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Atmospheric Measurement Techniques Discussions

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

Anonymous Referee #1

Received and published: 20 November 2014

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 very suitable for publication in AMT.

Overall comments:

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 measure-

ments 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)

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.

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

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

The repeated references to Ruthenberg et al 2014 are somewhat un-necessary 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.

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.

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.

Specific comments:

Abstract: Abstract: It would be clearer to say at the start of the abstract that the quartz

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fibre is exposed to a volume of ambient air which is then analysed

Abstract: "...all μgm$-$3 values based..." this could more correctly be written as " all reported concentrations"?

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?

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

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

Methods: Throughout the article, the size fraction of PM sampled is never mentioned. Is it PM10, PM2.5 or total PM?

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.

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 file 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.

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

Methods: p10940, "MDL for the TOR method is three times the standard deviation of 514 blanks (Desert Research Intitute, 2012)" – but all the blank values for TOR in the supplementary material are zero?

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.

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.

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.

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 be-

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fore that conclusion is true, i.e. testing the method against other methods of measuring OC.

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.

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

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Discussion Paper