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Comment

Interactive comment on “Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements from infrared spectra: organic carbon” by A. M. Dillner and S. Takahama

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Interactive comment on “Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements from infrared spectra: organic carbon” by A. M. Dillner and S. Takahama Response to Anonymous Referee #1

In general this is an interesting and well written paper with care taken to do statistical tests to check the basis of the calibration work they are trying to do. The main area which could be improved is making the context of the research much clearer and I have made some recommendations on how to do this. Once revised this should be

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very suitable for publication in AMT.

Response: Thank you for your positive and helpful comments regarding our paper. Responses and new text are shown immediately following each comment. No changes were made to the figures or supplemental material related to these comments so they are not included here.

Overall comments:

1. The authors have not communicated very well the underlying purpose of the experiments and explained the result in that context. Is the calibration of the FTIR measurements against the TOR being done in order to replace the TOR at most sites in the IMPROVE network whilst retaining several calibration sites where both methods are used (there is precedent for this in many other air quality monitoring networks e.g. in the UK automatic NO₂ measurements are supplemented with diffusion tubes). Response: The purpose is to demonstrate the feasibility of using FTIR to replace TOR. This is the first step towards proposing FTIR be used to measure OC (this paper) and EC (next paper) in monitoring networks. Text has been added to the abstract and the introduction to clarify this point. In addition, future work needed to make the proposal viable is included in the conclusions. Yes, the proposal will include maintaining a few sites with TOR. Thank you for your suggestion that IMPROVE follow the precedents of other air quality monitoring network. Added text below.

Abstract: This work marks an initial step in proposing a method that can reduce the operating costs of large air quality monitoring networks with an inexpensive, non-destructive analysis technique using routinely collected PTFE filter samples which, in addition to OC concentrations, can concurrently provide information regarding the composition of organic aerosol. This feasibility study suggests that the minimum detection limit and errors (or uncertainty) of FT-IR predictions of TOR OC are on par with TOR such that evaluation of long-term trends and epidemiological studies would not be significantly impacted.

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Introduction: This work is the first step in proposing a non-destructive method for reducing sampling and analysis costs for large particulate speciation monitoring networks. The method also provides a means of obtaining information about the carbonaceous aerosol at sampling sites that have only Teflon filter samples provided that new samples have similar aerosol composition to the samples in the calibration set.

Conclusions: Future work includes establishing that the calibration developed using samples from one year can be used to predict TOR OC during other years and developing a calibration that includes samples with a broader range of aerosol composition.

2. There was also little discussion about whether specific sites contributed to more of the variation than others or to the correction factors used in the TOR methods which were integral to the calibration. i.e. one method was being compared to a method with has “correction factors”. So it is not a scientific step forward per se to match a corrected dataset.

Response: The purpose of this method is to predict TOR OC so that long term data sets will not be impacted. For example, IMPROVE has used TOR since 1984. Although TOR uses correction factors, they are based on measurements taken in the field, and while imperfect, the factors reflect the best estimate of carbon adsorption on quartz filter within network financial constraints. The data show that the FTIR predictions of TOR-equivalent OC are based on a mechanistic relationship between the absorbance spectra by FT-IR and TOR OC values. In addition, FT-IR can be used to measure organic functional groups and from that calculate the OC and organic matter so that in addition to TOR OC, FT-IR can be used to measure the aerosol composition (Ruthenburg et al., 2014).

3. There is little mention of the alternative techniques to TOR and FTIR of which are higher cost on-line instrumentation e.g. an ACMS or an on-line total organic carbon analyser though lower manual analysis costs.

Response: The capital cost of these alternative techniques are prohibitive for IM-

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PROVE and CSN (and likely other large networks) for the foreseeable future. There are approximately 170 sites in the IMPROVE network alone. In addition, the priority for the networks is to keep a continuous data stream so reproducing TOR OC is imperative. ACMS which is based on a different principle than the TO methods, measures submicron (PM₁) non-refractory aerosol which is dependent on collection efficiency so the OC measured by the ACSM, is not the same as that measured from particles collected on a filter. Text shown below has been added to the introduction to describe the use of a continuous data stream of TOR OC data. Although methods exist for measuring OC directly from FT-IR spectra (Russell, 2003; Ruthenburg et al., 2014), calibrating to TOR OC provides TOR-equivalent OC data that will enable the continuation of long term trend analysis of particulate pollution and longitudinal epidemiological studies on the effects of particulate pollution on human health.

4. I would recommend making a significant edit on the introduction and conclusions to make the context of the experiment clearer and the application of the results more general rather than one method vs another. i.e. the context of actually quantitatively measuring OC without correction factors.

Response: The abstract, introduction and conclusions have been edited to make the context more clear, as noted above. The Ruthenburg paper describes our method for measuring OC without correction factors.

5. The repeated references to Ruthenburg et al 2014 are somewhat unnecessary and distract from the content of this paper. Though it is obviously a linked piece of work it really should only be referred to when it is relevant to the science being discussed in this paper.

Response: We have deleted references to Ruthenburg et al when it was not relevant to the science.

6. One long term question would be if the FTIR was to replace the TOR and the chemical climate shifts (not implausible) would the calibrations be able to cope.

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Response: On the time scale of a chemical climate shift, there may be changes in regulations and other analytical methods may even replace TOR OC. On a shorter time scale of slowly decreasing PM concentrations, we are investigating how well our calibration developed with samples from 2011 can predict samples from 2013. We also will recommend to the regulatory agencies that a small fraction of TOR analysis (~10% of sites), be continued to so that the calibration can be evaluated and modified if needed in the future. This will be addressed in future papers in which samples from the entire network will be available for developing the calibration.

7. Seven sites in the IMPROVE were used in this experiment but the representativity of those 7 sites in the context of the IMPROVE network is not established.

Response: This paper is only intended to show the feasibility of this approach. We are now analyzing one year of samples from all sites in the network for developing a calibration to be used for all sites. As stated above, we have added text to the conclusion to address the issue of a calibration suited to a broader range of samples

Specific comments:

8. Abstract: Abstract: It would be clearer to say at the start of the abstract that the quartz fibre is exposed to a volume of ambient air which is then analysed
Response: Done

9. Abstract: “. . .all μgm^{-3} values based. . .” this could more correctly be written as “ all reported concentrations”?
Response: Done

10. Abstract: The conclusion that the FTIR measurement can accurately predict the TOR measurement though interesting is not directly a step forward in atmospheric science. More importantly are the authors concluding that the FTIR measurement could replace the TOR measurements and if so can it only be done with calibration?
Response: As stated above, we have added text indicating that this is a step toward proposing FTIR as a method to replace TOR. A paper on TOR EC is forthcoming.

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Please see related responses to questions 1 and 2 above. In that the proposed method is a measurement technique which will facilitate further study of the atmospheric aerosol burden, we believe that this manuscript is suitable for the audience of AMT.

11. Introduction: P10933, line 6 First sentence: could the authors cite or refer to one of the major reviews whether by the WHO or other organisations for the reader to see the evidence of the health and AQ effects of PM Response: Done

12. Introduction: P10035, line 27: Though there is minimal adsorption of semivolatiles onto PTFE there is significant adsorption of semivolatiles onto sampled PM (and re-volatilisation). This should be noted in the text and discussed.

Response: The adsorption of semivolatiles onto sampled PM is likely similar between PTFE and quartz filters so we do not address this issue. We state that there is minimal adsorption onto PTFE filters because this is a difference between quartz and Teflon filters.

13. Methods: Throughout the article, the size fraction of PM sampled is never mentioned. Is it PM10, PM2.5 or total PM? Response: PM2.5. Thank you for catching this oversight. This information has been added to the first paragraph of section 2.1.

and produces filter samples of particles smaller than 2.5 μm in diameter (PM2.5).

14. Methods: A reference or url link to the network TOR data is missing. Is the data publically archived and if not where did the authors get it from? It would be good practice to put the date the data was received and from whom. It would also be good to see in the acknowledgements mention of the field teams who do the sample handling and site maintenance.

Response: The URL and download date have been added to section 2.1. The field teams have been added to the acknowledgements.

Section 2.1

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IMPROVE data was obtained from the Federal Land Manager Environmental Database (FED, <http://views.cira.colostate.edu/fed/Default.aspx>) on May 1, 2014.

Acknowledgements

Thanks to the IMPROVE team at UC Davis for performing the sample handling and site maintenance for all IMPROVE sites.

15. Methods: p10940, line 24: In the supplementary material, all the TOR blanks are zero. Here an MDL is quoted for them which would not be possible if all the values were zero. Is this correct or is there a typo error? Methods: it needs clarifying whether all the FTIR blanks were laboratory blanks or travel blanks. If both were done was there a difference between the 2 sets? If there were no travel blanks done this should be mentioned. Methods: p10940, “MDL for the TOR method is three times the standard deviation of 514 blanks (Desert Research Institute, 2012)” – but all the blank values for TOR in the supplementary material are zero?

Response: The three related questions above are address together here. The PTFE blanks are laboratory blanks and the word laboratory has been added to section 2.2.1. IMPROVE does not collect travel blanks. The blanks are assigned a TOR OC value of zero for calibration purposes. We don't have corresponding measured TOR laboratory blanks. We stated our assumption of zero carbon for PTFE blanks on lines 24-25 on page 10939 in the submitted manuscript. The reported MDL for FTIR is based on the FTIR values reported for the PTFE blanks. The TOR MDL is based on quartz filter laboratory blanks performed years before our work. The two sets of blanks (PTFE and quartz) are not related to each other.

16. Methods: p10937 line 1, Why is it a nominal flow rate? Are the flows not calibrated in the network?

Response: The nominal flow rate is provided for conversion from mass to concentration units if the reader so desires. The flow rates are continuously measured for each sam-

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ple in the network. These measured flowrates and actual sample times were used to convert atmospheric concentrations to filter loadings. The word measured was added to the text regarding adjustment of flows to clarify this point.

17. Results: p10943 “The ammonium is estimated assuming full neutralization solely by ammonium of reported sulfate and nitrate concentrations reported in the IMPROVE network data.” Given that there is a significant literature on the ammoniated salts of di- carboxylic acids and the fact that oxalate is one of the most abundant PM organic acids, is there a particular reason this speciation was ignored? Also ammonium chloride can be present depending on the location. Did the authors just base their assumptions on what was measured in the IMPROVE network? If so it would be interesting if they could use campaign or other atmospheric PM speciation data or models which has more PM speciation information to assess their assumptions.

Response: We used the available measured data from IMPROVE which does not include organic species to estimate ammonium. This value may be an underestimate when ammoniated salts and/or ammonium chloride are present and an over estimate if the sulfate and nitrate are not fully neutralized. However, our simple assumption provides insight into the impact of differences in ammonium/OC between the calibration and test set on predicted values.

18. Conclusions: the authors mention in the introduction correction factors used in the TOR method to account for charring and for adsorption of gas phase organics. Given that the calibration is done to the corrected TOR measurements and good agreement is given, it would be useful for the authors to comment on what the implications of this are for those correction factors. Was a calibration against uncorrected TOR done (or could it be done). Currently they have successfully calibrated against “corrected data”. The real challenge is to measure what is in the atmosphere without corrections.

Response: Text has been added to the conclusions that addresses the implications of the good agreement between TOR and FTIR are on the artifact and charring correc-

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tion. A calibration against uncorrected TOR data was not done but it could be done. However, the TOR data is corrected in an effort to mitigate error caused by sampling and analysis so that the reported data is closer to what is actually in the atmosphere than uncorrected data is. The aerosol FTIR papers in the introduction all measure carbon in the atmosphere without correction factors.

The higher errors in the low OC mass samples suggest that the use of a single value to artifact correct all samples collected in a month induces additional error in low OC samples. The low error in most samples suggests that the charring correction is consistently applied such that it can be accounted for with the statistics used to develop the calibration models.

19. Conclusions: as mentioned in my general comments, the bias and errors discussed are based on calibrating the FTIR method against a method which has “correction factors” therefore the authors need to make it clearer that the bias and errors refer to this comparison rather than directly measuring and calibrating that.

Response: Section 2.4 Methods for evaluating the quality of calibration defines the error and bias as being between TOR and FTIR. This section has been modified to further clarify that these metrics are based on comparison between the two methods.

The bias is the median difference between measured (TOR) and predicted (FT-IR) OC for the test set. Error is the median absolute bias.

20. Conclusions: The final sentence conclusion is only true if the correction factors in TOR OC are good and TOR is quantitative. Therefore I think that further work is required before that conclusion is true, i.e. testing the method against other methods of measuring OC.

Response: The concluding statement has been changed to say that it is a robust method for predicting TOR OC (rather than just OC) as this is the goal of the paper. Therefore, we conclude that FT-IR spectra calibrated to TOR OC using partial

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least squares regression is a robust method for predicting TOR organic carbon from particulate matter samples.

21. Figure 1: I see no need for all these references in the figure caption for the “previous work”. They should be either in the figure if relevant or in the text, or in a table.

Response: These references support the figure and we think are the appropriate way to communicate this information to the reader.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 10931, 2014.

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