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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Determining the spatial and seasonal variability in OM/OC ratios across the US using multiple regression" *by* H. Simon et al.

H. Simon et al.

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The authors thank the editor and reviewers for their thoughtful comments. We believe that in addressing these comments we have improved the manuscript. We have added more detail to our methods section and have addressed additional uncertainties in the revised manuscript. Responses to specific comments are provided below.

Comments from Reviewer 1

R1.1: In my opinion this is an interesting paper dealing with the calculation of OM/OC ratios from $PM_{2.5}$ speciation IMPROVE data treatment. The authors apply modified existing tools to re-evaluate data sets that allow to obtain partially different results

when compared with previous data treatment. In my opinion the papers merits publication but I recommend the following modifications:

A1.1: We appreciate the reviewer comment that the paper merits publication. See responses to specific comments below. Please note that we have replaced the page numbers used by Reviwer 1 with ACPD page numbers.

Major issues:

R1.2: Page 24654 line 24: Why Al was eminated from eq for soil dust? Al_2O_3 is a major constituent from clay minerals. As far as I know the ratio Si/Al decreases from PM_{10} to $PM_{2.5}$, indicating that proportionally Al is higher in $PM_{2.5}$ when compared with Si. Clay minerals may reach <2.5 microns.

A1.2: As mentioned on page 24657: **"we use an updated IMPROVE soil equation (compare Eqs. 2 and 7) which eliminates aluminum from the calculation because Al is not reliably measured by the IMPROVE XRF analysis (McDade, 2008)."** In the revised soil equation, the silicon multiplier is increased to account for aluminum at typical Si/Al soil ratios. Later, in Section 3.3 we describe a sensitivity analysis in which we used the version of the soil equation which included Al. This analysis showed that β_{OC} values were not substantially changed with the alternate version of the soil equation.

R1.3: Page 24655 line 12: Clarify use of nylon filters. Are these used in filter pack sets to correct artifacts? As far as I know nylon filters may trap gaseous HNO_3.

A1.3: Nylon filters do trap HNO_3 and that is the reason for using nylon. The configuration used in IMPROVE is a HNO_3 denuder followed by a nylon filter substrate. Ammonium nitrate will volatilize to NH_3 and HNO_3 as the temperature changes to warmer temperatures than when the sample was collected. Nylon will trap this volatilized HNO_3 thus eliminating the volatilization artifact.

We have added references in the text which outline the full IMPROVE measurement methodology. Also we have added language to the text clarifying that the nylon filter is downstream of a denuder.

R1.4: Page 24659 line 4: $CO_3^{=}$ in $PM_{2.5}$ should be nearly negligible.

We agree that the OM/OC ratio from carbonate is an unrealistic upper-bound for ambient OM/OC. Instead we now reference Turpin and Lim (2001) and set the upper-bound for OM/OC to 3.8 (upper-bound for OM/OC of aliphatic dicarbonyls).

R1.5: Same part of the text: In many papers EC is multiplied also by 1.1 for mass balance. In any case if you state that OM/OC may be 1, does this means that you are including EC here??? By definition?

A1.5: No, EC is not included in OM/OC since the denominator is OC instead of TC. The decision to set β_{EC} to 1 is described on page 24657. In addition, the sensitivity of our results to β_{EC} assumptions is explored in depth in section 3.3 and supplement section S3.

R1.6: Page 24674: IMPORTANT: In my opinion you need to add a section comparing your β_{OC} results with those obtained with other tools (AMS for example) from prior studies.

A1.6: The authors appreciate this comment and agree that comparison to other determinations of OM/OC is important. However, due to the length and amount of material covered in the current paper, we have decided that it is not feasible to add this analysis here. A future publication is planned to present a full comparison of β_{OC} results derived in this paper with OM/OC ratios that have previously been reported in the literature. This is mentioned on line 19 of page 24678.

R1.7: Page 24674, lines 6-7: I do not fully understand, SOA is present everywhere!!

A1.7: The reviewer is correct that SOA is present in all regions of the country. However, during the winter months SOA concentrations are higher in the Southeast that in other regions of the country (as reported by Yu et al., 2007). We have revised the text to clarify that wintertime SOA concentrations are higher in the Southeast but that SOA is present in other regions.

R1.8: Page 24674: Although you obtain statistically a majority of sites with a given β_{OC}, and only 12 with another trend, this does not mean that the more statistically significant coeff should be applied to everywhere. Clarify this issue. Locally obtained β_{OC} should be applied to local data.

A1.8: We have added a statement acknowledging that any particular site may deviate from this overall trend.

R1.9: Page 24678: Summary and future work: Why you do not suggest analyzing NH_4^+, in my opinion it is important for mass closure, eutrophization and for acidity!

A1.9: We direct the reviewer to page 24678, lines 21-24: **“First, our analysis shows the effect of the neutralization state on predicted mass associated with sulfate. These results suggest that sulfate is often not fully neutralized. Further studies to characterize ammonium concentrations could improve our ability to achieve mass closure with IMPROVE data.”**

Minor changes:

R1.10: Abstract line 8: 1.80 and 1.95

A1.10: This change has been made.

R1.11: Intro, page 24653 line 3: add references for ‘some earlier literature’

A1.11: Reference has been added.

R1.12: Page 24654. line 7: quartz microfiber and Teflon filters?

A1.12: The authors are unsure what the reviewer is asking and to which section he/she is referring. There appears to be no discussion of filter types at this point in the text. However, as addressed in A3.2, we have added Table 1 which now specifies the filter type on which each PM component is collected.

R1.13: Page 24676 Once and onwards: β_{OC} is defined, try to use only β_{OC} and not OC coefficients, the use of different ways to point a coefficient is confuse.

A1.13: Numerous occurrences of “OC coefficient”, “sulfate coefficient”, “nitrate coefficient”, and “soil coefficient” have now been changed to β_{OC}, β_{sulf}, β_{nit}, and β_{soil}.

Comments from Reviewer 2

R2.1: The manuscript by Simon and coworkers presents the results from a method to estimate the organic mass to organic carbon ratio (OM/OC) using ambient measurements from the IMPROVE network. The authors modify a previously published method and present averages and trends of OM/OC across the US and for different seasons.

OM/OC is an important parameter in aerosol characterization and measurement, and the paper is generally well-written and thorough. The modified method may also be useful to other researchers. I recommend publication in ACP after the following issues are addressed (including re-running the analysis if needed).

A2.1: We appreciate the comment that the paper is well-written and thorough. See responses to specific comments below.

R2.2: Line 11 on page 24652 (abstract) and later in the manuscript: the values of OM/OC of 1.29 and 1.32 for the winter in the Western and Central states appear unrealistically low. Similarly for the value of 1.37 a couple of lines later. The lowest OM/OC is associated with combustion of fossil fuels, which are thought to be comprised of lubricating oil and urburned or partially burned fuel (Tobias et al., 2001), which have an OM/OC of about 1.25 (as discussed in page 24659 of the present paper). Wood burning for heating is thought to be an important OM source in these regions during the winter, and the OM/OC of that source is quite a bit higher (the authors quote 1.7 in page 24659, but Turpin and Lim (2001) report 1.9-2.1 in their Table 4). Although much smaller than in summer, some SOA formation from fossil fuel and wood combustion will still occur in winter, increasing the OM/OC a little. The authors should comment whether they think such low ratios of 1.29-1.32, which would seem to correspond to OM dominated by fossil fuel combustion without barely any impact of wood burning or other sources, are realistic for the IMPROVE regional sites, or whether there could be some alternative explanation for them, including a low bias on the method. See also comment 4 below about filter artifacts.

A2.2: We agree that these low wintertime OM/OC ratios deserve exploration. We have added a paragraph to section 3.3 discussing possible reasons for OM/OC values near 1.3. In this paragraph we also address uncertainties in the regression analysis that could lead to erroneously low OM/OC estimates.

R2.3: Line 13 on page 24657. It is well-known that HNO_3 reacts with NaCl in sea salt forming $NaNO_3$ and displacing the Cl into the gas-phase, and the reaction is quite rapid (Gard et al., 1998; Bardouki et al., 2003; Finlayson-Pitts, 2003). For this reason

estimating the total sea salt mass from Cl is a very poor choice. Would it be possible to estimate it from Na instead? If yes, the analysis should be redone in that way. If not, this limitation needs to be highlighted in the manuscript.

A2.3: Sodium is generally poorly characterized by the IMPROVE XRF measurements and is therefore not recommended for use in these calculations. White (2008) did an extensive analysis of the use of chloride measurements to quantify sea salt mass at coastal IMPROVE sites. He found that at these sites, $1.8*Cl^-$ is an accurate way to quantify sea salt mass. He qualified this finding, stating that it may not hold at locations where sea salt is more aged. It is also important to note that most IMPROVE sites are in remote locations with low NO_y concentrations. HNO_3 displacement is less important under these conditions. We have added the following statement to acknowledge the limitation of using Cl as a sea salt tracer: **"It should be noted that although $1.8xCl^-$ has been shown to be a good estimate of sea salt mass at coastal IMPROVE sites, this calculation may underestimate sea salt concentrations at inland locations in which chloride has been displaced from the aged sea salt. However, since sea salt generally contributes little to $PM_{2.5}$ mass at most inland locations, this underestimation should not substantially affect the regression results."**

R2.4: Line 19 of page 24657. Non-soil potassium is likely to be due mostly to biomass burning sources, in which the potassium chemical form is typically KCl, which can react to form KNO_3 or K_2SO_4 (Gaudichet et al., 1995; Li et al., 2003) all of which have much higher species/K ratios. This needs to be accounted for in the revised manuscript.

A2.4: The reviewer raises a good point. However, we include NO_3 and SO_4 as explicit components of the mass balance for which direct chemical measurements have been made (i.e. we expect that any NO_3 and SO_4 contained as potassium salts would be measured by the ion chromatography and XRF analysis that are used to quantify these components). Therefore, if we also were to include this mass in a multiplier for KNON, we would be double counting that mass. In addition, potassium makes up such a small fraction of total $PM_{2.5}$ mass that the assumptions about the KNON multiplier should not affect the other regression coefficients. In fact, in the sensitivity analysis described in Section 3.3 in which KNON was eliminated from the regression calculation entirely, there was almost no change in the OC coefficient when compared to the baseline regression.

R2.5: Page 24678: the caveat given here about filter artifacts is very important and a key limitation of this work, and it should be added to the abstract and conclusions.

A2.5: The following statement has been added to the conclusions: **“All conclusions about OM/OC ratios from this paper rely on measurements made on quartz and Teflon filters. The reader is cautioned that there is uncertainty in these OM/OC estimates because they depend on accurate and complete OC artifact corrections on both filter types and techniques for quantifying these artifacts are still an active area of research.”** A brief statement was also added to the abstract acknowledging this uncertainty.

Minor issues

R2.6: Page 24653, a very relevant paper for this FTIR discussion is Polidori et al. (2008).

A2.6: Thank you for this reference. We have added this reference when discussing both FTIR spectroscopy and sequential extraction as techniques for determining OM/OC.

R2.7: Line 12 of page 24659, another good reference for the OM/OC of laboratory SOA is Chhabra et al. (2009). Several papers have reported OM/OC of ambient SOA which should also be cited here (Aiken et al., 2008; Sun et al., 2009; Huang et al., 2010).

A2.7: Thank you for these references. We have added the Chhabra reference to the discussion of OM/OC in laboratory SOA. We have also added a brief section describing the ambient OM/OC ratios reported in the other three references.

R2.8: Line 16 of page 24672: could the higher values of b$_nitbeduetothepresenceofotherformsofnitratesuchasKNO_3$ from the reaction of KCl in wood burning emissions?

A2.8: The reviewer brings up a good point. However the presence of KNO$_3$ cannot fully explain the high nitrate coefficients for two reasons: 1) potassium mass is already accounted for in our mass balance equation by the KNON and SOIL terms, so even if KNO$_3$ were present in the aerosol, this should not show up in the nitrate coefficient and 2) The ratio of molecular weights of KNO$_3$/NH$_4$NO$_3$ is about 1.26. Therefore the presence of KNO$_3$ might be expected to cause a nitrate coefficient up to 1.26 (KNO$_3$ is not expected be hydrated at relative humidities less than 50 percent found in the measurement laboratory). The higher values of β_{nit} mentioned on page 24672 are all much higher than 1.26 (ranging from 1.41 to 2.92). At this time we cannot justify these high values as physically meaningful.

R2.9: Line 19 of page 24673: is the presence of acidic sulfate during quarter 1 consistent with the annual cycle of NH$_3$ emissions? Could some acidic sulfate be neutralized in the filters when plumes of NH$_3$-rich air are sampled later?

A2.9: The predicted seasonal variation in sulfate neutralization is consistent with the availability of ammonia in the atmosphere. This availability is dependent on not only NH$_3$ emissions, but also ambient sulfate concentrations and transport/collocation of these two compounds in the atmosphere. In the Supplement we analyze molar ratio of NH$_4$ to SO$_4$ measured at STN monitoring sites. The seasonal and regional trends in this value as well as variation of RH in the measurement laboratory were used to analyze β_{sulf} values. Due to the length of this analysis we have omitted this from the main text of the paper and summarized the analysis with the statement: **“Further analysis presented in the supplement suggests that the trends predicted by the regression analysis can indeed be reasonably explained by the seasonal variation in laboratory RH where samples were weighed and in the degree of sulfate neutralization”.** We refer the reviewer to the Supplement for more details on this analysis. In response to the reviewers comment about neutralization on the filter, the samples are collected for 24 hours. It is certainly possible that if the air composition changes during the 24 hour sampling period that some chemistry could occur on the filter. However, the chemical characterization of the filter components should still represent an average composition for that period of time.

Comments from Reviewer 3

R3.1: In this paper, a modified multiple linear regression approach is applied to data from the IMPROVE network for estimation of OM/OC ratios across the United States. This study is a continuation of a previous data analysis using ordinary least squares (OLS) regression. OLS regression does not account for errors in the explanatory variables. To overcome this limitation so called error-in-variance models are applied in the present paper. The authors know regression modelling very well and the data analysis is done very carefully. However, there are some open questions that need to be addressed prior to publication in ACP (see below).

A3.1: Please see responses to specific comments below.

Major Comments:

R3.2: There is no instrumental section. The authors give some information about measurement techniques used within IMPROVE in section 1, but this is incomplete (e.g. no information about method for determination of OC and EC). I would appreciate a very short section with the basic information. I would also appreciate a table summarizing what constituents were determined from which filter material.

A3.2: The following text has been added to section 1: **"Specifically, the Thermal Optical Reflectance (TOR) combustion method is used to measure OC and EC, ion chromatography is used to measure SO$_4{}^{2-}, NO_3^-$, and Cl$^-$ and X-Ray Fluorescence (XRF) is used to measured elements with molecular weights between those of sodium and lead. Table 1 summarizes the IMPROVE measurements used for this paper and the filter type on which each PM component is collected. Details of the IMPROVE sampling and measurement methods are given by Malm et al. (1994) and in the IMPROVE data guide (http://vista.cira.colostate.edu/improve/Publications/OtherDocs/IMPROVEDataGuide/IMPROVEdataguide.htm)."**

R3.3: I have a major concern about interpretation of the absolute values of the

determined OM/OC ratios. My concern comes from the fact that thermal-optical determination of OC and EC as applied in this study must be regarded as a conventional approach for determination of OC rather than a correct determination of a chemically well defined PM fraction. The split between OC and EC strongly depends on the detailed realization of the measurement. The chosen temperature protocol and the method for charring correction (reflectance or transmission) have a rather large impact on the obtained value. On the other hand, the absolute values for OC have a direct impact on the estimate for coefficient β_{OC} when used in a regression model (the PM mass concentration explained by OC remains constant). As a consequence, the OM/OC ratio would be different from the reported values when e.g. a NIOSH temperature protocol instead of the IMPROVE temperature protocol would have been used. The authors should very clearly address this limitation. The authors might argue that best solutions were found for β_{EC} to be equal to 1 (discussion in the supplementary material), however, other values seem also possible and the "uncertainty" in fixing β_{EC} to 1 must be considered as being rather large. In my view, the regional and seasonal differences in β_{OC} are interesting and merit publication. However, the authors should avoid the interpretation of the absolute values. On p. 24658 the readers are cautioned against over-interpreting the regression coefficients which is good but not sufficient.

A3.3: We agree that the NIOSH vs. IMPROVE methods for determining OC and EC will lead to different OC/EC splits. We have therefore added the following caveat to section 2.2: **"It should also be noted that OC is operationally defined. Here, OC is measured with the IMPROVE TOR protocol which is now used at both CSN and IMPROVE network sites. Coefficients estimated from the analysis presented in this paper should only be applied to OC derived using the same or equivalent methods."**

However, it should be noted that the now widespread use of the IMPROVE protocol makes these results broadly applicable. In addition, we do not agree with that statement that "the 'uncertainty' in fixing β_{EC} to 1 must be considered as being rather large' or that the differences between IMPROVE and NIOSH OC measurements would have a large impact on the regression results here. These two protocols estimate very different EC concentrations, but very similar OC concentrations (see Chow et al (2001)). We addressed the issue of β_{EC} in detail in the supplemental information (as noted by the reviewer). Through several analyses we found that, in fact, β_{EC} has little effect on β_{OC}, so long as β_{EC} was within the range of 0.25 – 1.75 (note when EC is treated as an independent variable, some β_{EC} estimates are well outside of this range). We have no reason to believe that actual EC artifact is great enough to cause a β_{EC} outside this range (Chow et al report that average NIOSH EC/IMPROVE EC is about 0.4) and therefore feel that we have sufficiently addressed this issue. Throughout the paper we have been careful to address many limitations and uncertainties in the techniques and in the results section we focus on seasonal and regional trends, not on absolute values at specific sites. We feel that these facts in addition to the statement on page 24658 noted by the reviewer are sufficient for acknowledging the limitations of this work.

Chow, J.C., Watson, John, G., Crow, D., Lowenthal, D.H., and Merrifield, T. (2001). “Comparison of IMPROVe and NIOSH Carbon Measurements”, Aerosol Science and Technology, 34: 1, 23-34.

R3.4: The authors argue that volatilization of nitrate leads to $\beta_{nit} < 1$ (p. 24660 line18, and section 3.2). This is plausible since losses of nitrate due to volatilization should be different for nylon and Teflon filters. If volatilization of nitrate is important, the assumed linear effect of measured nitrate on measured $PM_{2.5}$ is questionable. The authors should address this issue.

A3.4: The reviewer brings up a good point about potential non-linear relationships between $PM_{2.5}$ and nitrate. The work done by Hering and Cass (1999) and Frank (2006) both show that absolute nitrate loss from Teflon filters is dependent on ambient temperature and RH conditions but not on nitrate concentration (as long as the calculated nitrate loss is not greater than the ambient nitrate concentration in which case 100 percent of the nitrate would be lost). However, the β_{nit} in this work represents an average nitrate loss over the time period of the data. The coefficient is a multiplicative

bias since the loss will always be a fraction of nylon nitrate (ratio of Teflon to nylon nitrate). That ratio will vary with ambient conditions including shipping and laboratory conditions.

However, we have explored the impacts of alternate model formulations which represent nitrate loss as a constant value for each data set. This analysis is presented in a supplement to the response to comments.

To acknowledge the complicating issues surrounding nitrate volatilization, the following text has been added to the main paper: **“It should also be noted that Hering and Cass (1999) report that the absolute amount of nitrate volatilization is a function of relative humidity and temperature, but not ambient nitrate concentration (as long as the calculated nitrate loss is less than total nitrate present). Nevertheless, we feel that using a proportional coefficient is a reasonable way to capture the average volatilization behavior for a given dataset acknowledging that nitrate volatilization depends on seasonal RH and temperature trends.”**

R3.5: In Eq. 5, KNON represents the mass of wood burning related potassium. The coefficient of KNON is fixed at 1.2 in order to account for potassium oxide from wood burning. However, there should be more mass related to emissions from wood burning than potassium oxide (and OM and EC that is represented in Eq. 5 by the corresponding terms). So it is not so obvious that the model as given in Eq. 5 is (a) appropriate (are all effects linear?) and (b) complete. Why is a model without intercept used? An obvious option would be to use a model with intercept, if no intercept is needed the confidence interval for the estimated intercept would then include zero. There are some questions related to the model selection, I therefore would very much suggest to include a careful analysis of the residuals for justification of the selected model (in the supplementary material, justification of selected model in main text).

A3.5: We do not agree that there should be more mass related to emissions from biomass burning than the components included in our calculations (potassium, organic aerosol, EC, ammonium sulfate, ammonium nitrate, and chloride). We point the reviewer to Reff et al (2010) which includes chemical speciation for emissions from various types of biomass combustion. According to Reff's speciation profiles for wildfires, agricultural burning, and prescribed burning, no chemical component missing from our analysis contributes more than 2 percent to emitted $PM_{2.5}$ mass. Thus, our model as given in Eq. 5 is complete (see discussion in A3.4 about linear relationship between $PM_{2.5}$ and nitrate and the supplement for discussion of the intercept). The reasoning behind the model selection was discussed and justified in detail in section 2.2. In addition, the work included extensive analysis of residual error values to build confidence in the appropriateness of our model selection (see sections 2.4.2 and 2.4.3). We expect that large non-linearities between model components and $PM_{2.5}$ would show up as high correlations between the residual error value and that component. We flagged all regressions in which such a correlation existed. Finally, in our results section we use residual error values to calculate NMB and NME. These relatively low NMB and NME values confirm that the data do actually fit the selected model quite well. In the supplement we report the NMB and NME for each regression, so that the readers themselves may determine if any particular regressions are unreliable due to poor model fit.

R3.6: The discussion of the estimated coefficients in section 3 is lengthy and not easy to read. The manuscript would gain if this section could be reduced to the most important facts. Please try to revise accordingly.

A3.6: We have reread section 3 with an eye toward succinctness and have made some minor modifications to shorten its length.

Minor comments

R3.7: Abstract, line 6: I would prefer the expression “variable selection” instead of “dataset selection”.

A3.7: We discuss two separate issues in our methodology: dataset selection (determining how to group our data, i.e. into site- and quarter-specific datasets) and variable or model selection. We have modified the abstract to include both of these issues in the list of common regression pitfalls addressed by this work.

R3.8: Page 24654, line 11: Please mention here on what type of filter $PM_{2.5}$ was

collected.

A3.8: See response A3.2.

R3.9: Page 24674, line 12: It is stated that β_{nit} cannot be precisely estimated in summer – what about the standard errors (or confidence intervals) for β_{nit}?

A3.9: We have added the following statement to the text: **“This is supported by the fact that the median error for β_{nit} is much larger in quarter 3 (0.34) than in other quarters (0.06 in quarter 1, 0.16 in quarter 2, and 0.08 in quarter 3).”**

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C12922/2011/acpd-10-C12922-2011-supplement.pdf

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