

Review of 'Quantification of major particulate matter species from a single filter type using infrared spectroscopy – Application to a large-scale monitoring network' by Debus et al:

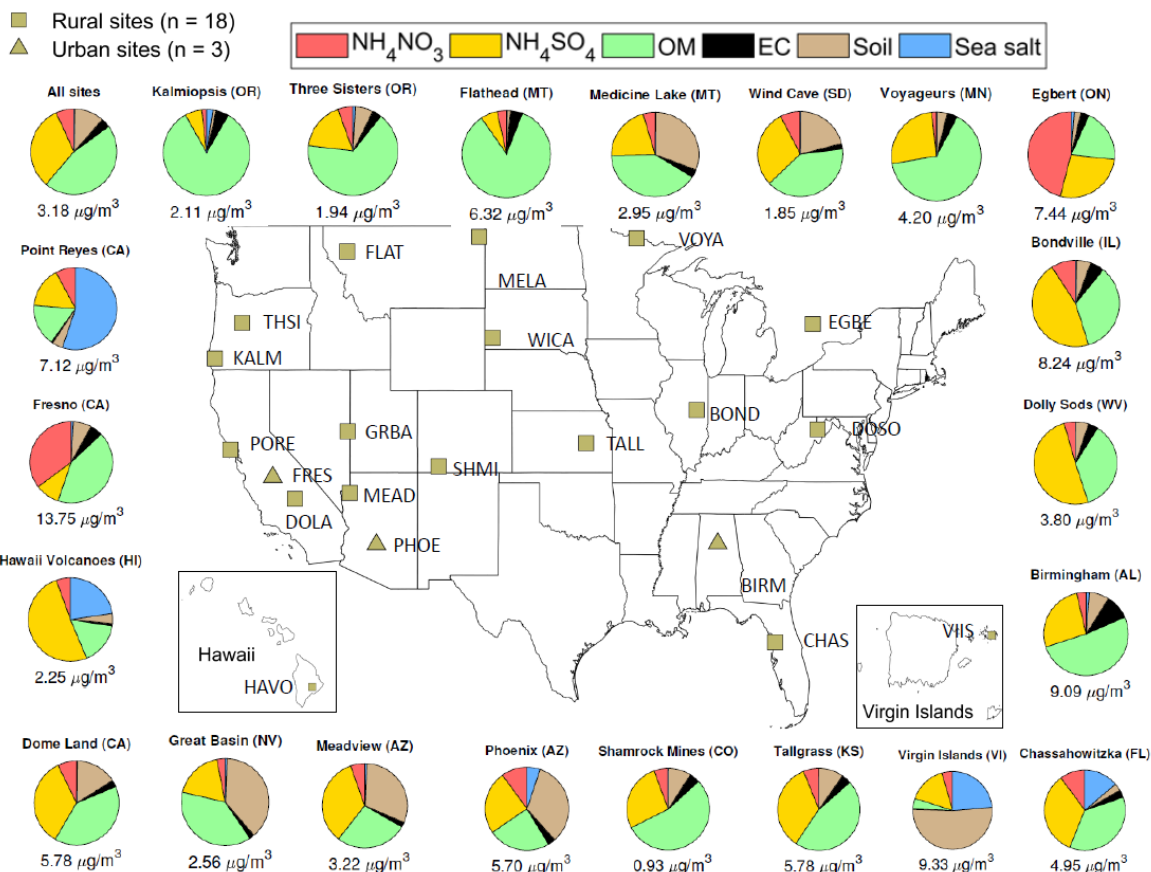
Reviewer #1

Overall, this paper clearly presents a novel solution to increase the efficiency of IMPROVE measurements using FTIR. The results are comprehensive, as well as surprisingly good and consistent, with a few relatively small exceptions.

Thank you for your supportive comments. Reviewer comments are in black, responses are in green and edits to the paper are in blue.

In addition to the method comparison, there is a brief discussion characterizing the different sites with their regional similarities, and a slightly awkward overview map showing the CONUS concentrations, but with problematic nitrate.

We hope the map and discussion are helpful. However, the maps is showing routine IMPROVE data with nitrate coming from IC on nylon filters, not problematic nitrate from PTFE filters. To clarify, we have modified the caption of the figure as follows. We have also tried to make the map less awkward by moving the Virgin Islands side to the southeast of the CONUS map and Hawaii to the southwest, more in line with their true geographic locations.



The composition is obtained from [routine IMPROVE \(non-FT-IR\)](http://vista.cira.colostate.edu/Improve/reconstructed-fine-mass/) measurements and the IMPROVE reconstructed fine mass equation (<http://vista.cira.colostate.edu/Improve/reconstructed-fine-mass/>).

The abstract omits that measurements of nitrate on the PTFE filter cannot adequately access particulate nitrate in the atmosphere. This is a pretty limiting feature and should be highlighted in the abstract, even if it has been reported previously, since it has significant impacts for this method.

Yes, good point. We have modified the abstract by adding the following sentence.

The major limitation is measuring nitrate as it is known to volatilize off of PTFE filters.

The method seems sound in terms of separating training and testing sets, but there are a few aspects that should be shown in more detail:

- 1) the outlier results should be shown in supplement.

Thank you for this request. We also thought it would be helpful and so included plots and discussion of the EC outliers in Section S2, page 5 of the supplemental material. The other

samples designated as outliers were excluded prior to evaluation by FT-IR because they are either not in the IMPROVE database or had contamination that was indicated with an SA (sampling anomaly) flag.

2) the comparison before the calibration to the limited sites (at least include in SI).

We appreciate your interest in these model results. We initially included the global model (which includes all sites) in the main paper but due to the length of the paper and large variety of analyses, we decided to move it to the supplemental material. A brief mention of this model is made in Section 2.5 of the paper and indicates that the results can be found in Section S1 in the supplemental material. In section 3.4, we compare predictions of the biomass burning samples between the biomass burning model and the global model in Figure 3. In section 3.3.1, we mention that the multilevel model performs similarly well to the global model found in supplemental material.

3) the statistics in the summary table should also be given including outliers and without biomass burning corrections, i.e. an untrained, uncorrected, full-dataset comparison.

Summary statistics for the Global model (which includes all samples) are shown in Table S1-1 in the supplemental material in Section S1.

If these things can be added, the paper would present a much more complete evaluation of the method for future potential users.

Specific Comments

Nitrate is one of the two most abundant inorganic anions that is quantified in the network (if not the most abundant component overall: see Fresno, Ebger sites) yet determining nitrate from PTFE has a large uncertainty due to volatilization of nitrate on the filter. It was suggested that nylon filters that are analyzed by IC can be used as a reference method but how would this affect costs since this paper promotes FTIR+PTFE as a cost effective single-filter/single-technique.

Thank you for these comments on nitrate, an important and abundant species in aerosols. The efforts presented here utilize IC from nylon filters as the reference method to attempt to measure ambient nitrate which as you noted, but these produce poor results. However, it's useful to have two estimates of nitrate: 1) "true nitrate" in the atmosphere as quantified by the nylon filter and 2) the nitrate on the Teflon filter, which corresponds to its contribution to the gravimetric mass, in principle, is useful as an independent laboratory calibration. We plan to work on this in the future. This cost of this development would be modest. This paper tries to describe the prediction of (1) from the measured signal on the Teflon filter through statistical calibration, which may be using composition particular to season/temperature to correct for the volatilized fraction. While still useful to obtain this estimate via single Teflon filter, there will be limits to how accurate this may be and should be acknowledged as part of reporting, as you suggested. We have added text shown below to address both the limitations of the method proposed in this

paper and address the topic of the value and means for measuring how much nitrate is on the PTFE filter given the volatility issue.

References to papers that successfully performed these alternative techniques for quantifying nitrate would be good to include (for quantifying ammonium nitrate: <https://www.tandfonline.com/doi/full/10.1080/02786820701272038>).

Thank you for suggesting this and including the reference. We have added the below text and references per your comment.

Unlike nylon filters for which nitrate is trapped on the surface, nitrate is known to evaporate from PTFE filters and extent of volatilization is dependent on temperature and relative humidity during and after sampling. This causes a discrepancy between the mass of nitrate deposited onto the nylon filter and the mass of nitrate on the PTFE filter (Eldred and Ashbaugh, 2004), therefore FT-IR calibrations with the nitrate measurements by IC from nylon filters as the reference should be used with caution. Although there are physical limitations to measuring ambient nitrate on PTFE filters, a measure of nitrate on PTFE filters which corresponds to its contribution to the gravimetric mass is useful for mass closure and data validation. FT-IR has been shown to be useful for measuring and evaluating nitrate under controlled laboratory conditions (ex. Wu et al., 2007). For network samples, nitrate could be measured using laboratory calibration standards and this effort will be addressed in future work.