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# Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements from infrared spectra: organic carbon

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## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

Organic carbon (OC) can constitute 50% or more of the mass of atmospheric particulate matter. Typically, the organic carbon concentration is measured using thermal methods such as Thermal-Optical Reflectance (TOR) from quartz fiber filters. Here, methods are presented whereby Fourier Transform Infrared (FT-IR) absorbance spectra from polytetrafluoroethylene (PTFE or Teflon) filters are used to accurately predict TOR OC. Transmittance FT-IR analysis is rapid, inexpensive, and non-destructive to the PTFE filters. To develop and test the method, FT-IR absorbance spectra are obtained from 794 samples from seven Interagency Monitoring of PROtected Visual Environment (IMPROVE) sites sampled during 2011. Partial least squares regression is used to calibrate sample FT-IR absorbance spectra to artifact-corrected TOR OC. The FTIR spectra are divided into calibration and test sets by sampling site and date which leads to precise and accurate OC predictions by FT-IR as indicated by high coefficient of determination ( $R^2$ ; 0.96), low bias ( $0.02 \mu\text{g m}^{-3}$ , all  $\mu\text{g m}^{-3}$  values based on the nominal IMPROVE sample volume of  $32.8 \text{ m}^3$ ), low error ( $0.08 \mu\text{g m}^{-3}$ ) and low normalized error (11%). These performance metrics can be achieved with various degrees of spectral pretreatment (e.g., including or excluding substrate contributions to the absorbances) and are comparable in precision and accuracy to collocated TOR measurements. FT-IR spectra are also divided into calibration and test sets by OC mass and by OM/OC which reflects the organic composition of the particulate matter and is obtained from organic functional group composition; this division also leads to precise and accurate OC predictions. Low OC concentrations have higher bias and normalized error due to TOR analytical errors and artifact correction errors, not due to the range of OC mass of the samples in the calibration set. However, samples with low OC mass can be used to predict samples with high OC mass indicating that the calibration is linear. Using samples in the calibration set that have a different OM/OC or ammonium/OC distributions than the test set leads to only a modest increase in bias and normalized error in the predicted samples. We conclude that FT-IR analysis with partial least squares

## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



regression is a robust method for accurately predicting TOR OC in IMPROVE network samples; providing complementary information to the organic functional group composition and organic aerosol mass estimated previously from the same set of sample spectra (Ruthenburg et al., 2014).

## 1 Introduction

Particulate matter (PM) has been implicated in increased morbidity and mortality and reduced visibility in numerous studies. As a result, its size-resolved chemical composition is measured during episodic measurement campaigns and over longer periods of time in many networks world-wide, including the IMPROVE network (Hand et al., 2012; Malm et al., 1994) in pristine and rural areas in the US, the Chemical Speciation Network/Speciation Trends Network (CSN/STN; Flanagan et al., 2006) in urban and sub-urban areas in the US, the SouthEastern Aerosol Research and Characterization network (SEARCH; Hansen et al., 2003) in urban and rural areas in the southeastern US, the Canadian National Air Pollution Surveillance network (NAPS; Dabek-Zlotorzynska et al., 2011) in primarily urban sites in Canada, and the European Monitoring and Evaluation Programme (EMEP; Torseth et al., 2012) throughout Europe. Typically, organic carbon (OC) and elemental carbon (EC) concentrations are measured on quartz filters using thermal optical reflectance (TOR; Chow et al., 2007), NIOSH 5040 (Birch and Cary, 1996), European Supersites for Atmospheric Aerosol Research (EUSAAR-2 protocol; Cavalli et al., 2010), or similar methods. PM is drawn through a quartz filter and a portion is subjected to a temperature gradient with two carrier gas regimes that operationally define the organic and elemental carbon (Chow et al., 2007). Charring of organic material during heating is corrected for using laser reflectance or transmittance (Cavalli et al., 2010; Chow et al., 2007). The measurement artifact caused by gas phase adsorption of organic material on the quartz filter may be corrected for by using blank or back-up quartz filters (Chow et al., 2010; Maimone et al., 2011; Turpin

## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



et al., 1994). Organic matter (OM) is estimated by multiplying the reported OC by an assumed OM/OC factor (Pitchford et al., 2007; Turpin and Lim, 2001).

Fourier transform-infrared spectroscopy (FT-IR) has been proposed as an alternative for quantification of organic matter in particles collected on filters (Russell, 2003; Ruthenburg et al., 2014). FT-IR measures abundances of bonds connecting carbon atoms with their heteroatoms, leading to characterization of functional groups including aliphatic and aromatic CH, carbonyl (C=O), alcohol OH (C–OH), carboxylic acid OH (C–OH) and others (Blando et al., 2001; Coury and Dillner, 2008; Maria et al., 2003). This bond abundance allows more direct estimates of OM and OM/OC ratios (Russell, 2003; Ruthenburg et al., 2014) compared to using TOR OC and an assumed OM/OC ratio. Organic functional groups in carbonaceous material absorb IR light in specific region(s) of the mid-IR spectrum (4000 to 400 cm<sup>-1</sup>). The amount of light absorbed is proportional to the moles of functional group. Based on initial work by Allen and colleagues (Allen et al., 1994), researchers (Coury and Dillner, 2008; Reff et al., 2007; Russell et al., 2009; Ruthenburg et al., 2014; Takahama et al., 2013) have shown that organic functional groups can be quantified even in complex mixtures of ambient or indoor aerosols. These studies have used laboratory-generated standards as reference material, each containing one or more organic compounds, to develop calibration models for quantifying functional group abundance.

Researchers in other fields have used FT-IR spectra to quantify properties such as total carbon (TC), organic carbon, or fatty acid content using calibrations developed from environmental (e.g., soil or food) reference samples. These samples were analyzed by FT-IR alongside an expensive or time-consuming conventional method to measure the property of interest. Partial least squares regression (PLSR) has been commonly used to develop calibration models that quantitatively predict these properties from the FT-IR spectra. In one example of this approach in the field of soil science (Madari et al., 2005), calibrations were developed for total carbon and organic carbon in soil samples using near-infrared (NIR) and diffuse reflectance mid-infrared spectroscopy (DRIFTS). Over 1000 samples from the Brazilian National Soil Collection

## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



were analyzed by a combustion method to determine TC and by a chromate oxidation method to determine OC. Calibrations of DRIFTS spectra developed through spectral pretreatments and subsets of samples based on carbon content, soil texture and soil class produced accurate predictions of soil TC and OC with high correlation to observations ( $R^2$  of 0.95 and 0.93, respectively).

Another application of this method in the food science field (Vongsvivut et al., 2012) used attenuated total reflectance FT-IR (ATR-FT-IR) spectra of fish oil supplements and PLSR to quantify the fatty acid content of the oil. Fatty acids are composed of organic functional groups including carbonyl groups, carboxylic acid OH groups and aliphatic CH groups. Because gas chromatography (GC), the common method for measuring fatty acids in oils, is time and labor intensive and uses hazardous chemicals, researchers sought a faster, less expensive, and more environmentally friendly method. Sixty-four samples were analyzed by GC and ATR-FT-IR and two-thirds of these were used to develop a calibration for fatty acids using PLSR. Predictive estimations ( $R^2 \geq 0.96$  compared to observed values) of total oil, total fatty acids, and two specific fatty acids in fish oil samples were made using this technique.

The work presented here proposes a similar approach for predicting OC in ambient aerosol samples. As described above, thermal optical methods provide OC measurements in air monitoring network ambient particle matter samples. Such networks simultaneously sample particles on PTFE filters for gravimetric mass and elemental composition analysis; the filters can also be used to obtain FT-IR spectra. In this work, OC is predicted from infrared spectra of filter samples of aerosols using PLSR. The methods are developed and tested using OC from gas phase adsorption corrected TOR analysis and FT-IR spectra from parallel PTFE filters from one year of samples from seven IMPROVE sites. The use of PTFE filters for FT-IR analysis has several benefits. FT-IR analysis is fast, relatively inexpensive and non-destructive to the samples. PTFE filters have minimal organic gas phase adsorption (Gilardoni et al., 2007; Turpin et al., 1994) and are commonly used in PM monitoring networks, such as the speciation networks mentioned above and the Federal Reference Method sampling



time at a nominal flow rate of 22.8 liters per minute which yields a nominal volume of 32.8 m<sup>3</sup>.

The FT-IR analysis is applied to 25 mm PTFE filters (Teflo, Pall Gelman) that are analyzed for gravimetric mass, elements and light absorption in the IMPROVE network.

5 The sample area is 3.53 cm<sup>2</sup>. Quartz filters collected in parallel to the PTFE filters are analyzed by TOR to obtain OC and EC mass in the IMPROVE network (Chow et al., 2007). The OC values are adjusted to account for charring of organic material during heating (Chow et al., 2007). Organic carbon values are adjusted to account for the  
10 gas phase adsorption artifact by subtracting the monthly median OC value from field blanks collected at a few sites in the network; during 2011 the monthly median OC values ranged from 4.1 to 6.7 μg OC. For this work, the OC values are also adjusted to account for flow differences between the quartz and PTFE filters. IMPROVE data was obtained from IMPROVE samples lacking either flow records for PTFE filters or TOR  
15 measurements are excluded, leaving 794 samples for this analysis.

In order to provide reference performance metrics for the evaluation of the FT-IR to TOR comparisons (see Sect. 2.4 for a description of the metrics), measurements from seven IMPROVE sites with collocated TOR measurements (Everglades, Florida; Her-  
20 cules Glade, Missouri; Hoover, California; Medicine Lake, Montana; Phoenix, Arizona; Saguaro West, Arizona; Seney, Michigan) are used.

## 2.2 FT-IR analysis

### 2.2.1 Spectra acquisition

794 PTFE ambient samples and 54 PTFE blank filters are analyzed using a Tensor 27 Fourier transform infrared (FT-IR) spectrometer (Bruker Optics, Billerica, MA) equipped with a liquid nitrogen-cooled wide-band mercury cadmium telluride detector. The sam-  
25 ples are analyzed using transmission FT-IR over the mid infrared wavenumber region of 4000 to 420 cm<sup>-1</sup> (see Ruthenburg et al., 2014 for more details). Absorbance spectra are calculated using a recent spectrum of the empty sample compartment as a zero

## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion







## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



are generated by varying the number of factors used to represent the matrix of spectra. A common approach for model selection and assessment is to divide the set of available samples into three groups: a training set for determining model parameters, a validation set for selecting the best model, and a test set for evaluating its performance or prediction errors (Hastie et al., 2009; Bishop, 2011; Witten, 2011). The first two sets are combined into what is called the calibration set; training and validation is handled by an approach known as  $K$ -fold cross validation (CV); (Arlot and Celisse, 2010; Hastie et al., 2009). In this approach, the calibration set is partitioned into  $K$  segments, and each of the  $K$  segments is used for validation while the remaining  $K - 1$  segments are used to train the model.

The minimum root mean square error of prediction (RMSEP; Mevik and Cedervik, 2004) is used to select the model with least prediction error. A value of  $K$  between 5 and 10 has often been chosen empirically for CV (Hastie et al., 2009); evaluation of TOR-equivalent OC estimates for  $K = 5, 8,$  and  $10$  showed very little difference in prediction error (Supplement, Sect. S3) so a value of  $K = 10$  is fixed for our protocol. This CV procedure permits development and selection of PLSR models using only the samples in the calibration set, and guards against over-fitting to a single set of samples. Blind evaluation is then carried out on the test set, which imposes no prior influence on the model development or selection.

The total number of samples in the calibration set is held fixed at  $2/3$  of the total filters for the “base case” (described in the following paragraph) and other cases used to evaluate which parameters impact prediction quality to ensure that particular models are not advantaged by more measurements. Included in this set are ambient and blank spectra, and the corresponding OC mass (which is assumed to be zero for the blank filters). Samples with TOR OC values below its method minimum detection limit (MDL) are excluded from the calibration set so as to not train the model to values with low signal-to-noise ratios. The total number of samples in the test set is  $1/3$  of the ambient and blank samples. The test set is used to assess the prediction quality and is not used in calibration development. Blank samples in the test set are used to calculate

the MDL. Performance metrics used to assess the quality and MDL determination are described in Sect. 2.4.

Multiple calibrations are developed by varying the spectra type used and by selecting filters for the calibration and test sets using different ordering regimes. We define a “base case” reference scenario, where the samples are chronologically stratified per site (i.e., ordered by date for each site), prior to selecting every third sample for inclusion in the test set. The remaining samples are placed in the calibration set. The base case is also defined to use the raw spectra. Other calibration models are described in the results section.

## 2.4 Evaluation of the quality of calibration

The quality of each calibration is evaluated by calculating four performance metrics: bias, error, normalized error and the coefficient of determination ( $R^2$ ) of the linear regression fit of the predicted FT-IR OC to measured TOR OC. FT-IR OC is the OC predicted from the FT-IR spectra and the PLSR calibration model. TOR OC is the artifact-corrected OC reported from TOR. The bias is the median difference between measured and predicted OC for the test set. Error is the median absolute bias. The normalized error for a single prediction is the error divided by the TOR OC value. The median normalized error is reported. The performance metrics are also calculated for the collocated TOR observations and compared to those of the FT-IR-OC to TOR-OC regression. The MDL and precision of the FT-IR and TOR methods are calculated and compared. The MDL of the FT-IR method is three times the standard deviation of the blanks in the test set (18 blank filters). MDL for the TOR method is three times the standard deviation of 514 blanks (Desert Research Intitute, 2012). Precision for both FTIR and TOR are calculated using the 14 parallel samples in the test set at the Phoenix, AZ site.

## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



### 3 Results

#### 3.1 Predicting TOR OC from infrared spectra

Figure 2 compares predicted FT-IR OC to measured TOR OC for the calibration and test set for the base case. The performance metrics for the calibration and test sets show good agreement between measured and predicted OC values. Prediction of the calibration set is expected to be better than the test set as the model is trained on these values. An ANOVA analysis between the calibration set predictions and the test set predictions indicate that while the predictions are not statistically different, the bias ( $p = 0.08$ ) and error ( $p < 0.001$ ) are. The performance metrics for the collocated TOR samples show good agreement between TOR samples collected at the same site and time. The precision between TOR samples is expected to be better than that between FT-IR OC and TOR OC because the TOR samples are collected on the same filter type and analyzed by the same method. However, since the collocated observations are from different sites than the FT-IR-OC and TOR-OC comparison (except Phoenix), a direct comparison (and ANOVA analysis) is not possible. The distribution of normalized errors for the calibration and test set and the collocated precision for the TOR samples are quite similar (Fig. S4 in the Supplement). The analysis suggests that the accuracy of FT-IR OC predictions is comparable to collocated TOR measurements.

Table 1 compares the MDL and precision of the FT-IR OC predictions and TOR OC measurements. The MDL for the FT-IR OC method using raw spectra (base case, Fig. 2) is higher than TOR but both methods have less than 3% of the samples below MDL. For the FT-IR OC method with raw spectra, 7 of the 268 ambient samples in the test set are below MDL; 4 for TOR. The MDL is calculated from 18 blank filters in the test set with 36 blank filters in the calibration set. However, the MDL is independent of the number (from zero to 36) of blanks in the calibration set (see Sect. S5 in the Supplement). The absolute precision is slightly better for FT-IR OC than for TOR OC. The mean predicted value for the blanks filters (last row of Table 1) is an order of magnitude lower than the 1st percentile of predicted OC values in this data set.

## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## 3.2 Predicting TOR OC using different spectral types

The analysis shown in Fig. 2 is performed on the raw spectra. Figure 3 shows the same prediction capability of the method using baseline corrected spectra and truncated spectra. All other inputs, including the samples used for the calibration and test sets, are not changed. The performance metrics (test set panel in Fig. 2 for raw spectra) are of the same order for all three cases. An ANOVA analysis of these three predictions produces  $p$  values of 0.99 ( $R^2$ ), 0.53 (bias) and 0.61 (error) indicating that the quality of predictions are not statistically different for these three spectra pretreatments. The distribution of normalized errors for the calibration and test set for both spectral pretreatments are shown in Fig. S4 in the Supplement and show that the distributions are quite similar to distribution of normalized errors when using the raw spectra.

Table 1 shows the MDL and precision values for these two cases. When compared to the raw spectra calibration, the MDLs for these two cases are lower than the raw spectra and both have only 2 samples below MDL. The mean blank values for the baseline corrected and truncated spectra case are higher and not centered around zero as are the raw spectra calibration. For baseline corrected cases, the mean blank is less than half of the 1st percentile of predicted OC values and for the truncated spectra, the mean blank is of the same order as the 1st percentile of predicted values ( $3.7 \mu\text{g}$ ). The precision is poorest using baseline corrected spectra. ANOVA of the blank values indicates that the blank predictions are significantly different ( $p < 0.001$  for prediction, bias and error).

## 3.3 Evaluating causes of bias and error by selecting the calibration and test sets based on measured parameters

In this section, we consider the role of the distribution of TOR OC, OM/OC and ammonium/OC on the quantification of OC. The magnitude of OC is considered since this is the property to be quantified. OM/OC is considered since it is indicative of the mix of primary and secondary organic aerosol composition. OM/OC is obtained from

## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



similar for the test and calibration sets. The bias and error indicate that the test set is well predicted for both the Base and Uniform cases. Similarly, for the case where the lowest and highest thirds of the values are used to predict the middle third (Non-uniform B), the bias and normalized error median and interquartile range are similar and small indicating good prediction of the test set. For the case when low OC mass samples are used to predict high OC mass samples (Non-uniform A), there is a small negative bias ( $-0.10 \text{ mg m}^{-3}$ ) and a larger range in bias for the test set. However, the normalized error is small and similar for the two sets highlighting the linearity of the calibration. For all of these cases, median OC masses for both sets are greater than  $15 \mu\text{g}$ . For the case when high OC mass samples are used to predict low OC mass samples (Non-uniform C), the median OC mass is less than  $15 \mu\text{g}$  in the test set. For this case the median bias is  $0.10$  to  $0.14 \mu\text{g m}^{-3}$  and the normalized error is between 40 and 50 % depending on the spectral types used. The range of errors (the higher errors are outside the bounds of the plot) is also considerably larger. The positive bias and normalized errors for low OC mass samples is expected due to some combination of higher analytical TOR and FT-IR errors, including TOR blank correction and PLSR fitting errors at low concentrations. For the samples below  $15 \mu\text{g}$ , the actual measurement artifact may be considerably less than the monthly median value used (Sect. 2.1), leading to an under-estimate of TOR OC which contributes to the positive bias in the FT-IR OC. The large sample to sample variability in measurement artifact in TOR may contribute to the higher variability in the error.

The top row of subplots in Fig. 5 shows the distribution of OM/OC in the test and calibration sets for the base case, the Uniform OM/OC case and the three Non-uniform OM/OC cases. The Base and Uniform cases have similar OM/OC distributions, a median bias of zero and low normalized error in the test and calibration sets indicating good prediction of the test set. When the highest and lowest 1/3 of the samples are used to predict the middle third (Non-uniform B), the median OM/OC are somewhat different between the calibration and test set but the test set has low bias and error indicating good prediction. However when there is a larger difference in OM/OC









## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



is large which means that more samples have larger biases than in the calibration set. However, the median OC for Phoenix is nearly 50  $\mu\text{g}$ , so the bias is small relative to the OC mass. The normalized error is also slightly higher for the Phoenix samples than the rest of the samples although the distribution of errors is similar for the calibration and test set indicating only a small effect on error. Phoenix has the largest difference in composition between it and the rest of the sites, yet the impact on the calibration metrics are small. This analysis carried out for OC/EC shows similar trends (Sect. S7 in the Supplement).

Only the Phoenix and Sac and Fox sites show differences in ammonium/OC between the test and calibration set; these are the same two sites impacted by OM/OC differences (Fig. 9). The calibration set for predicting Phoenix has higher ammonium/OC than Phoenix, the same pattern as Non-uniform C for ammonium/OC which was shown to have a small impact on predicted values. This suggests that the increased bias and error in Phoenix is due primarily to differences in organic composition not to ammonium interference. The calibration set for Sac and Fox has lower ammonium/OC than Sac and Fox. This is similar to Non-uniform A for ammonium/OC in which the calibration is not trained to disregard ammonium when determining OC, so a positive bias is observed and a larger normalized error and range of errors. Sac and Fox has only a small positive bias and increase in error and no increase in the range of error so the impact of ammonium, if present is small. However, the impact of the difference in OM/OC produces similar changes in bias and error as ammonium/OC, so for Sac and Fox, the small increases in bias and error compared to the calibration set may be due to either OM/OC or ammonium/OC or some combination of both.

We can therefore predict how well a site not included in the calibration will be predicted, based on the OC, OM/OC and ammonium/OC for the site. However, even for the most poorly predicted sites the median normalized errors are still fairly low, 17–25 % for sites with low OC mass and 11–14 % for Phoenix which has low OM/OC and 9–12 % for Sac and Fox due to some combination of low OM/OC and high ammonium/OC.

## 4 Conclusions

PTFE filters routinely collected in the IMPROVE network are non-destructively analyzed by FT-IR. The FT-IR spectra and parallel TOR OC measurements are used in partial least squares regression to develop calibrations to predict OC. All three spectral types produce high quality predictions. Blank filters in the test set are used to calculate MDL, but the number of blanks in the calibration set does not impact the value of the MDL. The calibration sets developed from samples ordered by site-date, OC or OM/OC and produce nearly bias-free predictions with low error. Samples with low OC mass predict OC in samples with high OC mass with low error because the calibration is linear. Errors for samples with low OC mass (less than  $15 \mu\text{g}$ , or  $0.45 \mu\text{g m}^{-3}$ ) are high primarily due to TOR OC analytical errors and artifact correction errors. Using the lowest 1/3 of OC samples in the calibration set may improve the prediction for some samples near the MDL but this modification to the calibration does not improve the overall performance of the calibration. Errors and bias are kept to a minimum by including samples in the calibration set that have a similar range of organic composition, as indicated by OM/OC or OC/EC, and a similar range of ammonium/OC as the samples to be predicted. Using a calibration set in which samples do not span the full range of OM/OC or ammonium/OC in the test set leads to higher bias and errors, but the bias and errors are still small. Therefore, we conclude that FT-IR spectra calibrated to TOR OC using partial least squares regression is a robust method for predicting organic carbon from particulate matter samples.

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## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## References

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## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama

**Table 1.** MDL and precision for FT-IR OC and TOR.

	TOR-OC	FT-IR OC raw spectra	FT-IR OC baseline corrected spectra	FT-IR OC truncated spectra
MDL ( $\mu\text{g m}^{-3}$ )*	0.05	0.14	0.11	0.08
% below MDL	1.5	2.6	0.7	0.7
Precision ( $\mu\text{g m}^{-3}$ )*	0.14	0.12	0.21	0.12
Mean blank ( $\mu\text{g}$ )	NR**	$0.1 \pm 1.5$	$1.9 \pm 1.2$	$2.8 \pm 0.9 \mu\text{g}$

\* Concentration units of  $\mu\text{g m}^{-3}$  for MDL and precision are based on the IMPROVE volume of  $32.8 \text{ m}^3$ .

\*\* Not reported.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

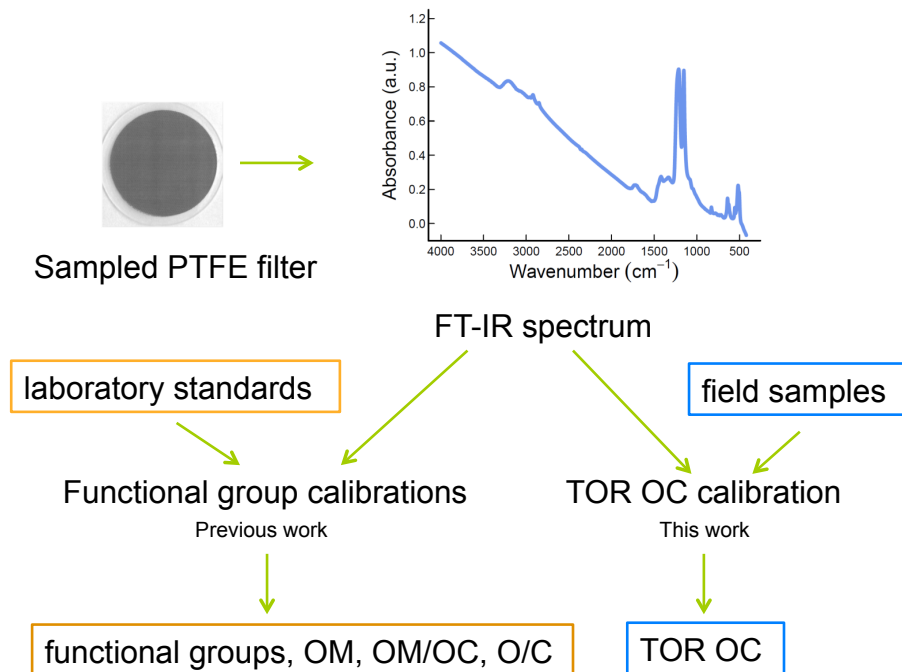
Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





**Figure 1.** FT-IR absorbance spectra from particulate matter collected on PTFE filters can be used for measuring OM, OM/OC, organic functional groups and, from the work presented here, TOR OC. Previous work on functional group calibrations includes: CH groups from saturated (Ruthenburg et al., 2014), unsaturated, and ring structures (Gilardoni et al., 2007; Maria et al., 2003; Russell et al., 2009); amine  $\text{CNH}_2$  (Liu et al., 2009; Maria et al., 2003); alcohol (Ruthenburg et al., 2014) and phenol COH (Bahadur et al., 2010; Russell et al., 2010; Takahama et al., 2013); organosulfate  $\text{COSO}_3$  by solvent-rinsing (Hawkins et al., 2010; Maria et al., 2003); organonitrate  $\text{CONO}_2$  groups (Day et al., 2010); carboxylic COH (Liu et al., 2009; Ruthenburg et al., 2014; Takahama et al., 2013), and carbonyl CO (Gilardoni et al., 2007; Maria et al., 2003; Ruthenburg et al., 2014; Takahama et al., 2013).

**Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements**

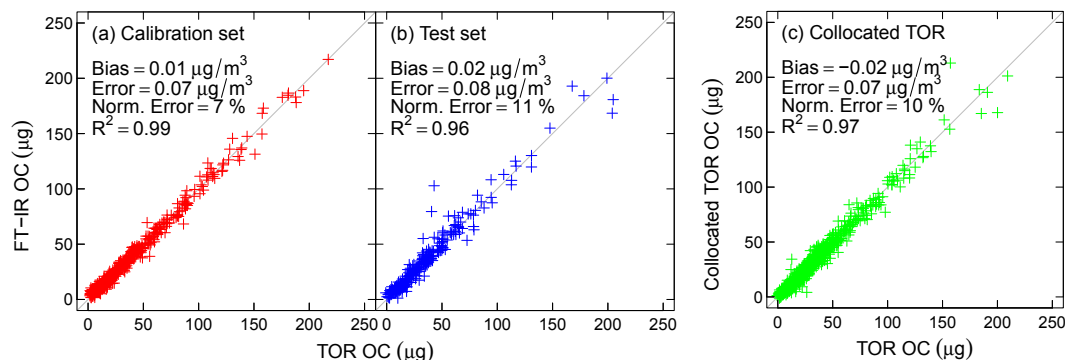
A. M. Dillner and S. Takahama

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	



## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama



**Figure 2.** Predicted OC for the calibration set **(a)** and test set **(b)**. The collocated TOR samples **(c)** are from sites with parallel quartz filters that are both analyzed by TOR. Only the Phoenix site has samples in the calibration, test and collocated data sets. There are 521 samples in the calibration set **(a)**, 265 samples in the test set **(b)** and 759 samples in the collocated TOR data set **(c)**. Concentration units of  $\mu\text{g m}^{-3}$  for bias and error are based on the IMPROVE nominal volume of  $32.8\text{ m}^3$ .

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

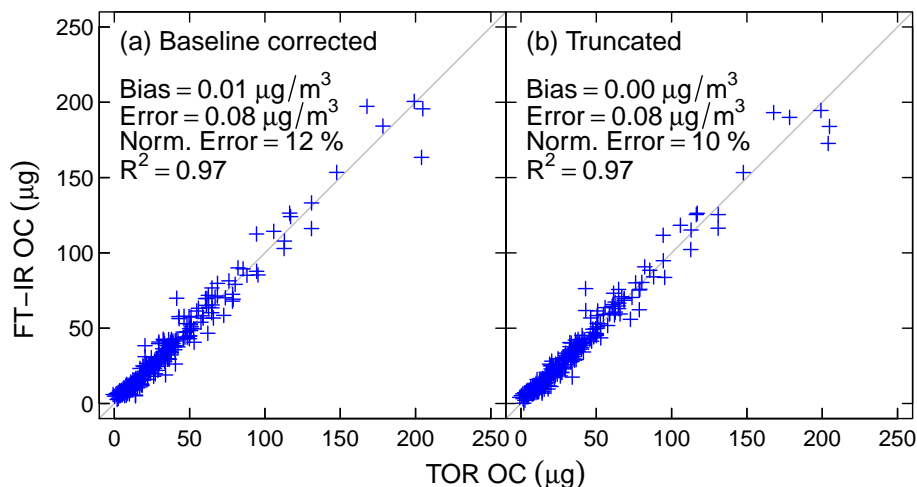
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements**

A. M. Dillner and S. Takahama



**Figure 3.** Predicted FT-IR OC vs. measured TOR OC for the base case test set with (a) baseline corrected and (b) truncated spectra. Concentration units of  $\mu\text{g m}^{-3}$  for bias and error are based on the IMPROVE nominal volume of  $32.8 \text{ m}^3$ .

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

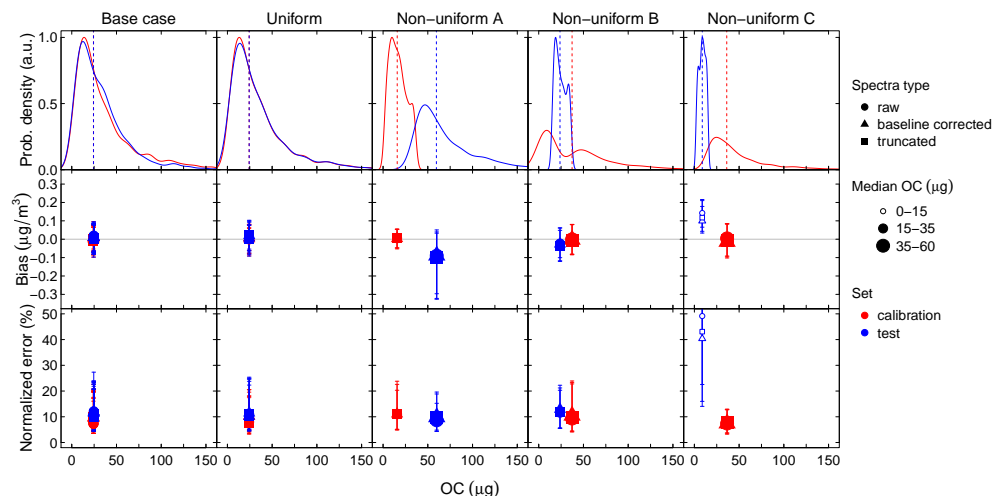
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama



**Figure 4.** The probability density distribution of OC and bias and normalized error (with the interquartile range shown by error bars) in the calibration (red) and test (blue) sets for five calibration cases: the Base case, the Uniform OC case and three Non-uniform OC cases. Vertical lines are the median of the OC mass distributions color-coded for calibration and test sets.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

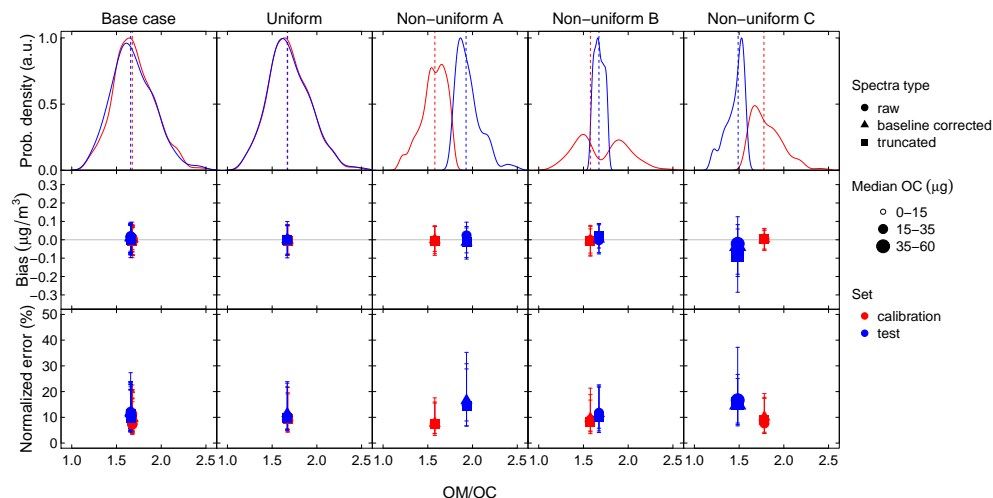
Printer-friendly Version

Interactive Discussion



## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama



**Figure 5.** The probability distribution of OM/OC and bias and normalized error (with the interquartile range shown by error bars) in the calibration (red) and test (blue) sets for five calibration cases: the base case, the uniform OM/OC case and three non-uniform OM/OC cases. Vertical lines on the probability distributions are the color-coded median of the OM/OC distributions.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

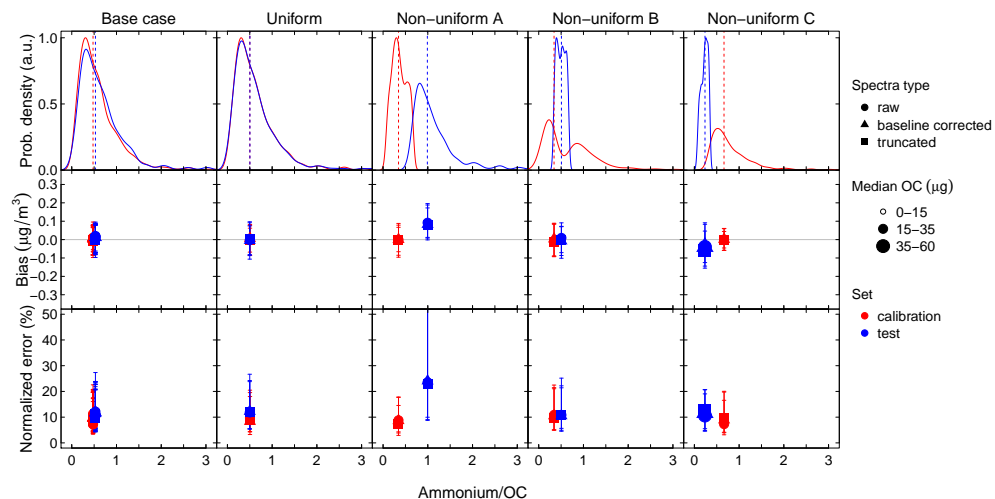
Printer-friendly Version

Interactive Discussion



## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama



**Figure 6.** The probability distribution of ammonium/OC and bias and normalized error (with the interquartile range shown by error bars) in the calibration (red) and test (blue) sets for five calibration cases: the base case, the uniform ammonium/OC case and three non-uniform ammonium/OC cases. Vertical lines on the probability distributions are the median of the ammonium/OC distributions.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

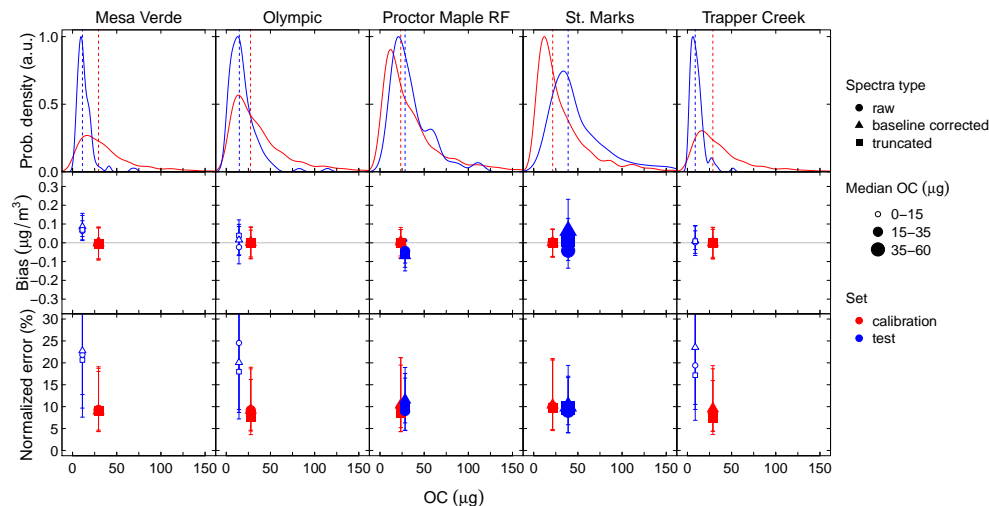






## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama



**Figure 8.** The distribution of OC and the bias and normalized error (with the interquartile range shown by error bars) in the calibration (red) and test (blue) sets for calibrations developed for each of five sites. Each calibration has all samples in the calibration set except for the site to be predicted. Vertical lines are the color-coded median of the OC distributions.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

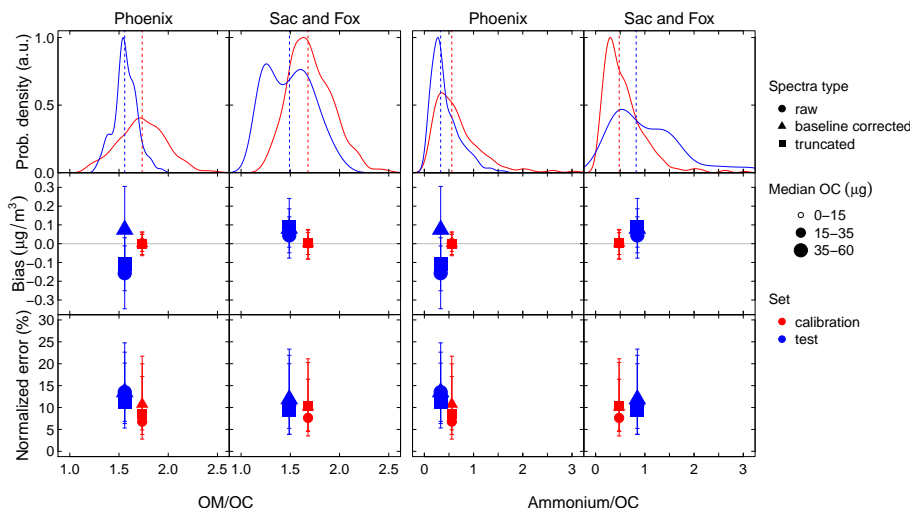
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Predicting ambient aerosol Thermal Optical Reflectance (TOR) measurements

A. M. Dillner and S. Takahama



**Figure 9.** The OM/OC and ammonium/OC distributions and the bias and normalized error (with the interquartile range shown by error bars) in the calibration (red) and test (blue) sets for calibrations developed for Phoenix and Sac and Fox. Each calibration has all samples in the calibration set except for the site to be predicted. Vertical lines are the median of the OM/OC or ammonium/OC distributions.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

