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RESEARCH TRIANGLE PARK, NC 27711

OFFICE OF  
AIR QUALITY PLANNING  
AND STANDARDS

November 17, 2010

MEMORANDUM

SUBJECT: Simplified Approaches for Calculation of Hourly PM<sub>2.5</sub> Light Extinction Values From Hourly PM<sub>2.5</sub> Mass and Relative Humidity Data and 24-hour PM<sub>2.5</sub> Composition Data

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TO: PM NAAQS Review Docket (EPA-HQ-OAR-2007-0492)

**Overview**

This memorandum explores simple procedures for calculating PM<sub>2.5</sub> light extinction, with the goal of identifying a procedure that produces hourly values that are comparable to those developed for the 15-city assessment in the final Urban Focused Visibility Assessment for the current PM NAAQS review (UFVA Section 3.3).<sup>1</sup> The possible benefits of moving to a simpler approach include: (1) more transparency in the required calculations, (2) less intensive data processing, (3) an increase in the number of monitoring sites that could meet the data requirements of the approach without adding new sampling equipment or additional laboratory analysis, and (4) an increase in the number of days per year for which the calculation of PM light extinction could be conducted.

This memorandum is based on the analysis that was first reported in Appendix 4B of the second draft of the PM Policy Assessment Document. Both that draft Appendix 4B and this memorandum use 2005-2007 data. Appendix 4B of the final Policy Assessment Document will be based on 2007-2009 data and will focus on the characteristics of two preferred simpler methods that have been selected based, in part, on the analysis described in this memorandum.

**Complexity of the UFVA Approach**

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<sup>1</sup> Particulate Matter Urban-Focused Visibility Assessment Final Document, EPA 452/R-10-004, July 2010. The PM<sub>10-2.5</sub> values for St. Louis in the UFVA were determined by difference between two nearby monitoring sites. Based on comments received on the draft UFVA to the effect that the PM<sub>10</sub> monitoring site used for St. Louis was not representative of the St. Louis urban area, EPA does not consider the PM<sub>10-2.5</sub> concentrations for St. Louis to be credible. The PM<sub>10</sub> light extinction results for St. Louis were, therefore, excluded from most tables and figures in the second draft Policy Assessment Document. However, for the assessment in this memorandum of various simplified methods to calculate PM<sub>2.5</sub> light extinction, St. Louis data were not excluded since all of the comparisons are for calculated PM<sub>2.5</sub> light extinction.

The UFVA approach to estimation of hourly PM<sub>2.5</sub> light extinction has the following complex aspects:

1. The SANDWICH mass balance model is used to estimate 24-hour average PM<sub>2.5</sub> sulfate, nitrate, and organic carbonaceous material (OCM) mass loading on the FRM filter for each Chemical Speciation Network (CSN) sample day.<sup>2</sup> This requires information on daily temperature and relative humidity. The sulfate and nitrate components are initially derived from the relevant CSN filters, with adjustments to represent FRM mass. FRM sulfate includes estimated particle bound water while the FRM nitrate loading may under-represent the ambient concentration of nitrate. These are re-adjusted in a subsequent step to represent ambient conditions prior to calculation of extinction.
2. The estimates of 24-hour average PM<sub>2.5</sub> elemental carbon and fine soil component concentrations are determined from the analysis of the relevant CSN filter.
3. Monthly mean diurnal variations of each of the major PM<sub>2.5</sub> components from CMAQ air quality simulation modeling results for the location of each monitoring site are applied to sample day-specific CSN 24-hour samples to create preliminary estimates of hourly component concentrations. For the UFVA, available output from a 2004 CMAQ modeling platform was used. This step can result, for example, in preliminary estimates of concentrations of sulfate that are fairly uniform throughout a day while concentrations of nitrate may show much more variation because of temperature effects on the gas/particle partitioning of nitrate.
4. Estimates of hourly PM<sub>2.5</sub> mass are developed by normalizing continuous PM<sub>2.5</sub> measurements to the 24-hour FRM filter mass.<sup>3</sup>
5. The preliminary estimates of hourly components from step 3 above are scaled up or down in equal proportion to reconcile their sum to the estimate of hourly PM<sub>2.5</sub> mass.
6. The resulting hourly PM<sub>2.5</sub> sulfate and nitrate component concentrations are adjusted to reflect actual atmospheric concentration, which is assumed to be represented by the CSN filter sulfate and nitrate measurements. (This step in effect un-does the estimated FRM sulfate mass enhancement due to particle bound water and the FRM nitrate loss introduced by the SANDWICH mass balance model.)
7. The original IMPROVE algorithm is used to estimate hourly PM<sub>2.5</sub> light extinction from hourly PM<sub>2.5</sub> component and hourly relative humidity values.

### **Analytical Approach in this Memo**

This analysis examines the difference between calculated hourly PM<sub>2.5</sub> light extinction values used in the UFVA and values generated using simpler approaches, explored in a step-wise fashion. In each step, one of the steps described above is omitted or simplified. All of the simpler

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<sup>2</sup> Frank, N., Retained Nitrate, Hydrated Sulfates, and Carbonaceous Mass in Federal Reference Method Fine Particulate Matter for Six Eastern U.S. Cities, *J. Air Waste Manage. Assoc.*, 56, 500-511, 2006.

<sup>3</sup> This memo is based on 2005-2007 data. The continuous PM<sub>2.5</sub> instruments operating in this period were not EPA-approved as Federal Equivalent Methods (FEMs). EPA-approved FEMs were first used in state networks in 2009. EPA staff envisions that in any future monitoring of hourly PM<sub>2.5</sub> mass to implement a visibility-based secondary PM NAAQS, EPA-approved continuous FEMs will be required. For both the UFVA and this memo, therefore, hourly PM<sub>2.5</sub> mass values from continuous instruments were adjusted day-by-day to match the 24-hour average PM<sub>2.5</sub> mass reported by the collocated filter-based sampler.

approaches (designated by letter of the alphabet and described below) use the original IMPROVE algorithm without the Rayleigh and  $PM_{10-2.5}$  terms.<sup>4</sup>

- Approach A. This designates the UFVA approach, but without the  $PM_{10-2.5}$  term in the IMPROVE algorithm.
- Approach B. This approach uses a simpler approach to estimating organic carbonaceous mass and nitrate than in the UFVA approach briefly described in the steps listed above. Table 1 contrasts in detail the steps in this simpler approach B (and approach F, below) to the steps of approach A. The key distinguishing features of approach B are (i) a multiplier of 1.7 is applied to the CSN measurement of organic carbon (after a correction for blank filter artifact) rather than estimating organic carbonaceous material by the mass-balance SANDWICH approach, and (ii) the hourly  $PM_{2.5}$  mass (still normalized to match the FRM value for the 24-hour  $PM_{2.5}$  mass as in the UFVA approach) is speciated using that day's CSN-measured component mix directly, with no correction for possible nitrate loss by the continuous instrument or the FRM.
- Approach D. This approach is the same as B except that the time-varying diurnal component profile from CMAQ is replaced by a flat profile for each sample day. This has the effect of giving each hour of the day the same percentage mix of components, but each CSN day is treated separately.
- Approach E. In this approach, step 3 above was modified. The preliminary estimates of hourly component concentrations for every day were calculated by applying the CMAQ diurnal profile to the monthly-average 24-hour concentration of that component (in  $\mu\text{g}/\text{m}^3$ ). This results in an estimate of the mass concentration of each component for each hour of "an average day." Then these values were adjusted by a common factor to match the hour-specific  $PM_{2.5}$  mass concentrations in each day. Thus, this method suppresses the information from the CSN data on how the 24-hour component mix varies day-to-day, but hours still vary in component mix due to the application of the CMAQ profiles.
- Approach F. This approach is the same as B except both flat diurnal  $PM_{2.5}$  component variation are assumed and monthly averaged  $PM_{2.5}$  component percentages are used in place of sample period-specific values from CSN data (i.e., the approach combines aspects of approaches D and E). The net effect is that every hour of a month is assumed to have the same percentage mix of components. For greatest clarity, the data sources and calculation steps used in this approach are listed in Table 2.
- Approach I. This approach simply uses the  $PM_{2.5}$  mass concentration times a single constant. This approach was included to show the performance of using  $PM_{2.5}$  mass

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<sup>4</sup> Note that the letter designations for the approaches are not contiguous. This is because EPA staff tested additional approaches that are not included in this technical memo. Note also that all of the figures include approach designators, as plan designators. The 1.7 multiplier for OC was selected for this memo after a brief assessment of what multiplier value would reproduce SANDWICH results on average. After the completion of this work, a more thorough analysis based on 2007-2009 CSN data only from sites that had converted to the IMPROVE carbon methods indicated that a multiplier of 1.6 is more appropriate when using OC data collected with the newer CSN carbon methods. The 1.6 value is used in the final version of the Policy Assessment Document.

without adjusting for particle composition and humidity effects on hygroscopic particles. The constant used for this approach was 4.35 m<sup>2</sup>/g.<sup>5</sup>

As the results below show, approaches B, D, E, and F produce hourly PM<sub>2.5</sub> light extinction values that are quite comparable to the hourly PM<sub>2.5</sub> light extinction values in the original UFVA (i.e., approach A). Approach F is of particular interest because it is the most simplified of the methods tested that make use of CSN measurements, and its use of monthly-averaged PM<sub>2.5</sub> component concentrations means that it can be applied every day, not just on days with CSN monitoring data (i.e., 1-day-in-3 or 1-day-in-6).<sup>6</sup>

Appendix 4B of the final Policy Assessment Document considers two approaches that are slight variations of approaches D and F, using 2007-2009 data instead of 2005-2007 data as used in this memo.

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<sup>5</sup> The value of 4.35 m<sup>2</sup>/g has no derivation of particular importance. If this approach were to be pursued further, more careful analysis would be appropriate, including analysis of the possibility of site-specific or region-specific constants.

<sup>6</sup> Note that Approach F as applied for this memo required the availability of filter-based FRM/FEM data for 24-hour concentration, and that most filter-based PM<sub>2.5</sub> monitoring sites do not operate every day. However, see the related comment at step (xi) of Table 2.

1 **Table 1. Detailed Comparative Description of Approaches A, B, and F for Estimating 1-hour PM<sub>2.5</sub> Light Extinction.**  
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UFVA Step <sup>7</sup>	Aspect of Approach	Approach A	Approach B	Approach F
1	Estimation of 24-hour organic carbonaceous mass	The SANDWICH method is used to subdivide the 24-hour PM <sub>2.5</sub> mass reported by the FRM for each day and site into hydrated ammonium sulfate, ammonium nitrate, elemental carbon, organic carbonaceous material (OCM), and fine soil. This is done using information from the CSN measurements, physical models, and day-specific temperatures and relative humidity. OCM is estimated as the residual needed to achieve mass balance after estimation of the other components.	Organic carbonaceous mass is assumed to equal the organic carbon value reported from CSN sampling, minus a blank filter correction that depends on sampler model and laboratory method for carbon but not on monitoring site, times 1.7.	Same as B
1, continued	Estimation of 24-hour elemental carbon mass	CSN elemental carbon concentration	Same as A	Same as A
1, continued	Estimation of 24-hour ammonium sulfate mass	CSN sulfate concentration, with day-specific SANDWICH estimates of associated ammonium and water.	Sulfate ion measurement from the CSN filter is multiplied by 1.375 to represent dry ammonium sulfate.	Same as B
1, continued	Estimation of 24-hour ammonium nitrate mass	Nitrate ion on the FRM Teflon filter is estimated by SANDWICH, with day-specific estimates of associated ammonium and water.	Nitrate ion measurement from the CSN filter is multiplied by 1.29 to represent dry ammonium nitrate.	Same as B

<sup>7</sup> The numbering of steps follows that used to describe the UFVA approach in section 3.3.1 of the UFVA.

<b>UFVA Step<sup>7</sup></b>	<b>Aspect of Approach</b>	<b>Approach A</b>	<b>Approach B</b>	<b>Approach F</b>
1, continued	Estimation of 24-hour fine soil/crustal mass	Calculated from CSN elements, but without Al (a difference from the IMPROVE approach)	Same as A	Same as A
2	Diurnal pattern of PM <sub>2.5</sub> components	The CMAQ-derived monthly normalized diurnal profiles for the sulfate, nitrate, elemental carbon, organic carbon and fine soil/crustal components (each of which averages to 1.0 across 24 hours) were multiplied by the day-specific SANDWICH-based estimates of the 24-hour average concentrations of the five PM <sub>2.5</sub> components, to get intermediate day-specific hourly estimates of the five components (including ammonium and water associated with sulfate and nitrate ion).	CMAQ-derived profiles were applied to the mass concentration of each of the five components in same way as in Approach A. However, as described above, in Approach B the sulfate, nitrate, and organic carbonaceous material components are defined and estimated differently than in Approach A.	No diurnal profiles are used.
3	Sum the 5 components	The hourly concentrations of these five components (including day-specific ammonium and water associated with sulfate and nitrate ion when the FRM Teflon filter is weighed) were added together, to get a sum-of-components estimate of hourly PM <sub>2.5</sub> mass for the day of the FRM/CSN sampling.	The hourly concentrations of the five components were added together, to get a sum-of-components estimate of hourly PM <sub>2.5</sub> for the day of FRM/CSN sampling. Note that water is not included.	Calculate the monthly-average percentage mix of the 5 PM <sub>2.5</sub> components, as follows: For each day of 24-hour CSN sampling, sum the five (dry) components. Calculate the fraction of sum-of-5 for each component. Average the fraction for each component across the CSN sampling days in the month.

<b>UFVA Step<sup>7</sup></b>	<b>Aspect of Approach</b>	<b>Approach A</b>	<b>Approach B</b>	<b>Approach F</b>
4	Hourly PM <sub>2.5</sub> concentration, consistent with 24-hour FRM concentration.	The hourly data from the continuous PM <sub>2.5</sub> instrument on the day of the FRM sampling were normalized by their 24-hour average, to get a normalized diurnal profile. This profile was applied to the 24-hour PM <sub>2.5</sub> mass reported by the FRM sampler, to get a preliminary, FRM-consistent estimate of hourly PM <sub>2.5</sub> mass for the day of the FRM sampling. This keeps the average of the valid 1-hour PM <sub>2.5</sub> values equal to the 24-hour value from the FRM sampler.	Same as A	Same as A, but see the comment on this topic in Table 2.
5, 6	Adjust preliminary estimates of hourly PM <sub>2.5</sub> component concentrations (reflecting CMAQ diurnal profiles and 24-hour measurements) to be consistent with estimate of hourly PM <sub>2.5</sub> mass.	The two estimates of hourly PM <sub>2.5</sub> mass from steps 3 and 4 were compared, hour-by-hour. Within each hour, the estimates of all five components from step 2 were increased or decreased by a common factor so that the sum of the five components after this adjustment was equal to the estimate of the hourly PM <sub>2.5</sub> mass from step 4. The adjustment percentage varied from hour-to-hour.	Same as A	Not applicable  Monthly-average percentage mix of PM <sub>2.5</sub> components is directly applied to the day-specific FRM-consistent hourly PM <sub>2.5</sub> mass.

UFVA Step <sup>7</sup>	Aspect of Approach	Approach A	Approach B	Approach F
7	Adjust the FRM-consistent estimate of sulfate to the CSN/IMPROVE-consistent basis expected by the IMPROVE algorithm.	Each hourly estimate of sulfate concentration on the FRM filter from step 6 (which includes estimates of associated ammonium and particle bound water) was adjusted so that it excludes water and reflects full neutralization and therefore is consistent with the reporting practices of the IMPROVE program and the IMPROVE algorithm.	No adjustment is needed, given that the factors of 1.375 and 1.29 already assume full neutralization and no water.	Same as B
8	Adjust the FRM-consistent estimate of nitrate to the CSN/IMPROVE-consistent basis expected by the IMPROVE algorithm.	<p>A similar adjustment as in step 7 (for sulfate) was made to each hour's nitrate concentration from step 6, so that the estimate of hourly nitrate would reflect actual atmospheric conditions and be consistent with the IMPROVE algorithm.</p> <p>This can result in the estimate of nitrate used in the IMPROVE algorithm being higher than the FRM-consistent estimate, for days on which the SANDWICH method predicts a loss of nitrate from the FRM filter.</p>	<p>No adjustment is made.</p> <p>Implication:</p> <p>On warm days when the FRM filter has lost nitrate mass, the estimates of hourly PM<sub>2.5</sub> will be lower than actual atmospheric mass. All hourly PM<sub>2.5</sub> components will be reduced, by the fraction that the lost nitrate is of total PM<sub>2.5</sub> mass.</p>	Same as B
Not numbered in UFVA	Estimation of PM <sub>2.5</sub> light extinction from estimates of hourly concentrations of PM <sub>2.5</sub> components.	Original IMPROVE algorithm, including f(RH) determined from hourly RH. Hours with RH >90% were excluded from design values and from most graphical displays of results.	Same as A	Same as A

**Table 2. Calculation Steps for Approach F.**

Calculation Step	Comments
(i) For each CSN sampling day, subtract OC artifact from OC measurement, and multiply by 1.7 to estimate organic carbonaceous material (OCM).	The values for the OC artifact ranged from 0.32 to 1.53 $\mu\text{g}/\text{m}^3$ , depending on sampler model. The artifact adjustment for the URG 3000N sampler is of most interest prospectively, because it is the single sampler now in use for carbon sampling in CSN. The URG 3000N was used only at about one-half of the 15 study sites and only in the second half of 2007. For those sites and days, an organic carbon artifact of 0.4 $\mu\text{g}/\text{m}^3$ was assumed for the purposes of the UFVA and this document, based on early experience with this sampler. EPA staff are currently exploring whether there is a better way to adjust for organic carbon artifact based on a more recent, larger field blank and back-up filter data set.
(ii) For each CSN sampling day, calculate fine soil/crustal $\text{PM}_{2.5}$ (FS) from CSN measurements of crustal elements Si, Ca, Fe, and Ti, using the formula $\text{Fine soil PM}_{2.5} = 3.73 \times [\text{Si}] + 1.63 \times [\text{Ca}] + 2.42 \times [\text{Fe}] + 1.94 \times [\text{Ti}]$	This 4-element approach to estimation of fine soil is the approach used in the SANDWICH method. It is a modification of the 5-element approach used in the Regional Haze program. It was originally selected for the SANDWICH method because of concern over the uncertainty of the [Al] measurements at IMPROVE sites. [Al] measurements using CSN methods are considered less uncertain than IMPROVE measurements. For Appendix 4B of the final Policy Assessment Document, EPA staff intends to revert to the 5-element approach used in the Regional Haze program.
(iii) For each CSN sampling day, multiply CSN measurement of sulfate ion (S) by 1.375, and multiply CSN measurement of nitrate ion (N) by 1.29, to reflect associated ammonium under an assumption of full neutralization.	
(iv) Sum the above estimates of the 5 components of $\text{PM}_{2.5}$ :  $\text{Sum} = 1.375 \times \text{S} + 1.29 \times \text{N} + \text{OCM} + \text{EC} + \text{FS}$	Here, S means sulfate ion and N means nitrate ion.
(v) For each CSN sampling day, calculate the 5 component factions:	

<p>sulfate fraction = <math>1.375 \cdot S / \text{Sum}</math>  Nitrate fraction = <math>1.29 \cdot N / \text{Sum}</math>  OCM fraction = <math>\text{OCM} / \text{Sum}</math>  EC fraction = <math>\text{EC} / \text{Sum}</math>  FS fraction = <math>\text{FS} / \text{Sum}</math></p>	
<p>(vi) Average the fraction for sulfate from step (v) across the CSN sampling days of that calendar month of that calendar year. Repeat for the other 4 components. Call these the monthly-average component fractions.</p>	<p>In the analysis reported in this memo, no minimum number of CSN samples was applied when calculating monthly-average component fractions. It may be more appropriate to apply a minimum requirement of four samples per month, which is usually 80% of the samples scheduled per month at a site using one-in-six-days sampling.</p>
<p>(vii) For each CSN sampling day, average the 24 values of 1-hour <math>\text{PM}_{2.5}</math> mass from the continuous instrument. Divide the 24-hour FRM value for <math>\text{PM}_{2.5}</math> mass by this average. Call this the “instrument scaling factor”.</p>	
<p>(viii) For each CSN sampling day, multiply each 1-hour <math>\text{PM}_{2.5}</math> mass value from the continuous instrument by the instrument scaling factor.</p>	<p>As explained in footnote 2, hourly <math>\text{PM}_{2.5}</math> mass concentrations from continuous instruments were adjusted on a day-by-day basis to match the 24-hour concentration reported by a collocated FRM/FEM filter-based sampler only for the purpose of this analysis. Prospectively, if only continuous instruments approved as federal equivalent methods (FEM) were allowed to be used for purposes of measuring hourly <math>\text{PM}_{2.5}</math> mass concentrations for purposes of estimating hourly <math>\text{PM}_{2.5}</math> light extinction, this adjustment presumably would not be needed. If the adjustment step were omitted, then FRM measurements would not be a required data source for this approach.</p>
<p>(ix) For each daylight hour of each day of that month (including days without CSN sampling) multiply the value of hourly <math>\text{PM}_{2.5}</math> mass from step (viii) by the monthly-average component fractions from step (vi).</p>	<p>The exclusion of hours with <math>\text{RH} &gt; 90\%</math> originated out of concern that a direct instrumental measurement of PM light extinction might result in high values of light extinction due to natural conditions of fog or precipitation. While approach F does not employ a light extinction instrument, the accuracy of hourly <math>\text{PM}_{2.5}</math> mass and RH measurements at such high values of RH is still a concern.</p>
<p>(x) Insert the results from step (ix) into the original IMPROVE algorithm, along with <math>f(\text{RH})</math> calculated based on same-hour RH. Omit the Rayleigh scattering term and the contribution from <math>\text{PM}_{10-2.5}</math>. Estimates of <math>\text{PM}_{2.5}</math> light extinction in hours with RH greater than 90% are not used in design value calculations and graphics presented in this memo.</p>	

## Comparative Performance of Simplified PM<sub>2.5</sub> Light Extinction Approaches

The performance assessment of simplified approaches for calculated PM<sub>2.5</sub> light extinction was accomplished by comparing hourly values of PM<sub>2.5</sub> light extinction generated by each approach to their corresponding paired values generated using the original UFVA method, which is labeled above as approach A. Annual box and whisker plots of the percentage differences between the paired values, as well as annual and monthly scatter plots and regression analysis of these paired data, were generated. Selected graphs and summary tables of regression statistics are included below to show the degree of comparability between the various approaches to the original estimates of PM<sub>2.5</sub> light extinction.

The box and whisker plots of the differences between calculated hourly PM<sub>2.5</sub> light extinction by approaches B, D, E, and F are shown in Figures 1 and 2. In the box and whisker plots of percentage difference, the percentage difference is calculated as follows:

$$\text{Percentage difference} = [(\text{simpler approach estimate}) - (\text{"A"} \text{ estimate})] / (\text{"A"} \text{ estimate}) * 100\%$$

Note that a few points in the box and whisker plots have extreme values for the percentage difference. These instances have been traced to the effect of rounding differences for very low values of PM<sub>2.5</sub> light extinction.

The patterns of relatively small bias for the 15 urban areas are notably similar in each of the plots. Keeping in mind that the differences in the approach are iterative with approach B differing from approach A only by not using the SANDWICH model to estimate organic component mass concentration and to adjust nitrate concentrations, while the three other approaches (i.e., D, E, and F) add additional simplifications, it is perhaps surprising that the city-to-city pattern of the box positions and sizes are remarkably similar for these four approaches. This suggests that the simplification between approaches A and B (i.e., replacing the SANDWICH model) is responsible for the greatest amount of differences in calculated hourly PM<sub>2.5</sub> light extinction between approach A and D, E, and F, or in other words, the additional changes introduced in the remaining three approaches did not much affect the resulting hourly values.<sup>8</sup>

The degree of comparability for paired hourly PM<sub>2.5</sub> light extinction between approach F and A, and between approach F and B values by month and urban area is evident in regression statistics (Tables 3 and 4). In both tables, the regression lines have slopes and R<sup>2</sup> values near 1.0, with small intercepts for most urban areas and months implying that the values are highly comparable. The western urban areas (e.g., Fresno, Houston, Los Angeles, Phoenix, Salt Lake City and Tacoma) have slopes and R<sup>2</sup> values for some months that imply a bias and/or noisier relationship between values calculated by approaches F and A.<sup>9</sup> As expected the regression relationships show that values calculated by approach F are more similar to those of approach B (Table 4)

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<sup>8</sup> In the box and whisker plots, some extreme values of the percentage change are due to rounding effects when the values involved were very small.

<sup>9</sup> One can speculate that the bias and/or noisier relationship for some months are in Fresno, Los Angeles, and Salt Lake City due to nitrate episodes, in Houston due to episodes of Saharan dust transport, and in Tacoma due to biomass burning episodes.

since neither uses the SANDWICH model, than to those of approach A (Table 3) which included the SANDWICH model estimates. Four scatter plots of calculated hourly  $PM_{2.5}$  light extinction for all months that compare approach F to approach A and approach F to approach B for Baltimore and Fresno are shown in Figure 3 as examples of the degree of comparability for eastern and western urban areas.

The analysis documented in this memo is not a comprehensive assessment of why there are greater differences between approaches A and B than between approaches B and any of D, E, and F. However, some explanations are suggested by the results themselves. The fact that hour-to-hour and day-to-day variations in the dry  $PM_{2.5}$  composition can be replaced by monthly averaged values without much loss of precision in calculated hourly  $PM_{2.5}$  light extinction suggests that these shorter term variations within a single month at a single monitoring site are usually not very influential. If day-to-day variations in the component mix are not very influential, this may imply that the different estimates of component percentage mix caused by use of the UFVA approach versus the simpler approach B may also not be very influential. By process of elimination, this suggests that the greater differences between approaches A and B may be due to the adjustment in the UFVA method to account for negative sampling artifact for ammonium nitrate. The UFVA method (approach A) can result in hourly sum-of-five-component-concentrations that average over 24 hours to a value greater than the FRM-reported  $PM_{2.5}$  mass, while approach B does not. This is consistent with the behavior for sites that have high ammonium nitrate (e.g., Fresno and Los Angeles). Another approach that properly accounts for nitrate loss effects but otherwise has the simplifications of approach F might be an even better method to calculate  $PM_{2.5}$  light extinction. In particular, if hourly data from continuous FEM reflect actual ambient nitrate concentrations during each hour, direct use of such data without normalization to match the 24-hour average reported by the FRM may produce better estimates of actual hourly  $PM_{2.5}$  light extinction during hours when light extinction is highest.

Another assessment has looked more closely at why the use of monthly averaged composition to estimate  $PM_{2.5}$  light extinction produces comparable results to the use of daily values.<sup>10</sup> In that assessment the terms of the IMPROVE algorithm were rearranged to show that light extinction equals  $PM_{2.5}$  mass times the sum of a dry extinction efficiency term and a moist extinction efficiency term. Both extinction efficiency terms depend on composition and the moist term also depends on relative humidity. The dry term can vary in theory from  $1 \text{ m}^2/\text{g}$  to  $10 \text{ m}^2/\text{g}$ , but is commonly in a range from about  $3 \text{ m}^2/\text{g}$  to  $4 \text{ m}^2/\text{g}$  for typical urban  $PM_{2.5}$  composition, which is dominated by sulfate, nitrate, and/or organic  $PM_{2.5}$ . The moist extinction efficiency term depends on the hygroscopic fraction of the  $PM_{2.5}$  mass (i.e., composed of sulfate and nitrate) so it ranges from 0 to 1.0, which varies regionally and seasonally, as well as day to day and hourly. The moist extinction efficiency term is the product of the hygroscopic fraction and a non-linear function of relative humidity that varies from  $0 \text{ m}^2/\text{g}$  (for relative humidity <40%) to  $9.5 \text{ m}^2/\text{g}$  (for relative humidity at 90%). It seems that most of the variations in light extinction associated with variations in the moist extinction efficiency are due to the relative humidity variability compared  $PM_{2.5}$  composition variability. Overall, this other assessment supports the conclusions from this analysis (i.e., that use of monthly mean  $PM_{2.5}$  composition values in the IMPROVE

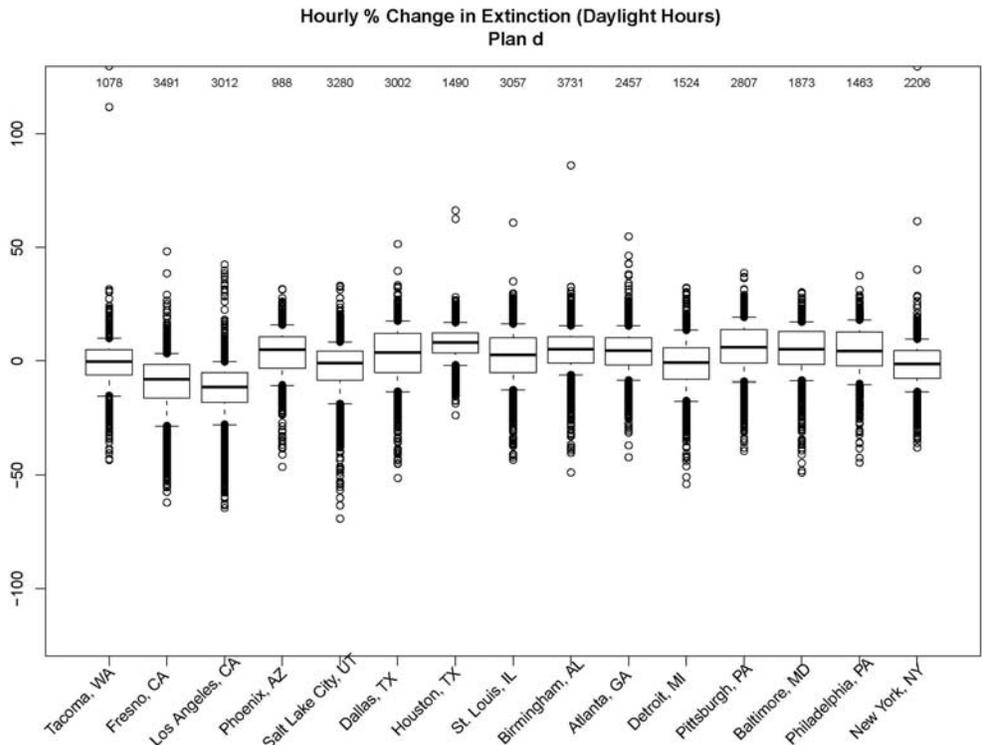
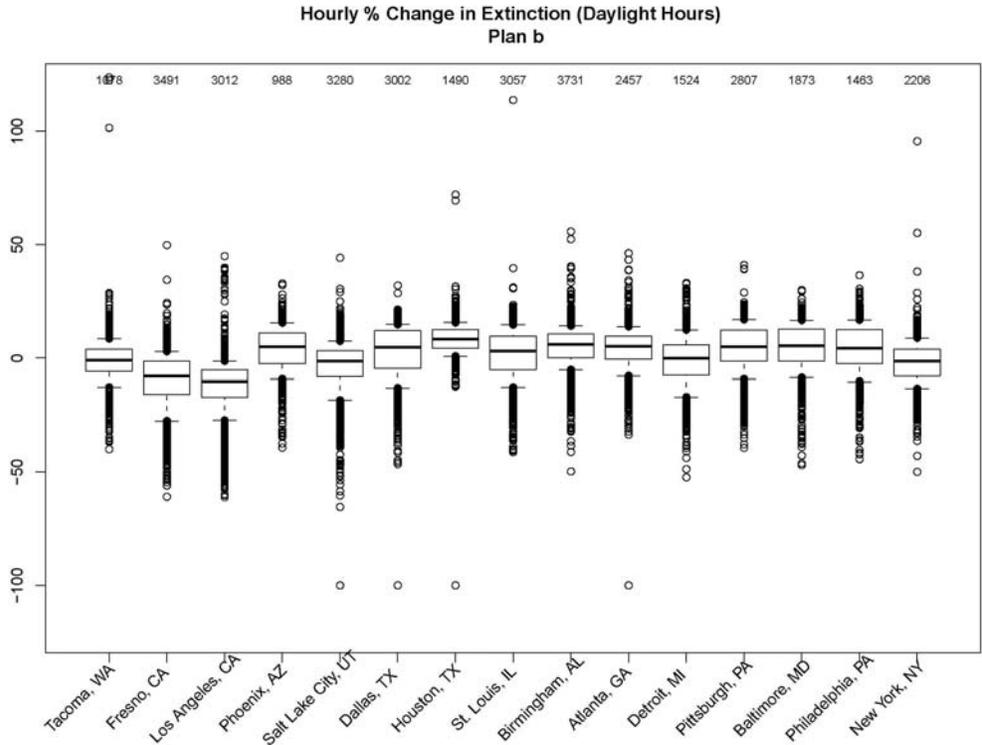
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<sup>10</sup> Memo: "Assessment of the Use of Speciated  $PM_{2.5}$  Mass-Calculated Light Extinction as a Secondary PM NAAQS Indicator of Visibility", Marc Pitchford, NOAA, November 17, 2010.

algorithm does not greatly degrade the estimation of  $PM_{2.5}$  light extinction compared to use of sample period specific  $PM_{2.5}$  composition).

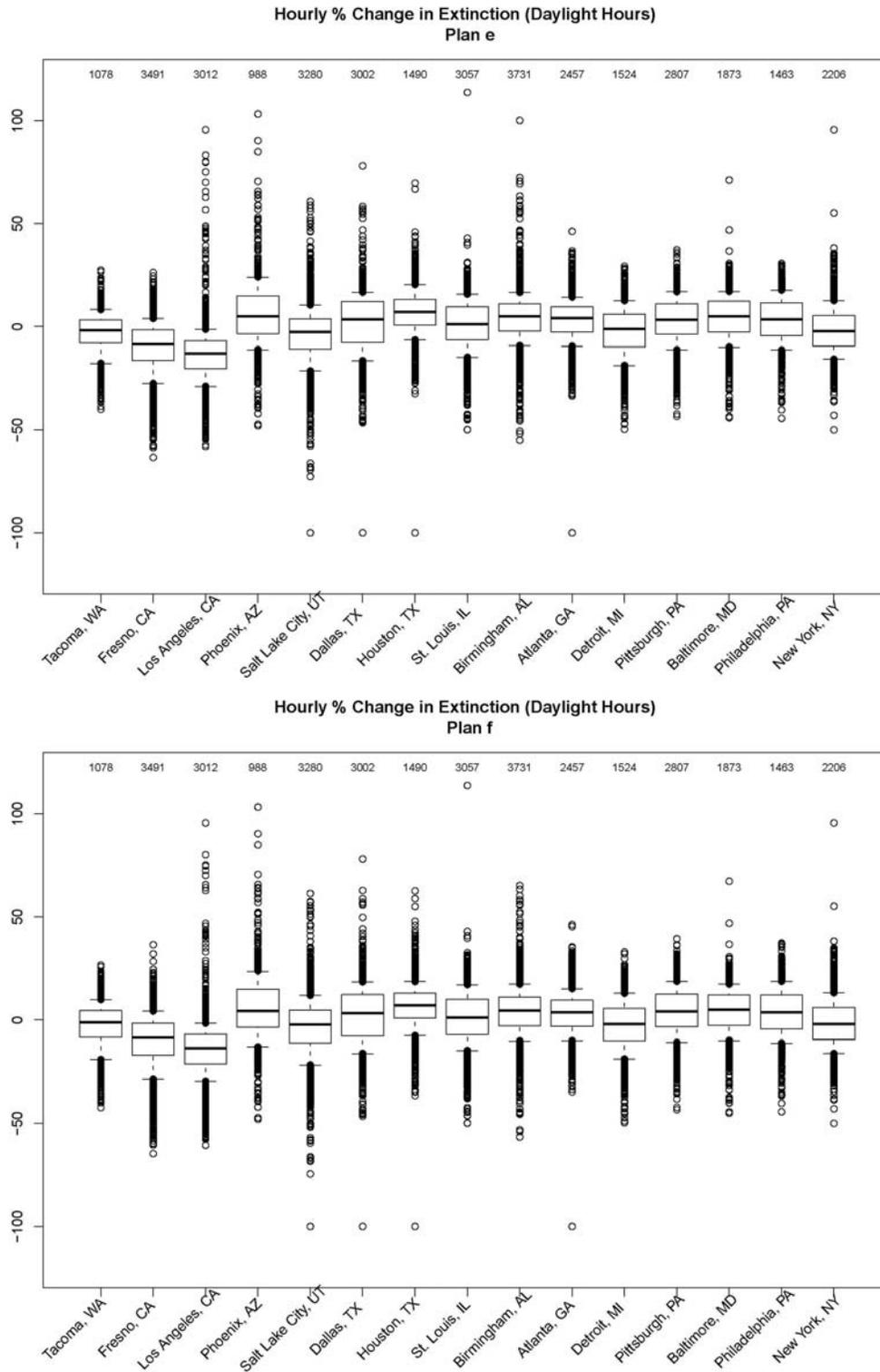
A final caveat is appropriate. In an attempt to capture diurnal variations in the component mix of  $PM_{2.5}$  as best as possible, the UFVA approach (approach A) made use of 2004 monthly-average diurnal profiles for each component. Individual hours in 2005-2007 could have a quite different component mix than predicted by the UFVA approach, even though the UFVA approach as best as possible reconciles the hourly component concentrations to the 24-hour average concentrations on the corresponding day as revealed by the CSN sample. Thus, using approach A as “truth” for comparison to another approach may not fully reveal the differences that could exist between that approach and a direct measurement of  $PM_{2.5}$  light extinction. Such a comparison does, however, give an indication of the additional variability caused by dropping complex calculation steps that are part of the UFVA approach.

**Figure 1. Box and whisker plot of the percent difference in calculated hourly PM<sub>2.5</sub> light extinction between approaches B and A (top plot), and between D and A (bottom plot) by urban area.**  
 (Approach B takes a simple approach to 24-hour-average component mix for each separate day and omits the UFVA correction for nitrate loss. Approach D adds the further simplification of the component mix being the same across all hours.)



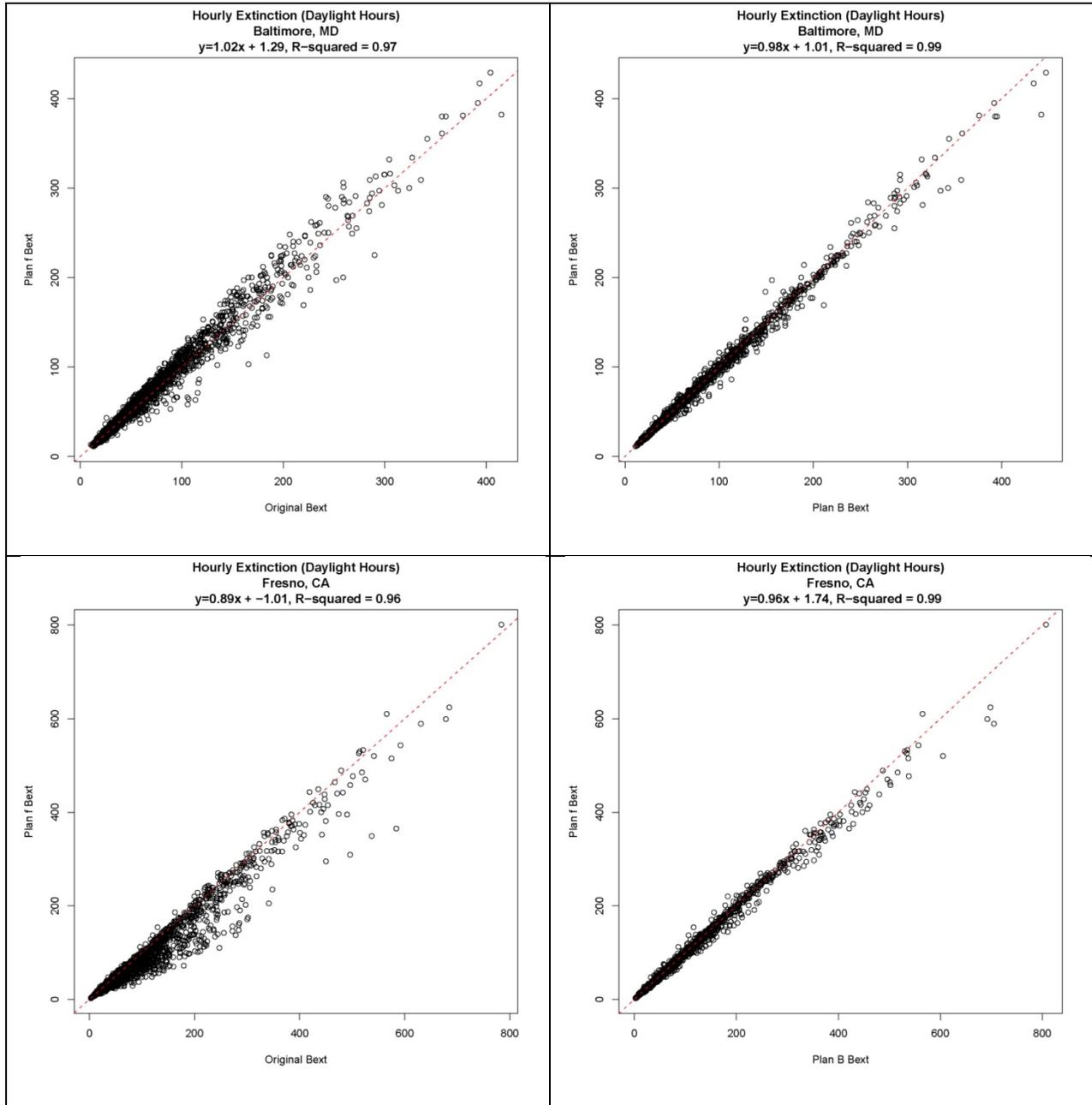
**Figure 2. Box and whisker plot of the percent difference in calculated hourly PM<sub>2.5</sub> light extinction between approaches E and A (top plot), and between F and A (bottom plot) by urban area.**

(Approach A is the original UFVA approach. Approach B takes a simple approach to 24-hour-average component mix for each separate day and omits the UFVA correction for nitrate loss. Approach D adds the further simplification of the component mix being the same across all hours.)



**Figure 3. Scatter plots of calculated PM<sub>2.5</sub> light extinction by approach F versus approach A (“original”, left) and versus approach B (right) for Baltimore (top) and Fresno (bottom).**

(Approach A is the original UFVA approach. Approach B takes a simple approach to 24-hour-average component mix for each separate day and omits the UFVA correction for nitrate loss. Approach F adds the further simplifications of the component mix being the same across all hours of the month.)



**Table 3. Linear regression equation and R<sup>2</sup> values for relating hourly PM<sub>2.5</sub> light extinction values calculated using approach F (x in the equation) to those using approach A (y in the equation) by month for 15 urban areas.<sup>11</sup>**

Month	1	2	3	4	5	6	7	8	9	10	11	12
Atlanta, GA	y=1.09*x +-0.73; Rsq=0.98	y=1.03*x +1.92; Rsq=0.98	y=1.01*x +-1.52; Rsq=0.97	y=1.06*x +-4.65; Rsq=0.98	y=1.02*x +-4.41; Rsq=0.97	y=0.99*x +-3.52; Rsq=0.97	y=0.96*x +-1.38; Rsq=0.96	y=0.98*x +-4.01; Rsq=0.98	y=0.98*x +-2.8; Rsq=0.98	y=0.97*x +0.42; Rsq=0.99	y=1.04*x +0.12; Rsq=0.96	y=1.04*x +0.63; Rsq=0.98
Baltimore, MD	y=0.99*x +1.25; Rsq=0.99	y=1.06*x +-3.6; Rsq=1	y=0.97*x +3.27; Rsq=0.99	y=1.02*x +0.41; Rsq=0.96	y=0.99*x +0.83; Rsq=0.9	y=0.98*x +-3.78; Rsq=0.96	y=0.94*x +-2.59; Rsq=0.98	y=0.88*x +2.1; Rsq=0.99	y=0.96*x +-3.25; Rsq=0.98	y=1.05*x +-2.77; Rsq=0.98	y=0.99*x +6.6; Rsq=0.99	y=1.02*x +0.14; Rsq=0.97
Birmingham, AL	y=1.09*x +-2.17; Rsq=0.97	y=1.04*x +0.7; Rsq=0.97	y=1.06*x +-2.82; Rsq=0.97	y=1.06*x +-3.91; Rsq=0.97	y=0.94*x +2.05; Rsq=0.97	y=0.98*x +-4.9; Rsq=0.98	y=1.02*x +-6.87; Rsq=0.97	y=0.9*x+ 2.31; Rsq=0.93	y=1*x+- 6.31; Rsq=0.98	y=1.06*x +-3.87; Rsq=0.97	y=1.05*x +-2.19; Rsq=0.98	y=1.02*x +0.36; Rsq=0.99
Dallas, TX	y=1.17*x +-0.86; Rsq=0.97	y=1.1*x+ 0.43; Rsq=0.98	y=1.14*x +-3.9; Rsq=0.96	y=1.04*x +-2.66; Rsq=0.97	y=1.03*x +-3.1; Rsq=0.96	y=0.93*x +0.75; Rsq=0.95	y=0.96*x +-0.01; Rsq=0.96	y=0.98*x +-0.63; Rsq=0.91	y=1.01*x +-3.02; Rsq=0.93	y=1.06*x +-2.35; Rsq=0.97	y=1.04*x +-1.16; Rsq=0.96	y=1.03*x +2.16; Rsq=0.99
Detroit, MI	y=1.02*x +2.24; Rsq=0.97	y=0.95*x +3.79; Rsq=0.99	y=0.99*x +2.13; Rsq=0.99	y=1.1*x+ -0.5; Rsq=0.96	y=0.92*x +5.42; Rsq=0.96	y=0.96*x +2.14; Rsq=0.96	y=0.99*x +0.17; Rsq=0.93	y=1.29*x +-18.07; Rsq=0.9	y=1.12*x +-8.63; Rsq=0.97	y=1.18*x +-3.36; Rsq=0.95	y=1.04*x +5.56; Rsq=1	y=0.94*x +4.14; Rsq=0.99
Fresno, CA	y=1.05*x +-0.76; Rsq=0.98	y=1.05*x +2.04; Rsq=0.99	y=1.15*x +4.9; Rsq=0.96	y=1.31*x +-4.13; Rsq=0.87	y=1.27*x +-2.92; Rsq=0.83	y=1.24*x +-5.26; Rsq=0.87	y=1.06*x +-0.97; Rsq=0.97	y=1.3*x+ -6.59; Rsq=0.86	y=1.39*x +-6.67; Rsq=0.89	y=1.48*x +-7.51; Rsq=0.94	y=1.07*x +5.44; Rsq=0.98	y=0.97*x +5.71; Rsq=0.99
Houston, TX	y=0.83*x +4.6; Rsq=0.96	y=0.97*x +-1.12; Rsq=0.99	y=0.9*x+ 0.8; Rsq=0.99	y=1.02*x +-3.72; Rsq=0.98	y=0.97*x +-2.87; Rsq=0.97	y=0.84*x +7.59; Rsq=0.92	y=0.76*x +11.38; Rsq=0.85	y=0.88*x +5.36; Rsq=0.93	y=0.99*x +-2.92; Rsq=0.98	y=1.06*x +-3.39; Rsq=0.99	y=1.07*x +-3.64; Rsq=0.95	y=1.06*x +-2.09; Rsq=0.98
Los Angeles, CA	y=1.18*x +-0.57; Rsq=0.98	y=1.1*x+ 2.01; Rsq=0.98	y=1.08*x +7.64; Rsq=0.96	y=1.14*x +2.11; Rsq=0.96	y=1.04*x +12.59; Rsq=0.96	y=1.33*x +-3.58; Rsq=0.86	y=1.26*x +-2.89; Rsq=0.92	y=1.38*x +-12.8; Rsq=0.84	y=1.4*x+ -9.14; Rsq=0.91	y=1.25*x +-0.9; Rsq=0.96	y=1.08*x +7.75; Rsq=0.98	y=1.09*x +5.38; Rsq=0.97

<sup>11</sup> After completion of the second draft PAD, an error related to SANDWICH processing of 2005-2007 PM<sub>2.5</sub> speciation data was discovered and corrected. This affected the UFVA method (also designated in this memo as approach A) predictions of hourly PM<sub>2.5</sub> light extinction to a small degree, but not the predictions using the approaches designated in this memo as B, D, etc. The comparisons between the latter approaches and approach A were also very slightly affected, as the reader may notice by careful comparison of results in this table and Tables 4 and 5 to similar results in the second draft PAD.

Month	1	2	3	4	5	6	7	8	9	10	11	12
New York, NY	$y=1.03*x+2.14;$ Rsq=0.98	$y=1.03*x+-1.36;$ Rsq=1	$y=1.01*x+3.61;$ Rsq=0.99	$y=1.1*x+-0.68;$ Rsq=0.98	$y=1.06*x+-1.45;$ Rsq=0.97	$y=1.1*x+-6.27;$ Rsq=0.96	$y=1.02*x+-7.94;$ Rsq=0.96	$y=0.98*x+-1.24;$ Rsq=0.97	$y=1.03*x+0.25;$ Rsq=0.96	$y=1.22*x+-7.93;$ Rsq=0.97	$y=1.07*x+0.64;$ Rsq=0.99	$y=1.05*x+1.63;$ Rsq=0.98
Philadelphia, PA	$y=0.95*x+3.2;$ Rsq=0.99	$y=1.01*x+-1.74;$ Rsq=0.99	$y=1*x+1.45;$ Rsq=0.99	$y=0.96*x+2.39;$ Rsq=0.94	$y=0.9*x+1.44;$ Rsq=0.98	$y=0.92*x+-0.44;$ Rsq=0.98	$y=0.91*x+1.75;$ Rsq=0.98	$y=0.85*x+5.59;$ Rsq=0.98	$y=0.89*x+1.3;$ Rsq=0.96	$y=0.95*x+3.85;$ Rsq=0.97	$y=1.05*x+1.94;$ Rsq=0.99	$y=0.96*x+3.08;$ Rsq=0.99
Phoenix, AZ	$y=1.21*x+-2.37;$ Rsq=0.89	$y=1.13*x+-1.38;$ Rsq=0.97	$y=0.88*x+1.25;$ Rsq=0.96	$y=0.85*x+1.94;$ Rsq=0.94	$y=0.93*x+0.87;$ Rsq=0.9	$y=0.88*x+1.65;$ Rsq=0.97	$y=0.77*x+4.02;$ Rsq=0.69	$y=0.92*x+0.62;$ Rsq=0.99	$y=0.86*x+0.48;$ Rsq=0.97	$y=0.92*x+1.18;$ Rsq=0.72	$y=1.05*x+-1.68;$ Rsq=0.92	$y=1.16*x+-2.69;$ Rsq=0.94
Pittsburgh, PA	$y=1.1*x+-3.63;$ Rsq=0.95	$y=0.99*x+1.91;$ Rsq=0.97	$y=0.98*x+0.09;$ Rsq=0.99	$y=1.09*x+-2.39;$ Rsq=0.97	$y=1.07*x+-5.49;$ Rsq=0.92	$y=0.95*x+-1.28;$ Rsq=0.97	$y=1.03*x+-9.91;$ Rsq=0.96	$y=0.94*x+-1.93;$ Rsq=0.97	$y=1.04*x+-7.42;$ Rsq=0.94	$y=1.02*x+-1.66;$ Rsq=0.97	$y=1.06*x+-1.21;$ Rsq=0.99	$y=0.99*x+2.34;$ Rsq=0.98
Salt Lake City, UT	$y=0.91*x+8.62;$ Rsq=1	$y=0.97*x+4.95;$ Rsq=0.99	$y=1.12*x+1.95;$ Rsq=0.97	$y=1.14*x+-1.2;$ Rsq=0.88	$y=0.98*x+0.92;$ Rsq=0.83	$y=1.02*x+0.98;$ Rsq=0.87	$y=1*x+0;$ Rsq=0.99	$y=0.98*x+-0.43;$ Rsq=0.97	$y=0.88*x+5.49;$ Rsq=0.87	$y=1.08*x+0.17;$ Rsq=0.93	$y=1.06*x+0.81;$ Rsq=0.97	$y=0.91*x+5.89;$ Rsq=0.99
St Louis, MO	$y=1.01*x+1.72;$ Rsq=0.99	$y=1.03*x+-0.14;$ Rsq=1	$y=1.06*x+-0.01;$ Rsq=0.98	$y=1.14*x+-3.92;$ Rsq=0.94	$y=1.08*x+-3.27;$ Rsq=0.93	$y=0.92*x+0.97;$ Rsq=0.95	$y=0.98*x+-2.77;$ Rsq=0.97	$y=1*x+-7.97;$ Rsq=0.98	$y=0.94*x+-0.89;$ Rsq=0.97	$y=1.19*x+-3.77;$ Rsq=0.95	$y=0.98*x+5.24;$ Rsq=0.97	$y=1*x+2.3;$ Rsq=0.99
Tacoma, WA	$y=1.02*x+0.02;$ Rsq=1	$y=0.99*x+0.65;$ Rsq=0.94	$y=1.07*x+-0.1;$ Rsq=0.97	$y=1.22*x+-3.78;$ Rsq=0.96	$y=1.18*x+-4.43;$ Rsq=0.92	$y=1.09*x+-0.14;$ Rsq=0.9	$y=1.1*x+-1.28;$ Rsq=0.94	$y=1.22*x+-4.35;$ Rsq=0.95	$y=1.06*x+0.02;$ Rsq=0.96	$y=0.99*x+0.69;$ Rsq=0.98	$y=1.03*x+1.52;$ Rsq=1	$y=1.02*x+2.46;$ Rsq=0.98

**Table 4. Linear regression equation and R<sup>2</sup> values for relating hourly PM<sub>2.5</sub> light extinction values calculated using approach F (x in the equation) to those using approach B (y in the equation) by month for 15 urban areas.**

Month	1	2	3	4	5	6	7	8	9	10	11	12
Atlanta, GA	y=1.01*x +0.4; Rsq=0.98	y=1.06*x +0.26; Rsq=0.96	y=1.02*x +0.15; Rsq=0.99	y=1.02*x +0.72; Rsq=0.99	y=1.02*x +0.83; Rsq=0.99	y=1.02*x +1.06; Rsq=0.99	y=1.02*x+ -0.38; Rsq=0.95	y=1.04*x +3.54; Rsq=0.98	y=1.02*x +0.74; Rsq=0.99	y=1*x+1. 11; Rsq=0.99	y=1*x+1. 2; Rsq=0.98	y=0.99*x +0.81; Rsq=0.99
Baltimore, MD	y=0.96*x +1.84; Rsq=0.99	y=1.09*x +5.5; Rsq=0.99	y=1.04*x +1.21; Rsq=1	y=1.01*x +1.15; Rsq=0.98	y=1.02*x +1.15; Rsq=1	y=0.99*x +0.73; Rsq=0.99	y=1.01*x+ -0.36; Rsq=0.98	y=1*x+0. 25; Rsq=1	y=1.02*x +1; Rsq=1	y=0.97*x +2.23; Rsq=0.98	y=0.99*x +2.99; Rsq=0.99	y=1.02*x +0.17; Rsq=0.98
Birmingham, AL	y=1.08*x +2.37; Rsq=0.98	y=0.98*x +3.39; Rsq=0.96	y=1.01*x +0.05; Rsq=0.99	y=1.07*x +2.22; Rsq=0.98	y=1*x+1. 38; Rsq=0.99	y=1.01*x +0.71; Rsq=0.99	y=1.06*x+ -4.76; Rsq=0.98	y=0.98*x +2.12; Rsq=0.95	y=1.02*x +2.17; Rsq=0.98	y=1*x+1. 46; Rsq=0.98	y=1.02*x +0.76; Rsq=0.99	y=1*x+1. 59; Rsq=0.99
Dallas, TX	y=1.08*x +1.32; Rsq=0.99	y=1.05*x +1.39; Rsq=0.99	y=1.06*x +1.42; Rsq=0.99	y=1.08*x +2.68; Rsq=0.98	y=1.04*x +1.58; Rsq=0.99	y=0.98*x +1.45; Rsq=0.95	y=0.99*x+ 0.46; Rsq=0.96	y=0.94*x +2.44; Rsq=0.91	y=1*x+ 0.52; Rsq=0.99	y=1.02*x +0.48; Rsq=0.99	y=1.03*x +0.71; Rsq=0.99	y=1.13*x +3.74; Rsq=0.99
Detroit, MI	y=1.06*x +4.02; Rsq=0.98	y=1.05*x +2.66; Rsq=1	y=1.03*x +1.35; Rsq=0.99	y=1.01*x +0.23; Rsq=0.99	y=0.99*x +0.13; Rsq=1	y=0.98*x +0.79; Rsq=0.99	y=1.02*x+ -0.65; Rsq=0.99	y=1.09*x +5.76; Rsq=0.97	y=1.02*x +0.88; Rsq=0.99	y=1.05*x +1.29; Rsq=0.99	y=0.99*x +4.66; Rsq=1	y=1.09*x +5.4; Rsq=0.95
Fresno, CA	y=1.06*x +5.57; Rsq=0.99	y=1.05*x +4.18; Rsq=0.99	y=1.03*x +0.85; Rsq=1	y=1.02*x +0.57; Rsq=0.99	y=1.02*x +0.24; Rsq=0.98	y=1.03*x +0.55; Rsq=0.99	y=1*x+ 0.76; Rsq=1	y=1.02*x +0.58; Rsq=0.99	y=1.04*x +1.01; Rsq=0.99	y=1.1*x+ -3.18; Rsq=0.99	y=1.05*x +4.61; Rsq=0.99	y=1.04*x +4.37; Rsq=0.99
Houston, TX	y=0.97*x +2.57; Rsq=0.99	y=1.08*x +1.78; Rsq=0.97	y=1.01*x +0.8; Rsq=0.99	y=1.04*x +0.93; Rsq=0.99	y=1.02*x +0.48; Rsq=0.98	y=0.9*x+ 8.05; Rsq=0.93	y=0.77*x+ 13.92; Rsq=0.81	y=0.92*x +7.13; Rsq=0.93	y=1.01*x +0.91; Rsq=0.99	y=1.05*x +1.77; Rsq=0.99	y=1.12*x +3.15; Rsq=0.99	y=1.14*x +2.39; Rsq=0.97
Los Angeles, CA	y=1.08*x +3.01; Rsq=0.99	y=1.04*x +1.62; Rsq=1	y=1.02*x +0.31; Rsq=0.99	y=1.05*x +3; Rsq=0.99	y=1*x+0. 89; Rsq=1	y=1.05*x +2.16; Rsq=0.99	y=1.03*x+ -0.3; Rsq=0.99	y=1.03*x +0.34; Rsq=0.99	y=1.06*x +1.65; Rsq=0.99	y=1.08*x +3.22; Rsq=0.99	y=1.06*x +0.62; Rsq=1	y=1.04*x +0.14; Rsq=0.99
New York, NY	y=1*x+ 0.52; Rsq=1	y=1.01*x +0.82; Rsq=1	y=0.99*x +0.86; Rsq=1	y=1.03*x +0.26; Rsq=1	y=1*x+0. 17; Rsq=0.99	y=1.07*x +3.4; Rsq=0.99	y=1.03*x+ -4.03; Rsq=0.99	y=1.02*x +2.4; Rsq=0.99	y=1.01*x +0.93; Rsq=1	y=1.06*x +3.4; Rsq=0.99	y=1.02*x +0.84; Rsq=1	y=1*x+ 1.08; Rsq=1

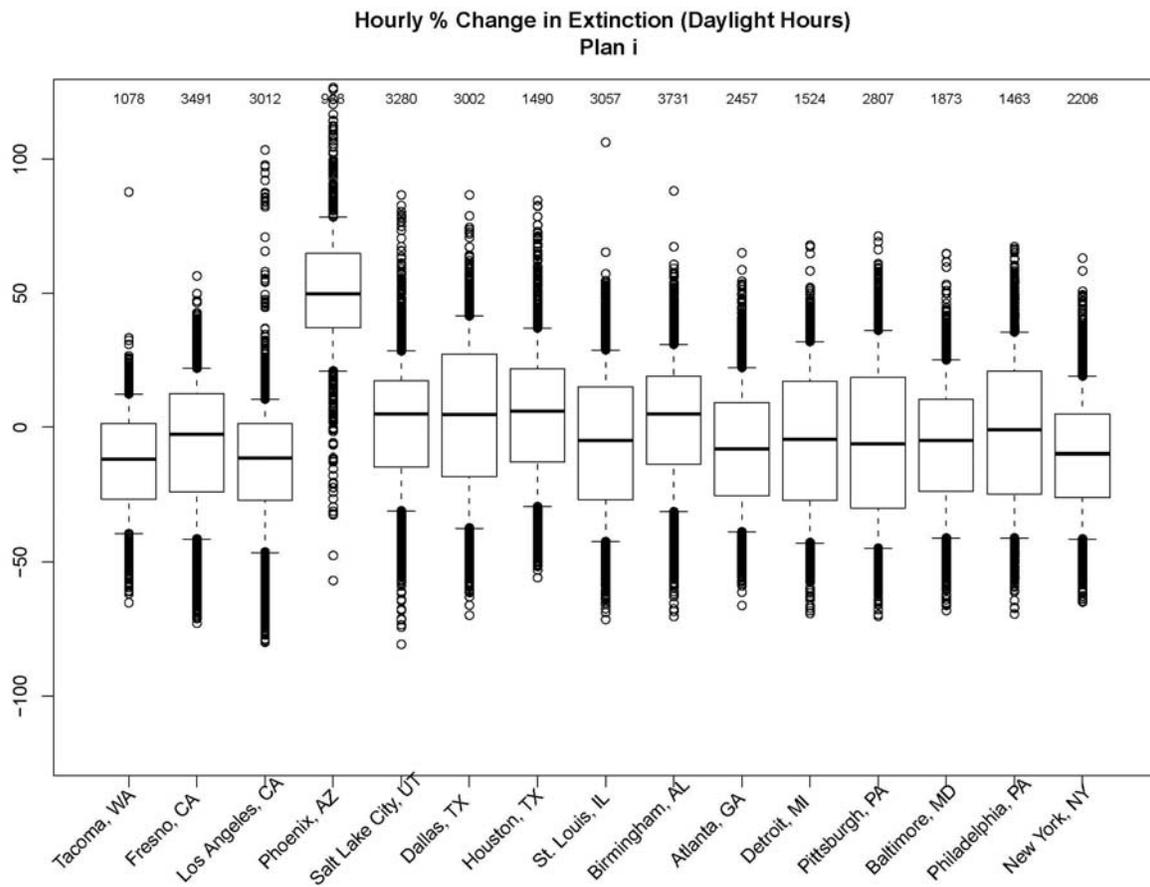
Month	1	2	3	4	5	6	7	8	9	10	11	12
Philadelphia, PA	$y=1.03*x$ +-1.63; Rsq=0.99	$y=1.02*x$ +-2.07; Rsq=0.99	$y=1.02*x$ +-0.65; Rsq=1	$y=1.05*x$ +-1.63; Rsq=0.98	$y=0.99*x$ +0.1; Rsq=1	$y=0.99*x$ +0.42; Rsq=1	$y=1.02*x$ +0.32; Rsq=0.98	$y=0.99*x$ +2.35; Rsq=0.99	$y=0.96*x$ +1.39; Rsq=0.99	$y=1.01*x$ +0.84; Rsq=1	$y=1.02*x$ +-0.83; Rsq=1	$y=1*x$ +0.41; Rsq=1
Phoenix, AZ	$y=1.17*x$ +-3.94; Rsq=0.93	$y=0.95*x$ +1.15; Rsq=0.99	$y=0.84*x$ +1.91; Rsq=0.97	$y=0.9*x$ +1.35; Rsq=0.94	$y=0.98*x$ +0.6; Rsq=0.96	$y=0.98*x$ +0.63; Rsq=0.98	$y=0.88*x$ +3.02; Rsq=0.81	$y=0.94*x$ +1.07; Rsq=0.99	$y=0.97*x$ +0.28; Rsq=0.98	$y=0.98*x$ +1.01; Rsq=0.89	$y=0.98*x$ +0.03; Rsq=0.96	$y=1.06*x$ +-3.32; Rsq=0.97
Pittsburgh, PA	$y=1.04*x$ +-0.57; Rsq=0.97	$y=1*x$ +0.78; Rsq=0.99	$y=1.01*x$ +0.29; Rsq=1	$y=1.05*x$ +-0.59; Rsq=0.99	$y=1.01*x$ +-0.88; Rsq=0.99	$y=1*x$ +0.02; Rsq=0.99	$y=1.02*x$ -3.12; Rsq=0.99	$y=1.04*x$ +-3.96; Rsq=0.99	$y=1.02*x$ +-1.58; Rsq=0.99	$y=0.98*x$ +2.1; Rsq=0.98	$y=1.05*x$ +-2.23; Rsq=0.99	$y=0.95*x$ +4.33; Rsq=0.98
Salt Lake City, UT	$y=1*x$ +1; Rsq=1	$y=1.02*x$ +-0.82; Rsq=1	$y=1.07*x$ +-0.81; Rsq=0.99	$y=1.05*x$ +-0.51; Rsq=0.95	$y=0.98*x$ +0.79; Rsq=0.96	$y=1.02*x$ +-0.44; Rsq=0.99	$y=0.97*x$ +0.77; Rsq=0.99	$y=0.96*x$ +0.74; Rsq=0.96	$y=0.75*x$ +8.1; Rsq=0.8	$y=0.97*x$ +1.37; Rsq=0.99	$y=1*x$ +0.22; Rsq=1	$y=1*x$ +0.24; Rsq=1
St Louis, MO	$y=1.04*x$ +-0.73; Rsq=0.99	$y=1.03*x$ +-0.62; Rsq=1	$y=1.08*x$ +-4.01; Rsq=0.99	$y=1.08*x$ +-2.89; Rsq=0.98	$y=1.04*x$ +-1.27; Rsq=0.97	$y=0.99*x$ +0.5; Rsq=0.99	$y=1.03*x$ -1.96; Rsq=0.99	$y=1.02*x$ +-3.12; Rsq=0.99	$y=1*x$ +0.23; Rsq=0.99	$y=1*x$ +1.02; Rsq=0.99	$y=0.93*x$ +4.74; Rsq=0.98	$y=1.09*x$ +-4.55; Rsq=0.98
Tacoma, WA	$y=0.97*x$ +1.51; Rsq=1	$y=1.08*x$ +3.92; Rsq=0.73	$y=1.02*x$ +0.31; Rsq=0.97	$y=1.03*x$ +-0.72; Rsq=0.99	$y=1.02*x$ +-0.71; Rsq=0.98	$y=1.02*x$ +-0.21; Rsq=0.99	$y=1.04*x$ -0.37; Rsq=0.98	$y=1.03*x$ +-0.58; Rsq=0.99	$y=0.98*x$ +1.41; Rsq=0.98	$y=0.97*x$ +0.92; Rsq=0.99	$y=1.02*x$ +-0.03; Rsq=1	$y=0.99*x$ +2.77; Rsq=0.97

## PM<sub>2.5</sub> Mass Concentration Used Alone to Calculate PM<sub>2.5</sub> Light Extinction

Approach I predicts PM<sub>2.5</sub> light extinction by merely multiplying the same hourly PM<sub>2.5</sub> values as used in approach A (continuous PM<sub>2.5</sub> instrument normalized to match the FRM 24-hour concentration) by a constant, 4.35 m<sup>2</sup>/g.<sup>12</sup> As shown in Figures 4 and 5, the results are not nearly as comparable as those calculated using approach F (or any of the methods that include composition and hourly relative humidity data).

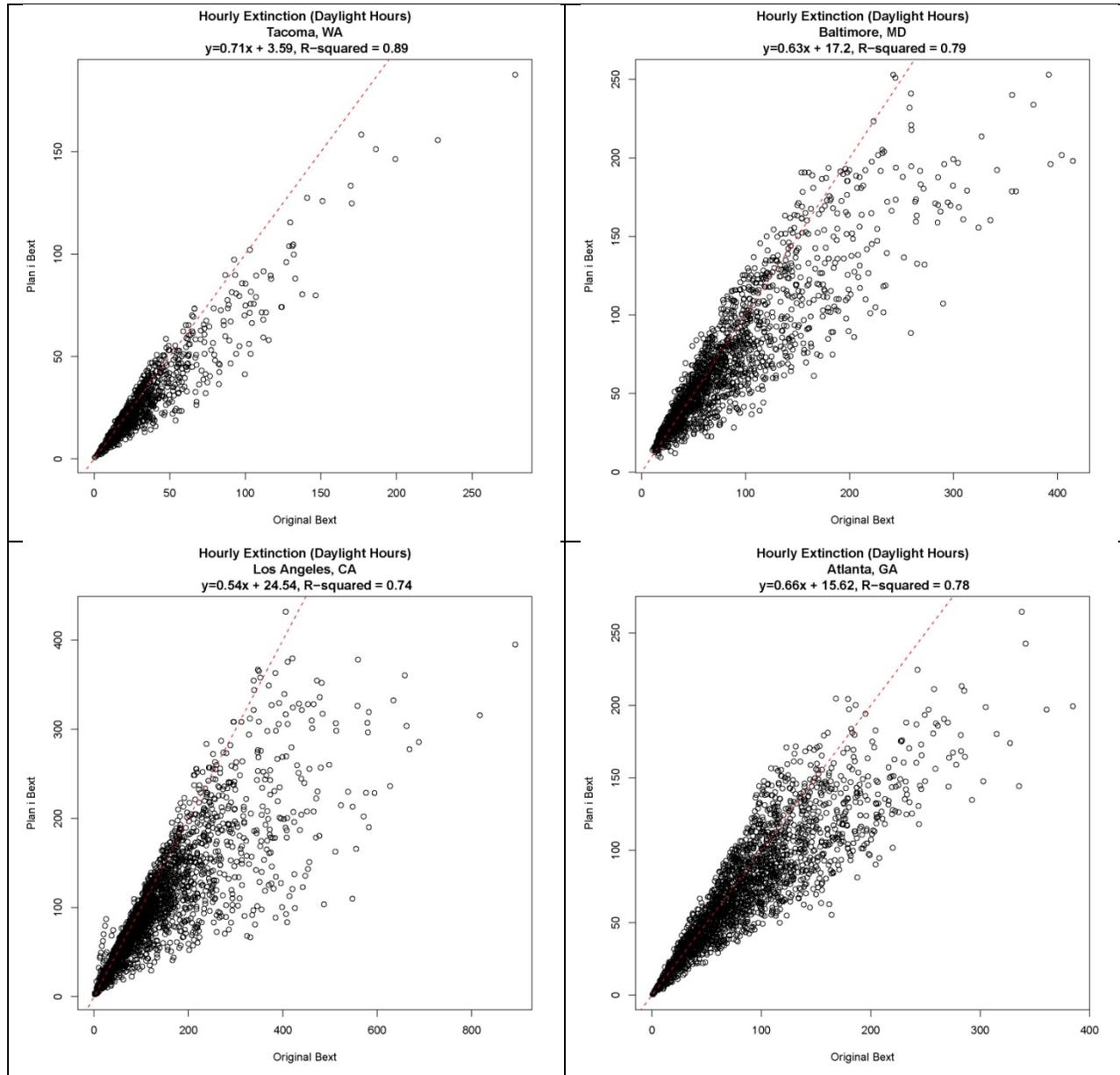
The variations in the relationships are even more evident in the monthly regression equations as shown in Table 5. The slopes range from about one half to nearly two with R<sup>2</sup> values that are often below 0.9 and as low as 0.4.

**Figure 4. Box and whisker plot of the percent difference in calculated hourly PM<sub>2.5</sub> light extinction between approaches I and A by urban area.**



<sup>12</sup> The value of 4.35 m<sup>2</sup>/g has no derivation of particular importance. If this approach were to be pursued further, more careful analysis would be appropriate, including analysis of the possibility of site-specific or region-specific constants. Selection of the best possible constant for a given monitoring site might remove the bias of approach I relative to approach A for that site, but would not reduce the spread of the errors.

**Figure 5. Scatter plots of hourly calculated PM<sub>2.5</sub> light extinction for approach I versus approach A (“original”) for four selected urban areas.**



**Table 5. Linear regression equation and R<sup>2</sup> values for relating hourly PM<sub>2.5</sub> light extinction values calculated using approach I (x in the equation) to those using approach A (y in the equation) by month for 15 urban areas.**

Month	1	2	3	4	5	6	7	8	9	10	11	12
Atlanta, GA	y=1.49*x+ -6.01; Rsq=0.91	y=1.45*x +-6.61; Rsq=0.85	y=1.25*x +-8.03; Rsq=0.85	y=1.33*x +-11.91; Rsq=0.85	y=1.2*x+ 7.04; Rsq=0.77	y=1.06*x+ 5.99; Rsq=0.65	y=0.87*x+ 25.82; Rsq=0.55	y=1.06*x+ 8.1; Rsq=0.62	y=1.21*x +-2.64; Rsq=0.75	y=1.22*x +-2.26; Rsq=0.89	y=1.53*x +-12.49; Rsq=0.91	y=1.56*x+ -13.12; Rsq=0.93
Baltimore, MD	y=1.28*x+ -8.13; Rsq=0.88	y=1.65*x +-31.12; Rsq=0.84	y=1.47*x +-17.18; Rsq=0.79	y=1.03*x +0.1; Rsq=0.79	y=1.05*x +6.54; Rsq=0.62	y=1.23*x+ -6.26; Rsq=0.7	y=1.1*x+ 1.47; Rsq=0.74	y=1.09*x+ 7.77; Rsq=0.85	y=1.33*x +-8.8; Rsq=0.81	y=1.49*x +-7.7; Rsq=0.72	y=1.66*x +-14.72; Rsq=0.94	y=1.34*x+ -5.97; Rsq=0.72
Birmingham, AL	y=1.29*x+ -5.76; Rsq=0.8	y=1.31*x +-7.25; Rsq=0.85	y=1.11*x +-5.05; Rsq=0.89	y=1.05*x +-2.93; Rsq=0.85	y=1.06*x +-6.34; Rsq=0.9	y=1*x+ 2.72; Rsq=0.82	y=1.09*x+ -0.42; Rsq=0.77	y=0.95*x+ 2.44; Rsq=0.77	y=1.16*x +-13.85; Rsq=0.8	y=1.24*x +-7.38; Rsq=0.87	y=1.17*x +-4.96; Rsq=0.89	y=1.2*x+ 0.65; Rsq=0.92
Dallas, TX	y=1.68*x+ -8.85; Rsq=0.84	y=1.93*x +-21.66; Rsq=0.88	y=1.53*x +-12.91; Rsq=0.79	y=1.34*x +-10.87; Rsq=0.75	y=1.16*x +-2.83; Rsq=0.69	y=0.86*x+ 3.04; Rsq=0.74	y=0.86*x+ 3.72; Rsq=0.75	y=0.96*x+ -2.36; Rsq=0.7	y=1.04*x +-2.03; Rsq=0.71	y=1.19*x +-2.94; Rsq=0.81	y=1.15*x +-2.83; Rsq=0.8	y=1.63*x+ -9.61; Rsq=0.93
Detroit, MI	y=1.19*x+ 11.68; Rsq=0.72	y=1.26*x +5.08; Rsq=0.85	y=1.12*x +7.21; Rsq=0.67	y=1.16*x +5.67; Rsq=0.86	y=0.79*x +11.4; Rsq=0.82	y=0.78*x+ 14.2; Rsq=0.84	y=0.99*x+ 8.98; Rsq=0.73	y=1.22*x+ 1.21; Rsq=0.55	y=1.22*x +-11.05; Rsq=0.72	y=1.42*x +-6.23; Rsq=0.79	y=1.69*x +-24.95; Rsq=0.92	y=1.13*x+ 18.7; Rsq=0.77
Fresno, CA	y=1.2*x+2 .32; Rsq=0.83	y=1.26*x +1.71; Rsq=0.84	y=1.43*x +0.17; Rsq=0.83	y=1.29*x +-2.1; Rsq=0.67	y=0.98*x +4.24; Rsq=0.54	y=1.01*x+ -1.51; Rsq=0.68	y=0.94*x+ -1.1; Rsq=0.93	y=1.13*x+ -5.1; Rsq=0.73	y=1.24*x +-4.61; Rsq=0.73	y=1.6*x+ 7.84; Rsq=0.71	y=1.22*x +8.23; Rsq=0.82	y=1.3*x+2 .8; Rsq=0.87
Houston, TX	y=1.29*x+ -2.32; Rsq=0.87	y=1.35*x +-6.35; Rsq=0.81	y=1.23*x +-7.63; Rsq=0.85	y=1.38*x +-18.36; Rsq=0.82	y=1.33*x +-19.81; Rsq=0.76	y=1.07*x+ -2.13; Rsq=0.77	y=0.54*x+ 20.69; Rsq=0.57	y=0.75*x+ 11.34; Rsq=0.43	y=1.21*x +-12.05; Rsq=0.82	y=1.3*x+ 10.7; Rsq=0.95	y=1.21*x +-7.66; Rsq=0.86	y=1.32*x+ -4.95; Rsq=0.88
Los Angeles, CA	y=1.41*x+ -5.87; Rsq=0.87	y=1.19*x +3.9; Rsq=0.85	y=1.24*x +6.92; Rsq=0.8	y=1.41*x +5.96; Rsq=0.78	y=1.4*x+ 3.52; Rsq=0.78	y=1.7*x+ 25.06; Rsq=0.57	y=1.22*x+ 5.35; Rsq=0.59	y=1.57*x+ -21.03; Rsq=0.5	y=1.38*x +-6.02; Rsq=0.71	y=1.43*x +-13.45; Rsq=0.81	y=1.47*x +-12.56; Rsq=0.86	y=1.17*x+ 6.8; Rsq=0.86
New York, NY	y=1.49*x+ -13.85; Rsq=0.9	y=1.17*x +-5.14; Rsq=0.92	y=1.39*x +-5.93; Rsq=0.87	y=1.21*x +-1.68; Rsq=0.89	y=1.2*x+ 2.33; Rsq=0.8	y=1.35*x+ -9.03; Rsq=0.78	y=1.17*x+ 0.72; Rsq=0.65	y=1.29*x+ -12.79; Rsq=0.79	y=1.37*x +-5.7; Rsq=0.89	y=1.89*x +-21.25; Rsq=0.83	y=1.39*x +0.87; Rsq=0.92	y=1.3*x+0 .85; Rsq=0.87

Month	1	2	3	4	5	6	7	8	9	10	11	12
Philadel phia, PA	y=1.36*x+ -8.52; Rsq=0.77	y=1.1*x+ 2.02; Rsq=0.79	y=1.03*x +1.75; Rsq=0.83	y=0.81*x +7.79; Rsq=0.68	y=0.88*x +4.55; Rsq=0.85	y=0.97*x+ 3.07; Rsq=0.78	y=1.03*x+ 1.63; Rsq=0.82	y=0.79*x+ 34.86; Rsq=0.69	y=0.8*x+ 10.76; Rsq=0.64	y=1.01*x +8; Rsq=0.86	y=1.27*x +1.02; Rsq=0.86	y=1.06*x+ 10.01; Rsq=0.76
Phoenix , AZ	y=0.83*x+ -2.5; Rsq=0.89	y=0.76*x +-1.53; Rsq=0.97	y=0.65*x +1.46; Rsq=0.96	y=0.56*x +2.12; Rsq=0.92	y=0.6*x+ 1.7; Rsq=0.88	y=0.62*x+ 1.11; Rsq=0.96	y=0.5*x+5 .73; Rsq=0.61	y=0.69*x+ 0.51; Rsq=0.97	y=0.6*x+ 0.85; Rsq=0.95	y=0.6*x+ 2.35; Rsq=0.58	y=0.76*x +-0.91; Rsq=0.91	y=0.97*x+ -2.05; Rsq=0.89
Pittsbur gh, PA	y=1.6*x+- 7.37; Rsq=0.75	y=1.22*x +0.01; Rsq=0.77	y=1.18*x +-1.9; Rsq=0.76	y=1.06*x +0.12; Rsq=0.74	y=1.06*x +0.38; Rsq=0.56	y=0.97*x+ 11.89; Rsq=0.67	y=1.06*x+ 10.46; Rsq=0.51	y=1.28*x+ -9.71; Rsq=0.74	y=1.18*x +-2.72; Rsq=0.62	y=1.16*x +2.65; Rsq=0.72	y=1.4*x+- 9.03; Rsq=0.82	y=1.47*x+ -6.82; Rsq=0.83
Salt Lake City, UT	y=1.38*x+ -4.77; Rsq=0.93	y=1.25*x +-0.91; Rsq=0.92	y=1.23*x +-0.88; Rsq=0.87	y=0.92*x +2.08; Rsq=0.75	y=0.73*x +4.3; Rsq=0.69	y=0.83*x+ 2.88; Rsq=0.79	y=0.9*x+0 .11; Rsq=0.98	y=0.88*x+ -0.16; Rsq=0.96	y=0.79*x +5.83; Rsq=0.87	y=1.1*x+ 2.25; Rsq=0.82	y=1.06*x +2.85; Rsq=0.92	y=1.12*x+ 9.08; Rsq=0.94
St Louis,, MO	y=1.5*x+- 0.32; Rsq=0.91	y=1.69*x +-23.16; Rsq=0.87	y=1.78*x +-23.32; Rsq=0.83	y=1.29*x +5.92; Rsq=0.69	y=1.24*x +-7.67; Rsq=0.73	y=0.88*x+ 8.95; Rsq=0.74	y=1.12*x+ -5.02; Rsq=0.75	y=1.07*x+ -2.69; Rsq=0.72	y=1.03*x +2.61; Rsq=0.74	y=1.7*x+- 15.07; Rsq=0.79	y=1.64*x +-13.94; Rsq=0.94	y=1.74*x+ -14.71; Rsq=0.82
Tacoma , WA	y=1.1*x+2 .32; Rsq=0.98	y=1.52*x +-2.25; Rsq=0.94	y=1.28*x +0.12; Rsq=0.92	y=1.37*x +-3.6; Rsq=0.86	y=1.15*x +-1.92; Rsq=0.71	y=1.1*x+2 .17; Rsq=0.63	y=1.03*x+ 2.64; Rsq=0.81	y=1.3*x+- 2.74; Rsq=0.68	y=1.07*x +2.74; Rsq=0.84	y=1.36*x +-0.96; Rsq=0.91	y=1.35*x +-1.99; Rsq=0.98	y=1.16*x+ 2.4; Rsq=0.96