 1964.

868 Schichtel, B. A., Malm, W. C., Bench, G., Fallon, S., McDade, C. E., Chow, J. C., and Watson, J. G.: Fossil
869 and contemporary fine particulate carbon fractions at 12 rural and urban sites in the United States, 113,
870 https://doi.org/10.1029/2007jd008605, 2008.

871 Senthil Kumar, R. and Rajkumar, P.: Characterization of minerals in air dust particles in the state of
872 Tamilnadu, India through ftir spectroscopy, 2013, 22221–22248, https://doi.org/10.5194/acpd-13-
873 22221-2013, 2013.

874 Snijders, T. A. B. and Bosker, R. J.: Multilevel Analysis: An Introduction to Basic and Advanced Multilevel
875 Modeling, SAGE, 370 pp., 2011.

876 Sorooshian, A., Wonaschütz, A., Jarjour, E. G., Hashimoto, B. I., Schichtel, B. A., and Betterton, E. A.: An
877 aerosol climatology for a rapidly growing arid region (southern Arizona): Major aerosol species and
878 remotely sensed aerosol properties, 116, https://doi.org/10.1029/2011jd016197, 2011.

879 Takahama, S., Schwartz, R. E., Russell, L. M., Macdonald, A. M., Sharma, S., and Leaitch, W. R.: Organic
880 functional groups in aerosol particles from burning and non-burning forest emissions at a high-elevation
881 mountain site, Atmos. Chem. Phys., 11, 6367–6386, https://doi.org/10.5194/acp-11-6367-2011, 2011.

882 Takahama, S., Dillner, A. M., Weakley, A. T., Reggente, M., Bürki, C., Lbadaoui-Darvas, M., Debus, B.,
883 Kuzmiakova, A., and Wexler, A. S.: Atmospheric particulate matter characterization by Fourier transform
884 infrared spectroscopy: a review of statistical calibration strategies for carbonaceous aerosol
885 quantification in US measurement networks, Atmos. Meas. Tech., 12, 525–567,
886 https://doi.org/10.5194/amt-12-525-2019, 2019.

887 Tuinstra, F. and Koenig, J. L.: Raman Spectrum of Graphite, 53, 1126–1130,
888 https://doi.org/10.1063/1.1674108, 1970.

889 Watson, J. G. and Chow, J. C.: A wintertime PM2.5 episode at the Fresno, CA, supersite, Atmospheric
890 Environment, 36, 465–475, https://doi.org/10.1016/S1352-2310(01)00309-0, 2002.

891 Weakley, A. T., Takahama, S., and Dillner, A. M.: Ambient aerosol composition by infrared spectroscopy
892 and partial least-squares in the chemical speciation network: Organic carbon with functional group
893 identification, 50, 1096–1114, https://doi.org/10.1080/02786826.2016.1217389, 2016.

894 Weakley, A. T., Takahama, S., Wexler, A. S., and Dillner, A. M.: Ambient aerosol composition by infrared
895 spectroscopy and partial least squares in the chemical speciation network: Multilevel modeling for
896 elemental carbon, 52, 642–654, https://doi.org/10.1080/02786826.2018.1439571, 2018a.

897 Weakley, A. T., Takahama, S., and Dillner, A. M.: Thermal/optical reflectance equivalent organic and
898 elemental carbon determined from federal reference and equivalent method fine particulate matter
899 samples using Fourier transform infrared spectrometry, 52, 1048–1058,
900 https://doi.org/10.1080/02786826.2018.1504161, 2018b.

901 White, W. H., Trzepla, K., Hyslop, N. P., and Schichtel, B. A.: A critical review of filter transmittance
902 measurements for aerosol light absorption, and de novo calibration for a decade of monitoring on PTFE
903 membranes, 50, 984–1002, https://doi.org/10.1080/02786826.2016.1211615, 2016.

904 Wold, S., Sjöström, M., and Eriksson, L.: PLS-regression: A basic tool of chemometrics, 58, 109–130,
905 https://doi.org/10.1016/S0169-7439(01)00155-1, 2001.

906 Yazdani, A., Dudani, N., Takahama, S., Bertrand, A., Prevot, A. S. H., El Haddad, I., and Dillner, A. M.:
907 Characterization of primary and aged wood burning and coal combustion organic aerosols in an
908 environmental chamber and its implications for atmospheric aerosols, 21, 10273–10293,
909 https://doi.org/10.5194/acp-21-10273-2021, 2021a.

910 Yazdani, A., Dillner, A. M., and Takahama, S.: Estimating mean molecular weight, carbon number, and
911 OM/OC with mid-infrared spectroscopy in organic particulate matter samples from a monitoring
912 network, 14, 4805–4827, https://doi.org/10.5194/amt-14-4805-2021, 2021b.

913 Zhang, X. L., Trzepla, K., White, W., Raffuse, S., and Hyslop, N. P.: Intercomparison of thermal-optical
914 carbon measurements by Sunset and Desert Research Institute (DRI) analyzers using the IMPROVE_A
915 protocol, 14, 3217–3231, https://doi.org/10.5194/amt-14-3217-2021, 2021.

916